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# Dynamic model of denitrification in natural wetlands on a global scale

Columba Martinez Espinosa

► **To cite this version:**

Columba Martinez Espinosa. Dynamic model of denitrification in natural wetlands on a global scale. Ecology, environment. Université Paul Sabatier - Toulouse III, 2021. English. NNT : 2021TOU30165 . tel-03693547

**HAL Id: tel-03693547**

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# THÈSE

En vue de l'obtention du  
**DOCTORAT DE L'UNIVERSITÉ DE TOULOUSE**

Délivré par l'Université Toulouse 3 - Paul Sabatier

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Présentée et soutenue par  
**Columba MARTINEZ ESPINOSA**

Le 8 octobre 2021

**Modèle dynamique de dénitrification dans les zones  
humides naturelles à l'échelle mondiale.**

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Ecole doctorale : **SDU2E - Sciences de l'Univers, de  
l'Environnement et de l'Espace**

Spécialité : **Ecologie Fonctionnelle**

Unité de recherche :  
**Laboratoire écologie fonctionnelle et environnement**

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# EXTENDED ABSTRACT

The biosphere is going through an environmental crisis triggered by our global energy-intensive development model. Understanding global ecosystem regulation processes and exchanges are the key challenges to enhance our resilience and reduce our impact on Earth. This thesis aims to assess the role of wetlands ecosystems in the global nitrogen cycle.

The global nitrogen cycle has been altered by the intensive use and under regulation of nitrogen fertilizers. On one hand, fertilizers have allowed food production for 7.8 billion people, but on the other hand is polluting surface and groundwater as well as increasing greenhouse emissions. That in turn is threatening biodiversity and ecosystems, as well as human health. In addition to increasing global temperatures and depleting the ozone layer.

Wetlands are present in all continents; they represent 4% of Earth's surface. They are high productive ecosystems that provide habitat for diversity of wildlife species and afford various ecosystem services (i.e. groundwater recharge, storing floodwater, stabilizing shorelines, filtering contaminants, removing nutrients and sediments from runoff). Approximately 40% of world species including humans depend on wetlands. Wetlands ecosystem functionality is declining globally as they have been under valued and their surface area has significantly decreased due to the conversion of these ecosystems to fields, urban areas, and river channels.

This PhD aims to contribute with the wetlands biogeochemical processes understanding that may improve wetlands effective management. Providing the first dynamic global assessment of wetlands capacity to mitigate nitrate ( $\text{NO}_3^-$ ) transport, through denitrification. The main regulatory process driven by the soil bacterial community that transforms nitrates in dinitrogen,  $\text{N}_2$  (g), with an obligated portion of nitrous oxide,  $\text{N}_2\text{O}$  (g), when oxygen is not available.

This PhD project contributes by an exhaustive literature review with a state of the art of the most recent trends and gaps to develop regarding denitrification in wetlands research. By modelling coupled with satellite Earth Observations and field data the development of denitrification model that assess the spatial and temporal evolution of nitrate regulation in wetlands (calibrated with field data). Furthermore, presents the potential hot spots and hot moment of denitrification in natural wetlands with their associated quantitative  $\text{N}_2\text{-N}+\text{N}_2\text{O-N}$  yearly contribution by different types of wetlands.

In summary, this PhD developed a new approach to monitor wetlands nitrogen dynamics and provide the first quantitative dynamic assessment of denitrification in natural wetlands at global scale. This approach includes a python module-based model that can be use and improve by the scientific community. In addition, it provides evidence to improve wetland management and value their ecosystem services. Moreover, estimates uncertainties and opportunities of satellite Earth Observations tools for global biogeochemical modeling. As a conclusion, the results of this thesis aim to contribute to the human knowledge and wetlands ecosystem protection, and policies prespectives.

# RÉSUMÉ DÉTAILLÉ

La biosphère traverse une crise environnementale déclenchée par notre modèle de développement mondial à forte intensité énergétique. Comprendre les processus de régulation et les échanges des écosystèmes globaux sont les principaux défis à relever pour améliorer notre résilience et réduire notre impact sur la Terre. Cette thèse vise à évaluer le rôle des écosystèmes des zones humides dans le cycle global de l'azote.

Le cycle global de l'azote a été modifié par l'utilisation intensive et la sous-régulation des engrais azotés. D'une part, les engrais ont permis de produire de la nourriture pour 7,8 milliards de personnes, mais d'autre part, ils polluent les eaux de surface et souterraines et augmentent les émissions de gaz à effet de serre. Cela menace à son tour la biodiversité et les écosystèmes, ainsi que la santé humaine. En plus d'augmenter les températures mondiales et d'appauvrir la couche d'ozone.

Les zones humides sont présentes sur tous les continents ; elles représentent 4 % de la surface de la Terre. Il s'agit d'écosystèmes hautement productifs qui fournissent un habitat à une grande diversité d'espèces sauvages et offrent divers services écosystémiques (recharge des eaux souterraines, stockage des eaux de crue, stabilisation des rivages, filtrage des contaminants, élimination des nutriments et des sédiments des eaux de ruissellement). Environ 40 % des espèces mondiales, y compris les humains, dépendent des zones humides. La fonctionnalité de l'écosystème des zones humides est en déclin au niveau mondial car elles ont été sous-évaluées et leur surface a considérablement diminué en raison de la conversion de ces écosystèmes en champs, en zones urbaines et en canaux de rivière.

Cette thèse vise à contribuer à la compréhension des processus biogéochimiques des zones humides afin d'en améliorer la gestion. Fournir la première évaluation dynamique globale de la capacité des zones humides à atténuer le transport des nitrates ( $\text{NO}_3^-$ ), par la dénitrification. Le principal processus de régulation est dirigé par la communauté bactérienne du sol qui transforme les nitrates en diazote,  $\text{N}_2$  (g), avec une partie obligatoire de protoxyde d'azote,  $\text{N}_2\text{O}$  (g), lorsque l'oxygène n'est pas disponible.

Ce projet de doctorat contribue par une revue exhaustive de la littérature à un état de l'art des tendances les plus récentes et des lacunes à développer concernant la recherche sur la dénitrification dans les zones humides. Par la modélisation couplée avec des observations terrestres par satellite et des données de terrain, le développement d'un modèle de dénitrification qui évalue l'évolution spatiale et temporelle de la régulation des nitrates dans les zones humides (calibré avec des données de terrain). En outre, nous présentons les points chauds et les moments chauds potentiels de la dénitrification dans les zones humides naturelles, ainsi que la contribution quantitative annuelle de  $\text{N}_2\text{-N}+\text{N}_2\text{O-N}$  qui leur est associée par différents types de zones humides.

En résumé, ce doctorat a développé une nouvelle approche pour surveiller la dynamique de l'azote dans les zones humides et fournir la première évaluation dynamique quantitative de la dénitrification dans les zones humides naturelles à l'échelle mondiale. Cette approche comprend un modèle basé sur un module Python qui peut être utilisé et amélioré par la communauté scientifique. En outre, elle fournit des preuves pour améliorer la gestion des zones humides et valoriser leurs services écosystémiques. En outre, elle estime les incertitudes et les opportunités des outils d'observation de la Terre par satellite pour la modélisation biogéochimique mondiale. En conclusion, les résultats de cette thèse visent à contribuer à la connaissance humaine et à la protection des écosystèmes des zones humides.

# RESUMEN EXTENDIDO

La biosfera está atravesando una crisis medioambiental provocada por nuestro modelo de desarrollo global intensivo en energía. Entender los procesos de regulación e intercambios de los ecosistemas globales es el reto clave para mejorar nuestra resiliencia y reducir nuestro impacto en la Tierra. El objetivo de esta tesis es evaluar el papel de los ecosistemas de humedales en el ciclo global del nitrógeno.

El ciclo global del nitrógeno se ha visto alterado por el uso intensivo y la escasa regulación de los fertilizantes nitrogenados. Por un lado, los fertilizantes han permitido la producción de alimentos para 7.800 millones de personas, pero por otro lado están contaminando las aguas superficiales y subterráneas, además de aumentar las emisiones de efecto invernadero. Eso, a su vez, está amenazando la biodiversidad y los ecosistemas, así como la salud humana. Además de aumentar la temperatura global y agotar la capa de ozono.

Los humedales están presentes en todos los continentes, representan el 4% de la superficie de la Tierra. Son ecosistemas muy productivos que proporcionan un hábitat para la diversidad de especies silvestres y prestan diversos servicios ecosistémicos (por ejemplo, recarga de aguas subterráneas, almacenamiento de aguas de crecida, estabilización de las costas, filtrado de contaminantes, eliminación de nutrientes y sedimentos de la escorrentía). Aproximadamente el 40% de las especies del mundo, incluidas las humanas, dependen de los humedales. La funcionalidad de los ecosistemas de los humedales está disminuyendo en todo el mundo, ya que han sido infravalorados y su superficie ha disminuido considerablemente debido a la conversión de estos ecosistemas en campos, zonas urbanas y canales fluviales.

Este doctorado pretende contribuir a la comprensión de los procesos biogeoquímicos de los humedales para mejorar su gestión eficaz. Proporcionando la primera evaluación dinámica global de la capacidad de los humedales para mitigar el transporte de nitrato ( $\text{NO}_3^-$ ), a través de la desnitrificación. El principal proceso regulador impulsado por la comunidad bacteriana del suelo que transforma los nitratos en dinitrógeno,  $\text{N}_2$  (g), con una porción obligada de óxido nitroso,  $\text{N}_2\text{O}$  (g), cuando no hay oxígeno disponible.

Este proyecto de doctorado contribuye mediante una revisión exhaustiva de la literatura con un estado del arte de las tendencias más recientes y las lagunas a desarrollar en relación con la investigación de la desnitrificación en los humedales. Mediante la modelización acoplada con observaciones de la Tierra por satélite y datos de campo, se desarrolla un modelo de desnitrificación que evalúa la evolución espacial y temporal de la regulación de los nitratos en los humedales (calibrado con datos de campo). Además, se presentan los potenciales puntos y momentos calientes de desnitrificación en los humedales naturales con su correspondiente contribución cuantitativa anual de  $\text{N}_2\text{-N}+\text{N}_2\text{O-N}$  por parte de los diferentes tipos de humedales.

En resumen, este doctorado ha desarrollado un nuevo enfoque para monitorizar la dinámica del nitrógeno en los humedales y proporcionar la primera evaluación dinámica cuantitativa de la desnitrificación en los humedales naturales a escala global. Este enfoque incluye un modelo basado en un módulo de Python que puede ser utilizado y mejorado por la comunidad científica. Además, proporciona pruebas para mejorar la gestión de los humedales y valorar sus servicios ecosistémicos. Además, estima las incertidumbres y oportunidades de las herramientas de observación de la Tierra por satélite para la modelización biogeoquímica global. Como conclusión, los resultados de esta tesis pretenden contribuir al conocimiento humano y a la protección del ecosistema de los humedales.





***"Scientia est potentia"***



# ACKNOWLEDGEMENTS

Esta tesis está dedicada a todas las mujeres del mundo, principalmente a las que no tienen acceso a la educación y a las mujeres científicas que se enfrentan a todas las desigualdades del sistema. También esta dedicada a todas las personas que cuestionan, luchan y resisten al capitalismo.

Una tesis es un proceso de aprendizaje personal y científico que involucra la interacción con muchas personas que con intención o sin intención colaboraron a este trabajo. Estudiar en otro país, donde desconocía el idioma y las costumbres, me hizo sentir como un intruso y pretendí ser fuerte y mantenerme siempre al pie del cañon cuando me sentía sola. Sin embargo, este sentimiento ha sido contrareestado gracias a todos los gestos de bondad y generosidad que me dieron muchas personas, que me han hecho sentir como en casa. Así que agradezco a todos aquellos desconocidos con los que crucé el camino y que con una sonrisa hicieron la diferencia en mi día a día.

Personalmente, quisiera agradecer a mis directores de tesis José Miguel Sanchez Pérez y Sabine Sauvage quienes me dieron la confianza para trabajar con ellos durante todo este tiempo y que han sido testigos de todos los altibajos de este trabajo.

A Ahmad Al bitar, por su gran ayuda y apoyo para la construcción del modelo. Además de su gran corazón y su confianza.

A los miembros de la SWS (Society of wetlands Scientist) especialmente a Jos T.A. Verhoeven y a Matthew Simpson por sus múltiples consejos, por compartir su pasión por los humedales y por el apoyo intelectual y financiero que me brindaron.

A Charles Vörösmarty, por recibirme en su laboratorio, por las enriquecedoras discusiones e intercambio de ideas que aportaron valor a esta tesis.

A Pieter que me dio la fuerza para empezar el doctorado y quien se despidió en el camino. Que tanto su presencia como su ausencia fueron un parteaguas en mi vida. Y me enseñaron a darle valor a las cosas importantes. Y quien siempre estará en mi corazón.

A Lucy, Fer, Mich, Mariana, Estefi, Pili, Mariana y Regina, por tanto apoyo moral, risas, amor y porque disfruto mucho su amistad. Gracias por esos mensajes de voz en crisis, en fiestas, en momentos de felicidad y llorar al teléfono logrando que la distancia se deshaga.

Viviana y Fabian, porque desde la maestría confiaron en mí y me mantuvieron en la mira para que no perdiera la esperanza de terminar el doctorado.

A Ricardo, Rodrigo, Víctor, Jerónimo, José Luis, Paola, Prada, Alessandro, Vanessa, Ceci y Jonjo por su amor y por hacerme parte de sus familias en repetidas ocasiones. Por las múltiples comidas deliciosas compartidas, consejos de vida, borracheras, viajes y bailes. Con el tiempo aprecio más saberlos tan cercanos y me encanta que sean todos artistas y científicos a la vez.

A Manon, Marilen y, Maite, quienes fueron mis grandes amigas en este periodo en Toulouse, con quienes descubri la vida cotidiana en esta ciudad y que siempre me tendieron la mano y me apoyaron en las situaciones difíciles con su energía y su sonrisa. Ver como crecieron sus familias, y darle la bienvenida a Albanita, Emil y Adei es una realización del tiempo y de lo bonito que es la vida. Aprendí lo difícil que es hacer compatible la maternidad con la academia, pero que sí se puede y necesitamos más mujeres en la ciencia.

A Abraham, mi único amigo mexicano en Toulouse, quien cocinaba comida mexicana deliciosa y siempre mantenía el ánimo de toda la pandilla (Daria, Gabi, Tiziana, Sujay, Laura). Además de enseñarme astrofísica, y programación.

A todos los amigos de Ecolab, Pankyes, a big big brother that never let me down. Juan Luis, por su gran corazón y paciencia, por ayudarme a entender todas las ecuaciones, aprender química, R, estadística, y ciencias. Jaime, por ser tan positivo, ser un gran compañero en la parte experimental y de campo además de ser un crack de la desnitrificación. A Rox y a Jeremy por ayudarme a lidiar con Python es repetidas ocasiones. A Xi, Juan, Francesco, Vanessa, Sarah, Theo, Benjamin, Oskar por todos los cafés, lunch, cervezas y tiempo compartido. A Ecolab y su equipo de gestión Frank, Annick, Thierry, Hugues, Virginie, Marijo por su apoyo y por siempre tratar de ayudarme y resolver los problemas.

A mi familia belga: los Wolfs-Scherleenk (Anton & Lana, Karen, Vera & Yaron, Ann y Peter), Mathil, Loic, Diego, Rafa, Annita, Beth, Lucy, Adrian por su amistad tan profunda, y sus visitas tan intensas.

A Bruno por escuchar y recordarme que vale la pena vivir y amar, además de saber cuándo es un buen momento para darme fuerza y amor.

A Marcelo y Nathalie quienes me han impulsado a seguir el camino de la investigación, a la UNAM, por enseñarme a valorar la educación pública, gratuita, ¡laica y para todos! Gracias por haberme mostrado el privilegio de estudiar en una Universidad Autónoma, donde la libertad de expresión forma parte de la educación y de la apropiación del lugar.

A México, CONACYT y el Café Son por financiar estos cuatro años de estudios e infinitas experiencias de vida.

Y finalmente a los amores más grandes que tengo, mi familia **los Martínez y los Espinosa todos los miembros incluidos. Pero especialmente a mi hermana Sara, mi mamá Columba y mi papá Abel.**

**Gracias, Merci, Thank you!**

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## LIST OF ABBREVIATIONS

CDTI	Centro para el Desarrollo Tecnológico Industrial
CNES	Centre National d'Etudes Spatiales
DEA	Denitrification enzyme activity
DNRA	Dissimilatory Nitrate Reduction to Ammonium
DOC	Disolved organic carbon
ESA	European Space Agency
FAO	Food and Agruculture Organization of the United Nations
GIAHS	Globally Important Agricultural Heritage Systems
GIS	Geographic Information Systems
GLWD-3	Global Lake Wetlands Database level 3
IUCN	International Union for Conservation of Nature
NBS	Natural based Solutions
Nr	Nitrate reactive
POC	Particulate organic carbon
Ramsar	Ramsar Convention on Wetlands
SM	Soil Moisture
SMOS	Soil Moisture and Ocean Salinity
SSS	Sea Surface Salinity
UN	United Nations
ASL	Above Sea Level
SMDM	Soil Moisture Denitrification Model
SMDM-PMM	Soil Moisture Denitrification Model Pyhton Module Model



## **HIGHLIGHTS BY CHAPTER**

### **CHAPTER II**

- Identification of the soundest satellite Earth Observations that could be useful for denitrification modelling.
- Construction of a conceptual model that integrates soil properties, wetlands diversity and the main weathering (i.e. Soil Temperature and Soil Moisture) influencing parameters from satellite data.

### **CHAPTER III**

- Collection of field data from the most important wetlands worldwide.
- Identification of the potential denitrification capacity of sampled soils.

### **CHAPTER IV**

- Development of a dynamic denitrification model that takes into account the diversity of wetlands typology, soil characteristics and that is sensible to soil moisture and temperature changes. It was called Soil Denitrification Model (SDM)
- Construction of a Python based model that integrates global databases and that allows the extrapolation of the model at global scale.
- Assumptions, limitations and uncertainties of SDM

### **CHAPTER V**

- SDM was applied at global scale, and it provides the first dynamic global estimation of denitrification spatialized.
- It identified the sensibility of denitrification to soil moisture and temperature, identifying the main hot spots and the different ecosystem efficiencies.

## **POINTS FORTS PAR CHAPITRE**

### **CHAPITRE II**

- Identification des observations terrestres par satellite les plus pertinentes qui pourraient être utiles pour la modélisation de la dénitrification.
- Construction d'un modèle conceptuel qui intègre les propriétés du sol, la diversité des zones humides et les principaux paramètres d'altération (c'est-à-dire la température et l'humidité du sol) à partir de données satellitaires.

### **CHAPITRE III**

- Collecte de données de terrain dans les zones humides les plus importantes du monde.
- Identification de la capacité potentielle de dénitrification des sols échantillonnés.

### **CHAPITRE IV**

- Développement d'un modèle de dénitrification dynamique qui prend en compte la diversité de la typologie des ZONES humides, les caractéristiques du sol et qui est sensible aux changements d'humidité et de température du sol. Il a été appelé Modèle de dénitrification des sols (SDM).
- Construction d'un modèle basé sur Python qui intègre des bases de données mondiales et qui permet l'extrapolation du modèle à l'échelle mondiale.
- Hypothèses, limites et incertitudes du SDM.

### **CHAPITRE V**

- SDM a été appliqué à l'échelle globale, et il fournit la première estimation dynamique globale de la dénitrification spatialisée.
- Il a identifié la sensibilité de la dénitrification à l'humidité et à la température du sol, en identifiant les principaux points chauds et les différentes efficacités des écosystèmes.

FRANÇAIS

INTRODUCTION GENERALE

### CONTEXTE

L'évolution du modèle économique vers un modèle économique de consommation qui suppose des ressources illimitées n'a pas toujours été la règle et n'a jamais été la seule option. Le changement climatique et la crise environnementale actuelle sont la conséquence de la diffusion de ce modèle économique qui ignore les limites de la Terre. L'impact humain atteint des niveaux qui pourraient être difficiles à inverser (Butchart et al., 2010).

La pollution actuelle des eaux de surface par les métaux traces, les pesticides et les éléments biogéniques comme le carbone, les nitrates et le phosphore est aujourd'hui et pour l'avenir, l'un des problèmes environnementaux majeurs dans un contexte de changements globaux. Les émissions de gaz à effet de serre augmentent la température mondiale et appauvrissent la couche d'ozone. Ces changements accentuent les dommages causés à la biodiversité et aux écosystèmes et posent des problèmes de santé humaine. Pour faire face à la crise environnementale, il est essentiel de réduire l'incertitude quant à l'ampleur des effets du changement planétaire et de reconnaître les processus clés qui peuvent atténuer notre impact (Ciais et al., 2014) En outre, il s'agit de promouvoir une planification judicieuse des politiques à l'échelle régionale, nationale et mondiale.

La recherche à grande échelle, qui comprend la modélisation et les expériences, est une approche fondamentale pour intégrer des expériences multifactorielles et multi-niveaux pour paramétrer des processus connus, se produisant à grande échelle et sur de longues périodes de temps (Ponce-Campos et al., 2013). En outre, elle peut améliorer la capacité d'observation des liens mal compris entre les processus dans la gamme critique des facteurs environnementaux en interaction, sur une gamme plus large d'écosystèmes (Lechuga-Crespo et al., 2020). Le développement de la compréhension au niveau des processus en une capacité de prédiction de la réponse des écosystèmes est essentiel pour parvenir à un changement global, et pour mieux comprendre les interactions entre la biosphère et l'atmosphère qui ne pouvaient pas être évaluées auparavant (Bobbink et al., 2010; Hu et al., 2017).

Le présent travail se concentrera sur la compréhension de la dynamique des écosystèmes des zones humides naturelles en lien avec le cycle de l'azote, l'humidité du sol et les changements de température au cours des dix dernières années à partir du paradigme de la zone critique à l'échelle mondiale.

*"La zone critique est l'environnement terrestre proche de la surface, depuis le fond des eaux souterraines en circulation jusqu'au sommet de la végétation, qui accueille les interactions*

*complexes impliquant la roche, le sol, l'eau, l'air et les organismes vivants qui régulent les ressources nécessaires à la vie" (Brantley et al., 2007).*

Dans ce contexte, les écosystèmes des zones humides jouent un rôle important dans la zone critique, ils sont présents sur tous les continents à l'exception de l'Antarctique et ils ont été désignés comme les "reins du paysage" pour reconnaître les services écosystémiques importants, les valeurs d'habitat et tous les processus biogéochimiques qui s'y déroulent (Mitsch et al., 2009).

En ce qui concerne le changement climatique, le cycle du carbone est le principal indicateur de changement, et les zones humides sont des écosystèmes clés dans ce cycle. D'un côté, les écosystèmes des zones humides émettent 20 à 25 % des émissions mondiales de méthane (GIEC, 2013), de l'autre, ils ont la plus grande capacité parmi tous les écosystèmes terrestres, à séquestrer du carbone (Mitsch et al., 2013). Néanmoins, l'augmentation des températures fait fondre la neige et active le pergélisol, augmentant la productivité des tourbières par respiration aérobie, convertissant certaines tourbières boréales en sources radiatives de CO<sub>2</sub>, compromettant ainsi la fonction de puits de carbone des zones humides (Davidson et Janssens, 2006).

En outre, un autre impact du changement climatique sur les zones humides est l'élévation du niveau de la mer, qui écrase la côte. Il a été estimé que si le niveau de la mer s'élevait de 100 cm, la moitié des zones humides actuellement désignées comme étant d'importance internationale par la convention de Ramsar seraient menacées en 2080 (Nicholls, 2004). Afin d'établir une corrélation entre le changement climatique, l'impact anthropique et la fonctionnalité de l'écosystème des zones humides, il convient de comprendre la résilience de ces écosystèmes.

*"La résilience est l'ampleur de la perturbation qu'un écosystème est capable d'absorber sans passer à un autre état et perdre sa fonction et ses services" (Carpenter et al., 2001).*

Cette définition examine le comportement des systèmes et transmet une vision du degré de constance d'un système. Ce point de vue concerne une quantification à long terme de la performance non variable des écosystèmes, ensuite, en se concentrant sur l'atteinte de cette constance, les événements critiques semblent être des oscillations d'amplitude et de fréquence (Holling, 1973).



Privilégier une approche holistique au niveau de l'écosystème constitue un changement fondamental pour une évaluation de la résilience de l'écosystème, avec des impacts positifs et négatifs potentiels des valeurs et services structurels, fonctionnels et utilitaires de l'écosystème (Amthor et Huston, 1998 ; Neubauer et Megonigal, 2015).

### ÉCOSYSTEMES DES ZONES HUMIDES

Dans ce travail, la définition et la classification des zones humides de la Convention de Ramsar sont utilisées comme lignes directrices. Ramsar est la convention internationale la plus reconnue et la plus étendue qui a promu le premier accord environnemental international. Cette convention a été établie le 3 (mois) 1971, dans la petite ville iranienne de Ramsar. C'est toujours le seul traité mondial qui empêche les pays qui y adhèrent d'exploiter de manière négligente et égoïste leur patrimoine naturel souverain (Matthews, 1993).

La Convention de Ramsar (article 1.1) stipule que *"les zones humides sont des étendues de marais, de tourbières ou d'eau, naturelles ou artificielles, permanentes ou temporaires, où l'eau est stagnante ou courante, douce, saumâtre ou salée, y compris des étendues d'eau marine dont la profondeur à marée basse ne dépasse pas six mètres"* (Matthews, 1993).

En outre, dans le but de protéger des sites cohérents, l'Article 2.1 prévoit des sites supplémentaires à inscrire sur la liste Ramsar des zones humides d'importance internationale :

*"peuvent comprendre des zones riveraines et côtières adjacentes aux zones humides, ainsi que des îles ou des étendues d'eau marine d'une profondeur supérieure à six mètres à marée basse situées dans les zones humides"* (Matthews, 1993).

La distinction des zones humides par rapport aux écosystèmes terrestres et aquatiques est due au fait que les zones humides sont un écotone, c'est-à-dire un habitat "de bordure", une zone de transition entre les terres sèches et les milieux aquatiques (Hammer et Bastian, 1989). Pendant la saison de croissance, il y a de l'eau stagnante, soit à la surface, soit dans la zone racinaire. Ce fait est crucial et limite la végétation capable de s'adapter aux sols hydriques (Worbes et al., 1992), où les périodes d'anoxie du sol sont longues, que supportent des plantes spécialisées des zones humides, les hydrophytes (Burton et Tiner, 2009).

Le terme "plaine d'inondation" est un terme générique utilisé pour désigner un ou plusieurs types de zones humides situées dans une zone généralement plate à côté d'un cours d'eau. Les zones humides de plaine d'inondation ne sont pas répertoriées comme un type de zone humide

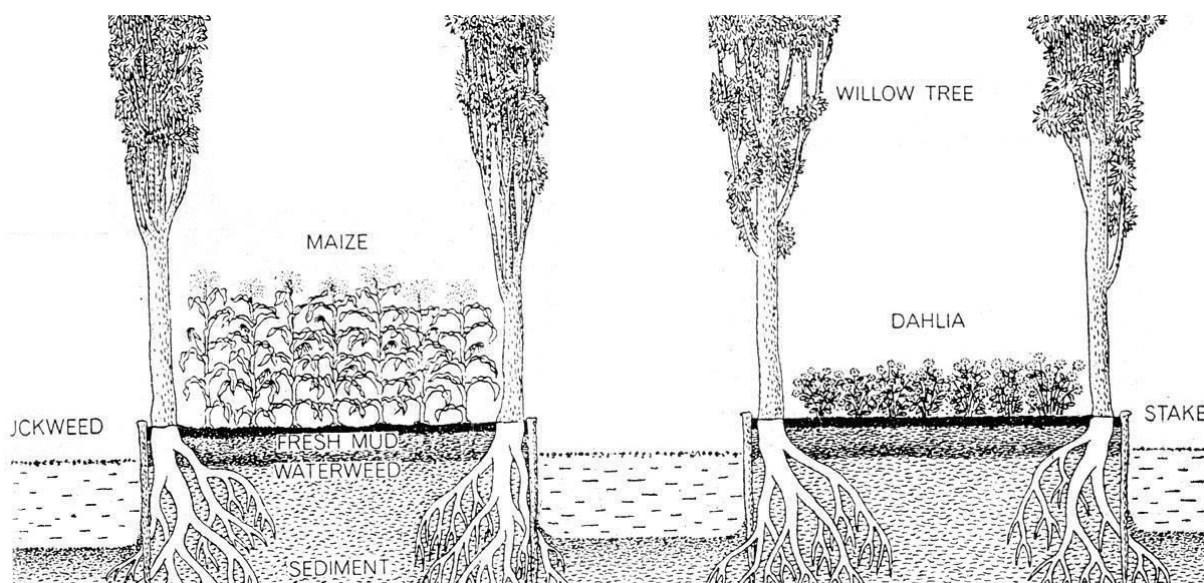
spécifique dans le présent document. Elle s'étend de la rive du fleuve aux bords extérieurs de la vallée. Parmi les exemples de zones humides de plaine d'inondation, on peut citer les prairies inondées de façon saisonnière (y compris les prairies humides naturelles), les zones arbustives, les zones boisées et les forêts (Ramsar, 2004).

Les zones humides sont connues pour leur capacité de stockage du carbone, mais il a été observé et signalé que chaque type de zone humide a sa propre capacité. En ce qui concerne les zones humides d'eau douce, les tourbières sont les contributeurs les plus importants, suivies des sols marécageux et enfin des sols marécageux. Cela suggère que la communauté et la diversité végétales sont un facteur important qui doit être pris en compte dans le bilan carbone mondial (Marín-Muñiz et al., 2014).

Les estimations mondiales de l'étendue des zones humides varient de 0,29 million de km<sup>2</sup> (Friedl et al., 2002) à 9,78 millions de km<sup>2</sup> (Lehner et Doll, 2004) de zones humides, soit environ 5 à 8 % de la surface terrestre. La plus grande partie des zones humides se trouve dans les régions boréales du nord, suivies des latitudes tropicales et enfin des latitudes tempérées.

### LES ZONES HUMIDES ET LE DEVELOPPEMENT HUMAIN

De nombreuses cultures dans le monde vivent au sein et dépendent des zones humides, aujourd'hui comme depuis plusieurs siècles. Un exemple remarquable d'un ancien système socio-écologique durable développé sous l'empire aztèque est une technique d'exploitation agricole dans les marécages (Cox et al., 2020). Ils disposaient d'un réseau de canaux et d'îles artificielles, appelés chinampas. Les canaux étaient creusés pour faciliter l'écoulement de l'eau, et la boue riche en nutriments était placée sur l'île. Le maïs, les haricots, les pommes de terre, les tomates et le poivre étaient les principales cultures. Des saules bordaient les îles pour éviter l'érosion. Cette conception optimisait les ressources en eau, et le système de rotation des cultures assurait la fertilité du sol (Figure 1). Cette technique existe toujours, elle a été reconnue par la FAO comme un système de patrimoine agricole d'importance mondiale (GIAHS) (FAO, 2017).

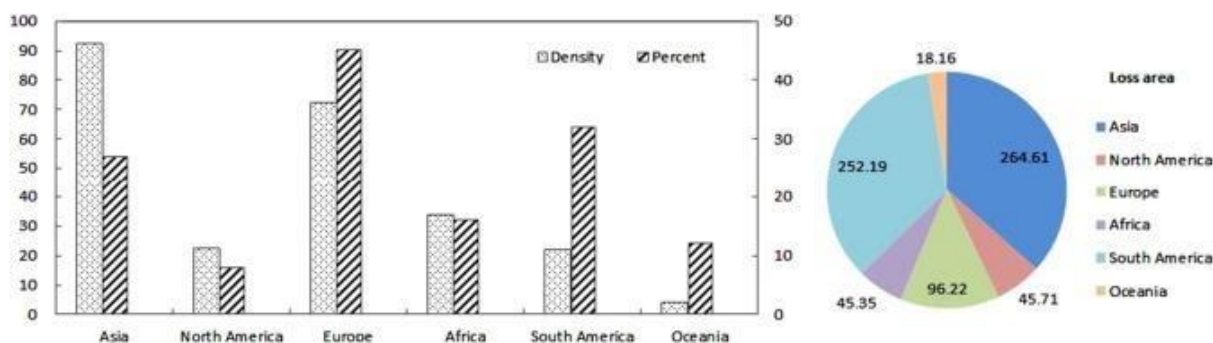


**Figure 1.** Schéma de la structure traditionnelle de la chinampa, à partir d'images Pinterest en libre accès, consultées le 22-02-2021.

En Asie, les techniques anciennes concernant la culture du riz sont très répandues en Chine, en Corée, au Japon et aux Philippines. La moitié de la population mondiale est nourrie par des systèmes de rizières (Aselmann et Crutzen, 1989; Luo et al., 2014). Ces terrasses sont très productives et la plupart des techniques anciennes sont encore appliquées. La moitié de la surface terrestre du Bangladesh est couverte de zones humides d'eau douce et d'eau salée. Les étangs d'aquaculture et les pratiques agricoles de jardins flottants sont des techniques anciennes qui ont également permis l'accès aux terres aux communautés les plus pauvres (FAO, 2015).

Néanmoins, au cours du siècle dernier, les zones humides ont été détruites à un rythme alarmant dans l'ensemble du monde développé et en développement (Global Forest Watch, 2021; Richards et Friess, 2016; Trancoso et al., 2009). En raison des difficultés techniques liées au suivi et à l'extension des zones humides, il est difficile de déterminer avec précision la perte globale des zones humides. La première estimation mondiale sur le long terme des zones humides a enregistré une perte comprise entre 54 et 57 % depuis 1900, et 87 % depuis 1700. Le taux de diminution le plus élevé de la perte de zones humides a été enregistré au cours du 20ème siècle et au début du 21ème siècle (Davidson, 2014).

La vaste population exigeant des niveaux élevés de nourriture et de logement a entraîné l'accélération du développement de l'agriculture et l'urbanisation a été la principale cause de pertes graves de zones humides dans le monde entier. La plus grande perte de zones humides s'est produite en Asie, mais la situation la plus grave se trouve en Europe (Figure 2) (Hu et al., 2017).



**Figure 2.** Le pourcentage de perte de zones humides et la densité de population entre les différents continents (unité de surface: 104 km<sup>2</sup>) d'après (Hu et al., 2017).

Cependant, une grande campagne pour le changement de paradigme et la protection de ces précieux écosystèmes est en train de devenir la norme. Des zones humides naturelles saines et fonctionnelles sont essentielles aux moyens de subsistance des humains et au développement durable (Gardner et Finlayson, 2018).

Les zones humides ont été incluses dans les objectifs durables des Nations unies car elles ont été identifiées comme très précieuses pour stabiliser les réserves d'eau, atténuant ainsi les inondations et les sécheresses. En outre, elles nettoient les eaux polluées, protègent les rivages et rechargent les nappes phréatiques. Leur protection et leur suivi sont inclus dans l'objectif N°6: "Assurer la disponibilité et la gestion durable de l'eau et de l'assainissement pour tous" (PNUD, 2017).

En outre, les zones humides construites deviennent populaires, et de nombreuses recherches ont été développées pour réaliser le traitement des eaux usées avec des solutions à base naturelle (NBS). La gestion des zones humides nécessite une compréhension complète des aspects scientifiques des zones humides en interaction avec les cadres juridiques, institutionnels, culturels et économiques.

Dans la présente étude, l'accent sera mis sur le rôle des zones humides naturelles dans les processus du cycle de l'azote. La particularité des zones humides est la fréquence élevée de l'anoxie dans le sol. Cette condition ralentit la décomposition de la matière organique et pousse la communauté bactérienne à dégrader les nitrates pour obtenir de l'oxygène et ensuite dégazer principalement du N<sub>2</sub>, et une petite fraction de N<sub>2</sub>O, ce processus est appelé dénitrification (Marín-Muñiz et al., 2014). La section suivante contextualise le cycle de l'azote dans les zones humides et met l'accent sur la dénitrification au sein du cycle de l'azote.

## ÉTUDE DU CYCLE DE L'AZOTE DANS LES ZONES HUMIDES

Le cycle de l'azote dans les zones humides est l'un des cycles chimiques les plus importants et les plus étudiés dans les zones humides. En raison de la présence d'azote dans différents états d'oxydation, et des fluctuations continues des environnements anoxiques-oxiques, comprendre le rôle des zones humides dans le cycle global de l'azote est donc essentiel pour comprendre le cycle lui-même (Song et al., 2014; Van Cleemput et al., 2007).

Mesurer la dénitrification dans les zones humides à l'échelle mondiale est un processus composé de deux parties : les mesures in situ sont nécessaires et obligatoires mais les réaliser à l'échelle mondiale est coûteux et non réalisable ; la modélisation représente un outil important et donne la possibilité d'extrapoler des observations ponctuelles dans les dimensions temporelles et spatiales. L'utilisation de ces deux techniques peut enrichir la possibilité d'estimer (quantitativement) et de prévoir la résilience des zones humides naturelles et leur pertinence dans le cycle global de l'azote. La section suivante explique les forces et les faiblesses de chacune d'entre elles et leur complémentarité dans la présente étude.

Cette thèse est composée de deux parties, une partie est basée sur une expérience de terrain qui était essentielle pour comprendre la sensibilité du processus en cours, collecter des données afin de réaliser une expérience de laboratoire. La deuxième partie était le développement d'un modèle de dénitrification, qui représente la première tentative d'estimer à l'échelle globale, de manière dynamique, la dénitrification des zones humides naturelles. Les données de terrain de la première partie de la thèse ont ensuite été utilisées pour calibrer et valider le modèle.

## OBJECTIFS

L'objectif de cette thèse est d'améliorer nos connaissances sur la dynamique de la dénitrification dans les sols des zones humides. D'abord par une expérience de terrain, puis par le développement et l'application d'un modèle qui quantifie la capacité de dénitrification dynamique des sols naturels des zones humides à l'échelle mondiale, en combinant des observations terrestres et un modèle parcimonieux. Les objectifs spécifiques sont:

Par une recherche exhaustive des recherches les plus pertinentes menées ces dernières années sur l'étude de la dénitrification dans les zones humides à l'échelle globale. Par l'identification de l'écart à développer et l'opportunité de la présente thèse à développer (Chapitre II).

Par une expérience de terrain dans la plaine d'inondation amazonienne, comprendre les limites et les forces du travail de terrain, ainsi que la nécessité d'un suivi des données de terrain pour mieux quantifier l'impact anthropique et mieux identifier les particularités de chaque site d'étude (Chapitre III).

En développant un modèle physique simplifié, calibré avec les échantillons de sol (Chapitre III), quantifier et identifier la dynamique spatiale et temporelle du rôle des zones humides amazoniennes dans le cycle global de l'azote (Chapitre IV).

En appliquant à l'échelle mondiale le modèle physique (Chapitre IV) pour identifier les moments chauds et les points chauds du dégazage de dénitrification dans les écosystèmes naturels des zones humides, reconnaître l'importance des zones humides dans le cycle global de l'azote (Chapitre V).

Les conclusions et les perspectives du présent travail sont résumées et les pistes possibles pour continuer à développer la recherche sont présentées (Chapitre VI).

## INTRODUCTION GENERALE

# CHAPTER I

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## GENERAL INTRODUCTION



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## ABSTRACT

This chapter presents the theoretical framework of this thesis. It explains the why this work is relevant in the current environmental crisis. It continues defining the key concepts of the thesis that will be used all along the manuscript. Then, definition of the selected ecosystems (i.e. wetlands) and typology is provided. Subsequently, wetlands are linked to human development and to the current environmental context specifically to the nitrogen cycle. Afterwards a chemical description of the nitrogen cycle and each of the steps of the cycle is explained. Emphasis is placed on the process to be studied (denitrification) and why wetlands are key in the global nitrogen cycle. The approaches (fieldwork and modelling) that will be used to study this process are explained in general terms, giving the limitation of each approach and the reasoning for this thesis to combine fieldwork and modelling. The chapter ends by stating the main objectives of the thesis, and how they will be addressed.

## RESUME

Ce chapitre présente le cadre théorique de cette thèse. Il explique pourquoi ce travail est pertinent dans le contexte de la crise environnementale actuelle. Il continue à définir les concepts clés de la thèse qui seront utilisés tout au long du manuscrit. Ensuite, une définition des écosystèmes sélectionnés (i.e. les zones humides) et une typologie sont fournies. Par la suite, les zones humides sont liées au développement humain et au contexte environnemental actuel, en particulier au cycle de l'azote. Ensuite, une description chimique du cycle de l'azote et de chacune des étapes du cycle est expliquée. L'accent est mis sur le processus à étudier (dénitrification) et sur les raisons pour lesquelles les zones humides sont essentielles dans le cycle global de l'azote. Les approches (travail de terrain et modélisation) qui seront utilisées pour étudier ce processus sont expliquées en termes généraux, en donnant les limites de chaque approche et la raison pour laquelle cette thèse combine travail de terrain et modélisation. Le chapitre se termine par l'énoncé des principaux objectifs de la thèse et la manière dont ils seront abordés.

## RESUMEN

Este capítulo presenta el marco teórico de esta tesis. Explica el porqué de la relevancia de este trabajo en la actual crisis ambiental. Continúa definiendo los conceptos clave de la tesis que se utilizarán a lo largo del manuscrito. A continuación, se definen los ecosistemas seleccionados (es decir, los humedales) y su tipología. Posteriormente, se relacionan los humedales con el desarrollo humano y con el contexto ambiental actual, concretamente con el ciclo del nitrógeno. Consecutivamente, se explica una descripción química del ciclo del nitrógeno y de cada una de sus etapas. Se hace hincapié en el proceso que se va a estudiar (desnitrificación) y en por qué los humedales son clave en el ciclo global del nitrógeno. Se explican de forma general los enfoques (trabajo de campo y modelización) que se utilizarán para estudiar este proceso, indicando las limitaciones de cada uno de ellos y el razonamiento para que esta tesis combine trabajo de campo y modelización. El capítulo finaliza exponiendo los principales objetivos de la tesis y cómo se abordarán.

## CONTEXT

The economic model evolution towards an economic model of consumption that assumes unlimited resources has not always been the rule and it has never been the only option. Climate change and the current environmental crisis, is the consequence of the spreading out of this economic model that ignores Earth's limits. Human impact is reaching levels that may be difficult to reverse (Butchart et al., 2010).

Current surface water pollution by trace metals, pesticides and biogenic elements like carbon, nitrates and phosphorus is now and for the future, one of the major environmental problems in a context of global changes. Greenhouse gas emissions are elevating the global temperature and depleting the ozone layer. These changes are enhancing biodiversity and ecosystems damage, as well as human health issues. Reduction of uncertainty about the magnitude of global change effects and recognition of the key processes that can mitigate our impact, are crucial to make front to the environmental crisis (Ciais et al., 2014). Additionally, to promote sound policy planning at regional, national and global scale.

Large-scale research that include modelling and experiments is a fundamental approach to integrate multifactor, multilevel experiments for parameterization of processes know to occur at large scale and over long time periods (Ponce-Campos et al., 2013). In addition, it may improve the observation capacity of poorly understood linkages among process across the critical range of interacting environmental factors over a broader range of ecosystems (Lechuga-Crespo et al., 2020). Developing process-level understanding into a predictive capability of ecosystem response is central for achieving global change, and to better understand interactions between de biosphere and the atmosphere, that before could not be assessed (Bobbink et al., 2010; Hu et al., 2017).

The present work will be focus on the understanding natural wetlands ecosystem dynamics related to nitrogen cycle, soil moisture and temperature changes in the last ten years from a critical zone paradigm at global scale.

*The critical zone is the near-surface terrestrial environment from the bottom of circulating groundwater to the top of vegetation, hosts the complex interactions involving rock, soil, water, air, and living organisms that regulate life-sustaining resources* (Brantley et al., 2007).

In this context, wetlands ecosystems play an important role in the critical zone, they are found in all continents except the Antarctica and they have been referred as “kidneys of the landscape”

to acknowledge the important ecosystem services, habitat values and all the biogeochemical processes on them (Mitsch et al., 2009).

Regarding climate change, carbon cycle is the main indicator of change, and wetlands are key ecosystems within this cycle. On one side, wetland ecosystems emit 20 to 25 percent of global methane emissions (IPPC, 2013), yet they have the highest capacity of carbon sequestration of any other terrestrial ecosystems (Mitsch et al., 2013). Nevertheless, increasing temperatures is melting the snow and activating permafrost rising peatland productivity by aerobic respiration converting some boreal peatlands in radiative sources of CO<sub>2</sub> compromising wetlands carbon sink function (Davidson and Janssens, 2006).

In addition, another impact of climate change on wetlands is the sea level rise, that is squeezing the coast, it has been estimated that if sea level were to rise by 100 cm, half of wetlands currently designated as international important by Ramsar convention will be threatened in 2080 (Nicholls, 2004). In order to correlate the climate change, anthropogenic impact and the functionality of wetlands ecosystem, the resilience of these ecosystems has to be understood.

*Resilience is the magnitude of disturbance an ecosystem is able absorb without shifting to an alternative state and losing function and services*

This definition examines the behaviour of systems and transmit a vision of the degree of constancy of a system. This point of view concern to a long-term quantification of the non-variable performance of ecosystems, and then with the focus on achieving constancy, the critical events seems to be the amplitude and frequency oscillations (Holling, 1973).

## WETLANDS ECOSYSTEMS

In this work, wetlands definition and classification from Ramsar Convention are used as guideline. Ramsar is the most recognised and widespread international convention that promoted the first international environmental agreement. This convention was first established the 3rd 1971, in the little Iranian town of Ramsar. It is still the only world-wide treaty which restrains the countries joining it from the careless, egoistic exploitation of their sovereign natural patrimony (Matthews, 1993).

The Ramsar Convention (Article 1.1) states that *“Wetlands are areas of marsh fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres”* (Matthews, 1993).

In addition, for the purpose of protecting coherent sites, the Article 2.1 provides that wetlands to be included in the Ramsar List of internationally important wetlands:

*“may incorporate riparian and coastal zones adjacent to the wetlands, and islands or bodies of marine water deeper than six metres at low tide lying within the wetlands”* (Matthews, 1993).

The distinction of wetlands from terrestrial and aquatic ecosystems is due to the fact that wetlands are an ecotone i.e. an “edge” habitat, a transition zone between dry lands and aquatic environments (Hammer and Bastian, 1989). During growing season, there is standing water, either at the surface or within the root zone. This fact is crucial and limits the vegetation able to adapt to hydric soils (Worbes et al., 1992), where anoxic soil periods are long and support specialized wetlands plants (hydrophytes) (Burton and Tiner, 2009).

The term “Floodplain” is as a generic term used to refer one or more wetlands types located in a generally flat area next to a river or stream. Floodplain wetlands are not listed as a specific wetland type herein. It stretches from the riverbank to the outer edges of the valley. Some examples of floodplain wetlands are seasonally inundated grassland (including natural wet meadows), shrublands, woodlands and forests (Ramsar, 2004).

Wetlands are known for their capacity of carbon stock; however, it has been observed and report that each kind of wetlands have their own capacity. Related to freshwater wetlands, peatlands are the most important contributors followed by swamp soils and finally marsh soils. Suggesting

that the plant community and diversity is an important factor that needs to be considered in global carbon budget (Marín-Muñiz et al., 2014).

Global estimates wetlands extent vary from 0.29 million km<sup>2</sup> (Friedl et al., 2002) to 9.78 million km<sup>2</sup> (Lehner and Doll, 2004) of wetlands or about 5 to 8 percent of the land surface on Earth. The greatest portion of wetlands are found in the northern boreal regions, followed by the tropical latitudes and the temperate latitudes at last.

## WETLANDS TYPOLOGY

For Ramsar convention, the first level of classification, divide the wetlands in three main types: (i) Marine/Coastal wetlands, (ii) Inland wetlands and (iii) Human-made wetlands. Inland wetlands are then divided in permanent (rivers and lakes) or non-permanent. Freshwater and coastal/saline wetlands can be classified as swamps (forested wetlands), marshes (non-forested wetlands), and peatlands (bog and fens) (Ramsar, 2010) (Figure 3). The present work is centred in natural non-permanent wetlands, meaning swamps, marshes and peatlands, subsequently described.

### SWAMPS

They are also known as flooded forests; trees and other woody plants dominate them. They can be intertidal, or freshwater, they are found along coastal areas, rivers and lakeshores. Tree height is an indicator of swamp status; if the trees are taller than a shrub, it is considered a primary swamp, otherwise they are Shrub-Scrub Swamps dominated by trees less than 10 m height (Mitsch and Gosselink, 2015).





- *Mangroves*: Subtropical and tropical coastal ecosystems dominated by halophytes trees, shrubs and other plants growing in brackish to saline tidal waters (Mitsch and Gosselink, 2015).



- *Várzea*: A seasonally flooded forest in the Amazon River basin. It usually refers to forest flooded by white-water (sediment-laden) river water (Junk, 1997).


## MARSHES

A frequently or continually, inundated wetlands characterized by emerging herbaceous vegetation adapted to saturated soil conditions. In European terminology, a marsh has a mineral soil substrate and does not accumulate peat (Mitsch and Gosselink, 2015). There are two types of marshes:

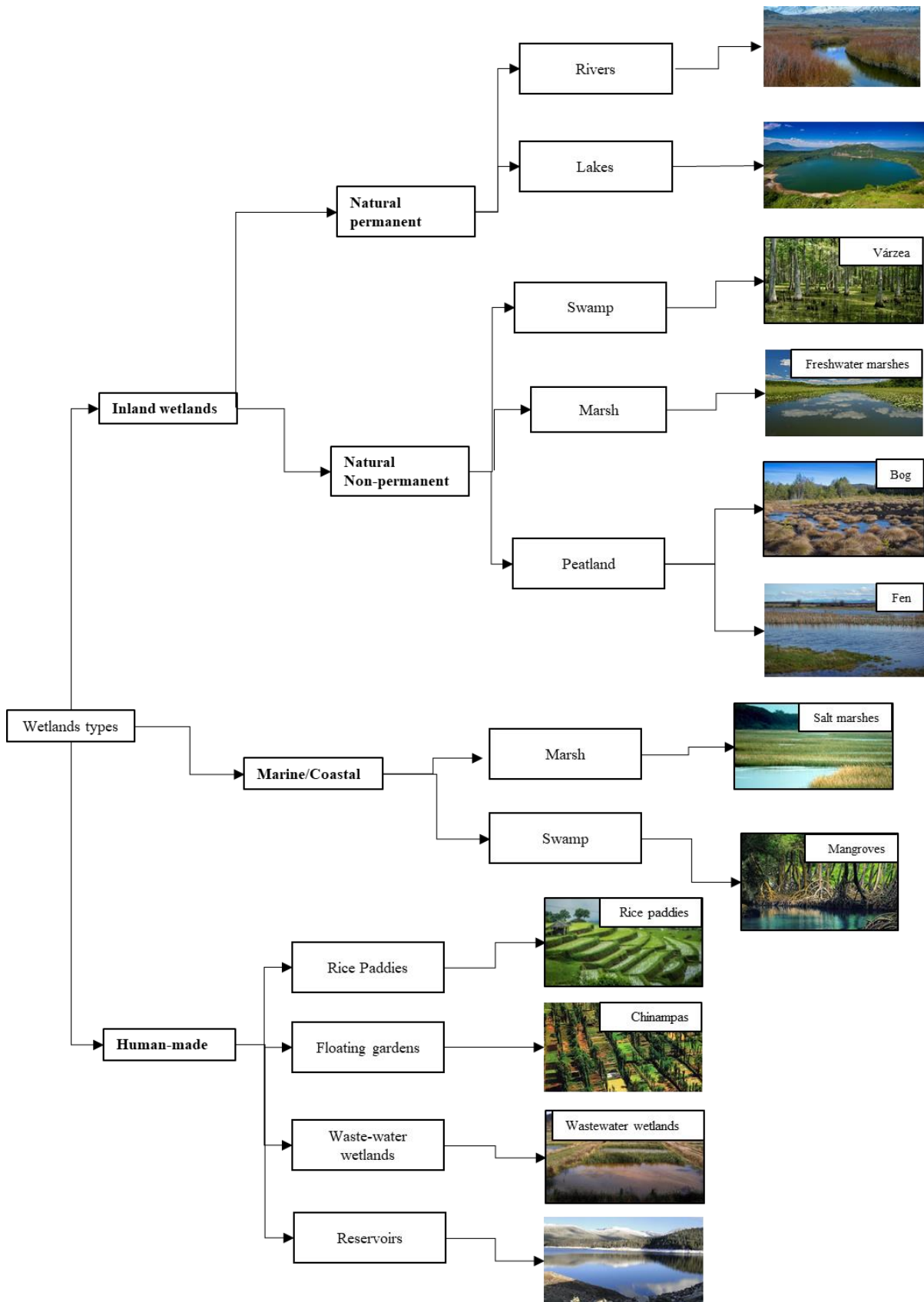
	<ul style="list-style-type: none"> <li>• <i>Salt marshes</i>: a halophytic grassland on alluvial sediments bordering either saline water bodies where water level fluctuates tidally or non-tidally (Deegan et al., 2012a).</li> </ul>
	<ul style="list-style-type: none"> <li>• <i>Tidal freshwater marsh</i>: marsh along rivers and estuaries close enough to the coastline to experience significant tides by non-saline water. Vegetation is similar to non-tidal freshwater marshes (Yang et al., 2013).</li> </ul>

## PEATLANDS

This term is a generic denomination of any wetland that accumulates partially decayed plant matter (peat), within this terms there are different kind of wetlands (Mitsch and Gosselink, 2015):

	<ul style="list-style-type: none"> <li>• <i>Bog</i>: A peat-accumulating wetland that has no significant inflows or outflows and supports acidophilic mosses, particularly <i>Sphagnum</i>, they dominate boreal peatlands (Johnson et al., 2015).</li> <li>• <i>Fen</i>: A peat-accumulating wetland that receives some drainage from surrounding mineral soil and usually supports marsh-like vegetation (Gorham, 1991).</li> </ul>
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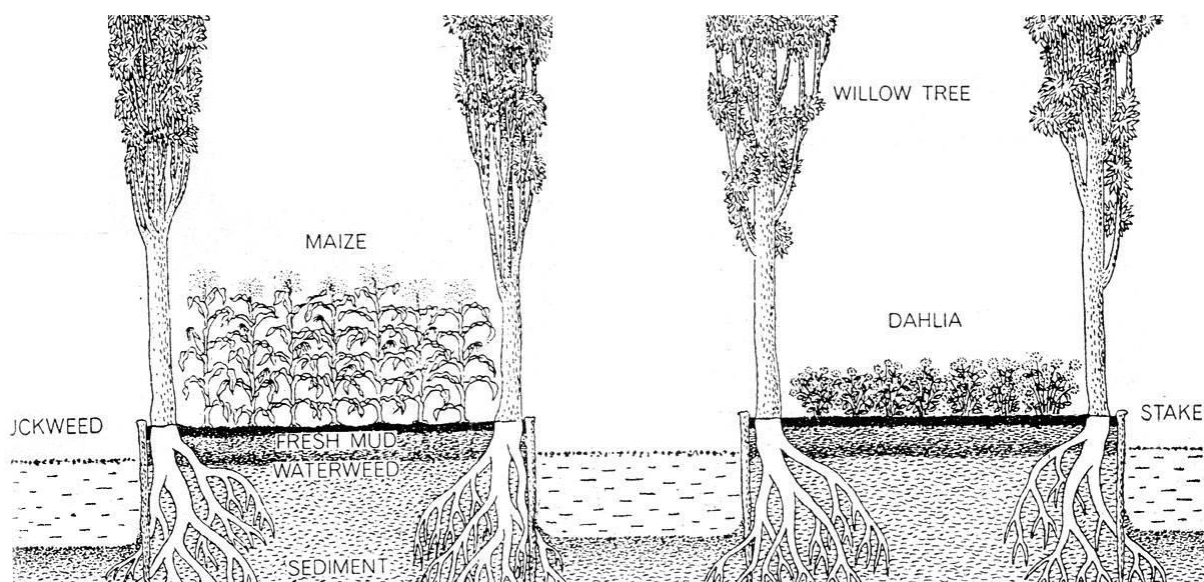
GENERAL INTRODUCTION



**Figure 3.** Wetland typology with some photographs as examples of each kind of wetlands. Photos from free access google images consulted: 22-02-2021.

## WETLANDS AND HUMAN DEVELOPMENT

Many cultures all around the world have lived among and even depend on wetlands for centuries. A remarkable example of an ancient sustainable social-ecological system developed during Aztec empire is a technique to farm in the swamps (Cox et al., 2020). They had a network of channels and artificial islands, called *chinampas*. The channels were dug to facilitate water flow, and the nutrient-rich mud was placed on the island. Maize, beans, potatoes, tomatoes and pepper were the main crops. Willow trees bordered the islands to avoid erosion. This design optimized the water resources, and the crop rotation system maintain the soil fertility (Figure 4). This technique still existing, and it had been recognized by FAO, as an Agricultural Heritage System of Global Importance (AHSGI) ( FAO, 2017).



**Figure 4.** Scheme of the traditional chinampa structure, from free access Pinterest images, consulted 22-02-2021.

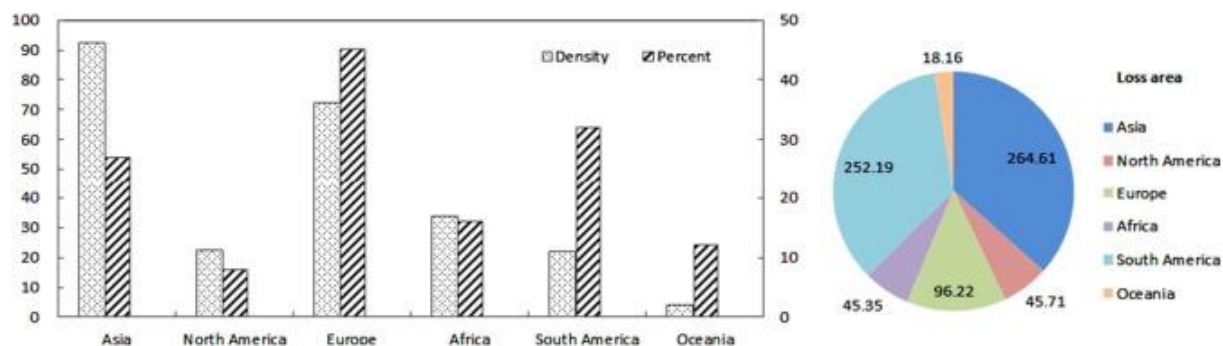
In Asia, ancients' technics regarding rice culture are widespread in China, Korea, Japan and Philippines. Half of the world population is fed by rice paddy systems (Aselmann and Crutzen, 1989; Luo et al., 2014). These terraces are very productive and most of the ancient techniques are still been applied. Half of Bangladesh's land surface is covered by freshwater and saltwater wetlands. Aquaculture ponds and floating garden agriculture practices are ancient techniques that have also permitted to give an access to lands to the poorest communities (FAO, 2015).

Nonetheless, in the last century, wetlands have been destroyed at alarming rates throughout the developed and developing world (Global Forest Watch, 2021; Richards and Friess, 2016; Trancoso et al., 2009). Due to the technical hitches for monitoring and wetland extension, is difficult to determine precisely wetlands global loss. The first wetlands long-term global



estimation recorded a loss between 54-57% since 1900, and 87% since 1700. With the highest declining rate of wetlands loss during the 20<sup>th</sup> and early 21<sup>th</sup> centuries (Davidson, 2014).

The vast population demanding high levels of food and housing result in the acceleration of the development of agriculture and urbanization was the main cause of the sever loss of wetlands worldwide. The greatest wetland loss happened in Asia, but the most serious situation is in Europe (Figure 5) (Hu et al., 2017)



**Figure 5.** The percentage of wetland loss and population density (inhabitants/km<sup>2</sup>) among different continents (unit of area: 10<sup>4</sup> km<sup>2</sup>) from (Hu et al., 2017).

However, a big campaign for paradigm change and protection of these valuable ecosystems is becoming the norm. Healthy, functioning natural wetlands are critical to human livelihoods and sustainable development (Gardner and Finlayson, 2018).

Wetlands have been included as part of United Nations sustainable goals as they have been identified very valuable for stabilize water supplies, thus mitigating both floods and drought. In addition, they cleanse polluted water, protect shorelines, and recharge groundwater. Their protection and monitoring is included in goal N.6 “Ensure availability and sustainable management of water and sanitization for all” ( UNDP, 2017)

Moreover, Natural based Solutions (NbS) term refers to actions to protect, promote sustainable management, and restore natural or modified ecosystems that address societal challenges effectively and adaptively, simultaneously providing benefits to human well-being and biodiversity. These NbS, shouldn't be confused with smaller scale urban green solutions as constructed wetlands. However, all these measures are contributing to reduce pollution and ecosystem degradation (Cohen-Shacham et al., 2016). Wetland management requires a complete understanding of the scientific aspects of wetlands in interaction of the legal, institutional, cultural and economic frameworks.

In the present study, the focus will be the role of natural wetlands regarding nitrogen cycle processes. The particularity of wetlands is high frequency of anoxia in soil. This condition slows down the decomposition of organic matter and drive bacterial community to degrade nitrates to obtain oxygen and then degas mainly  $N_2$ , and a small fraction of  $N_2O$ , this process is called denitrification (Marín-Muñiz et al., 2014). The next section contextualized nitrogen cycle in wetlands and emphasises denitrification within the nitrogen cycle.

## NITROGEN CYCLE

Nitrogen is a biogeochemical cycle by which nitrogen is converted into multiple chemical forms as it circulates through biotic (biosphere) and abiotic (lithosphere, atmosphere and hydrosphere) compartments of the Earth (Galloway et al., 2013).

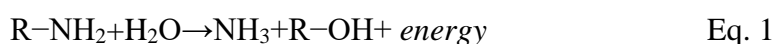
Nitrogen cycle is of particular interest to ecologists because nitrogen has limited availability for biological use. Leading to a range of metabolic, evolutionary and symbiotic strategies of bacteria and plants to optimize the nitrogen offered (LeBauer and Treseder, 2008). Availability can affect the behaviour of microbial communities, which have a central role in ecological systems dynamics (Philippot et al., 2013). In turn, primary production, decomposition and biodiversity is affected (Galloway et al., 2003).

Dinitrogen ( $N_2$ ) is the most abundant gas of Earth's atmosphere (80%), however in this chemical form is not available for the majority of living organisms (99%) (Galloway et al., 2003). The conversion of  $N_2$  (nonreactive N), into reactive N (Nr) or biologically available forms is a process that naturally (undisturbed scenario) was carried out by lightning and by nitrogen-fixing bacteria. Lightning fixes  $< 10 \text{ TgN.yr}^{-1}$  (Galloway et al., 1995) and has not been affected by human activities. Instead, biological nitrogen fixation (BNF) the main natural process ( $\sim 128 \text{ TgN.yr}^{-1}$ ) is variable to environmental dynamics and has been perturbed by human activities. BNF represents a regulatory factor on the availability of nutrients for primary production in every ecosystem (Galloway et al., 2004).

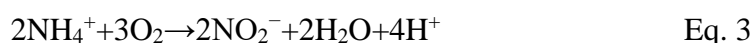
In undisturbed, natural soils, roughly 95 % of the nitrogen is found in living material (i.e. plants, animals, and microorganism). They contain rich nitrogen compounds as amino acids, nucleic acids, and proteins in their tissues. Is then the decomposition of these organisms that form soil organic matter. If organic matter is rich in nitrogen, organic material is transformed to inorganic ammonium and nitrate forms which plants and other soil organisms use (mineralization). When organic matter has low levels of nitrogen they will be consume or immobilize (C:N ratio greater than 40:1).

In wetlands, nitrogen fixation can occur in overlying waters, in the aerobic soil layer, in the oxidized rhizophore of the plants, and on the leaf and stem surfaces of plants. Bacterial nitrogen fixation can be carried out by nonsymbiotic bacteria, or by symbiotic bacteria *Rhizobium*, or by certain actinomycetes. Bacterial fixation is the most significant pathway for nitrogen fixation in salt marsh soils, while nitrogen-fixing bacteria are virtually absent from the low pH peat of northern bogs. Cyanobacterias (blue-green algae) are common nitrogen fixers in wetlands, occurring in flooded delta soils, in northern bogs and in rice cultures.

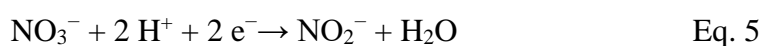
Nitrogen **mineralization** is a generic term that refers to **ammonification** (Eq. 1) and ammonia hydrolysis (Eq. 2), ammonium  $[\text{NH}_4^+]$  and ammonia  $[\text{NH}_3]$  are closely related. When pH is high ammonia is favoured as gas form once is formed it quickly volatilized. With low to moderate pH soluble ion (ammonium) is favoured. Ammonium does not easily leach, and is an exchangeable cation, and is an energy-rich compound. Moreover, it can be trapped between layer of clay minerals that exhibit shrinking and welling (i.e. ammonium fixation).

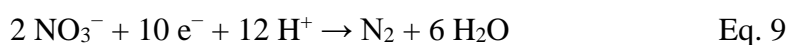
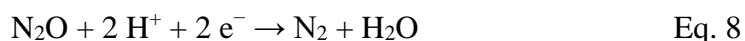
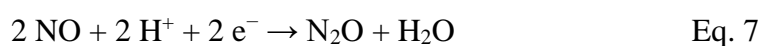
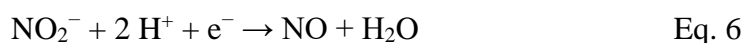


In the presence of oxygen, ammonium is first transformed to nitrite  $[\text{NO}_2^-]$ , by oxidizing bacteria such as *Nitrosomonas* (Eq. 3) and the oxidation of nitrite to nitrate  $[\text{NO}_3^-]$ , by *Nitrobacter* (Eq. 4), these two steps are needed for a full **nitrification**.



Nitrates are negatively charged anion and as such, is repelled by negatively charged soil colloids. Nitrate salts are highly soluble, so nitrates move with soil water and can be easily leached through soil. Additionally, nitrates can be chemically reduced through **denitrification**. In poorly aerated soils, when soils are saturated with rain or flooded by irrigation or river overflow denitrification can be a major mechanism for nitrogen loss. Denitrifies are heterotrophic bacteria, that need food and oxygen, when oxygen is not freely available, then denitrifies are capable to strip the oxygen from nitrates molecules, by a chain reaction catalysed by enzymes (Eq. 5-8). The whole process can be expressed as a balanced redox reaction (Eq. 9).



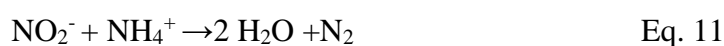


**Dissimilatory Nitrate Reduction to Ammonia** is the conversion from mobile nitrates to the less-mobile ammonium (Eq. 10).

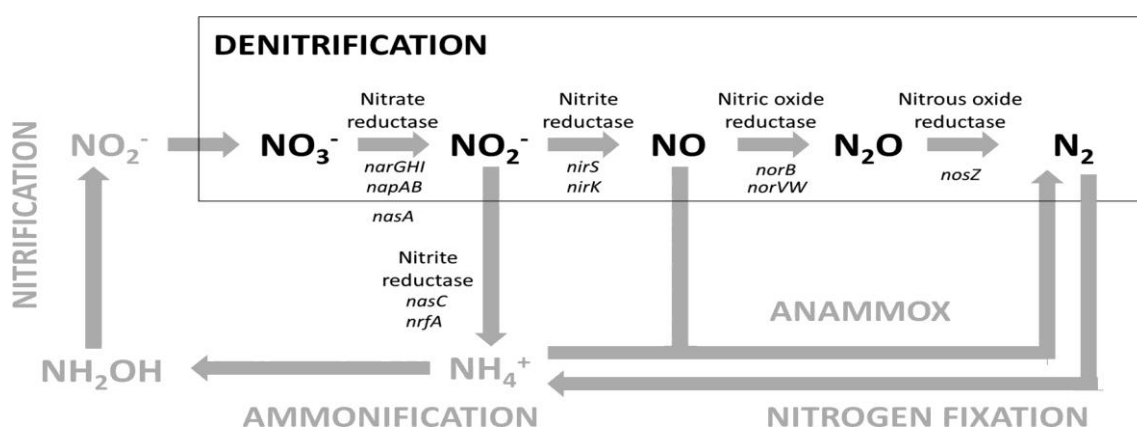


This process yields energy to the bacteria capable of carrying out this process. Megonigal et al., 2004, has reported that high availability of organic carbon and/or low nitrate concentrations favour DNRA over denitrification.

**Anammox** (for anaerobic ammonium oxidation) involves nitrite-nitrogen (rather than nitrate-nitrogen as the oxidant (Eq. 11)). This process is important in soils where denitrification is limited by lack of organic carbon (Megonigal et al., 2004). In wetlands it has been observed the presence of bacterial anammox genes (Ligi et al., 2015) but the estimation of their contribution is not yet quantified, but it is suggested that anammox converting ammonium to dinitrogen gas may be compensate for the relatively low rates of denitrification (Song et al., 2014).



Altogether, the reactions and various forms of nitrogen explained above with emphasis on denitrification are summary in Figure 6.



**Figure 6.** Simplified nitrogen cycle, with denitrification highlighted. Denitrification starts in the reduction of nitrates ( $\text{NO}_3^-$ ) to dinitrogen ( $\text{N}_2$ ). The enzymes involved in the denitrification pathway are listed next to the reaction they catalyse, image from Alvarez et al., 2014.

Nitrogen is the most important nutrient required by plants, and large amounts are needed. The Haber-Bosch process, developed in 1913, is now the primary source of nitrogen in fertilizers. About as much nitrogen is fixed by this process as is fixed by all natural processes combined (Galloway et al., 2004). The use of artificial nitrogen fertilizers, fossil fuel combustion, release of nitrogen in wastewater have dramatically altered the global nitrogen cycle (Kuypers et al., 2018). Causing negative effects in the natural environment but also human health (Butchart et al., 2010; Townsend et al., 2003).

Increasing levels of deposition of reactive nitrogen (Nr) in terrestrial and aquatic ecosystem has overcome the resilience of many natural ecosystems around the world. Aquatic ecosystems are suffering acidification, eutrophication and toxic issues for animals (Deegan et al., 2012; Huang et al., 2017; Smith, 2003). Investigation for controlling nutrient flow to the coastal areas had proposed that revision of agronomic approaches or wetlands creation and riparian restoration are the most effective measurements. In the case of the Mississippi river basin where the hypoxic zone of 14 350 km<sup>2</sup> appears annually in the Gulf of Mexico, denitrification in wetlands was a particularly process recognized in the recommendation. Proposing that two million hectares (less than 1% of Mississippi River Basin) of restored and created wetlands and riparian buffers will carry out enough denitrification to substantially reduced the nitrogen inflow to the Gulf of Mexico (Mitsch et al., 2001). Efforts restoring wetlands are increasing, however, the hypoxia zone in the Gulf of Mexico continues to grow, as the nitrate influx is becoming more and more important (Murphy et al., 2013).

Nitrogen cycle in wetlands is one of the most important and studied chemical cycles in wetlands. Due to the presence of nitrogen present in different oxidation states, and continues fluctuations of anoxic- oxic environments. Including the role of wetlands in the global nitrogen cycle is therefore key to understand the cycle itself (Song et al., 2014; Van Cleemput et al., 2007).

Measuring denitrification in wetlands at global scale is a process composed by two parts: in situ measurements, but doing so at global scale is costly and not feasible. Modelling, which represents an important tool and gives extrapolation opportunity of punctual observations in temporal and spatial dimensions. The use of both technics may enrich the possibility of estimate (quantitatively) and predict natural wetlands resilience and relevance in the global nitrogen cycle. Next section will explain the strengths and weakness of each one and their complementary in the present study.

## STUDYING NITROGEN CYCLE IN WETLANDS

This thesis is composed by two parts, one part is based on a fieldwork experience that was critical to understand the sensibility of the process in hand, collect data and carry on a laboratory experiment. The second part was developing a denitrification model, which will represent the first attempt to estimate at global scale a dynamic approach of natural wetlands denitrification. The field data from the first part of the thesis was later on used to calibrate and validate the model.

## FIELDWORK

Traditionally in life and environmental sciences, fieldwork is assumed to be the most important and often essential component of research delivering a real-world relevant content (McCall, 2006) and enabling the deep learning which comes from systematic field observation a main pillar of scientific method (Herrick, 2010). The term fieldwork has different meanings within environmental sciences.

*Fieldwork refers to primary research that occurs ‘in the field’ – that is, outside the controlled settings of the laboratory or theory. Frequently fieldwork includes ‘field experiments’ (McCall, 2006).*

*A second meaning has reference to the period of preliminary work and/or data collection that does take place in field settings, as distinguished from other phases of those same studies (such as design, analysis, and write-up) that take place in more conventional and research-controlled settings (McCall, 2006)*

Even though fieldwork is not replaceable and is fundamental in understanding the ecosystem behaviour, it can be limited when responding to the quantification of ecosystem resilience towards the global change (Miller et al., 2020). Fieldwork may be limited to specific areas, and a big bias of fieldwork data is encounter when upscaling to global approach. A huge gap of long-term data records in the global south is evident due to the lack of resources (Ríos-Saldaña et al., 2018). Moreover, there is no a consensus for observation measurements or collecting data protocols what increments the bias and the difficulties to compare the data in different sites, by different people and in different epoch. The gaps of the data that had not been recorded on the past cannot be filled up and alternatives to respond need to be developed. To counterbalance

these issues environmental modelling research strategy may be relevant for a global scale approach (Laniak et al., 2013).

## MODELLING

Scientific research resides in the accumulation of observations of systems and system behaviour under undisturbed circumstances and during experimental manipulations. The scientific method lays in four main conditions: (i) observations, (ii) experimentation, (iii) context, (iv) cross-referencing and connecting threads of the other three points (Wainwright and Mulligan, 2002). Observations provide the evidence upon which hypothesis can be generated about the structure and operation (function) of the systems. These hypotheses can be tested against new observations and, where they prove to be reliable descriptors of the systems or system behaviour, then they may eventually gain recognition as proven theory of general law as far as that is possible (Wainwright and Mulligan, 2002).

Modelling supports in the conceptualization and exploration of the behaviour of objects or processes and their interaction as a method of better understanding these and generating hypotheses concerning to them. Modelling also supports the development of (numerical) experiments in which hypotheses can be tested and outcomes predicted. In science, understanding is the goal, and models serve as tools towards that end (Baker, 1992).

*A model is a simplified representation of a system, which takes into account only the properties considered essential and sufficient to represent the phenomena to be studied* (Wainwright and Mulligan, 2002).

Modelling is not an alternative to observation. Yet, under certain circumstances, can be a powerful tool in understanding observations, as well as in developing/testing theory. Direct observations will always be closer to truth and must remain the most important component of scientific investigations (Klemeš, 1997).

The design of the whole model results from a compromise between realism, the databases available for validation and the precision necessary and sufficient to meet the objective of the model. Any model is inseparable from its function. Therefore, a preliminary analysis of the system is mandatory in order to identify the key processes. “*What is a model for?*” is a crucial questions since the model is above all intended to respond to the problems posed (Anderson and Bates, 2001).

The best model is always that which achieves the greatest realism with the least parameter complexity (parsimony) and the least model complexity. Realism can be measured objectively as agreement between model outputs and real-world observations or less objectively as the process insight or new understanding gained from the model. Parsimony (using no more complex a model or representation of reality than is absolutely necessary), has been a guiding principle on scientific investigations and is a prerequisite for effective scientific explanation (Lark, 2001).

### ENVIRONMENTAL MODELLING AND SPATIOTEMPORAL ANALYSIS

The context for environmental modelling at present is (mainly) the concern relating to human-induced climate change, and land degradation. These are application-driven investigations that provide an important means by which scientist can interact with and influence policy at local, national and international levels. Models can be a baseline of ensuring environmental protection, as long as we are careful about how the results are used (Bair, 2001).

There is other understanding-driven investigations that use models to develop our understanding of the processes of the environment around us. Processes are not observable features, but their effects and outcomes are (Richards, 1990). Models can thus be used to evaluate whether the effects and outcomes are reproducible from the current knowledge of the processes. This approach is not straightforward, as it is often difficult to evaluate whether process or parameter estimates are incorrect, but it does at least provide a basis for investigation. Of course, understanding-driven and application-driven approaches are not mutually exclusive, and the application driven is directly linked to the understanding. (Wainwright and Mulligan, 2002).

Modelling as a research tool, provides an important link between theory and observation, and provides a platform of testing ideas of how the world works. This link is important in that environmental scientist generally deal with temporal and spatial scales that are beyond the limits of observation of the individual. Environmental modelling deals with representation of processes that occur in the real world in space and time.

Model construction can be done by two different approaches, bottom up or top down. A bottom up model where the parts of the system are defined in detail. Once the parts are designed and developed, then these parts or components are linked together to prepare a bigger component.



The focus of this type of model is on identifying and resolving smallest problems and then integrating them together to solve a bigger problem (Castella et al., 2007).

On the other hand, top-down model is a system designed approach where starts from the system as a whole. Then this system is divided into smaller sub-applications with more details. Top down focus is on breaking the bigger problem into smaller one and then repeat the process with each problem. Top-down models are an interesting option to describe processes, especially when data availability is limited (Young, 2003).

In the present work, a combination of both approaches was used. First, a bottom up approach was adopted to develop a process-based model. This model includes emission references and spatial extrapolation of field flux measurements. When applying the model, a global scale a top down approach was used. Upscaling the model aims to give an estimation of the global wetland contribution to the nitrogen cycle, and identification of the hot moments and hot spots, yet not to be compared with punctual measurements. A strict top down model regarding the N<sub>2</sub>O emissions, are the once built up by climate and atmospheric transport modelling that constitute the greenhouse gas inventories (i.e. FAOSTAT, EDGAR, IPCC) (Syakila and Kroeze, 2011; Tian et al., 2020).

### ERRORS AND UNCERTAINTIES

No measurement can be made without error. There is always an element of interference when recording an observation. Thus, the act of observation perturbs what we are measuring. Furthermore, the devices used to measure will have their own uncertainties of measurement, even if they are the state-of-the-art electronic devices (Refsgaard et al., 2007).

To counter this problem, we may repeat the measurement to provide an average. Sampling theory suggests that a greater number of measurements will provide a better representation, with the standard error decreasing with the square root of the number of measurements made. However, a larger number of samples will take a longer time to make, and thus to have possible temporal changes to contend with in giving added error. Invasive methods will cause system perturbation and some parameters may be particularly sensitive (Dale and Van Winkle, 1998).

Non-invasive methods are likely to have a larger error but they prevent disturbance and a larger number of measurements being taken in a specific area, which is problematic if we are interested in spatial variability or if we wish to simulate at larger scale. In that case, the choice

for rapid results techniques, which perhaps provide less precise measurements, could be a solution. Taking into account the error and precision, precision in the sense of the exactness with which a measurement is taken (Bärlund and Tattari, 2001).

To summarize, all measurements should have their associated error cited, so that the implications can be considered and care be taken in interpreting results. Field measurements are often prone to error, because of the difficulty of collecting data and controlling environmental hazards. Error is an important part of the modelling process, and it must be incorporated within the framework of any approach taken. Uncertainty evaluation must be done as far as possible (Kavetski et al., 2003). Modelling is an art and can increase our understanding of environmental systems, but it requires great care and must be followed systematically (Wainwright and Mulligan, 2002).

### SATELLITE REMOTE SENSING

Remote sensing field is large and many definitions have been attributed to this term, meaning that it is the art or science of telling something about an object without touching it (Fischer et al., 1976). The remote sensing to be discussed here is related to the observation of Earth's land and water surface.

*“Remote sensing is the practice of deriving information about the Earth's land and water surfaces using images acquired from an overhead perspective, using electromagnetic radiation in one or more regions of the electromagnetic spectrum, reflected or emitted from the Earth's surface.”* (Campbell and Wynne, 2011)

Nowadays, many corporations and national governments operate platforms (satellites) with sensors specifically designed for observation of Earth's surface. Remote sensing is a powerful tool for its capacity of providing observations of large areas in a single image, fine detail and systematic repetitive graphic infrastructure, a useful way to detect, quantify and monitor land and water dynamics in the spatial and temporal dimensions.

### EARTH OBSERVATIONS

In the present study, we are looking for the dynamic of non-permanent wetlands, to identify the activation/deactivation of the denitrification process. Therefore, a parameter able to show wetlands dynamics in the soil moisture (i.e. extension variations and saturation periods). It is widely known that satellite data is relevant for its capacity of recording Earth's surface dynamically. The sensor should be able to record changes of soil water, even if vegetation is

present. Soil moisture measurements from L-band for Weather Satellite Data Receiving System seems to be the best tool. Showing large contrast between water and land. In addition, the influence of the vegetation on the signal is low. At L-Band, the emissivity may vary from almost 0.5 for a very wet soil to almost 1 for a very dry soil. (Kerr et al., 2010). These kinds of measurements are collected from the SMOS mission, explained in the next section.

### SMOS MISSION

The Soil Moisture and Oceanic Salinity (SMOS) mission was led by European Space Agency (ESA) in collaboration with the Centre National d'Etudes Spatiales (CNES) in France and the Centro para el Desarrollo Tecnológico Industrial (CDTI) in Spain. SMOS was launched on November 2, 2009. It carries a single payload, an L-Band 2-D interferometric radiometer operating in the 1400-1427-Mhz protected band. The instrument receives the radiation emitted from Earth's surface, which can then be related to the moisture content in the first few centimetres of soil over land, and to salinity in the surface water of the oceans (SSS) (Kerr et al., 2010).

## OBJECTIVES

The objective of this PhD is to improve our knowledge towards denitrification dynamics in wetlands soils. First by fieldwork experience and then developing and applying a model that quantifies dynamically denitrification capacity of natural wetlands soils at global scale, combining Earth Observations and a parsimonious model. The specific objectives are:

1. By an exhaustive search of the most relevant research carried out in recent years on the study of denitrification in wetlands on a global scale. The identification of the gap to develop and the timely of the present thesis to be develop (Chapter II).
2. By a fieldwork experience in the Amazonian floodplain, understand the limitations and strengths of fieldwork, as well as the need of monitoring field data to better quantify the anthropogenic impact and to better identify the particularities of each study site (Chapter III)
3. By developing a simplified physical model, calibrated with the soil samples (Chapter III) quantify and identify the spatial and temporal dynamics of Amazonian wetlands' role in the global nitrogen cycle (Chapter IV).
4. By applying worldwide, the physical model (chapter IV), identify the hot moments and hot spots of denitrification outgassing in natural wetlands ecosystems, to recognize the importance of wetlands in the global nitrogen cycle (Chapter V)

Conclusions and perspectives of the present work are summarized and possible ways to keep developing research lines are presented (Chapter VI).

## GENERAL INTRODUCTION

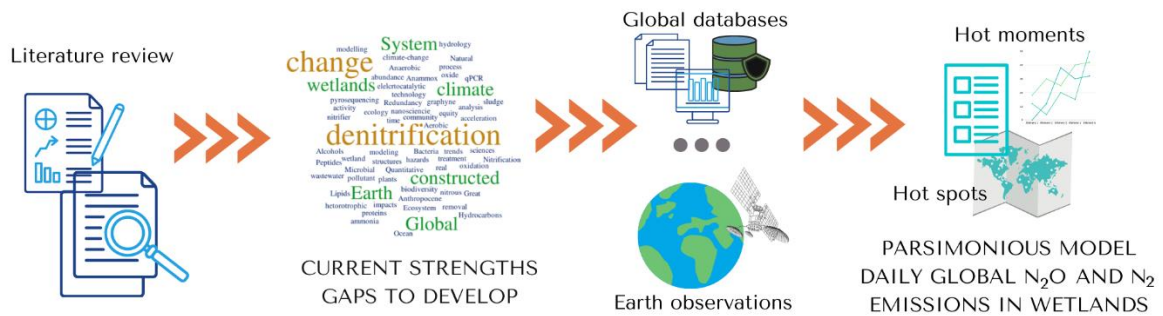
# CHAPTER II

## DENITRIFICATION IN WETLANDS: A REVIEW TOWARDS A QUANTIFICATION AT GLOBAL SCALE

How much do we know about  
**WETLANDS' ROLE**



IN THE GLOBAL NITROGEN CYCLE?



### ABSTRACT

This chapter is a quantitative literature review that identified the trends of the research focused on wetlands denitrification at global scale in the last fifty years. This chapter was thought to identify the main gaps of global modelling, and compile the most relevant global databases that are suitable for global modelling of denitrification in wetlands.

As a conclusion of this chapter, a conceptual model was constructed. The needed input data was identified and the most suitable and updated databases available (i.e. global databases and satellite data) to be used were identified. This literature review gives a solid basis and context of the need of valorising natural wetlands ecosystems and quantifies their role in the global nitrogen cycle.

### RÉSUMÉ

Ce chapitre est une revue quantitative de la littérature qui a identifié les tendances de la recherche sur la dénitrification des zones humides à l'échelle mondiale au cours des cinquante dernières années. Ce chapitre a été pensé pour identifier les principales lacunes de la modélisation globale, et compiler les bases de données globales les plus pertinentes qui conviennent à la modélisation globale de la dénitrification dans les zones humides.

En conclusion de ce chapitre, un modèle conceptuel a été construit. Les données d'entrée nécessaires ont été identifiées et les bases de données disponibles les plus appropriées et les plus récentes (c'est-à-dire les bases de données mondiales et les données satellitaires) à utiliser ont été identifiées. Cette revue de la littérature donne une base et un contexte solides à la nécessité de valoriser les écosystèmes naturels des zones humides et de quantifier leur rôle dans le cycle global de l'azote.

### RESUMEN

Este capítulo es una revisión bibliográfica cuantitativa que identifica las tendencias de la investigación centrada en la desnitrificación de los humedales a escala global en los últimos cincuenta años. Este capítulo fue pensado para identificar las principales lagunas de la modelización global, y compilar las bases de datos globales más relevantes que son adecuadas para la modelización global de la desnitrificación en los humedales.

Como conclusión de este capítulo, se construyó un modelo conceptual. Se identificaron los datos de entrada necesarios y las bases de datos más adecuadas y actualizadas disponibles (es decir, bases de datos globales y datos de satélite) que se utilizarán. Esta revisión bibliográfica proporciona una base sólida y un contexto de la necesidad de valorizar los ecosistemas de humedales naturales y cuantificar su papel en el ciclo global del nitrógeno.

### VALORISATION

This chapter has been already published:

Martínez-Espinosa, C., Sauvage, S., Al Bitar, A., Green, P. A., Vörösmarty, C. J., & Sánchez-Pérez, J. M. (2020). Denitrification in wetlands: A review towards a quantification at global scale. *Science of the Total Environment*, 142398.

<https://doi.org/10.1016/j.scitotenv.2020.142398>

## ABSTRACT

Research to understand the nitrogen cycle has been thriving. The production of reactive nitrogen by humans exceeds the removal capacity through denitrification of any natural ecosystem. The surplus of reactive nitrogen is also a significant pollutant that can shift biological diversity and distribution, promotes eutrophication in aquatic ecosystems, and affects human health. Denitrification is the microbial respiration in anoxic conditions and is the main process that removes definitively nitrates from the ecosystem by returning of reactive nitrogen (Nr) to the atmosphere as  $N_2$  and  $N_2O$  emissions. This process occurs in the oceans, aquatic ecosystems and temporary flooded terrestrial ecosystems. Wetlands ecosystems are rich in organic matter and they have regular anoxic soil conditions ideal for denitrification to occur.

In the current paper, we provide a meta-analysis that aims at exploring how research around global nitrogen, denitrification and wetlands had evolved in the last fifty years. Back in the time, wetland ecosystems were seen as non-exploitable elements of the landscape, and now they are being integrated as providers of ecosystem services. A significant improvement of molecular biology techniques and genetic extraction have made the denitrification process fully understood allowing constructed wetlands to be more efficient and popular. Yet, large uncertainties remain concerning the dynamic quantification of the global denitrification capacity of natural wetland ecosystems. The contribution of the current investigation is to provide a way forward for reducing these uncertainties by the integration of satellite-based Earth Observation (EO) technology with parsimonious physical based models.

### Keywords

Nitrogen cycle, denitrification, wetlands, global nitrogen, earth observations.



## INTRODUCTION

Nitrogen, together with carbon, hydrogen, oxygen and phosphorus constitute the core elements that sustain life, and they are the most abundant elements on Earth (Fowler et al., 2013). The pathway of these elements along the different compartments of the abiotic Earth (atmosphere, lithosphere and hydrosphere) interacting with the biotic component are called biogeochemical cycles (Van Cappellen, 2003). The understanding of nitrogen biogeochemical cycle has been a long process, the discoveries of the different species were elucidated in a time span of around 300 years (Galloway et al., 2013). Dinitrogen ( $N_2$ ), the most abundant form of nitrogen in an inert form not available for the majority of living organisms (Craine et al., 2015; Vitousek et al., 1997).

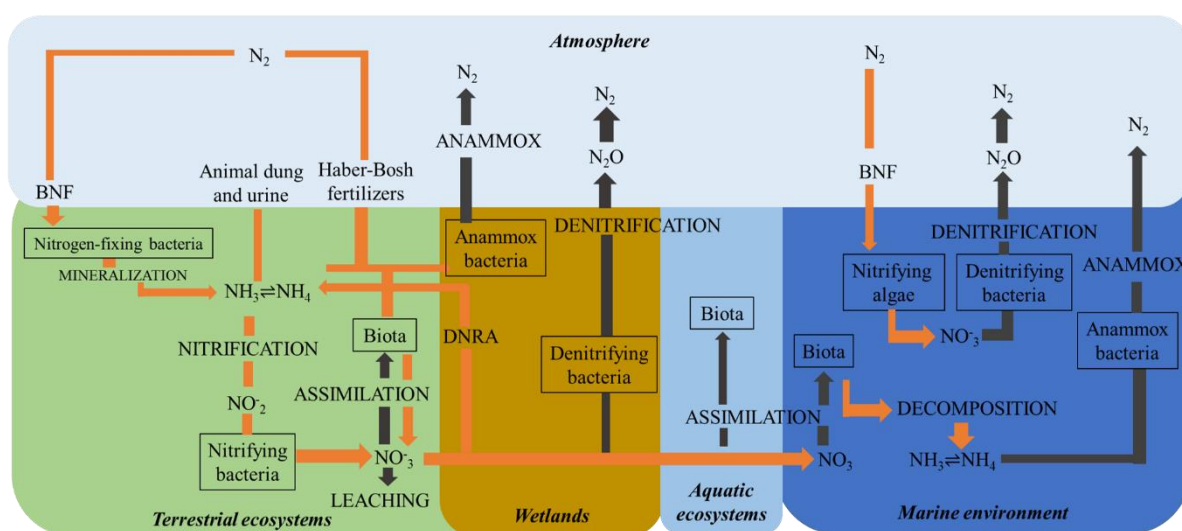
In 1880, Biological Nitrogen Fixation (BNF) was discovered and identified as principal pathway to convert inert nitrogen to reactive Nitrogen (hereafter Nr) (Erisman et al., 2008a) meaning that crop yield and insuring food security for the growing population depended on BNF. Since then, Nr was identified as a critical element for food production, this main concern pushed research towards developing alternatives (Smil, 2001). The turning point of this limitation was the synthesis of ammonia ( $NH_3$ ) from dinitrogen ( $N_2$ ), the well-known Haber-Bosh process developed in 1913 (Tilman et al., 2011). This synthetic fertilizer became popular and increased exponentially food production. Nowadays 50% of the human population's food consumption depends on it (Erisman et al., 2008a). By the 1970's the overall production of synthetic fertilizer surpassed terrestrial BNF (Galloway et al., 2013). Besides the positive impact on food production, artificial Nr brought with it numerous negative impacts including (i) biodiversity of terrestrial ecosystems (Hooper et al., 2012); (ii) soil acidification (Foley et al., 2005); (iii) eutrophication in aquatic and coastal ecosystems (Smith, 2003); (iv) greenhouse gas effect (Beaulieu et al., 2011; Bouwman et al., 2002), (v) acid rain (Denmead et al., 2010), (vi) smog and stratospheric ozone depletion (Vitousek et al., 1997), and (vii) detriments to human health (Powlson et al., 2008). One of the most remarkable impact of Nr is the current anthropogenic greenhouse emissions of  $N_2O$ , which are estimated to have increased from  $0.7 \text{ TgN.yr}^{-1}$  in 1860 to  $6.9 \text{ TgN.yr}^{-1}$  in 2006 (Ciais et al., 2014; Davidson and Kanter, 2014; Tian et al., 2018). Agricultural sector is responsible for ~60%  $N_2O$  emissions, cropping is linked to intense irrigation, yet these emissions can be compensated with the crop yield (Denmead et al., 2010). Nevertheless, the main source of greenhouse gases is coming from the industry (Trost et al., 2016), the production of mineral N fertilizer is one of those energy and greenhouse gas intensive processes (Lal, 2004).

To counteract the negative impacts of  $N_r$ , several governmental and international institutions like the Environmental Protection Agency (EPA) in U.S., the European Environmental Agency (EEA) from the European Commission, and United Nations Environmental Programme (UNEP) formulated legislations recognizing and attempting to limit the impacts of nitrogen on water quality, air quality and human health (Eulefeld, 1979). The two straightforward solutions known are: (i) stopping synthetic fertilizer production and (ii) enhancement of conversion of  $N_r$  back to nonreactive form ( $N_2$ ). However, the intended goals have not been achieved yet (Conijn et al., 2018). A legislative framework based on policies limiting excessive use of fertilizer, promotion of circular economy models and developing support for N waste recycling technologies can improve N management (Brownlie et al., 2015). Besides technology, ecosystem based solutions are able to mitigate in a variety of ways the anthropogenic impact (Cohen-Shacham et al., 2016; UNEP and TNC, 2014; Vörösmarty et al., 2018).

The major natural process carried out by microorganisms in the lithosphere able to convert  $N_r$  to  $N_2$  with a little percentage of  $N_2O$  (when completed) (Canfield et al., 2010) is called heterotrophic denitrification discovered in 1886 by Ulysse Gayon and Gabriel Dupetit. (Elmerich, 2007; Payne, 1986). Denitrification is considered as a regulating service, and it has been well understood at microbiological level, being key to produce technology that reproduces the optimum conditions needed to execute this process in controlled conditions i.e. constructed wetlands. Many advantages of the use of this technology had improved water quality worldwide as a cost effective and low maintenance alternative (Vymazal, 2011a). Yet, quantification of denitrification in natural wetlands is much more complex, and straightforward identification of conditions and variables affecting the process are still developing (Han et al., 2017; Malique et al., 2019).

Denitrification also occurs in dry soils that become inundated during irrigation or floods, having specific denitrification peaks. Wetlands instead have a continuous inundation dynamics that allows the process to happen regularly (Czuba et al., 2018; Howarth et al., 1996; McDonald et al., 2011; Saunders and Kalff, 2001). Aquatic ecosystems like rivers and lakes also effectuate denitrification especially in the sediment part (Sun, 2015; Viner, 1982), as well as, in marine environments where it was identified that up to 50 per cent of the total nitrogen turnover is due to another process called anammox (Galloway et al., 2013, 2004; Kuenen, 2008). In 1977 anaerobic ammonium oxidation (anammox) was hypothesized by Engerlbert Broda, and finally observed in 1986 in a wastewater treatment facility (Kuenen, 2008). Anammox organisms have the ability to combine ammonium and nitrite or nitrate to form  $N_2$ . becoming the second natural process known to return  $N_r$  to the atmosphere (Burgin and Hamilton, 2007).

Nitrogen cycle is summarized in Figure 7, starting with the conversion of  $N_2$  atmospheric to reactive Nitrogen mainly by three processes: the natural input namely Biological Nitrogen Fixation (BNF), fertilizers (Haber-Bosh process) and the deposition of animal dung and urine. Once in the biosphere, the  $N_r$  is diversified through different reactions (nitrification, assimilation, anammox and denitrification), according to the bacterial community present in the soil and environmental conditions. The biosphere is divided by four main compartments: (i) terrestrial ecosystems, (ii) wetlands as ecotones ecosystems, (iii) aquatic ecosystems, and (iv) coastal and marine environment according to the process dynamics. Finally, biosphere output is emitted as  $N_2O$  or  $N_2$  to the atmosphere.



**Figure 7.** Simplified diagram of the biogeochemical nitrogen cycle. Lithosphere is divided in terrestrial, wetlands and aquatic ecosystems and hydrosphere as a marine environment. In orange, the fluxes into the biosphere and in black the outputs.

The distinction of wetlands from terrestrial and aquatic ecosystems is due to the fact that wetlands are an ecotone i.e. an “edge” habitat, a transition zone between dry lands and aquatic environments (Hammer and Bastian, 1989). The Ramsar Convention (Article 1.1) states that “Wetlands are areas of marsh fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres” (Matthews, 1993), despite the ambiguity of this definition, this is the all-embracing definition, that has not been bettered. Wetlands can be classified following their structural or functional characteristics (Mitsch and Gosselink, 2015). A primary goal of these classifications is to define physical limits for the purposes of inventory, assessment and management (Cowardin, 1979). Ramsar Convention divides wetlands in two main groups, (1) marine/coastal wetlands - tidal marshes

(marine and freshwater) and mangrove swamps, (2) inland wetlands - freshwater marshes, freshwater swamps, and peatlands (Matthews, 1993). This classification is very wide, but cover the major wetlands diversity worldwide. The largest areas of the world's wetlands are found in both boreal and tropical regions and the least amount are found in temperate zones. Extension of the world's wetlands is 7 to 10 million km<sup>2</sup>, or about 5 to 8 percent of the land surface of Earth (Lehner and Doll, 2004; Ramsar, 2004).

The interest of this review regarding wetlands denitrification is established on the subsequent aspects: (I) *Spatial Distribution*: their placement in the landscape, as transitional ecosystems between terrestrial and aquatic ecosystems, plays an important role in the hydrological dynamics of a basin, the water residence time is longer, as they are found mainly in the lowlands, or flat areas (Band et al., 2001; Carpenter et al., 1998; Czuba et al., 2018) in addition, wetlands are distributed along the whole latitude gradient (Hu et al., 2017a; Lehner and Doll, 2004); (II) *Biogeochemical cycles*: due to “wet” conditions, the soil is mainly anoxic; therefore many turning of the core elements occur in these ecosystems, one of the most relevant is carbon sinking and methane production, and less mentioned but significant, the turnover of N<sub>r</sub> to N<sub>2</sub> to the atmosphere (Bridgham et al., 2013a; Galloway et al., 2003; Mitchell et al., 2013); (III) *Biodiversity*: wetlands ecosystems are very diverse and cover only ~1% of Earth's surface, but they provide a home to > 40% of the world's species (Butchart et al., 2010; Hooper et al., 2012). This review is divided in three main sections, first, a bibliometric analysis (Section 2) that presents a quantitative approach of the most significant research papers which resulted from the eleven research exercises effectuated, and applying two temporal filters (last ten years and five years) gave information about the trends and evolution regarding this topic. Furthermore, we highlighted and analysed more precisely the crucial contribution of the top ten research papers regarding the three main components of the topic reviewed i.e. nitrogen cycle - *global context* (Section 2.1), denitrification - *process of interest* (Section 2.2) and wetlands -*target ecosystems* (Section 2.3). As a synthesis of our study, an in-depth investigation of the most recent tools (Earth Observations) and its convenience for the topic in hand led to suggest a novel method based on modelling to achieve the quantification of daily wetlands' denitrification on a global scale with associated limitations. (Section 3).

## METHODOLOGY

### BIBLIOMETRIC ANALYSIS

#### LITERATURE REVIEW CRITERIA

Guidelines for integrative literature review were followed (Pickering and Byrne, 2014; Torracco, 2005). Firstly, identification of the literature was done using Web of Science (WoS) as a database on the 05-04-2019. This dataset represents the most significant source of the last fifty years' citation history, and has become the premier gateway to search and discovery for the world's research resources (Li et al., 2012).

Initially broad keywords (nitrogen cycling, global nitrogen, denitrification, wetlands soils, wetland\* modelling,) were used to cover the total resources availability of the topic at hand. These keywords can be grouped into three main topics. First, the nitrogen cycling, global nitrogen and denitrification, which are linked to the process. Second, 'wetlands soils' is selected to narrow the results to the ecosystem wanted and exclude terrestrial, aquatic and marine denitrification, and third the wetland\* modelling to exclude particular study cases, and mainly obtain quantifying tools for nitrogen budgets and past, present and future anthropogenic impact on the nitrogen fluxes and greenhouse gas emissions.

Subsequently, pairs of keywords (denitrification + wetlands, denitrification + modelling, nitrogen + wetland\*, global + wetlands, global wetlands + modelling, nitrogen cycle + wetland\*) were used with the same research method in order to obtain more specific results.

Three-step results selection was applied, first no restriction on the time span or other criteria was used. Then, time span filters were applied, to select the top articles of last ten years (2010-2019), and the last five years (2015-2019). Articles resulted in the top five most cited articles of the broad keywords being selected, and analysed, while for the second batch of keywords, the top ten most cited articles were selected. This systematic selecting methodology was applied throughout all research exercises (no filtered, 2010-2019, and 2015-2019). The discipline maps from the Web of science were also extracted for each research result of each general concept keywords (appendix Chapter II). A total of 225 articles resulted from these research exercises (appendix Chapter II), after removing the duplicates, 164 articles were analysed. The number of citations reported corresponded to the date the research exercises were carried out. No further update is shown.

## LITERATURE ANALYSIS

Analysis of keywords, methods, findings and future prospective was done for every peer-reviewed article on the top of citations of every searching exercise. The articles analysed were categorized depending their aim and contribution in six categories, (i) literature review: when the objective is to summarize the research done previously and they contribute with an update situation regarding the gaps to develop, (ii) novel tools: when the research concluded in an innovation and it contributes with a tool that can be used for a wide range of research objectives, (iii) model: when compilation of data is used to extrapolate a process, and assumptions are made; (iv) experiment: when different conditions are proven physically in natural or artificial conditions and give new data set for denitrification under different conditions, (v) discoveries: when various methodologies lead to identification of new natural elements, phenomena, or organisms, and (vi) eco-politics: when scientific knowledge is analysed under political terms (public policies, government commitments and legislation). Top research items contributions were extracted, discussed and the current gaps to develop and limitations of each category (Nitrogen, Denitrification and Wetlands) were identified. As a conclusion of this analysis, an in-depth investigation of the most recent tools (Earth Observations) and its convenience for the topic in hand led to suggest a novel method to achieve the quantification of daily wetlands' denitrification on a global scale.

## RESULTS

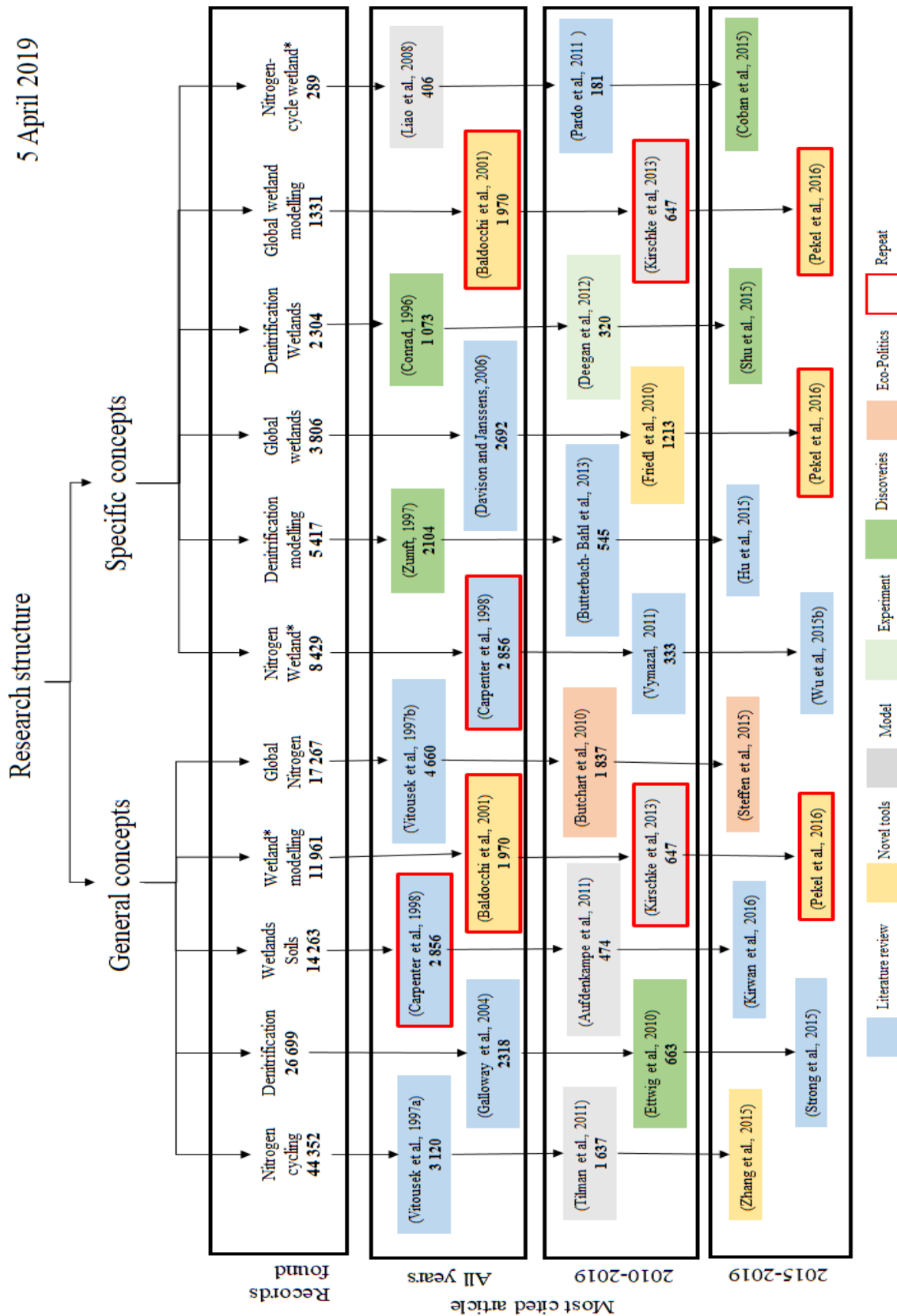
### RESEARCH POPULARITY

From the research exercises carried out, 225 articles representing the top ten articles for each research were selected. After removing duplicates 164 articles were analysed (see Appendix Chapter II A.2. - Table A2.1 and A2.2). The set of keywords referring to the “*general concepts*” gave a number of records always above 10 000 results, contrary to the group of “*specific concepts*”, where the total records found were below 10 000 on each research exercise. Some articles resulted repetitively as the most cited references. *Wetland\* modelling* and *global wetland modelling*, gave the same top references with every filter as shown in Figure 8.

The time span of top publications analysed in the present review goes from Conrad, 1996, with a scientific piece that describes in detail the microbiological processes occurring in the soil, that produce atmospheric trace gases, and ends with a high resolution (30 m) satellite imaging database from 1984-2015 of the global surface water (Pekel et al., 2016).

Pekel et al, 2016; resulted three times the most cited article when running different keyword sets (*wetland\* modelling, global wetlands* and *global wetland modelling*), meaning that is an important input dataset for the description and dynamics of wetlands surface in long term. The high number of citations prove the popularity that Earth Observation data has gained in the last decade.

*Nitrogen cycling* scored the greatest number of results (44 352), followed by *Denitrification* (26 699) with around half of the record found by the first keywords set. The least number of results found corresponded to *Nitrogen cycle wetlands* (289) that represents less than 1% of the total results of *Nitrogen cycling* keyword. Regarding discipline and distribution of the records found in each search exercise of the established *general concepts*, Environmental Sciences resulted always in first place (as expected), with a percentage that varied from 20 to 33%. Ecology resulted in second place in all the research exercises, except for Denitrification, where the second place was Engineering Environmental. The predominant presence of denitrification in the water treatment community (constructed wetlands) can cast a shadow on the scientific advancements in denitrification in natural wetlands. The total percentage of results regarding each *specific concept* indicated that most of the research among these concepts have been done on nitrogen + wetlands (39%), and the least in nitrogen cycle + wetlands (1%). Diagrams illustrating these percentages are found in Appendix Chapter II (Figure A.2.1 and A.2.2).



**Figure 8.** Diagram showing the top cited articles of each search exercise, on the top, the total of records found per each research exercise. First level is the most cited of all years since 1974 until the day of the research (5/04/19), second level is when a date filter (2010-2019) was applied. In third level, the second date filter (2015-2019). The numbers under each reference are the number of citations. The colors of each box refer to the kind of article i.e. Literature review (blue), novel tools (yellow), model (grey), experiment (light green), discoveries (green), and eco-politics (orange). In red margin, the articles that resulted as top articles in more than one searching exercise.



#### KEYWORDS VARIETY

The top-articles keywords of all research exercises were extracted, and word clouds were generated for each time span filter (Figure 9 a-c). The research with no filter, gave only one word as the most frequent “*Nitrogen*”, while the rest of the keywords were mentioned with almost no repetition. Regarding the last ten and five years, more keywords appeared to be in common, among the research articles. The resulting keywords, redirected some of the keywords used in the research exercises. These results show a progression from a general description of the nitrogen cycle towards more focused analysis of the “denitrification” in “wetlands” environment in the context of “global change”. Likewise, the present analysis showed a shift from process-based papers toward more systemic approach papers. This could be associated with the increasing number of multidisciplinary holistic approach papers that combine anthropogenic impacts and the role of biodiversity in nitrogen-related promoting the valorization of natural wetlands for water purification. In parallel, there is an increase in studies to develop technology to optimize constructed wetlands.



**Figure 9.** Word clouds created with the keywords of the top articles in each research exercise. **a.** no filter, **b.** 2010-2019, **c.** 2015-2019. The biggest word represents the most frequent, and the size gets smaller with lower frequencies. The colours represent the number of repetitions the keyword was found. Dark blue (one time), light blue (2-3 times), green (4 times), yellow (five or more times).

Based on these quantitative results, it is evident that nitrogen is an element that interacts with many aspects of human development, a part of being essential for all kinds of living organisms. Nitrogen centred vision is shown from the most popular research papers resulting from this analysis (Figure 9a). Giving the general panorama of the potential interactions that could be further explored in detail. The most relevant interactions were: (i) human alteration of nitrogen cycle (Vitousek et al., 1997a, 1997b); (ii) greenhouse emissions past, present and future scenarios and its impact in climate alteration patterns (Baldocchi et al., 2001; Galloway et al., 2004); (iii) the closest relation of the nitrogen cycle with temperature (Davidson and Janssens, 2006); (iv) consequences of production methods promoting plant invasion (Liao et al., 2008) as well as pollution sources (Carpenter et al., 1998).

Further on, the common output of research (Figure 9b) agree about the power of humans altering the nitrogen cycle and threatening biodiversity (Butchart et al., 2010). Wetlands begin to be mentioned as key ecosystems (Vymazal, 2011a). N<sub>2</sub>O (Butterbach-Bahl et al., 2013; Pardo et al., 2011) and CH<sub>4</sub> (Ettwig et al., 2010; Kirschke et al., 2013) emissions occurrence and its consequences is accounted for climate change. Global observations from satellites (Friedl et al., 2010) began to be used for environmental dynamics. Then, Tilman et al., (2011), proposed a possible sustainable long-term global agriculture method. In this period, the top research consent in the unsustainability of the system and the need of a prompt intervention to stop and restore the damages.

Going forward in time (Figure 9c), the most recent research becomes a feedback of what was done previously. It attempts to explain in detail and more precisely the nitrogen cycle, using state of the art tools. At micro level (i.e. gene identification, molecular techniques) reporting precise description of denitrification process (Hu et al., 2015; Zhang et al., 2015), innovative technology of constructed wetlands (Coban et al., 2015; Shu et al., 2015; Wu et al., 2014), and energy alternatives (Strong et al., 2015). Along with macro level (i.e. satellite data) high-resolution observations of global dynamics. In the following subsections, a qualitative analysis of the just mentioned research pieces, integrated to our three main interest topics is presented.

## NITROGEN CYCLE

*keywords: Nitrogen cycling; Global Nitrogen*

In these two research exercises the most cited articles are two literature reviews; written by the same researcher (Vitousek et al., 1997b, 1997a). These articles account for the general human impact on the global nitrogen cycle recognized at that time. Reporting already numbers that are by far impactful, showing a vast issue that amends the whole Earth system.

The first one, entitled “*Human Domination of Earth’s Ecosystems*” (Vitousek et al., 1997a), with 4660 citations (WoS, 05/04/19). It is a comprehensive report showing the interconnection of human population increasing (size and resource use) and the production means (human enterprises) influences in different ways: (1) land transformation, (2) global biogeochemistry, (3) biotic additions and losses, (4) climate change, and (5) loss of biological diversity. The paper citations has been constantly increasing since publication and is now at about 250 citations per year (“Human Domination of Earth’s Ecosystems | Semantic Scholar,” 2020). It was by then reported that atmospheric nitrogen fixed by the Haber-Bosh process was already more than all natural terrestrial sources combined (80 TgN.yr<sup>-1</sup> in 1990) and expected to increase to 135 TgN.yr<sup>-1</sup> by 2030 (Galloway et al., 1995). The consequences caused by the excess use of fertilizers were by that time identified, described and reported.

Increased CO<sub>2</sub> emissions were a direct impact of the industrial revolution. It was already depicted at that time that the ascending emission rate of CO<sub>2</sub> was causing a greenhouse effect and began to impact the climate, and projections about future climate change in the next century were elucidated (Change and Houghton, 1996). However, little was mentioned about other type of greenhouse gases like N<sub>2</sub>O. As mentioned in Vitousek et al., (1997) the responsibility held by humans was reemphasized, our actions were already delineating our fate, and it is in the hands of the human population to do something about environmental degradation in a human-dominated Earth.

The second most relevant research, published earlier that same year was entitled “*Human alteration of the global nitrogen cycle, sources and consequences*” with 3120 citations (5/04/19), reports the nitrogen cycle in ecological terms, giving information about the importance of nitrogen as a key element controlling the primary production and species composition and functions in the different ecosystems (terrestrial, freshwater and marine). It emphasizes the punctual and non-punctual current global anthropogenic impact sources, mainly by the addition of nitrogen to the biosphere with activities like extensive use of fertilizers and nitrogen fixing crops. Projecting that emissions of the potent greenhouse (NO<sub>x</sub>) from fossil fuels by 2020 will be ≈ 46 TgN.yr<sup>-1</sup> (Galloway et al., 1994) and by 2004 the emissions were already 41 TgN.yr<sup>-1</sup> (Galloway et al., 2004).

These investigations gave certain scientific evidence; to inform about environmental consequences of human activities e.g. soil fertility loss, increased rate of carbon stored in terrestrial ecosystems, accelerated losses of biological diversity (microorganism, plants, and animals) giving strong advice about the long-term decline of air quality and coastal marine fisheries (Deegan et al., 2012b).

Vitousek et al., 1997a, recognised wetlands and riparian areas as significantly important nitrogen traps, and they appealed for restoration of such areas as compensation of past actions when channelling of many streams and wetlands drainage to increase the area of agricultural land was officially supported. With a panorama like that already back in 1997, the research kept moving forward, the four articles to be analysed hereafter are more diverse and correspond to the last ten and five years. Two of them are related to novel technology (Zhang et al., 2015; Tilman et al., 2011), one is a model that forecast the adaptation and transfer of high-yielding technologies to main croplands (i.e. maize, wheat) doing so at a global scale, land clearing would only increase by only  $\sim 0.2$  billion ha, greenhouse gas emissions of  $\sim 1 \text{ Gt y}^{-1}$ , and global N use of  $\sim 225 \text{ Mt y}^{-1}$  enhancing soil fertility (Tilman et al., 2011). Secondly, Zhang et al. (2015) showed the development of a metal-free bi-functional membrane using a mesoporous carbon foam co-doped with nitrogen and phosphorus to produce oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that can be adapted to a constructed wetland.

On the other hand, Butchart et al., (2010) and Steffen et al., (2015) provided a more interdisciplinary approach regarding the global nitrogen alteration. First, Butchart et al., (2010) investigated the goals targeted to reduce the rate of biodiversity loss committed by world leaders in 2002 through the Convention on Biological Diversity. The indicators included human resource consumption, invasive alien species, nitrogen pollution (deposition and transport), overexploitation, and climate change impacts, they were supposed to be reduced by 2010, but none of them has been achieved in 2010. Instead, the pressure on biodiversity increases, showing (i) a decline of vertebrates and birds (habitat specialist and shorebirds) population trends worldwide. (ii) Loss of terrestrial forest and mangroves extent, and (iii) coastal ecosystem degradation (seagrass beds and coral reefs). Deposition of  $\text{Nr}$  is affecting species distribution worldwide; unfavourable for sensitive species, and often favourable invasive species (Bobbink et al., 2010). The conclusions of this analysis emphasised the need to substantially strengthen and implement policies that fully integrate biodiversity into broad-scale land-use planning to reverse the environmental detriment and improve the environmental management accounting for their economic value. Enhancement of multi-actor decision-making and increase and sustain investments that tackle biodiversity loss, and monitor global biodiversity will lead to sustainable management of natural ecosystems.

Later on Steffen et al., (2015) updated the trends of the *Great Acceleration* report of the International Geosphere-Biosphere Programme, published in 2004, showing the socioeconomic and Earth System trends from 1750 to 2000, updated to 2010. It is remarkable that the atmospheric concentrations of the three greenhouse gases –carbon dioxide, nitrous oxide and

methane— are now well above the maximum observed at any time during the Holocene (Ciais et al., 2014). The Nitrogen cycle since the Haber-Bosh process was introduced, it is also out of the range of the Holocene range (pre-industrial scenario).

Even with the solid evidence of our impact and power (Steffen et al., 2015; Vitousek et al., 1997a, 1997b), models and projections (Galloway et al., 2004; Tilman et al., 2011), novel technology (Jeong et al., 2011; Xiang et al., 2011; Zhang et al., 2015) and indicators of losses of biodiversity and rapid increase of environmental detriment (Butchart et al., 2010; Sala et al., 2000) Earth System indicators point out no responsibility towards developing impacts, but how long can this present form can go on? This steady pace that may break at any moment. There has been previous evidence that this economic model is ruled by periods of growth, collapse, and reorganization (Costanza, 2006).

## DENITRIFICATION

*keywords: Denitrification; Denitrification modelling, Denitrification wetlands*

The three keywords used to cover denitrification topic gave as most cited articles four *literature reviews* (Butterbach-Bahl et al., 2013; Galloway et al., 2004; Hu et al., 2015), four *discoveries* (Conrad, 1996; Ettwig et al., 2010; Shu et al., 2015; Zumft, 1997) and one long term *experiment* (Deegan et al., 2012b). Denitrification is the target process of the present review, therefore, this section is the link between the previous (2.1 Nitrogen) and the following (2.2 Wetlands). In addition, some papers mentioned in this section were also relevant and appeared in the top five of some of the other research exercises (Appendix Chapter II, Table A.2.3).

Galloway et al. (2004) ranked as the top article of *Denitrification* and second place in *Nitrogen cycling*. This research developed a model that quantifies the global N budget from ~15 TgN.yr<sup>-1</sup> in 1860 to ~156 TgN.yr<sup>-1</sup> in the early 1990's. Projecting that by 2050 anthropogenic reactive nitrogen (Nr) creation will be ~270 TgN.yr<sup>-1</sup>. Giving regional continental N budgets as well as marine N budgets. Models are a representation of nature, not a perfect reflection of it, as usually happens with models, there are many assumptions made and there is always room for improvement. In this case, this model recognizes a large gap in knowledge regarding the rates of natural biological nitrogen fixation, amount of Nr storage in most environmental reservoirs, and production rates of N<sub>2</sub> by denitrification. Pointing out that the biggest unknown in the N cycle in managed and unmanaged ecosystems is the rate of denitrification and its relationship to Nr creation rates and ecosystem characteristics that control Nr cycling and storage (Galloway et al., 2004).

Nevertheless, Zumft (1997) described in a very detailed investigation, all molecular and genetic basis for the denitrification processes to happen. Describing the properties of nitrate respiration, bacterial diversity, and regulatory processes. However, isolation and full understanding of N<sub>2</sub>O reductase were still a challenge.

Later on, improvement of techniques of DNA (Deoxyribonucleic acid) isolation, coding sequences and protein extraction Ettwig et al., (2010) were able to identify a new intra-aerobic denitrification pathway of nitrite reduction to dinitrogen gas without a nitrous oxide reductase, not necessarily restricted to methane-oxidizing bacteria. This pathway under dynamic oxic/anoxic conditions, with recalcitrant substrates, certainly offers ecological advantages. In addition, this discovery may lead to a discussion about the early Earth life and evolution of anaerobic to aerobic respiration. Extending our understanding of hydrocarbon degradation under anoxic conditions and gives a novel path of production of N<sub>2</sub>. This pathway was found in a species named *Candidatus methylomirabilis oxyfera*, further research is expected to explore its presence, and abundance in soils.

In the same vein, Shu et al., (2015) carried out an experiment on 6 different types of anaerobic sludge, to identify the microbial communities and abundances. The identification was possible through novel microbiological techniques i.e. pyrosequencing and real time quantitative polymerase chain reaction (qPCR). The results of this study showed the coexistence, and high abundance of two bacterial communities involved in nitrogen removal: anaerobic ammonium oxidation (anammox), and Archaea ammonium oxidation (AOA) revealing alternative significant paths that have been neglected. As a next step, the coexistence and interaction of denitrification and dissimilatory nitrate reduction to ammonium (DNRA) for simultaneously nitrogen and organic matter removal in artificial wastewater treatment bioreactors should be investigated Shu et al. (2015).

Strong et al., (2015) proposed after an extensive review the possibility of either using methane as a final product or using it as an energy resource. One of the possibilities is using methane as a low-cost carbon source to facilitate denitrification in biological wastewater denitrification systems. Proving that various consortia of bacteria are capable of using methane as the sole carbon source for denitrification both aerobically and anaerobically. This possibility has been studied in experimental conditions, the detailed microbiological elucidation of denitrification pathways and controls need to be better understood in natural conditions to assume the same. The complexity of soils and variety of environmental conditions makes it difficult to model and predict accurately. A field-scale study in Central Iowa identified the soil variability on a watershed scale, to study the spatial distribution of soil properties, to identify the yield potential,

hydrological responses, transport of herbicides and  $\text{NO}_3^-$  to surface or groundwater, helping to understand the hotspots of denitrification at watershed scale. These results could be extrapolated to another similar landscape configuration Cambardella et al., (1994).

Moreover, Conrad (1996), established the soil microorganism as controllers of atmospheric trace gases ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{OCS}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}$ ), in this research, soil denitrification is widely described. To classify the different processes, a basic classification is proposed: not water-saturated (upland soil), and water saturated soils, generally anoxic (wetland soil) and three different categories of soil processes (chemical, enzymatic and microbial), both key to facilitate understanding of the different trace gas exchange. The ecological interaction and complexity of a soil matrix with the atmosphere is acknowledged as macroscale processes between systems but controlled predominantly on a microscopic level. The soil hosts a large amount of microorganisms, perhaps only 1 to 10% of existing soil bacterial species are known (Brock, 1987). Therefore, understanding microscopic processes in soils (Koegel-Knabner et al., 2010) is of major interest for biogeochemical cycle studies and gas exchange modelling (Bakken et al., 2012; Huang and Gerber, 2015). The quantification and estimation of atmospheric budgets from field fluxes is not trivial, several integration efforts to integrate flows over larger areas and extended periods have been published, and are still being improved. Advances in identification of diversity of microbial communities across ecosystems, plant-soil interaction, and insights of regulation of the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ , with novel technology (isotope tracing, and metagenomics) have increased our understanding and measurement precision of  $\text{N}_2\text{O}$  and  $\text{N}_2$  emissions. However, our knowledge is mainly based on studies in controlled laboratory conditions, and there is still a lot to know about  $\text{N}_2\text{O}$  and  $\text{N}_2$  emissions controls and rates at field to landscape scales (Butterbach-Bahl et al., 2013; Butterbach-Bahl and Dannenmann, 2011).

On a global level, a meta-analysis of ambient  $\text{N}_2\text{O}$  emissions based on 23 studies revealed no clear dose-response effect for N deposition and  $\text{N}_2\text{O}$  emissions (Liu and Greaver, 2009). Nonetheless, a significant increase of  $\text{N}_2\text{O}$  emissions (average of 216% across all ecosystems) is caused by N fertilization (ranging from 10 to 562 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$ ) (Butterbach-Bahl et al., 2013). Additionally, the same review, exposed that all terrestrial ecosystems have a higher N-induced emission factor (1.43-1.90) compared with the factors calculated for agriculture, which was ranging from 1.0 to 1.2. Under enrichment conditions in terrestrial ecosystems, the enhancement of  $\text{N}_2\text{O}$  emissions was estimated at  $0.0087 \pm 0.0025$  kg  $\text{N}_2\text{O-N}$   $\text{ha}^{-1}$   $\text{yr}^{-1}$  per 1 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$ , and tropical forest emitted more  $\text{N}_2\text{O}$  under N enrichment (on average + 739%) (Liu and Greaver, 2009). Emission rates of  $\text{NO}$  and  $\text{N}_2\text{O}$  in wetlands soils have been proven to

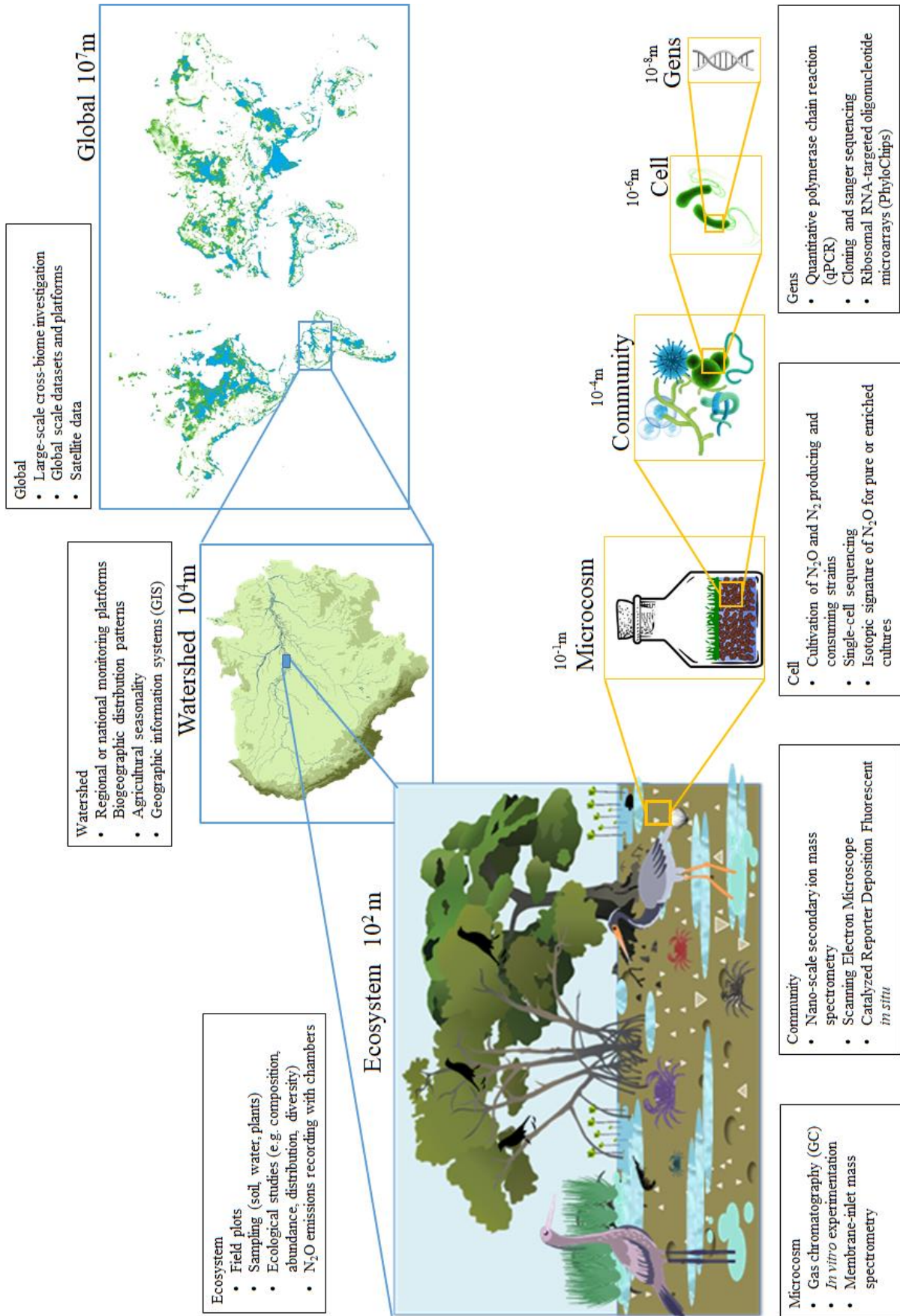


be small compared with aerated soils; this is because a larger percentage of these gases are further reduced by denitrification to  $N_2$ , nonetheless, wetland soils are especially important sources of atmospheric  $CH_4$  (Bridgman et al., 2013b). Surprisingly, Conrad, (1996) reported that submerged rice fields seem to sink  $N_2O$  (occasionally) (Minami and Fukushi, 1984). Even though wetland soils are submerged, yet  $O_2$  penetrates from the surface, creating a thin oxic layer. In addition, roots of aquatic plants with gas vesicular systems also transport oxygen into deeper soil layers. These two processes create a vertical redox gradient, characterized by dominance of the electron acceptors  $O_2$ ,  $NO_3^-$ ,  $Mn^{4+}$ ,  $Fe^{3+}$ ,  $SO_4^{2-}$ , and  $CO_2$ . This also promotes well-defined habitats for different groups of trace gas-metabolizing microorganisms (Zehnder and Stumm, 1988). Regarding specifically the denitrification products, the ratio of  $N_2$  to  $N_2O$  produced increases with the saturation of the soil pore and space with water, in experimental conditions. Still, the ratio obtained in controlled conditions cannot be converted to in field estimations, because of the large variability in environmental factors that affect the denitrifying process (Weier et al., 1993). However, it has been established that denitrification is one of the ecosystem services that wetlands and coastal marshes offer, retaining and eliminating the surplus of nitrogen (fertilizers) thereby decreasing the quantity that arrives in the oceans. Yet, nutrient enrichment has become a global problem for coastal ecosystems (Deegan et al., 2012b) and is causing soil acidification in many croplands (Guo et al., 2010). A nine-year experiment carried out by Deegan et al., (2012) to quantify the whole ecosystem nutrient-enrichment, proved that current nutrient loading rates have overwhelmed the capacity of marshes to remove nitrogen without deleterious effects.

Recently Hu et al. (2015), in a review article compiled the most recent knowledge about key microbial regulation pathways towards understanding  $N_2O$  formation and how to predict emission rates in terrestrial ecosystems. They argued and advocated for an urgent incorporation of microbial traits into biogeochemical ecosystem modelling, to produce a more reliable  $N_2O$  emissions assessment. As a final point, for better understanding of denitrification in wetlands, it is necessary to integrate processes at different spatial scales, using different experimental protocols and novel tools and technology to approach the different range of processes needed for a holistic comprehension as shown in Figure 10, where the upscaling of processes is explained. The main driver is determined at genetic level ( $10^{-8}$  m), a lot of progress has been made identifying the genes that codify the enzymes that carry out anaerobic respiration, using  $NO_3^-$  as an oxygen donor molecule in anoxic conditions and producing  $N_2$ . These genes are not species specific, instead, there is a wide range of microorganisms, living in the same soil community able to denitrify ( $10^{-6}$  m). Microcosm experiments ( $10^{-2}$  m), have been useful to

identify and isolate the organisms in controlled conditions. Once in the natural conditions, at ecosystem level ( $10^2$  m), information about real abiotic dynamics e.g. temperature, soil moisture, inundation, etc. occurring in parallel can be observed and measured. Moreover, it is possible to understand the interaction of the denitrifying organisms with other biotic elements. The vegetal structure will define the rate of organic matter produced as well as nutrients consumed. The same microorganisms will behave differently according to the type of wetland (e.g. swamps, marshes, floodplains, etc.). The ecosystem level is where ecological experimentation and in situ emissions can be recorded (Gorski et al., 2020; Qin et al., 2017; Seitzinger, 1994). Integrating wetlands ecosystems to a landscape or watershed ( $10^4$ m), information regarding input and output fluxes, pollution sources, origin of the organic matter, time of residence and spatial distribution of processes can be understood. The largest dimension for the study of denitrification is at Earth scale ( $10^7$ m). Modelling and compilation of data of many ecosystem and landscape level studies can give more information about denitrification and its role to the regulated fluxes into the oceans in a more integrative context and with a long term dynamic vision (Fabre et al., 2020; Trepel and Palmeri, 2002).

Hence, integration of information and multidisciplinary research, at different spatial-temporal scales need to be promoted. How to simplify microorganism's biological processes ( $10^{-6}$  m) on a global scale ( $10^7$  m)? How to upscale from controlled laboratory conditions and field case studies to a global change scenario? Translation of this knowledge into models has begun, thanks to the increasing improvement of analysing tools and datasets availability worldwide. Earth's atmosphere is a fluid layer composed of different gases, this composition changes according to the biosphere activity. In the past, it had changed from anoxic to oxic, and in the present it is changing. The current change is caused by humans, is the main cause of global warming, harming the other living organisms and promoting ozone depletion. The adaptation and survival of life as we used to know it, depends on human- nature interaction. Quantifying and predicting is one of the major priorities in science, aiming to reduce the global  $N_2O$  emissions. Promoting effective policies and novel mitigation actions (Hu et al., 2015).



**Figure 10.** Methodological framework of the different dimensional range of processes involved in wetlands soil denitrification.

## WETLANDS

*keywords: Wetlands soils, wetland modelling, global wetlands, global wetland modelling, nitrogen cycle wetland\*, nitrogen wetlands*

The six keywords used to cover wetlands topic gave as most cited articles five *literature reviews* (Carpenter et al., 1998; Davidson and Janssens, 2006; Kirwan et al., 2016; Pardo et al., 2011; Vymazal, 2011a; Wu et al., 2015a), three *novel tools* (Baldocchi et al., 2001; Friedl et al., 2010; Pekel et al., 2016), three *models* (Aufdenkampe et al., 2011; Kirschke et al., 2013; Liao et al., 2008) and one *discovery* (Coban et al., 2015). *Wetland\* modelling* and *global wetland modelling* gave the exact same top references. This section aims to summarize denitrification research exclusively in wetlands, due to the ambiguity of the definition; the term wetlands can be referred to constructed wetlands or natural ecosystems. Substantial differences among artificial and natural wetlands are acknowledged and the purpose of the current review is towards natural wetlands, even though the process is the same, a short subsection is dedicated to constructed wetlands but the scope of the present review is to address research advances towards natural wetlands.

The majority of the studies analysed, gave information on a global scale regarding: (i) pollution sources and consequences (Carpenter et al., 1998; Liao et al., 2008; Pardo et al., 2011), (ii) biogeochemical cycles (mainly carbon and methane) (Aufdenkampe et al., 2011; Baldocchi et al., 2001; Kirschke et al., 2013); (iii) Natural wetlands dynamics (Davidson and Janssens, 2006; Kirwan et al., 2016); (iv) global mapping of surface water (Pekel et al., 2016) and remote sensing global land cover algorithm (Friedl et al., 2010); and (v) constructed wetlands assessment (Coban et al., 2015; Vymazal, 2011; Wu et al., 2015).

### NATURAL WETLANDS

As mentioned before, the Earth is dominated by humans, and the overload of nutrients and pollutants have arrived to all the corners of the world (Smith, 2003). Because of hydrological alteration and their spatial location in a watershed, wetlands are highly impacted in an indirect manner (Richter et al., 1996). Carpenter et al., (1998) reported based on an extensive literature review that phosphorus and nitrogen are the main nonpoint pollution, coming mainly from uplands (agriculture and urban activities) causing a large eutrophication problem in rivers, lakes (Paerl et al., 2011), estuaries (Smith, 2003) and coastal oceans anoxic events worldwide (Jenkyns, 2010). In their review they had compiled enough scientific evidence to confidently say that nonpoint pollution on surface waters and wetlands can be decreased by reducing the surplus, by optimization of agricultural and urban wastewater (Carpenter et al., 1998). Till now

main studies have been dealing with decreasing P and N input and could allow natural ecosystems to reverse the eutrophication (Paerl et al., 2011). However, recovery process rates are slow and highly variable among water bodies (Carpenter et al., 1998).

Natural wetlands are very diverse in ecological terms, but their functionality and service provision are similar. On one hand, wetland ecosystems provide many *provisioning services* (wetland- dependent fish, shellfish, fur-bearing animals, waterfowl, timber, and peat), *regulating services* (moderating effect of floods, improve water quality, protect coastlines from storms, hurricanes, and tsunamis, climate regulation and aquifer recharge) and *cultural services* (recreation, ecotourism, aesthetics and cultural heritage) which contribute to human well-being (Sarukhán et al., 2005). On the other hand, biogeochemical cycles are mainly common, due to their hydro periodicity and high soil moisture, which allows us to group them together (Kögel-Knabner et al., 2010). Nowadays, these ecosystems have been highly impacted by humans, anthropogenic nitrogen deposition and emission had modified species composition and losses of N –sensitive species; shifting in favour of exotic invasive species (Pardo et al., 2011), these new established plants alter carbon and nitrogen cycles across all ecosystems, and their impact needs to be investigated deeper (Liao et al., 2008).

In synthesis, wetlands share low mineralization rates (Bridgham et al., 1998; Kumar et al., 2018), continues anoxic/oxic conditions (Richter et al., 1996; Walter et al., 2000) leading to stratification of soil redox potential and microbial distribution (Conrad, 1996), abundance of soil organic matter (Page et al., 2011) and high dependence to temperature changes (Benoit et al., 2015; Davidson and Janssens, 2006; Mitsch et al., 2013b).

Integration of riverine ecosystems, such as wetlands, streams rivers and lakes, as connecting ecosystems between land, oceans and atmosphere, may improve carbon budget modelling, and quantification of human-accelerated chemical weathering of minerals in watersheds that affects coastal zone acidification (Aufdenkampe et al., 2011). Models at watershed scale that integrate wetlands have shown that the performance improves, if the role of wetlands is included, the nutrients outputs are more accurate to what is reported in situ as emissions (vertical fluxes) and exports to the oceans (horizontal fluxes). Different watershed compartments and their spatial distribution of nutrient transformation are more detailed (Bernard-Jannin et al., 2017; Czuba et al., 2018; Hansen et al., 2018; Yao et al., 2017). Kirschke et al. (2013) calculated decadal budgets for methane sources and sinks between 1980 and 2010, using a combination of atmospheric chemical transport models, ecosystem models, climate chemistry models and inventories of anthropogenic emissions. Their result showed three contrasting emission scenarios (differing in fossil fuel and microbial emissions), to explain the decadal variability in

atmosphere methane levels detected, their budgets overestimates the total natural emissions, so definitive conclusions cannot be drawn, but trends of changes during these three decades were clearly visible. The dataset was extended from 2010 to 2017 (Saunois et al., 2019).

Overestimation and uncertainty in global scale analysis is unavoidable, but quantification and report of it is important to improve future research. A positive case found in this analysis was a meta-analysis of marsh elevation change at global scale, and indicated that marshes are generally building at rates similar to or exceeding historical sea level rise; and process-based models predict survival under a wide range of future sea level scenarios. Before this research, marsh vulnerability had been overstated (Kirwan et al., 2016). To improve modelling and reduce uncertainty, compilation of monitoring data in a wide range of ecosystems worldwide is needed. In this direction, FLUXNET (Baldocchi et al., 2001), provides infrastructure for compiling, archiving and distributing carbon, water and energy flux measurements, and meteorological, plant and soil data, collected from 140 operational sites on a long term and continuous basis. This platform has many potential research outputs, yet is mainly focused on carbon, quantifying net CO<sub>2</sub> exchange at ecosystem level (Baldocchi et al., 2001) nothing similar has been achieved for nitrogen. Soil carbon reservoirs in peatlands, wetlands represent a significant portion of global carbon soil stock, and represent more carbon than the currently present in the atmosphere (Dargie et al., 2019). Due to low decomposition rates, provoked by anaerobic conditions (Page and Baird, 2016), inputs (leaf and root detritus) are higher than outputs (dominated by efflux of CO<sub>2</sub>) although methane (CH<sub>4</sub>) efflux and hydrologic leaching of dissolved and particulate carbon compounds can also be important (Davidson and Janssens, 2006; Mitsch et al., 2013b; Page et al., 2011). The activation (permafrost) or increase rate (wetlands, peatlands) of organic matter decomposition in organic soils is a dormant danger (Gorham, 1991). To be able to predict the sensibility on a global change scenario with increasing temperatures of these ecosystems and organic matter decomposition rate change Davidson and Janssens, (2006) presented a kinetic model that aim to explain the behaviour of decomposition rate according to the temperature, first they proposed Arrhenius equation as the solution, establishing the Q<sub>10</sub> of decomposition equal two. Hence, theoretical and experimental evidence showed that the Q<sub>10</sub> = 2 is valid only under specific conditions, and was insufficient explaining the environmental response and substrate concentration affinity of the enzymes that have been proven important on decomposition activation/increasing process. As a conclusion of this review, merging concepts of substrate availability and temperature sensitivity may provoke new measurement and modelling approaches for soil C dynamics using a Michaelis-Menten kinetic. (Davidson and Janssens, 2006). Importance of natural wetlands as carbon

reservoirs and methane sources has improved, more data is available and better understanding of their processing have been achieved.

Specific study cases of denitrification around the world with a wide range of modelling tools and field data have been reported in many wetlands types as mangroves, floodplains and peatlands, but a global dynamic model of denitrification integrating different types of wetlands has not yet been proposed. Wetlands N turnover specifically ( $N_2$  and  $N_2O$  emissions) has not yet been understood, quantified and modelled at the level achieved regarding carbon cycling ( $CH_4$  emissions) being a gap to develop for current research. The multiple processes of environmental constraint that govern availability of substrates should be described and studied at global scale coupling of nitrogen and carbon within the context of climate change.

### CONSTRUCTED WETLANDS

The main objective of constructed wetlands is to reduce dissolved and particulate pollutants. Constructed wetlands for wastewater treatment started to be developed back in the early 1950's and the first full system was implemented in Germany during the late 1960's (Vymazal, 2011a), since then they started to be commonly used in Europe and later on implemented in North America and Australia. The main objective of constructed wetlands is to reduce dissolved and particulate pollutants, since their invention, investigation has never stopped, and an extensive range of constructed wetlands have been developed, always in the search of the most efficient system, and better suited to the specific wastewater quality. Although, some gaps have not been achieved, such as high phosphorus removal or contaminants removal like pesticides in agro-systems (Huang et al., 2017; Imfeld et al., 2009; King et al., 2015; Tournebize et al., 2017; Vymazal and Březinová, 2015). Regarding nitrogen significant improvements have been achieved (Coban et al., 2015; Vymazal, 2011a). On the other hand, constructed wetlands represent a sustainable solution to improve wastewater quality, they are land-intensive, low energy and less-operational requirements alternative to conventional treatment systems (Wu et al., 2015a). The advances regarding the identification of microbial communities and optimal conditions in constructed wetlands can be useful to elucidate some conditions that are present in natural wetlands as well as assembling main technological advances for its monitoring and study, processes modelled, pollution and management issues and opportunities.

## DISCUSSION

### TOWARDS GLOBAL WETLANDS DENITRIFICATION MODELLING

Regarding the denitrification process specifically, the challenge has been on the upscaling and transposition. An isolated, controlled environment is not representative of a natural soil multi-process matrix. When translating that to ecological terms, the study and effect of each bacteria coming together with many processes occurring simultaneously with or without dependence makes an extremely elaborated scenario to study. To achieve this complexity, efforts have been made to describe the soils characteristics and emissions, and composition of microbial biota communities in soils, but microbiological soil diversity is vast and so far, only ~10% of the total soil species that may exist have been described (Conrad, 1996). At watershed scale, physical modelling tools are used to spatialize and quantify the denitrification processes (Hoang et al., 2017; Van Breemen et al., 2002; Van Veen et al., 1984). The algorithms (models) rely on a set of geostatistical-mapped data to force the hydrological and biogeochemical modules calibrated using in situ measurements. The complexity and number of involved processes results in a high uncertainty in the outputs and generally the results are not applicable globally due to the lack of global homogenous in situ observations.

Thereby, alternative approaches can be used to constrain the modelling algorithms. In fact, the last two decades witnessed a sheer increase in the Earth Observation (EO) capacities as a supporting tool for the geospatial and modelling activities in weather and climate modelling, oceanography, hydrology (McCabe et al., 2017). The open data policy on EO data from many organisations like the European Commission through the Copernicus program, national space agencies as Centre National d'Etudes Spaciales (CNES) and National Aeronautics and Space Administration (NASA) across their EO satellite platforms and weather organisations as European Organisation for the Exploitation of Meteorological Satellites (EUMETSAT) and National Oceanic and Atmospheric Administration (NOAA) had a very positive impact (Zhu et al., 2019). EO data is either used directly in data-driven/parsimonious models or numerically assimilated into physical modelling like in the production of weather reanalysis data (Dee et al., 2011), hydrological modelling (Lievens et al., 2015; Schumann et al., 2009), carbon budget (Scholze et al., 2019), and water quality (Pastor et al., 2003).

The main abiotic variables that explain denitrification where ground daily data at global scale is limited or inexistence can be reached by EO imaging, being a key tool for improving modelling approach at global scale. Section 3.1 explains in detail these variables, i.e. flooded area extension, soil moisture conditions, soil and water surface temperatures, soil characteristics



(soil texture, type and carbon content), and vegetation dynamics that are relevant to model denitrification. In addition, a collection of the currently existing EO based dynamic (Table 1) and static (Table 2) observations. Section 3.2 explains their adequacy or limitations for the evaluation of the denitrification at global scale.

**Table 1.** Selected collection of global dynamic EO datasets for denitrification modelling in wetlands.

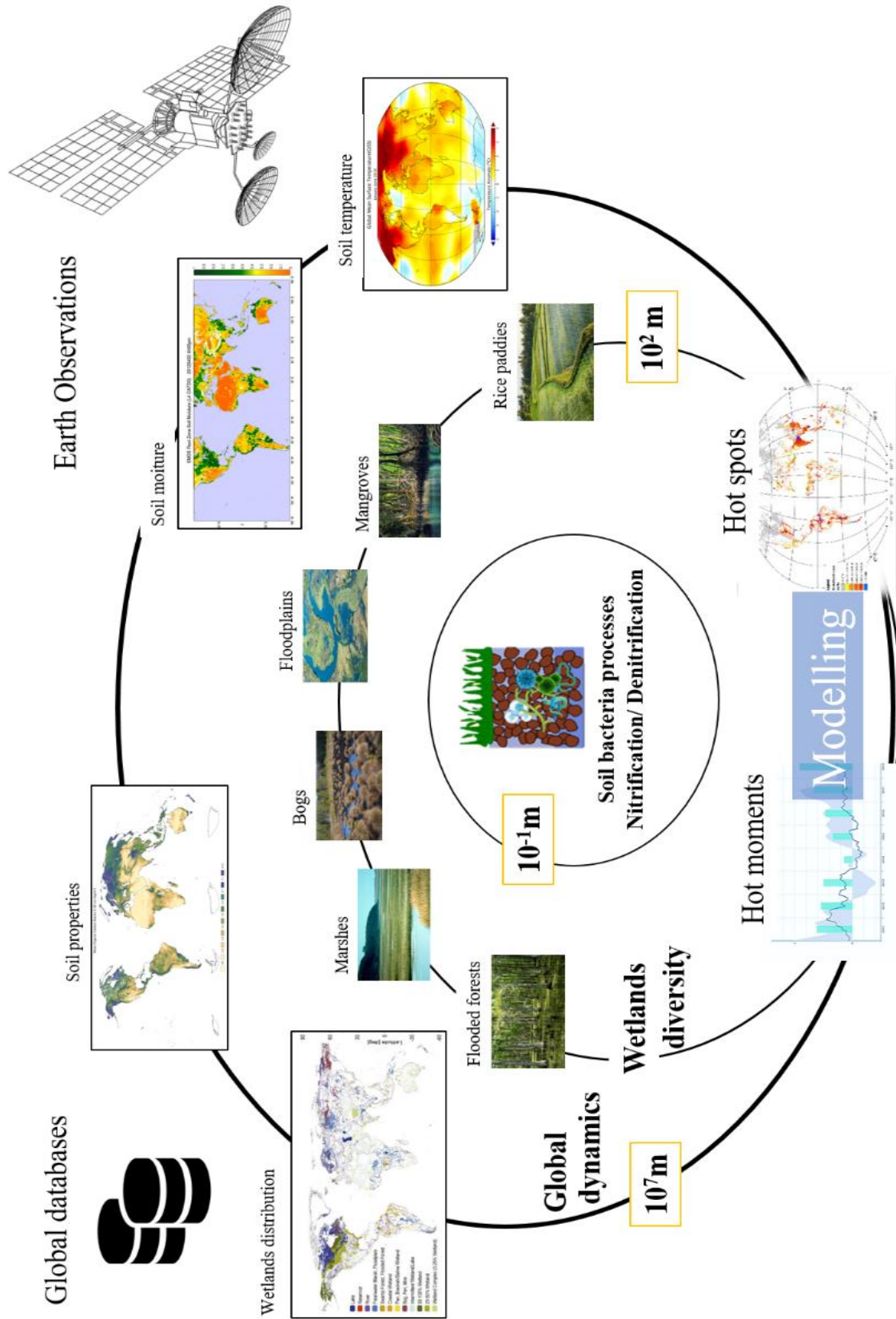
Observed variable	Dataset name	Spectral domain	Sensors	Spatial resolution	Temporal resolution	Temporal span	References
Wetlands extents	GSW	VIS / LST	LandSat series	30 m	Variable	1984-2015	Pekel et al., (2016)
	MOD44W	VIS	MODIS	250 m	monthly	2001-	Carroll et al., (2017)
	GIEMS	MW	ERS/SSMI/AS CAT...	25 km	monthly	1993-2007	Prigent et al., (2007)
	SWAMPS	MW	ERS/SSMI/AS CAT	25 km	Monthly	1992-2013	(Schroeder et al., 2015)
	G-SWAF	MW	SMOS	25 km	Weekly	2010-2020	Al Bitar et al., (2020)
Water heights	Hydroweb	MW altimeter	Jason-2/-3/Altica, Sentinel-3	-	-	-	Donlon et al., (2012); Lambin et al., (2010)
Soil moisture	CCI-SM	MW	ERS/SSMI/AS CAT/ AMSR-E	0.25°	variable	1978-2020	(Dorigo et al., 2017)
	SMOS L3 SMOS-IC	MW	SMOS	25 km	3 days	2010-2020	Al Bitar et al., (2017); Fernandez-Moran et al., (2017)
	SMAP-L3SMP	MW	SMAP	36 km	3 days	2015-2020	Entekhabi et al., (2010)
Land surface temperature	LandsatLST	TIR	Landsat5-7	30 m	16 days	1984-2017-	Malakar et al., (2018)
	TCDR-LST	TIR	MSG1-SEVIRI	3 km	15 min	2004-2015	LSA SAF, (2019)
Vegetation	MODIS LAI	VIS	MODIS	500m	8 days	2002-2020	Myneni et al.,(2015)

**Table 2.** Selected collections of global static datasets for denitrification modelling in wetlands.

Variable	Dataset	Spatial resolution	References
Water land cover maps	GC	0.005°	Broxton et al. (2014); Friedl et al. (2010)
	GLWD	30 sec	Lehner and Doll, (2004)
Soil properties	Soilgrids	250 m	Hengl et al., (2017)
	DSMW	5 arc min	Van Engelen et al., (2005)
	WISE 30sec	30 arc sec	Batjes, (2015)

The use of EO combined with numerical models for land use changes, and long term ecosystem dynamics have been widely done. Guilhen et al., (2020) applied such an approach over the Amazonian basin to quantify denitrification emissions at monthly scale (CO<sub>2</sub>, N<sub>2</sub> and N<sub>2</sub>O) over wetlands using a surface inundation EO product, at 25 km resolution. While this approach provided relevant results over the tropical Amazonian basin an adaptation will be required for a global scale application as shown in Figure 11 where the combination of inventory data and

EO at global scale will tackle different process at specific space and time via empirical equations and geographical information system software, to spatialize the denitrification process in a diverse range of wetlands at global scale; at a daily temporal step. This model would require the use of several databases to be accomplished. In Appendix A.3-Table A.3.2, a collection of possibilities with the associated properties is provided. The limitation and suitability of each of them for the modelling of this specific process has to be proven. A priori, we suggest that soil moisture dynamic datasets seem to be the most suitable parameter for detailed denitrification and precise hot moments due to its time span (daily), and capacity to sense soil moisture under vegetated areas in a depth of 30 cm. The present proposed approach has the potential to contribute to the understanding of denitrification dynamics at global scale that so far has been the least monitored transformation for nitrogen biogeochemical cycling modelling.



**Figure 11.** Illustration of the proposed multi-scale conceptual model. Each ring represents different spatial scale (i.e. soil, wetlands and Earth) where parameters and information regarding dynamics of denitrification process in wetlands soils worldwide is occurring.

## EARTH OBSERVATIONS DATA IN SUPPORT OF DENITRIFICATION STUDIES

### Surface Water

Wetlands extents can exhibit large seasonal variations, which has a direct impact on denitrification quantification, thus monitoring the surface water extents is an important information. This can be achieved using EO data in the optical and microwave (active or passive) domains or a combination of the two. We consider here the datasets that provide open water extents at a sub-monthly time resolution. For this reason, static land cover datasets like Globe Cover (GC) (Broxton et al., 2014; Friedl et al., 2010) and Global Lakes and Wetlands Database (GLWD) (Lehner and Doll, 2004) while widely used for the identification of wetland ecosystems do not meet this requirement. Worth mentioning, as it appeared second in this bibliometric review, that the GC product, which is part of the International Geosphere-Biosphere Programme (IGBP) program, is obtained using images from the Moderate Resolution Imaging Spectroradiometer (MODIS) at a spatial resolution of  $0.005^\circ$  covering years 2001 to 2012. Dynamic water surface masks derived from MODIS optical acquisitions are also available at 500 m resolution from the MOD44W product (Carroll et al., 2017). Recently, the Landsat-derived Global Surface Water (GSW) dataset (Pekel et al., 2016) has raised considerable attention for the description of wetlands from a high resolution (30m) optical EO. It appeared as the most cited article of recent times (2015-2019) on three of the research exercises (*wetland\* modelling, global wetlands and global wetland modelling*) of the present bibliometric analysis proving the importance that EO data has gained in the last decade. GSW provides global surface water dynamics over the past 32 years, obtained through three million high-resolution optical (30 m) Landsat satellite images. In GSW, an expert system, that corrects for Normalized Difference Vegetation Index (NDVI), Hue-Saturation-Value (HSV) colour and space transformations, is used to tag at global grid pixels into three classes: water, land or non-valid observations. The non-valid observations are associated to snow, ice, cloud or sensor-related issues. Since it is based on optical data, the GSW dataset has a lower temporal resolution over tropical and high-latitude regions. In addition, water surfaces under dense or floating vegetation are not well depicted even under clear sky conditions. These constitute the main two limitations for its application for denitrification studies. Outside these limitations, GSW dataset provides relevant and high resolution information about surface water changes (Yamazaki and Trigg, 2016).

To work around the limitations of optical EO, passive and active microwave has been used for the monitoring of inundated areas at large scale. Prigent et al., (2007) used a combination of active and passive microwave from SSMI/AMSR-E and ERS/ASCAT to derive the Global

Inundation Extent from Multiple-Satellites (GIEMS) dataset. (Schroeder et al., 2015) derived the Surface Water Microwave Product Series (SWAMPS) product from the ERS/SSM/I and ASCAT brightness temperatures. Parrens et al., (2017) demonstrated the ability of L-Band microwave brightness temperatures (Al Bitar et al., 2017) from SMOS to provide the SMOS Water Fraction (SWAF) under the vegetation in the Amazonian basin. An enhanced algorithm using multi-angular and dual-polarization brightness temperatures has been applied to obtain a global dataset G-SWAF (Al Bitar et al., 2020). All of the above products suffer from the coarse spatial resolution of the microwave sensors (>25km). For this several fusion or disaggregation algorithms have been developed (Aires et al., 2017; Parrens et al., 2019). They rely on complementary information from Digital Elevation Models (DEM) from for example the Shuttle Radar Topography Mission (SRTM) in combination to optical data to convert the fractional information to a water mask at higher resolution. A complementary information to the surface water extents is the surface water height, as the denitrification will depend on the water depth. Water height is observed over land using.

## SOIL MOISTURE

While for denitrification, open surface water maps images are essential to determine anoxic soil condition, a complementary information is needed to pinpoint when soil moisture in the 0-30 cm is at 80% of soil saturation before the inundations, where in fact, the activation of the biogeochemical processes is reached (Yang et al., 2019). Soil moisture in the first layer of the soil (0-5 cm) can be obtained from microwave radiometers (Kerr et al., 2012; Njoku and Chan, 2006), radar backscatter (Tomer et al., 2015; Wagner et al., 2013) or proxy optical acquisitions. The availability of global acquisition in C-Band SAR from SENTINEL-1 and future L-Band global data from NASA-ISRO Synthetic Aperture Radar (NISAR) opens the way for high-resolution soil moisture but currently no global high spatial and temporal resolution product is available at the submittal of this paper.

The available global surface soil moisture datasets are provided from microwave radiometers or scatterometers at a coarse spatial resolution >25 km and high revisit frequency (1-3 days) with all-weather capacities (except during very strong precipitation) (Al Bitar et al., 2017; Dorigo et al., 2017; Entekhabi et al., 2010). The ESA CCI SM (European Space Agency Climate Change Initiative Soil Moisture) (Dorigo et al., 2017) is an ongoing effort to provide a long time series soil moisture product from the fusion of multiple sensors (SSM/I, AMSR-E, ASCAT, SMOS, SMAP). Obtaining deeper soil moisture (root zone soil moisture) information would require higher frequency radiometers like in P-Band (Garrison et al., 2018) which is not available currently. On the other hand, parsimonious water balance models (Kerr et al., 2016) and assimilation into Land Surface Models (LSM) Crow et al.,(2018) can provide relatively accurate estimates.

## LAND SURFACE TEMPERATURE

Link to a flooding event, the soil surface temperature plays an important role in the activation of the biogeochemical processes (Benoit et al., 2015; Davidson and Janssens, 2006; Saad and Conrad, 1993; Shen et al., 2020). Bachand and Horne, (1999) suggested a temperature–activity coefficient of 1.15 to 1.22 depending on water temperature. EO can provide Land Surface Temperatures (LST) over canopies, soil, or water bodies using thermal infrared observations. High resolution sensors like ECOSTRESS aboard the International Space Station (ISS), Landsat, ASTER aboard MODIS Terra, provide this information at higher than 150m resolutions but at a low temporal frequency >12 days or not globally. Moderate resolution sensors like MODIS, MOD11 and Sentinel-3 SLSTR provide LST at high temporal frequency (1-3 days) and 500m to 1km spatial resolution. The meteorological satellites (e.g. METEOSAT,

GEOS & GMS) due to their geostationary orbits provide LST at a very high temporal (15 minutes) and low spatial (< 3km) resolutions (Sobrino and Romaguera, 2004). Still, the cloud cover and atmospheric water content affects the retrievals hamper all optical sensors for LST. In these conditions the climate reanalysis data based on in-situ and EO observations (METEOSAT for ECMWF) assimilation into climate models appear as a good alternative for direct EO data (Balsamo et al., 2015). However, the current reanalysis products do not take explicitly into account the change in the water bodies extents and have biased temperatures over actual dynamic water bodies.

#### VEGETATION DYNAMICS AND TYPE

Presence of vegetation plays an essential role in the nitrogen budget and thus the denitrification process (Nilsson et al., 2020). In constructed wetlands, vegetation is used to reduce the nitrous rate in the water and acts as a sink term. Vegetation uptake depends also on the vegetation type (Bachand and Horne, 1999). Observations of vegetation dynamics are mainly assessed using EO in the visible domain. Normalised Difference Vegetation Index (NDVI) is the most used indicator to determine low vegetation density. It is generally linked to the Leaf Area Index (LAI). MODIS LAI has been applied to wetlands monitoring (Jia et al., 2009; Yan et al., 2008). For dense vegetation and tropical forests, the optical based NDVI saturates, in these conditions low frequency (P or L-Band) Synthetic Aperture Radar (SAR) (Bouvet et al., 2018) or passive microwave are used (Njoku and Chan, 2006). The more recent data from Sentinel-2 (visible) and Sentinel-1 (C-Band SAR) provides the opportunity for global high temporal (5 days) and spatial resolution (20 m) vegetation (Hu et al., 2020).

#### SOIL CHARACTERISTICS

It has been proven that the rates of N<sub>2</sub>O vary among soils at the same wet conditions (Pihlatie et al., 2004), in case of paddy soils, nitrification seems to happen in aerobic/anaerobic conditions, but the net nitrification rate was recorded at 60% WHC (53% WFPS) (Yang et al., 2019). Thus, ancillary static soil properties maps are needed to parametrize the denitrification (Colombani et al., 2020) (Appendix A.3 -Table A.3.2). The first comprehensive global soil map is the Food and Agriculture Organization of the United Nations (FAO) Soil Map (Van Engelen et al., 2005a), delivered now as the Digital Soil Map of the World (DSMW). Recognising the need of an updated database the FAO and the International Institute for Applied Systems Analysis (IIASA) created the Harmonized World Soil Database (HWSD) (Nachtergaele et al., 2010). Batjes, (2015) used a Taxotransfer procedure over HWSD to produce the WISE30sec database which includes estimates of global carbon stocks that is a mandatory criteria for

denitrification (Burgin et al., 2011; Huang and Gerber, 2015; Kumar et al., 2018). More recently machine learning was used in combination to EO and the WoSIS database to produce the SoilGrids 250 m database (Hengl et al., 2017). Large discrepancies exist between the aforementioned datasets (Tifafi et al., 2017) showed that the use of the different datasets induces large uncertainties in the carbon budget, it is expected that this result would also provide large uncertainties for denitrification studies.

### LIMITATIONS OF EARTH OBSERVATIONS

#### TEMPORAL RESOLUTION

At monthly scale, seasonality can be noticeable and it can be related to agricultural fertilizers inputs (Lu and Tian, 2017) or climate conditions. However, the accuracy to detect the activation moments is not met, and could lead to possible overestimation of wet pulses length. Moreover, an underestimation of nutrient removal linked to discharge on each event is not accounted. Thus, daily to weekly temporal scale represents an important requirement to determine useful inundation patterns.

#### SPATIAL SCALE

Denitrification occurs from very local to large scales. Current observation capacities at global scale, allows only the large-scale processes to be modelled by all the needed variables (Table 1). It is not expected that the entire set of variables will be ever observed at very high resolution as in some cases this requirement cannot be physically met. For example, the use of high frequency radiometers is adequate for soil moisture remote sensing but it is limited by the very low amount of energy that is observed ( $10\text{-}14\text{ W.m}^{-2}$ ). Limits may be pushed to deca-kilometric resolutions but not sub-kilometric. In order to work around these limitations, fusion methods that combine the accuracy of coarse scale information and the spatial resolution of visible and SAR sensors are commonly used for many of the mentioned variables (Parrens et al., 2019; Peng et al., 2017; Tomer et al., 2016)

### CURRENT STATE AND FUTURE OPPORTUNITIES

The current literature review analysis provides an opportunity to identify how wetlands research on the global nitrogen cycle had changed over time. Initially no relation of wetlands and nitrogen cycle was recognised; the focus of the research at global scale was mainly towards the discovery of different species and turning points, once they were elucidated, limitation of reactive nitrogen (Nr), and the recognition of human dependence and limitation due to natural



processes velocity for food production drove research into this topic. Once artificial N<sub>r</sub> was produced and widespread for food production, no dependence on BNF existed anymore and agriculture production became faster. This originated a larger problem, allowing the human population to increase exponentially. The impact of these facts was noticeable in the nineteenth century and realization of management errors committed were recognised i.e. pollution of surface and groundwater, greenhouse gas emissions, loss of biodiversity and forest cover.

Later on, wetlands passed from being dried out to open space to more agricultural fields to a gradual valorisation of these ecosystems, as services providers. Currently, they are starting to be integrated in the hydrological models, as key ecosystems for their relevance in the nitrogen cycle as natural processors of N<sub>r</sub> to N<sub>2</sub> improving water quality and diminishing eutrophication of aquatic and coastal ecosystems. However, wetlands need to be better understood and more protection efforts have to be implemented. The potential of these ecosystems as water purifiers, had inspired the development of technology as constructed wetlands, they represent a low-cost technology that can be adapted for treating any residual water.

In the last ten years, the research has become more quantitative, experiments and models have been developed. An important research effort regarding the identification of microbial communities that perform denitrification and anammox processes with high-tech DNA sequences has been reported. Models with different purposes, most of them aiming to isolate and quantify the source variety of pollutants and ecosystems alteration of N<sub>r</sub> at local and global scale in current and future scenarios of climate change are developing.

Denitrification approach at watershed level, including wetlands as ecosystems could be by far the most precise method if data is available. At this scale, dynamics can be understood under the light of hydrological processes. However, not all the watersheds at global scale have been monitored with the same frequency nor precision. Particularly in the southern world; many watersheds are not monitored. Global modelling is a big challenge, but recent analytical tools and field evidence are getting more precise, and the range of study cases across climates and wetland typology are consolidating the understanding of these ecosystems and their dynamics. The most recent research recorded provided more precise tools to observe change in large areas (e.g. Pekel et al., 2016), or artificially enhance biological activity (e.g. Zhu et al., 2010). Both novel tools are improving the research and if these advantages are applied, they could deflate the current environmental crisis.

Nowadays, a complementary approach is emerging by the use of parsimonious models with EO data. It is possible to have dynamic information, trace trends (i.e. seasonality & inter-annual)

and record information on large-scale areas that are difficult to sample. Availability of data at daily scale (e.g. 3 days) through a long period of time (e.g. 30 years), with high spatial resolution (e.g. 30 m) allows researchers to link this process's changes with extreme natural events like droughts, floods, and also anthropogenic impact. Even though modelling at global scale means large uncertainties, satellite data is improving and the accuracy is enhanced.

Promotion of interdisciplinary research will speed up the holistic comprehension of global wetlands' denitrification. Specialized and in-depth knowledge is needed for developing parsimonious modelling in a global change scenario linked to conservation, restoration and mitigation actions.

Anthropogenic impact is increasing at a higher rate than the understanding of natural processes, investments on ecosystem conservation and prompt research to mitigate and reverse these impacts has to be promoted. Ecosystem-based solution concept should be wide spread and endorsed, Sustainable Development Goals should be used as a political tool to improve protection of natural ecosystems, in case wetlands.

### ACKNOWLEDGEMENTS

The research presented in this paper is funded by CONACYT (The Mexican National Council for Science and Technology) in the frame of a PhD research grant (Scholar/Scholarship reference: 625261/ 471711 2017-2021) at Université Toulouse III -Paul Sabatier, Toulouse, France. We would also like to thank the Environmental Initiative research unit of CUNY, New York, USA for their hospitality during a research stay funded by the Laboratoire Ecologie fonctionnelle et environnement, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France. To Michelle Bruce and Arnaud Mansat for their skills in visualizing graphics and figures that contributed to improve the present manuscript. To Bruno Schoerlin for his valuable comments and constructive criticism of the manuscript, as well as providing a custom-designed desk for writing the manuscript.



# CHAPTER III

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## LABORATORY N<sub>2</sub>O AND N<sub>2</sub> EMISSIONS FROM CENTRAL AMAZONIAN FLOODPLAIN SOILS.



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**ABSTRACT**

This chapter presents the fieldwork and laboratory experimentation that was carried out during this thesis. The motivation for executing this fieldwork was due to the lack of data in the tropical big basins that was limiting denitrification model development. Central Amazonian floodplain was chosen due to several factors: (i) it is the biggest watershed worldwide with the largest floodplain; (ii) optimal temperature conditions all year long, (iii) low anthropogenic disturbance compare to the other biggest watersheds worldwide; (iv) two types of wetlands represented in the area (freshwater marshes and flooded forests); (v) one clear inundation period.

We present the first laboratory controlled N<sub>2</sub>O emissions from Amazon flooded forest and freshwater marshes soils covering different rivers (Amazon, Solimões, Negro and Madeira rivers). The N<sub>2</sub>O and N<sub>2</sub> emissions observed in N<sub>2</sub> atmosphere free and in unlimited nitrate and carbon concentrations prove that organic soils had a higher emission range and that there is an inhibition of N<sub>2</sub> if nitrates are abundant. The average denitrification of our samples with no addition of nutritive solution was  $0.21 \pm 0.13 \mu\text{g N (N}_2\text{O} + \text{N}_2\text{)}.g^{-1}.h^{-1}$  of which  $0.11 \pm 0.10 \mu\text{g N}_2\text{O-N}.g^{-1}.h^{-1}$  values that were above the few studies reported in the Amazonian floodplain and Peruvian Amazonian swamps. When comparing our potential denitrification results with other studies, the results from treatment 1 (T1) were in the same range as the one observed by them. Yet, results of the last treatment with the highest concentrations of nutritive solutions, our values are twice as high, what we so we hypothesize that it is due to the inhibition of complete denitrification by high nitrate concentrations; and N<sub>2</sub>O production by other processes such as Anammox. Our study demonstrates that there is a major gap in our understanding of natural N<sub>2</sub>O emissions in Amazonian wetlands, and that denitrification is influenced by soil type, soil and water pH, availability of inorganic N, microbial community, etc. It also emphasizes the potential risk that moderate disturbance of the natural conditions would create an increase in greenhouse gas emissions (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) that would be a devastating feedback on climate change. The significant relationships and nitrate saturation coefficients were then used for calibrating the global denitrification model

## RÉSUMÉ

Ce chapitre présente les travaux de terrain et les expérimentations en laboratoire qui ont été réalisés au cours de cette thèse. La motivation pour exécuter ce travail de terrain était due au manque de données dans les grands bassins tropicaux qui limitait le développement de modèles de dénitrification. La plaine inondable de l'Amazonie centrale a été choisie en raison de plusieurs facteurs: (i) c'est le plus grand bassin versant du monde avec la plus grande plaine d'inondation; (ii) des conditions de température optimales tout au long de l'année, (iii) une faible perturbation anthropique comparée aux autres grands bassins versants du monde; (iv) deux types de zones humides présentes dans la région (marais d'eau douce et forêts inondées); (v) une période d'inondation claire. Nous présentons les premières émissions de N<sub>2</sub>O contrôlées en laboratoire à partir de sols de forêts inondés et de marais d'eau douce amazoniens couvrant différentes rivières (Amazone, Solimões, Negro et Madeira). Les émissions de N<sub>2</sub>O et de N<sub>2</sub> observées en atmosphère de N<sub>2</sub> libre et en concentrations illimitées de nitrates et de carbone prouvent que les sols organiques ont une gamme d'émission plus élevée et qu'il y a une inhibition du N<sub>2</sub> si les nitrates sont abondants. La dénitrification moyenne de nos échantillons sans ajout de solution nutritive était de  $0,21 \pm 0,13 \mu\text{g N (N}_2\text{O} + \text{N}_2\text{)}.g^{-1}.h^{-1}$  dont  $0,11 \pm 0,10 \mu\text{g N}_2\text{O-N}.g^{-1}.h^{-1}$ . Ses valeurs sont supérieures aux quelques études rapportées dans la plaine inondable amazonienne et les marais amazoniens péruviens. En comparant nos résultats de dénitrification potentielle avec d'autres études, les résultats du traitement 1 (T1) étaient du même ordre de grandeur. Pourtant, les résultats du dernier traitement avec les concentrations les plus élevées de solutions nutritives, nos valeurs sont deux fois plus élevées, nous supposons que cela est dû à l'inhibition de la dénitrification complète par les concentrations élevées de nitrate; et la production de N<sub>2</sub>O par d'autres processus tels que l'Anammox. Notre étude démontre qu'il existe une lacune importante dans notre compréhension des émissions naturelles de N<sub>2</sub>O dans les zones humides amazoniennes, et que la dénitrification est influencée par le type de sol, le pH du sol et de l'eau, la disponibilité de l'azote inorganique, la communauté microbienne, etc. Ce chapitre met également l'accent sur le risque potentiel qu'une perturbation modérée des conditions naturelles crée une augmentation des émissions de gaz à effet de serre (CO<sub>2</sub>, CH<sub>4</sub> et N<sub>2</sub>O) qui serait une rétroaction dévastatrice sur le changement climatique. Les relations significatives et les coefficients de saturation en nitrate ont ensuite été utilisés pour calibrer le modèle global de dénitrification.

## RESUMEN

Este capítulo presenta el trabajo de campo y la experimentación de laboratorio que se llevó a cabo durante esta tesis. La motivación para realizar este trabajo de campo se debió a la falta de datos en las grandes cuencas tropicales que limitaba el desarrollo de modelos de desnitrificación. Se eligió la llanura aluvial de la Amazonia central debido a varios factores (i) es la mayor cuenca hidrográfica del mundo con la mayor llanura de inundación; (ii) condiciones óptimas de temperatura durante todo el año, (iii) baja perturbación antropogénica en comparación con las otras mayores cuencas hidrográficas del mundo; (iv) dos tipos de humedales representados en la zona (pantanos de agua dulce y bosques inundados); (v) un claro período de inundación. Presentamos las primeras emisiones de  $N_2O$  en condiciones controladas en laboratorio en suelos de bosques inundados y pantanos de agua dulce de diferentes ríos (ríos Amazonas, Solimões, Negro y Madeira). Las emisiones de  $N_2O$  y  $N_2$  observadas en atmósfera libre de  $N_2$  y en concentraciones ilimitadas de nitrato y carbono demuestran que los suelos orgánicos tienen un mayor rango de emisión y que existe una inhibición del  $N_2$  si los nitratos son abundantes. La desnitrificación media de nuestras muestras sin adición de solución nutritiva fue de  $0.21 \pm 0.13 \mu\text{g N (N}_2\text{O + N}_2) \text{ g}^{-1} \cdot \text{h}^{-1}$  y  $0.11 \pm 0.10 \mu\text{g N}_2\text{O-N} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  valores que estuvieron por encima de los pocos estudios reportados en la llanura aluvial amazónica y en los pantanos de la Amazonia peruana. Al comparar nuestros resultados de desnitrificación potencial con otros estudios, los resultados del tratamiento 1 (T1) estaban en el mismo rango que el observado por ellos. Sin embargo, los resultados del último tratamiento con las concentraciones más altas de soluciones nutritivas, nuestros valores son el doble de altos, por lo que hipotetizamos que se debe a la inhibición de la desnitrificación completa por las altas concentraciones de nitrato; y la producción de  $N_2O$  por otros procesos como Anammox. Nuestro estudio demuestra que hay un gran vacío en nuestra comprensión de las emisiones naturales de  $N_2O$  en los humedales amazónicos, y que la desnitrificación está influenciada por el tipo de suelo, el pH del suelo y del agua, la disponibilidad de N inorgánico, la comunidad microbiana, etc. También se hace hincapié en el riesgo potencial de que una alteración moderada de las condiciones naturales genere un aumento de las emisiones de gases de efecto invernadero ( $CO_2$ ,  $CH_4$  y  $N_2O$ ) que supondría una retroalimentación devastadora para el cambio climático. Las relaciones significativas y los coeficientes de saturación de nitratos se utilizaron para calibrar el modelo de desnitrificación global.

## CHAPTER III



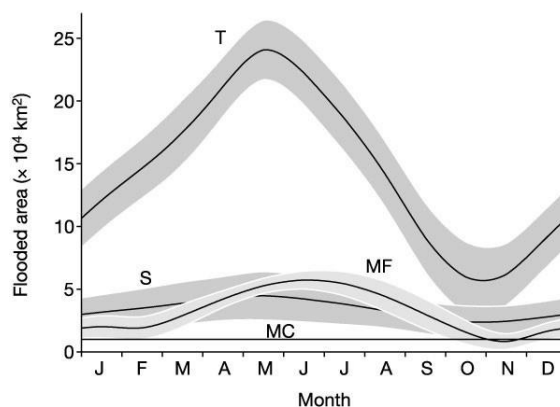
## INTRODUCTION

The Amazon basin covers an area of about 7,000,000 km<sup>2</sup>, Amazon river discharges roughly fifteen to twenty percent of the world's annual freshwater into the ocean (Pekárová et al., 2003), and Amazonian floodplain forests cover an area of more than 97,000 km<sup>2</sup> (Hamilton et al., 2002). Dimensions of this basin, reflects the meaning of water movement and abundance in life shaping global biogeochemical cycles (Vörösmarty et al., 1989). This basin hosts 40% of the world's remaining rainforest, 25% of global terrestrial biodiversity and more fish species than any other river system (Trancoso et al., 2009). As a tropical basin, mean annual temperature is 26.6°C with little variations; average rainfall is 2100 mm per year (Ribeiro and Adis, 1984). Together, these conditions are optimal for autotroph growth in the whole basin, therefore, the Amazon basin biodiversity and abundance of *terra firme* forest is the richest on Earth (Junk and Piedade, 1993). Even though floodplains are less diverse than their adjacent terrestrial ecosystems, flora diversity is estimated at 1000 species (Parolin et al., 2004).

Amazonian floodplains are directly linked to the lateral flood pulses (Junk et al., 1989; Keizer et al., 2014). A very regular monomodal flood pulse defines a rich specific species distribution and zonation along the flooding gradient of the central amazon floodplains (Kubitzki, 1989). These pulses are the main force that determine the biota and its interactions with the river and terrestrial ecosystems in this basin (Anjos et al., 2008). Resulting in two main vegetation cover, forested floodplains (swamps) versus floodable savannahs (freshwater marshes). Floodplains can also be characterized by the amount of dissolved and suspended content (i.e. nutrient-rich, floodplains of white water rivers versus nutrient –poor black water river or floodplains inundated by rainwater) (Fernandes-Corrêa and Furch, 1992). Vegetation represents the largest pool of nutrients and organic matter in the Amazon (Worbes et al., 1992).

The long and intense lateral flood pulse are due to a combination of geomorphology and hydrological connectivity (Martinez and Le Toan, 2007; Noe et al., 2013; Tockner and Stanford, 2002). At watershed scale, floodplains have shown significance to regional carbon biogeochemistry. It has been reported that the CO<sub>2</sub> outgassing from rivers and wetlands of the central Amazon basin has been estimated to be  $1.2 \pm 0.3 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$ , extrapolating across the entire basin this flux  $0.5 \text{ Gt C yr}^{-1}$  is at least 10 times the fluvial export of organic carbon to the ocean (Richey et al., 2002). The carbon source for the outgassing comes from riparian and flooded forest, that fluctuates seasonally with inundation changes. CO<sub>2</sub> emissions is an example of the important role of floodplains in the Amazonian basin. However, less is known regarding

CH<sub>4</sub> and N<sub>2</sub>O. These gases also fluctuates seasonally, and accurate estimation of methane and nitrous oxide emissions from Amazonian wetlands requires knowledge of seasonal changes of organic matter (Devol et al., 1990) and vegetation as well as flooding seasonality (Rosenqvist et al., 2002). The hydrographic (Figure 12) of the central Amazonian floodplains is partitioned by hydrographic environments, showing a different temporal behaviour. Tributaries located in the north reach their peak in June or July whereas south tributaries typically reach their peak in April or May (Richey et al., 2002).



**Figure 12.** Spatially integrated annual sequences of surface water area for hydrographic environments as determined from JERS-1 radar data and multi-year hydrographic records. Hydrographic environments are divided into: Amazon mainstem channel (MC); the mainstem floodplain (MF); the channels and floodplains of tributaries over 100 m wide (T); and the streams and riparian zones less than 100 m wide (S). Shaded regions represent 67% confidence intervals determined by Monte Carlo error propagation of both measurement uncertainties and interannual variability in river stage data from (Richey et al., 2002).

Biota adaptation to floodplain soils begins with the adaptability to flood pulses and changes of the water table, which causes drastic changes in the bioavailability of nutrients, oxygen content, and concentration of phytotoxins (Herbert et al., 2015). The reduced oxygen (O) content, during anoxic periods promoted by inundated soils, is rapidly consumed by roots and microorganisms. Oxygen depletion reduces soil redox potential, increases levels of CO<sub>2</sub> and solubility of mineral substances, simultaneously, the biological anaerobic nitrogen pathways are activated (Canfield et al., 2010). Microbiota living in these soils exchange their mechanisms in order to survive in altering hypoxic and oxygenated conditions. Plants have developed a range of structural, physiological, and phenological adaptations, which resulted in a variety of growth strategies (Evans and Wallenstein, 2012). According to Huang and Gerber, 2015 it is widely known that C and N cycles are intimately related in wetlands, nevertheless further measurements in situ should be performed to better understanding the influence of N turning points in wetlands (Guilhen et al., 2020; Updegraff et al., 1995).

Nitrates reaches the floodplains in the dissolved and particulate load from the rivers during floods and from the atmosphere as dry deposition via N fixation and precipitation. Anthropogenic sources have been reported as negligible and nitrogen have been reported as limiting factors for primary production (Furch and Junk, 1997). Aerobic microbiological process of nitrification take place during wetlands' dry period. However, during wet periods, the anoxic conditions trigger three different processes: denitrification, dissimilatory nitrate reduction (DNRA) and Anammox, of which denitrification as the main process in wetlands ecosystems (van den Berg et al., 2017).

The relevance of understanding these processes is crucial in the global change scenario. Current CO<sub>2</sub> and N<sub>2</sub>O emission coming from anthropogenic origin are doubling the natural emissions, and they keep increasing (Cramer et al., 2001; Liu and Greaver, 2009; Tian et al., 2018) Nitrous oxide is the third most important long-lived greenhouse gas (GHG) and an important stratospheric ozone depleting substance. Agricultural practices and the use of N-fertilizers have greatly enhanced emissions of N<sub>2</sub>O, recent global estimation estimates an N<sub>2</sub>O emission increase by 1.6 (1.4-1.7) TgN y<sup>-1</sup> between 2000-2005 and 2010-2015, however since 2009 N<sub>2</sub>O emissions increased substantially at a faster rate than estimated by the Intergovernmental Panel on Climate Change (IPCC) emission factor (EF). The regions of East Asia and South America made the largest contribution to the global increase (Thompson et al., 2019).

The IPCC provides guidelines for estimating regional and global N<sub>2</sub>O emissions, which are calculated by multiplying N loading with the indirect emission factors (EF)(IPCC, 1996). These EFs had been adapted after several studies called for the IPCC's revision. The indirect N<sub>2</sub>O emission factor associated with N leaching and runoff (EF<sub>5</sub>: kg N<sub>2</sub>O-N per kg of NO<sub>3</sub><sup>-</sup>-N) incorporate three components: (i) groundwater and surface drainage (EF<sub>5g</sub>); (ii) rivers (EF<sub>5r</sub>); (iii) and estuaries (EF<sub>5e</sub>). In a 2006 IPCC report the EF<sub>5</sub> factor was set to 0.75 (IPCC, 2006). Then, in the last IPCC report (2019), the EF<sub>5r</sub> and EF<sub>5e</sub> were adapted to 0.26 according to 91 data observations compiled by (Tian et al., 2019), and a mean value of the EF<sub>5g</sub> for ground and surface drainage was 0.60.

A recent model based on Earth Observation estimates an yearly average wetlands denitrification and associated emissions of N<sub>2</sub>O and CO<sub>2</sub> over the entire watershed at 17.8 kgN.ha<sup>-1</sup>.yr<sup>-1</sup>, 0.37 gCO<sub>2</sub>-C.m<sup>-2</sup>.yr<sup>-1</sup> and 0.18 g N<sub>2</sub>O-N m<sup>-2</sup>.yr<sup>-1</sup> (Guilhen et al., 2020). Using a N<sub>2</sub>O/N<sub>2</sub> emission ratio of 0.1. However, they remark the need of local observations to validate these estimations, and they agree that the main drivers for denitrification are organic carbon concentration in the

soil solution and extent of flooded area. Better understanding of bacteria functioning and emissions from natural ecosystems is fundamental for comprehension of wetlands resilience, their valorisation and imminent protection. At global scale Amazon floodplains represent a significant floodplain area, their pristine conditions in current times is of major relevance for the biogeochemical nitrogen cycle, and may be an important sink of N<sub>2</sub>O emissions

The present study aimed to contribute with field measurements of N<sub>2</sub>O emissions, collecting in situ data of soil characteristics (i.e. soil organic carbon, bulk density and nitrate soil concentration), diversity of wetlands ecosystems of the central floodplain, and quantify the actual and potential N<sub>2</sub>O emissions of these floodplains in laboratory-controlled conditions.

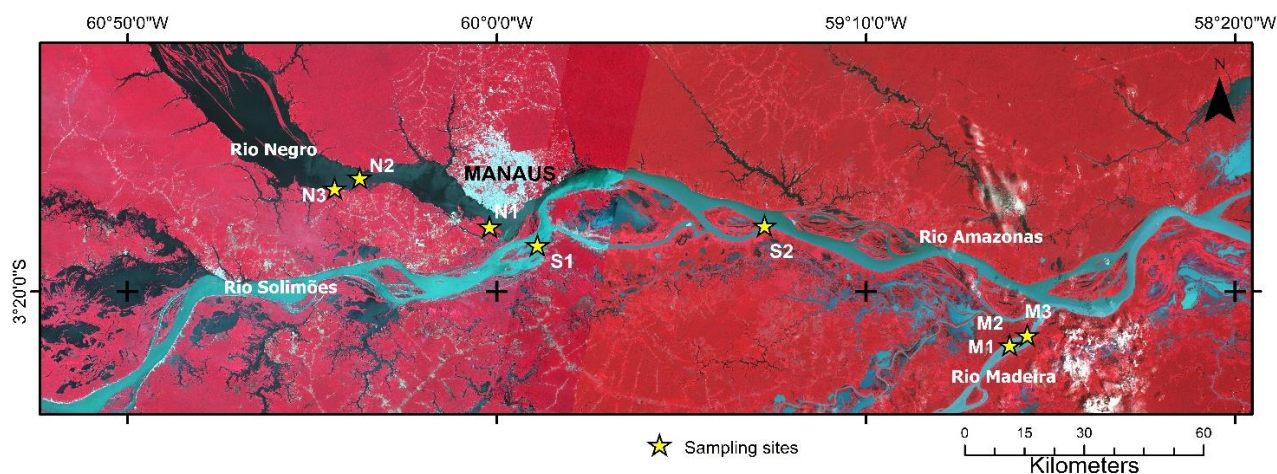
## MATERIALS AND METHODS

### STUDY SITE

A fieldwork campaign was carried out from 14<sup>th</sup> to 24<sup>th</sup> February 2020 along small range of the Amazon River and three of its main tributaries (Rio Negro, Rio Solimões and Rio Madeira). The tributaries studied in the present research, were a northern tributary (Rio Negro), and two southern tributaries (Rio Solimões and Madeira).

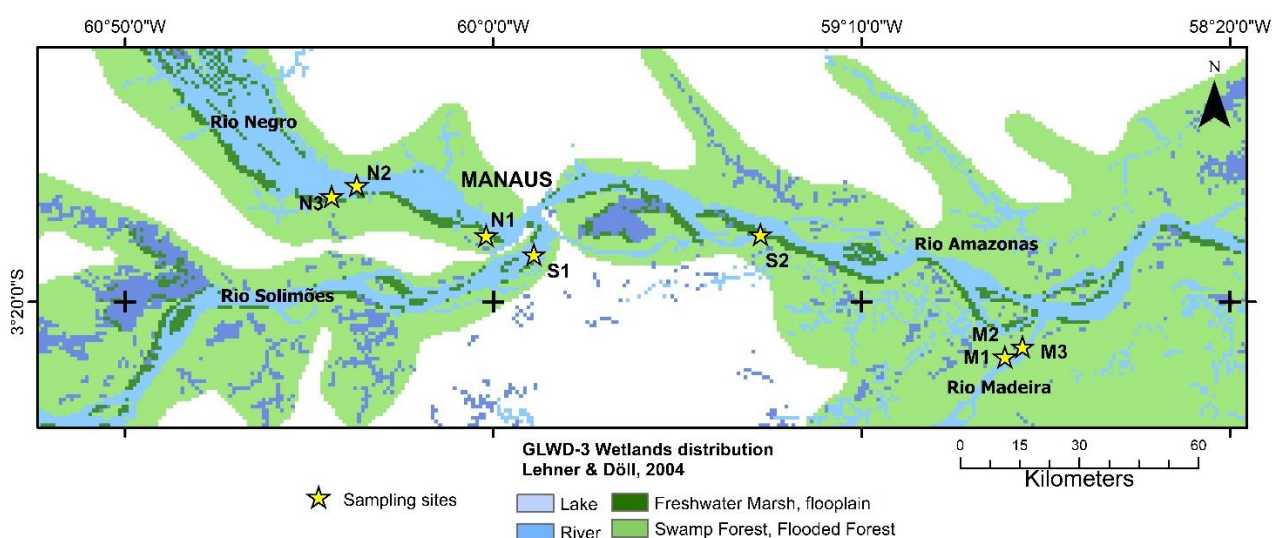
Rio Negro's source is in Colombia, it's name comes from the black colour of its water, consequence of its high level of iron and organic matter due to humus decomposition from forest soils with makes it acidic (pH= 5.5) and warm (28-30°C). Diversely, Solimões river is the part of the Amazon river that crosses the tri-border area of Peru, Colombia and Brazil and ends at Manaus. Its water is mainly muddy, charged in silt, neutral water (pH=7) and temperature of 20-22°C. Its flow is three times more important than Rio Negro mean annual flow (103 000 m<sup>3</sup>.s<sup>-1</sup> versus 29 300 m<sup>3</sup>.s<sup>-1</sup>). The confluence of these two rivers give birth to the Amazons river. The mixture of the two rivers is not obvious, however this is completed with the arrival of Rio Madeira, an even muddier river, found 150 km downstream. Rio Madeira, is the longest affluent of the Amazons, with a mean annual flow of 32 000 m<sup>3</sup>.s<sup>-1</sup>, and has its source in the Andes mountain range.

False-colour satellite image (Figure 13) illustrates the different colours of the rivers, and the confluence of these rivers. The eight sampling points were chosen taking into account the diversity of the study site explained above. Two sites were placed in Negro river (N2, N3), and one just in front of Manaus (N1), then one site in Solimões (S1) and the other one after Manaus, in the main stream but still in the Solimões side (S2), the last three sites were taken downstream in the Madeira river (M1-M3).



**Figure 13.** False-colour satellite image, of two Landsat-8 images courtesy of the U.S. Geological Survey, 2015-09-11 showing the different watercolour of each affluent river of the Amazons, sample sites indicated.

In addition to the water quality differences of these three rivers, there are two different types of wetlands ecosystems represented in this region, where the fieldwork was carried out. Figure 14 is the illustration of floodplains and flooded forest distribution; the sample sites also captured the ecosystem diversity.

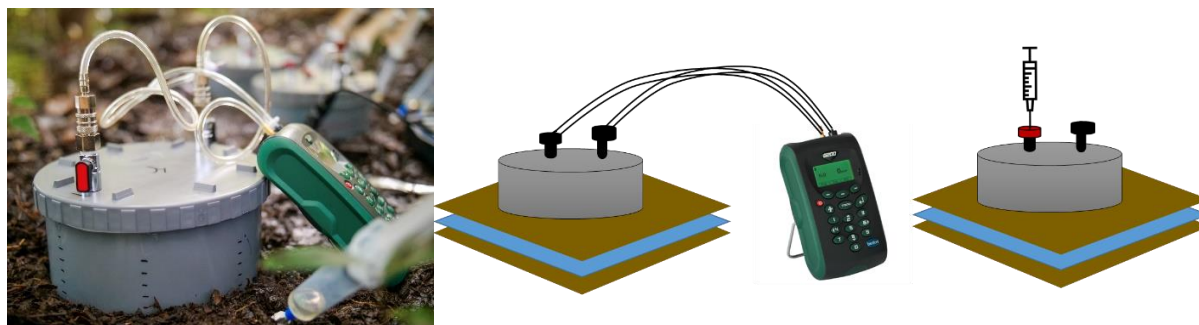


**Figure 14.** The two main wetland types, floodplain (light green) and flooded forest (dark green), lakes (dark blue) and river (light blue) distributed in the sampling area (Lehner and Doll, 2004).

## EXPERIMENTAL DESIGN

The  $N_2O$  fluxes were measured using the closed chamber technique, as described in Rochette, 2011. In each sampling site three chambers were placed. The chambers (diameter 25 cm and height 10 cm) were hermetically closed for 3 h, by fitting them into the soil to minimize the lateral diffusion of gases as explained by Hutchinson and Livingston, 2001. Gas samples were taken via a septum in the chamber lid and placed in 20 ml pre-evacuated vials at 0, 30, 60 and 180 min to test the linearity of headspace gas accumulation (Figure 15). One of the chambers

via a septum in the chamber lid was connected to a G200 N<sub>2</sub>O device that records real-time N<sub>2</sub>O with a minimum concentration of (1 ppm) (Figure 15). The gas samples were transported to Toulouse, France, and concentrations of N<sub>2</sub>O were quantified by gas chromatography, using a HP-6890 gas chromatograph (GC).



**Figure 15.** Chamber installed in the field photo by Arnold Mansat, followed by an illustration of the closed chamber technique, showing 25 x 10 cm chamber with two exits on the upper part, two chambers were not connected to the G200 device, and gas samples were taken with a syringe.

At each site, three independent small soil cores of about 10 cm long and 5 cm diameter were manually taken with a metal cylinder from the A horizon (0-10 cm) of eight different central Amazonian floodplains. Sampling depth was selected since the majority of the plant roots are concentrated in the uppermost 10 cm (Koschorreck and Darwich, 2003). Interstitial water samples were taken from each site, as well as redox potential, temperature and pH measurements. Soil and water samples were kept in ice; later transported to Toulouse, France and stored at 4°C before their analysis.

To carry out the experimentation subsequently explained (sections 2.2 and 2.3) sixty grams of each soil type were divided into three 125 ml glass flasks, having ~ 20 g per flask (n=3 each soil type). Biological activity was re-established in stored 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 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 G200 N<sub>2</sub>O device for quantifying N<sub>2</sub>O emission from soil activity, when limiting conditions. For the potential denitrification in unlimited conditions, concentrations recorded were above the sensibility of the real-time device (G200). Therefore, it was used as the only reading device for the rest of the experiments.

## LABORATORY DENITRIFICATION RATE

In order to quantify the denitrification, acetylene inhibition method as describe in Tiedje et al., 1989 was applied. The headspace of each container was replaced by helium (He). The flasks were incubated during three hours at 25°C, shaking the flasks every half an hour. Gas samples of the headspace of all flasks were taken for N<sub>2</sub>O analysis using 20 ml for evacuated vials for gas chromatography and 30 ml for G200 direct detection.

Subsequently the flasks were opened and aerated for five minutes, then again closed, the headspace replaced by He and 20 ml of C<sub>2</sub>H<sub>2</sub> (g) was added to each flask in order to inhibit the nitrous oxide reductase enzyme. Soil samples were again incubated, then after 3h, 20 ml of gas samples were extracted for measurement.

Potential denitrification ( DEA=*Denitrifier Enzyme Activity*) was measured using acetylene-inhibition technique (Balderston et al., 1976; Koschorreck and Darwich, 2003; Tiedje et al., 1984). To achieve potential denitrification rates, soil cores were incubated during three hours at 25°C, under anaerobic condition, replacing the headspace with helium (He), 20 ml of acetylene (C<sub>2</sub>H<sub>2</sub>) was added to each flask at the beginning of incubation. In order to identify the nitrate concentration needed to achieve the potential denitrification, five different treatments with progression of nutrient solutions (CH<sub>3</sub> COOH and KNO<sub>3</sub>) were applied. Concentrations are shown in Table 3 and were applied from 1 to 5.

**Table 3.** Treatments with different concentration of nitrates and carbon solution applied progressively from less to more.

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

A N<sub>2</sub>O content of the headspace was determined every half an hour within the following three hours. 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<sup>-3</sup>. Potential denitrification rates were calculated from the linear increase of the N<sub>2</sub>O content in the flask and expressed as µg N<sub>2</sub>O g<sup>-1</sup>.h<sup>-1</sup>. All data is expressed per gram of sediment on a

dry basis. The total N<sub>2</sub>O production (Eq. 1) was calculated by the N<sub>2</sub>O gas fraction and liquid fraction measured in ppm, and then converted to µg N<sub>2</sub>O gas (Eq. 1.1) and liquid (Eq. 1.2) as follows,

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

With

$$N_2O_g = \frac{(2,211 \cdot 10^{-8} \cdot M_{ppm}) - (4,35 \cdot 10^{-9})}{\frac{0,00468}{1,817 \cdot 10^{-3}}} \cdot 1000 \quad \text{Eq. 1.1}$$

$$N_2O_l = (1,536 \cdot 10^{-9}) \cdot M_{ppmv} \cdot W_v \cdot 10^6 \quad \text{Eq. 1.2}$$

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-N<sub>2</sub>O, N-N<sub>2</sub>O+N<sub>2</sub> and N-N<sub>2</sub>O production ratio were calculated in dry sediment basis as follows,

$$k_{N-N_2O} = \frac{N_2O_t}{DS} * \frac{28}{44} \quad \text{Eq 2}$$

If C<sub>2</sub>H<sub>2</sub> added,

$$k_{N-N_2O+N_2} = \frac{N_2O_t}{DS} * \frac{28}{44} \quad \text{Eq 3}$$

$$k_{N-N_2} = k_{N-N_2O+N_2} - k_{N-N_2O} \quad \text{Eq 4}$$

where  $k_{N-N_2O}$  refers to the production rate of N<sub>2</sub>O (µg N g<sup>-1</sup> h<sup>-1</sup>) when there is no inhibition with acetylene, and  $DS$  is the dry soil weight (g), when acetylene is applied then the N<sub>2</sub>O ratio recorded is  $k_{N-N_2O+N_2}$  which is the sum of (N<sub>2</sub> and N<sub>2</sub>O) and is also expressed in µg N g<sup>-1</sup> h<sup>-1</sup>, then  $k_{N-N_2}$  referees only to the N<sub>2</sub> production ratio (µg N g<sup>-1</sup> h<sup>-1</sup>), as subtraction of the two previous equations.

#### DATA ANALYSIS

Results are reported as mean ± SD. Principal component analysis (PCA) was executed for natural emissions. Differences between sites, locations, and treatments were assessed using 1-way ANOVA (Tukey post-hoc was applied). Pearson's correlation was used to establish relationships between site-mean emission vs. soil properties the p-value was calculated, only the significant correlations (α=0.05) are presented.



## RESULTS

## SOIL CHARACTERISTICS





The eight sites sampled in the central Amazonian floodplain showed a large range of values in the soil properties analysed (Table 4). For example, regarding C content, one of the main factors controlling denitrification, Negro river samples (N1, N2, N3) vary from 0.17 to 190 (g C kg<sup>-1</sup> soil), in the Solimões river, the values ranged from 6.37 to 89 (g C kg<sup>-1</sup> soil) and in the Madeira river 0.64 to 12.65 (g C kg<sup>-1</sup> soil). The lowest value was found in the sandy beach (N2). Aligned to these results the ratio C/N showed that the flooded forest of the Negro river (N1, N3) had the highest ratio, followed by the Solimões sites and the Madeira, with the lowest value found in the sandy beach (N2).

**Table 4.** Central Amazonian sampled floodplain soil characteristics.

Site: Rio Negro, N1- Flooded forest	3°18' S, 60°06' W	Soil	Soil: Rio Madeira, M1 Freshwater marsh	3°45' S, 58°84' W	Soil
					
		Organic matter (g · g <sup>-1</sup> ) 47.66 Bulk density (kg · dm <sup>-3</sup> ) 0.40 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.03 Organic Carbon (g · kg <sup>-1</sup> ) 190.28 Porosity 0.85 C/N ratio 16.17			Organic matter (g · g <sup>-1</sup> ) 2.18 Bulk density (kg · dm <sup>-3</sup> ) 1.27 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.15 Organic Carbon (g · kg <sup>-1</sup> ) 4.41 Porosity 0.52 C/N ratio 7.99
Soil: Rio Negro, N2- Sandy beach	3°09' S, 60°36' W	Soil	Soil: Rio Madeira, M2 Freshwater bush marsh	3°45' S, 58°84' W	Soil
					
		Organic matter (g · g <sup>-1</sup> ) 1.47 Bulk density (kg · dm <sup>-3</sup> ) 1.68 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.12 Organic Carbon (g · kg <sup>-1</sup> ) 0.18 Porosity 0.37 C/N ratio 1.42			Organic matter (g · g <sup>-1</sup> ) 6.47 Bulk density (kg · dm <sup>-3</sup> ) 1.10 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.15 Organic Carbon (g · kg <sup>-1</sup> ) 12.66 Porosity 0.59 C/N ratio 7.44
Soil: Rio Negro, N3- Flooded forest	3°06' S, 60°30' W	Soil	Soil: Rio Madeira M3 Freshwater bush marsh	3°43' S, 58°80' W	Soil
					
		Organic matter (g · g <sup>-1</sup> ) 5.61 Bulk density (kg · dm <sup>-3</sup> ) 1.35 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.07 Organic Carbon (g · kg <sup>-1</sup> ) 17.13 Porosity 0.49 C/N ratio 15.43			Organic matter (g · g <sup>-1</sup> ) 4.83 Bulk density (kg · dm <sup>-3</sup> ) 1.62 Mineral N-NO <sub>3</sub> <sup>-</sup> (mg · l <sup>-1</sup> ) 0.14 Organic Carbon (g · kg <sup>-1</sup> ) 0.64 Porosity 0.39 C/N ratio 4.52

CHAPTER III

Table 4. Continues

Soil: Rio Solimões S1 Flooded forest	3°22' S, 59°90' W	Soil	Soil: Rio Solimões S2 Freshwater bush marsh	3°18' S, 59°39' W	Soil
		Organic matter (g · g <sup>-1</sup> )			Organic matter (g · g <sup>-1</sup> )
		22.19			3.41
		Bulk density (kg · dm <sup>-3</sup> )			Bulk density (kg · dm <sup>-3</sup> )
		0.77			1.29
		Mineral N (mg · l <sup>-1</sup> )			Mineral N (mg · l <sup>-1</sup> )
		0.033			0.10
		Organic Carbon (g · kg <sup>-1</sup> )			Organic Carbon (g · kg <sup>-1</sup> )
		89.16			6.37
		Porosity			Porosity
		0.71			0.52
		C/N ratio			C/N ratio
		11.08			10.24

The highest N<sub>2</sub>O production was recorded in the flooded forest of the Negro river located the closest to Manaus city (N<sub>2</sub>O = 0.32 ± 0.1 μg N g<sup>-1</sup> h<sup>-1</sup>). This rate was almost the double compared to N3, S1, M1 and M2. The sandy beach did not show any emission. Concerning N<sub>2</sub> emission, four sites (N3, S2, M1 and M2) shown higher rate of N<sub>2</sub> than N<sub>2</sub>O. The site with the highest N<sub>2</sub> emission was the flooded forest of the Negro river (N3) with a rate of 0.23 ± 0.02 μg N g<sup>-1</sup> h<sup>-1</sup>. The sandy beach (N2) shown no emissions and the freshwater bush marsh (M3) shown the least (Figure 16).

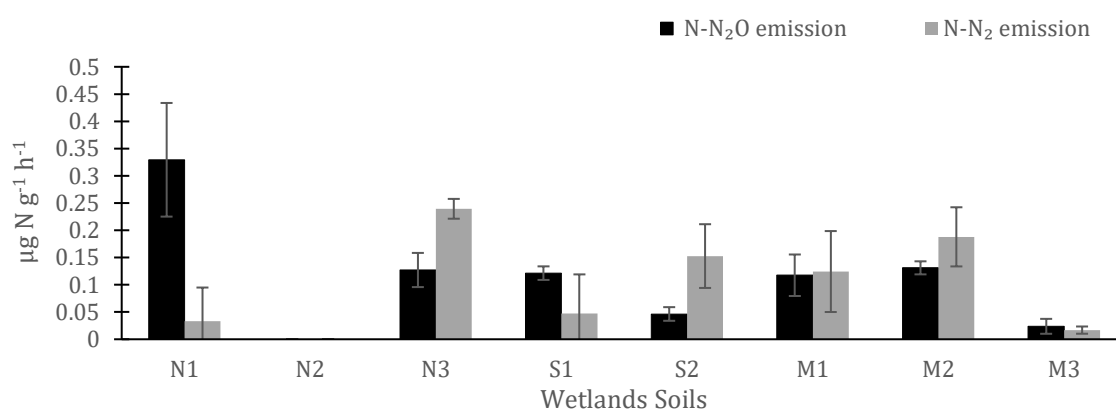


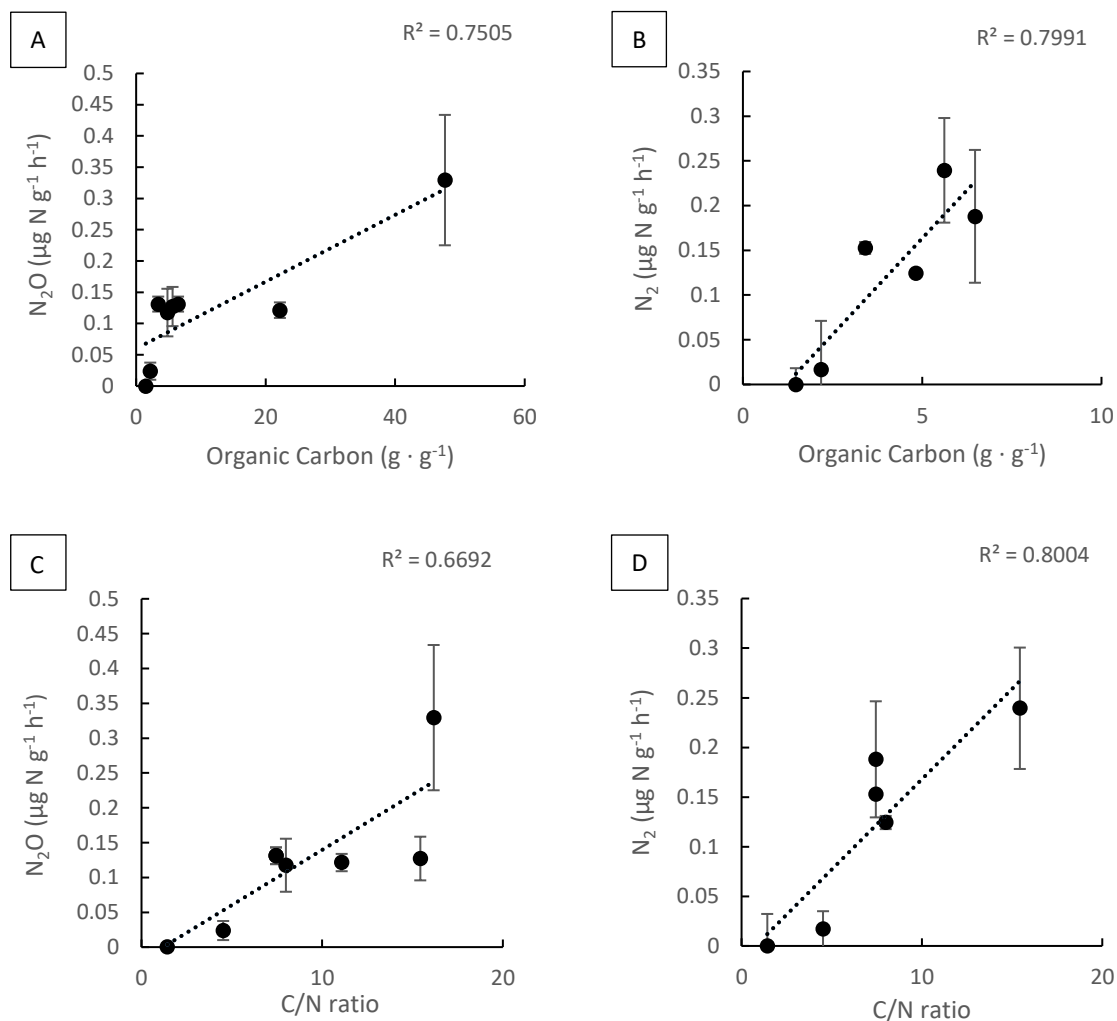
Figure 16. Mean and Standard Error of N<sub>2</sub>O and N<sub>2</sub> production rate of soil samples of each wetlands with no nitrates or carbon added in Laboratory controlled conditions (25°C and complete soil water saturation) (n=3) and N<sub>2</sub> atmosphere free (N = Negro, S=Solimoes, M= Madeira, + number site).

The results above show that each sites have their own production rates and that the ratio of production (Table 5) is variable from site to site., however no significant difference among sites are recorded. The flooded forests N1 and S1 had a ratio production that favoured N<sub>2</sub>O. The freshwater marsh S2 had a higher N<sub>2</sub> production (0.23), soil N2 show no emissions.

**Table 5.** N<sub>2</sub>O-N<sub>2</sub> Ratio natural emissions in controlled laboratory conditions

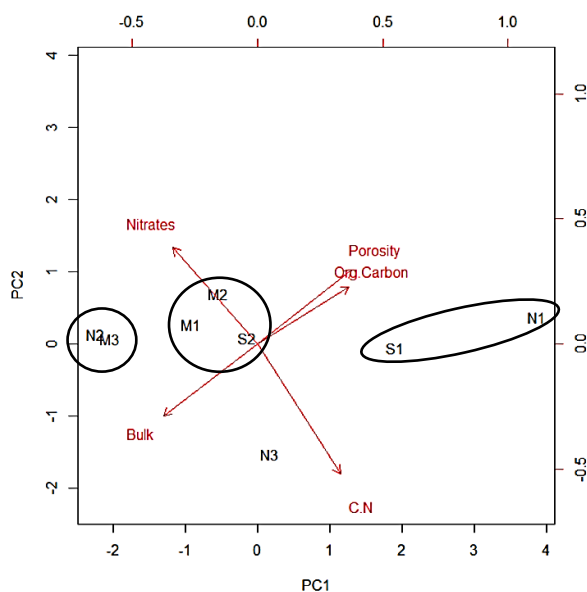
	N1	N2	N3	S1	S2	M1	M2	M3
<i>N<sub>2</sub>O-N<sub>2</sub> ratio</i>	99%	-	5%	3%	25%	9%	7%	14%

Correlation analysis of the mean values (n=3) of each soil type (n=8) are presented in Figure 17 A-E. N<sub>2</sub>O emission were negative correlated to bulk density ( $R^2 = 0.82$ , p-value= 0.001) and positive correlated to organic carbon content ( $R^2 = 0.75$ , p-value= 0.005) and therefore also to porosity ( $R^2 = 0.82$ , p-value= 0.001) and C/N ratio ( $R^2 = 0.66$  p-value= 0.014). N<sub>2</sub> emissions from the whole samples were not significant correlated to any of the soil properties analysed. So, in order to test if mineral soils N<sub>2</sub> emissions could be correlated with the soil properties, organic soils (N1 and S1) were excluded. Doing so, it was observed that the mineral soils (n=6) have positive correlation to N/C ratio ( $R^2 = 0.8$  p value= 0.016), followed by organic carbon content ( $R^2 = 0.79$  p value= 0.01).



**Figure 17. A-E** Significant correlations ( $p$ -value  $< 0.05$ ) between soil characteristics and N<sub>2</sub>O, from mineral and organic soils ( $n=8$ ) and N<sub>2</sub> emissions only for mineral soils ( $n=6$ ).

Once with all the results, a principal component analysis was carried out, in order to identify which soil characteristics, influence the N<sub>2</sub>O and N<sub>2</sub> emissions observed (Figure 18). Three main groups were identified, sample site N2 recorded zero emissions and M3 recorded the least, which is negatively related to nitrate concentration porosity and organic carbon. An intermediate group composed of two sites located in the Madeira River (M1, M2) and the site located in the main stream on the Solimões side (S2), this group is positively influenced by nitrates and negatively influenced by C/N ratio. S1 and N1 are located close to the confluence and the main components that define this group are porosity and organic carbon. Negro river sample (N3) was not grouped with the other sites and it is mainly influenced by C/N ratio.



**Figure 18.** Ordination plot based on PCA, showing the soil characteristics measured and the distribution of the samples:  $N_i$ =Negro sites,  $S_i$ =Solimões sites, and  $M_i$ =Madeira sites. PC1 represents 83% of the variance of the dataset and PC2 explains 8%.

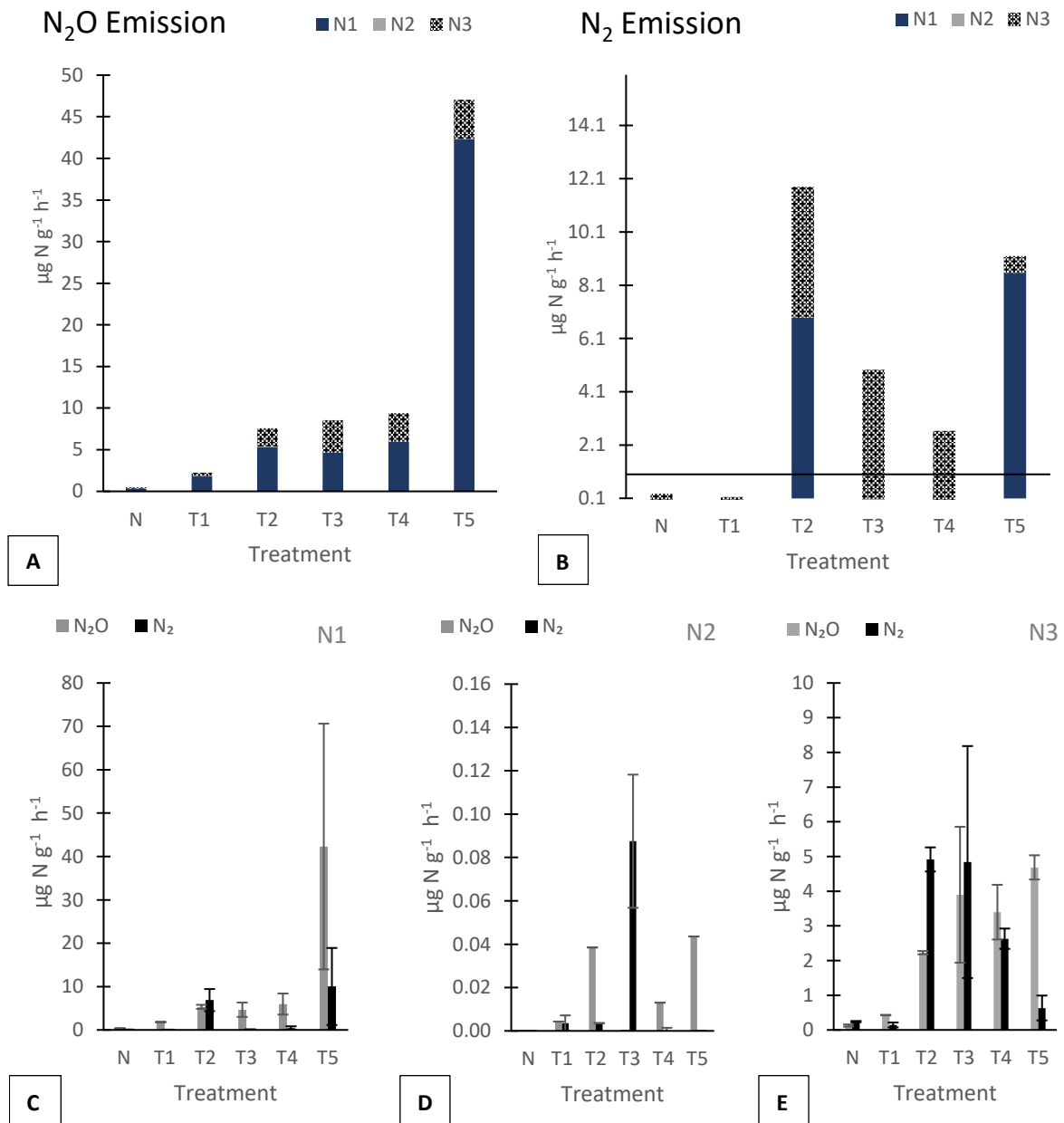
### POTENTIAL EMISSIONS

$N_2O$  and  $N_2$  emissions were recorded in different treatments (T1-T5) (Table 3). Results in this subsection are presented by river and then by gas ( $N_2$  and  $N_2O$ ). Figure 19 A-E, corresponds to Negro soil samples, Figure 20 A-D to Solimões soil samples and Figure 21 A-E to Madeira Natural emissions (N) from previous section are integrated in this section as reference of no addition of nutrient solution (control).

#### NEGRO RIVER WETLANDS SOILS $N_2O$ - $N_2$ EMISSIONS

Flooded forest-N1 continue to be in main contributor of Negro river  $N_2O$  emission (Figure 19.A). In T5 the emissions increased four-fold. Flooded forest-N3 did not respond the same way, highest emission was recorded in T3 (Figure 19.E), with a large variation (standard error), in the subsequent treatments there was a decrease. At the last, the sandy beach showed very low activity, with a highest mean value of  $0.45 \pm 0.39 \mu\text{g N g}^{-1} \cdot \text{h}^{-1}$  in T4.

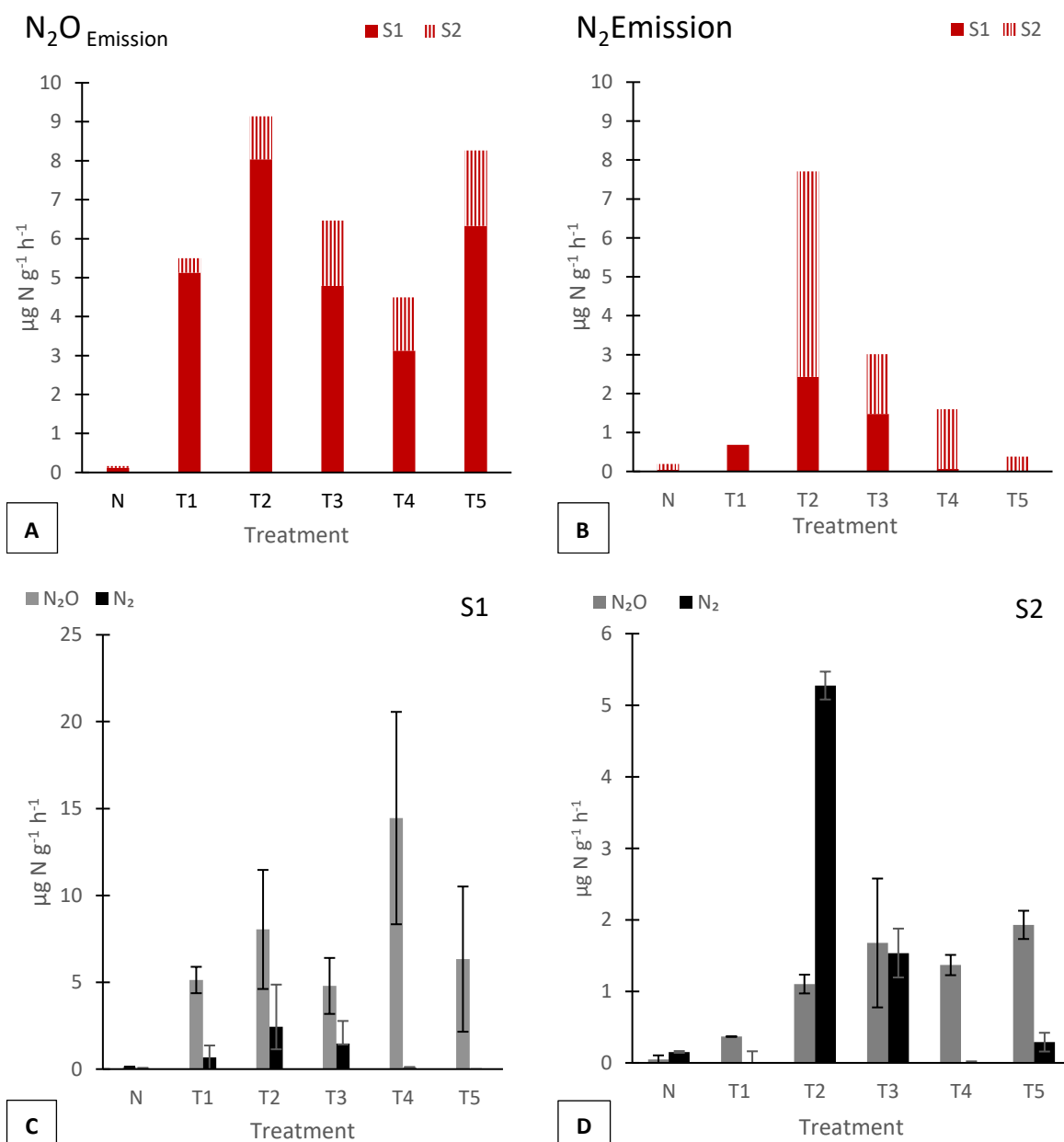
The pattern related to  $N_2$  is not the same; the maximum emission is reached in T2, with a similar contribution of the two flooded forests (N1 and N3). Looking at each site separately, N3 emission reaches its peak in T3, but variability among replicates is higher. N1 had more  $N_2$  emission in T5, but the total emission in T5 is mainly  $N_2O$ . The sandy soil also had its peak in T3; still the quantity is very low in any case.



**Figure 19.** Negro river wetlands soils sampled **A** Compile N<sub>2</sub>O emission, **B**. Compile N<sub>2</sub> emission. Total emissions from no addition of nutrient solution (N) and different treatments (T1-T5) on the three sites sampled, N1, N2 and N3. **C-E** Histograms with standard error bars of N<sub>2</sub> and N<sub>2</sub>O emissions by sites.

SOLIMÕES RIVER WETLANDS SOILS  $N_2O$  - $N_2$  EMISSIONS

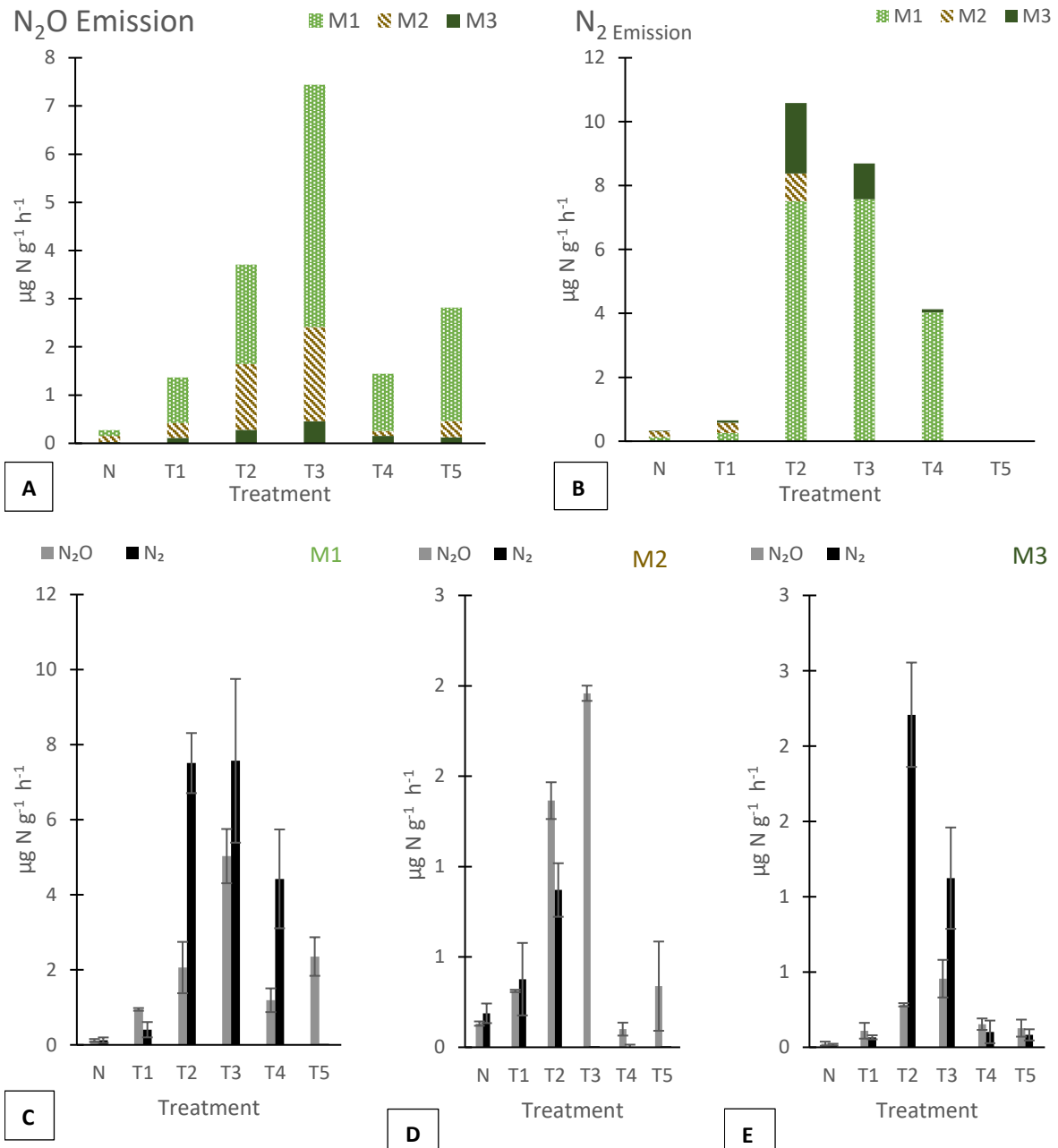
Same as the flooded forest in the Negro river (N1), flooded forest (S1) was the main contributor of Solimões river  $N_2O$  emission (Figure 20 A). In this case, the peak was reached in T2, and after a decline is observed and then a second peak in T5. When observing the  $N_2$  emission, the freshwater marsh (S2) takes advantage, same as  $N_2O$ ,  $N_2$  peaks in T2 then emission decline in both sites. Less disparity in  $N_2$  and  $N_2O$  total emission rate comparing the Negro river samples, yet higher uncertainties are observed in the  $N_2O$  emission.



**Figure 20.** Solimões River wetlands soils sampled **A** Compile  $N_2O$  emission, **B**. Compile  $N_2$  emission. Total emissions from no addition of nutrient solution (N) and in different treatments (T1-T5) on the two sampled sites, S1, S2. **C-D** Histograms with standard error bars of  $N_2$  and  $N_2O$  emissions by sites.

MADEIRA RIVER WETLANDS SOILS  $N_2O$  - $N_2$  EMISSIONS

The three Madeira's wetlands are freshwater marshes and their response to treatments was alike. The freshwater marsh (M1) had the highest emissions of N<sub>2</sub>O and N<sub>2</sub> (Figure 21 A-B). In T3, the three samples reach their peak of N<sub>2</sub>O emission followed by a steep decrease. Null N<sub>2</sub> emissions were recorded in T5 for M1 and M2 samples. Freshwater marsh (M1 and M3) recorded higher N<sub>2</sub> than N<sub>2</sub>O emissions in T2 and T3. The freshwater marsh (M2) record none or very low N<sub>2</sub> after T2.



**Figure 21.** Madeira River wetlands soils sampled **A** Compile N<sub>2</sub>O emission, **B**. Compile N<sub>2</sub> emission. Total emissions from no addition of nutrient solution (N) and in different treatments (T1-T5) of three sites. **C-E** Histograms with standard error bars of N<sub>2</sub> and N<sub>2</sub>O emissions by sites (M1-M3).



In summary, the results above show that in potential conditions, the emission ratio changes varying from 24-789%. The N<sub>2</sub>O-N<sub>2</sub> ratio in potential conditions is shown in Table 6.

**Table 6.** N<sub>2</sub>O-N<sub>2</sub> Ratio in potential emissions (T5) in controlled laboratory conditions

	N1	N2	N3	S1	S2	M1	M2	M3
N <sub>2</sub> O-N <sub>2</sub> ratio	48%	9%	72%	8%	78%	2%	6%	5%

## DISCUSSION

The present study aimed to contribute with field measurements of N<sub>2</sub>O emissions in the central Amazonian floodplain. However, in situ quantification of N<sub>2</sub>O with or without acetylene inhibition was too low to be recorded with the G200. Conversely, under lab conditions, N<sub>2</sub>O and N<sub>2</sub> emissions were observed in the slurries with no addition of nutritive solution. This difference could be due to certain causes, chambers had a larger surface than the flasks of the lab, in addition, soil structure and bulk density plays an important role in gas exchange (Pedersen and Sand-Jensen, 1992). In the field, the soil structure was not perturbed, meaning that oxic areas in the root zone may have been active, which was not the case for the soil's samples in the laboratory. Redox potential was measured as indication of anoxia, yet, a big uncertainty about soil redox potential homogeneity is difficult to control. Meaning that, in the field, there was no guarantee of complete anoxia in the surface sampled, or the sampling time was not enough to record 1 ppm of N<sub>2</sub>O.

The fieldwork was useful to collect samples (i.e. soil and water), observe the diversity of wetlands ecosystems of the central floodplain, and quantify the actual and potential N<sub>2</sub>O emissions of these floodplains in traditionally laboratory-controlled conditions. Once in controlled conditions, eliminating the uncertainty of anoxia and with no intervention of plants, N<sub>2</sub> and N<sub>2</sub>O emission from soil-denitrifies bacteria community was recorded. The wetlands soils sampled had a wide range of soil properties, from poor carbon content soil (N2) to very rich carbon soil (N1). The production ratio N<sub>2</sub>O-N<sub>2</sub> from the soil samples of the Madeira River (M1, M2, M3) was the one that varied the least, as the wetland typology was alike (freshwater marshes) as shown in the PCA.

Production ratio recorded of all samples were above the ratio estimated as default mineral soils under zero fertiliser N addition (Bouwman, 1996) (i.e., approx. 1 kg N<sub>2</sub>O-N ha<sup>-1</sup>yr<sup>-1</sup>) or the specific indirect emission factor (EF<sub>5</sub>) for rivers established in the IPPC-1996 report (2.5%). Wetlands soils (freshwater marsh or flooded forest) of the present study cannot precisely be considered within these EFs. The EF that refers to estuaries, refers to wetlands only to the semi-

enclosed coastal bodies of water, having free connection to the open ocean, and within which seawater is measurably diluted by freshwater derived from land drainage (Lauff, 1967). The EF of Solimões freshwater marsh (S2=, 0.023) had a production rate lower but closer to the reported by the IPCC-2019, but the rest of the soil samples had higher rates ranging from 0.035 to 0.091. Our EFs are highly different from the current IPCC-2019 default EF<sub>5f</sub>/ EF<sub>5e</sub>. This inconsistency may be reasonable, since the IPCC aims to be used on a larger scale, and aims to be valid across regions, being poorly constrained, which could be subject to significant error at local scale. Yet they are useful when accomplishing global scale assessments (Outram and Hiscock, 2012; Zhang et al., 2020).

The above presented explanatory powers of wetlands physico-chemical indicators among Amazonian floodplain wetlands soils underscore that the main microbial processes contributing to wetlands soil emissions may vary across different environmental conditions and soil typology. N<sub>2</sub>O emissions maybe the compilation of different microbial processes, including incomplete denitrification, nitrification, as well as dissimilatory nitrate reduction (DNRA) (van den Berg et al., 2017). As a constant, N<sub>2</sub>O production is frequently favoured by sufficient carbon sources and limited by N supply in line with other studies that reported the same dynamics (Nizzoli et al., 2018; Bernard-Jannin et al., 2017; Davidsson et al., 1998).

Quantification of denitrification enzymatic activity variability of wetlands soils gave information of the range of N<sub>2</sub>O-N<sub>2</sub> emissions that can be observed in a large area as the central Amazonian floodplain if nitrates and carbon are not limited. The three different ecosystems evaluated in the Negro river behave differently. N1 is more sensitive to nitrates, as the organic carbon content was already high. This result is aligned to what has been recently reported, as reaction of nitrogen-rich organic soils (Pärn et al., 2018). The sandy beach even if the activity was low, there was some emission, meaning that there is a denitrifying bacteria community. Flooded forest (N3), reach N<sub>2</sub> emission peak at T3, then a ratio overturn, producing more N<sub>2</sub>O than N<sub>2</sub>. The water from Negro river has a pH = 5.5, in our experiment the water was pH=7, this means that in field conditions denitrification is inhibited by the acid waters even if nitrates are available (Pärn et al., 2018).

Negro flooded forest (N1) had its peak at T5, also Solimões flooded forest (S1) had a high peak of N<sub>2</sub>O in T5. These two samples are organic soils, (>12% soil organic carbon) (FAO, 2005). As a persistent reaction in all samples, high concentration of nitrates (T4 and T5) constraints

N<sub>2</sub> emission. A bell-shaped distribution with a maximal emission in the in-between treatments (T2-T3), or an increasing tendency of N<sub>2</sub>O emission with higher nitrates concentrations.

Our results showed that wetlands soils are very reactive to nitrate and carbon changes and the predominant emission is N<sub>2</sub>O if concentrations are high. Interpreting these results in field conditions, would mean that if anoxic conditions and availability of nitrates, denitrification is conducted. When nitrates concentration is  $\leq 0.5 \text{ mg N l}^{-1}$ , N<sub>2</sub> is mainly emitted in the case of freshwater marshes. If nitrates are abundant ( $>20 \text{ mg N l}^{-1}$ ) a high risk of rising N<sub>2</sub>O emission and reducing N<sub>2</sub> emission is expected in flooded forest and freshwater marshes. The rise of nitrate concentration in natural conditions not only promotes emission of N<sub>2</sub>O, but also affects biodiversity. In surface water, a strong decrease in hydrophyte biodiversity is observed above a nitrate concentration of  $2 \text{ mgN l}^{-1}$  (James et al., 2005), same limit concentration apply for invertebrates health (Camargo et al., 2005). As far as freshwater eutrophication, concentration levels above  $1.5 \text{ mgN l}^{-1}$  are considered to be a potential risk (Billen et al., 2018).

At a larger scale, besides the heterogenic reported in this study, the Amazonian floodplain is well-known for its resilience to nitrate concentration (Parolin et al., 2004; Wittmann et al., 2011). Additionally to their high denitrification capacity due to their long saturation periods, soils properties and nitrification limitation, that could be very efficient nitrate removal at the watershed scale (Fisher and Acreman, 2004; Guilhen et al., 2020), yet ecological integrity of wetlands ecosystems have their limits. Another important function of wetlands, specially flooded forest or swamps is the capacity of removing large amounts of carbon dioxide due to the continued flooded conditions. Amazonian flooded forest represents almost half of tropical flooded forests, therefore disturbing tropical wetlands specially peatlands (i.e. organic soils) adding nitrates increase greenhouse gases fluxes (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) (Leifeld and Menichetti, 2018).

Pärn et al., 2021, carried out a study in the Peruvian amazon flooded forests, showing that moderate drying in this ecosystem may create a devastating feedback on climate change through CO<sub>2</sub> and N<sub>2</sub>O. The average denitrification of our samples with no addition of nutritive solution was  $0.21 \pm 0.13 \mu\text{g N-N}_2\text{O} + \text{N-N}_2 \text{ g}^{-1} \text{ h}^{-1}$  of which  $0.11 \pm 0.10 \mu\text{g N-N}_2\text{O} \text{ g}^{-1} \text{ h}^{-1}$ . In order to compare these results with other studies carried out in the Amazon basin, our results were converted to reference units resulting in  $6.5 \times 10^4 \pm 4.8 \times 10^4 \mu\text{g N-N}_2\text{O} + \text{N-N}_2 \text{ m}^{-2} \cdot \text{h}^{-1}$ , of which  $2.95 \times 10^4 \pm 1.8 \times 10^4 \mu\text{g N-N}_2\text{O} \text{ m}^{-2} \cdot \text{h}^{-1}$ .

Our experimental results are 2-fold what has been reported in Peruvian Amazonian swamp forest by Pärn et al., 2021 ( $360$  and  $420 \mu\text{g N-N}_2\text{O m}^{-2}\cdot\text{h}^{-1}$ ) and 1- fold the soil  $\text{N}_2\text{O}$  emissions from floodplain soils ( $1420 \pm 1900 \mu\text{g N}_2\text{O-N m}^{-2}\cdot\text{h}^{-1}$ ) (Figueiredo et al., 2019).

Regarding our DEA results, an average of  $2.9 \times 10^3 \pm 2.5 \times 10^3 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  was observed in T5. Comparing these results with a previous study from Koschorreck and Darwich, (2003), carried out a monitoring study in Marchantaria Island ( $3^\circ 13.947'S$  and  $59^\circ 56.765'W$ ), an island in the Amazon river near Manaus, Brazil, in 1996, reporting a DEA maximum value of  $50 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  in the transition phase between aquatic and terrestrial phase in bare sediments. With a range below  $5 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  in the terrestrial phase (i.e. before flooding) and  $17 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  after flooding. In our case, the sandy beach sample, that can be the closest to bare sediment, reported a maximum DEA of  $210 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  in T5, and a  $2.7 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  in T1 and zero emission when no addition of nutritive solution.

Regarding flooded forest DEA, our average value of N1, N3 and S1 samples in T5 was  $4.86 \times 10^3 \pm 1.27 \times 10^3 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$ , and T1  $175.46 \pm 58.42 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$ . While they reported a maximum of  $100 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  shortly after flooding. The freshwater marshes DEA showed no clear seasonal trend, and the maximum value was  $80 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$ , while our average value of M1, M2, M3 and S2 samples in T5 resulted in  $2.11 \times 10^3 \pm 2.01 \times 10^3 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$ , and  $30 \pm 25 \text{ nmol N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$  in T1.

Our laboratory records are above all the records reported by in situ previous studies. The difference regarding the emission with no addition of nutritive solution can be explain by the diffusion factor, which we enhanced by shaking the samples, resulting in a probable overestimation of natural emissions compared to undisturbed field conditions. Regarding the DEA results, our values are within the range compared to bare sediment samples, but the forest and freshwater marshes show a higher rate of  $\text{N}_2\text{O}$  emissions in T5, but values obtained in T1, are similar to the once reported in the literature. Differences regarding T5 and T1, can be explained by the inhibition of total denitrification due to high concentration of nitrates (Blackmer and Bremner, 1978), and/or the production of by anammox pathway, where the  $\text{N}_2\text{O}$  are also produced. Nevertheless, the second hypothesis cannot be confirmed, as we did not carry out a genetic analysis to identify the presence of genes correlated to these alternative processes.

The difference between our results and the previously reported in the literature can be explained due to several factors. The acetylene inhibition technique (AIT) is commonly used and is still widely (and validly) used for comparisons of sites and experimental treatments in both

terrestrial and aquatic contexts. In a positive sense, the AIT methods are reasonably robust, especially for systems with moderate or high  $\text{NO}_3^-$  levels (DEA). The AIT helped to identify the environmental regulation of denitrification e.g., control by oxygen,  $\text{NO}_3^-$ , carbon (C), soil moisture, pH, and other factors (Groffman et al., 2006) and even as an indirect measure of microbial functional diversity (Cavigelli and Robertson, 2000). The AIT have also produced understanding of the “hotspot” nature of denitrification, where small areas of soil cores, ecosystems and landscapes account for a very high percentage of areal denitrification (McClain et al., 2003; Parkin, 1987).

In the downside, this technique have intrinsic uncertainties. The main issue is that AIT underestimate the emissions due to an incomplete inhibition, inhibition of nitrification. Further work is needed to test whether the incomplete inhibition is dependent on soil type and environmental conditions (Qin et al., 2012).

From the available methods to quantify denitrification, they all have some limitations and are problematic for different reasons in different places and temporality. The most used techniques are (1) acetylene-based methods, explained before; (2)  $^{15}\text{N}$  tracers; is considered to be the one of the best methods for soil studies, but its application has been limited by the laborious procedures and expensive instrumentations. Still, it is remarkable that in agreement with these studies, Amazonian floodplains and swamps represent an important  $\text{N}_2\text{O}$  source, at local and global scale.

The sites analysed had different vegetation composition, from primary flooded forest, bush freshwater marshes, herbaceous marshes and sandy beach. The influence of vegetation on soil nitrogen availability in seasonally flooded habitats are related to N-input by mineralization, N-output by assimilation, aeration of the rhizosphere or modification of water movement and sedimentation/erosion is notorious. Our results do not allow complete nitrogen budget calculation of these sites. However, by comparing sites with different vegetation structures we can get an insight into the influence of vegetation on the soil nitrogen turnover. The campaign took place before the flooding season (February, 2020). This fact is reflected in low presence of inorganic nitrogen in all sampling sites, however it have been reported that high peak nitrogen mineralization and soil respiration are observed shortly after wetting of a dry soil as a consequence of rapid mineralization of dead organic material which accumulate during dry periods (West et al., 1989). Moreover, with flooding the water might supply or leach nutrients to/or from the soil and vegetation, which can also influence the presence/absence of inorganic

N in soil (Koschorreck and Darwich, 2003). To better understand the seasonal changes in the N-pools a monitoring of the sites has to be carried out, leading to explaining the causes and moments of pH variation, respiration peaks, and different nitrogen turnover peaks.

## CONCLUSIONS AND FURTHER RESEARCH

The present study tested static chamber protocol for in situ soil denitrification assessment; however, this method was not successful due to difficulties assuring total anoxia, precariousness of field material and lack of sampling at different times of the year. However, traditional laboratory protocol was explanatory as natural emissions and DEA were recorded. Meaning active denitrifier bacteria community in total anoxia and unlimited resources. Within the eight sampled sites, the two main wetlands typologies (flooded forest and freshwater marshes) were sample, from the three main tributaries (Negro river, Solimões and Madeira) of the Amazonian river system capturing a large range of field conditions that play an important role on the nitrogen cycle, especially denitrification. Emission  $N_2O$ - $N_2$  ratios were higher than IPCC -2019 default values for  $EF_{5R}$  and  $EF_{5E}$ . In wetlands soils emissions are limited by nitrates and carbon availability, a higher  $N_2$ - $N_2O$  emission is observed when nitrates and carbon are unlimited, meaning a high reactivity to nitrate concentration. Even though the large variance of wetlands ecosystems sampled, potential emissions showed two kinds of  $N_2O$  and  $N_2$  feedbacks, regarding wetland typology. In all cases, wetlands have a limiting capacity of  $N_2$  emission at higher nitrate concentration, which favours  $N_2O$  emission. Flood pulses have a critical effect on soil physical and chemical properties. These changes have different effect depending the vegetation and can be buffer by litter layer or fine soil texture. Yet, flooding pulses are the main regulator of nitrogen dynamics. Our results demonstrate that there is a major gap in our understanding of natural  $N_2O$  emissions in Amazonian floodplains. More efforts to produce measurement-based estimates and a regular assessment to eliminate current gaps in this important region is imperative and indispensable to improve the global  $N_2O$  budgets. Monitoring  $CO_2$ ,  $CH_4$  and  $N_2O$  emissions in Amazonian wetlands, as they are the largest area of floodplain on Earth, with low anthropogenic disturbance will help to promote wise-use of wetland ecosystems, considering the resilience of wetlands and capacity of nitrate transformers to  $N_2$  emissions. Highlight the possible effects of enhanced  $N_2O$  emission that should be prevented and prioritized. They represent an efficient nitrate removal area at the watershed scale, but their disturbance will mean a devastating feedback on climate change through  $CO_2$  and  $N_2O$ . Advocate for protective measurements to maintain these ecosystems in their optimal conditions and ecological integrity is mandatory and urgent.



# CHAPTER IV

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## DEVELOPMENT OF THE SOIL DENITRIFICATION MODEL (SDM) FOR NATURAL WETLANDS ECOSYSTEMS.



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## ABSTRACT

This chapter presents the soil denitrification model (SDM). This model was developed within the framework of the present thesis. It is based on a model originally developed to describe the hydro-biochemical exchanges between surface waters and the hyporheic zone of floodplains (Peyrard et al., 2011). The improvements made in the present study correspond to: (i) the inclusion of soil moisture and temperature from satellite Earth observations with a daily temporal resolution and a spatial resolution of 1 km and (ii) the distinction of soils under different wetland types (i.e., flooded forests, freshwater marshes, brackish wetlands, peatlands, and complex wetlands). These two changes are critical to expanding wetland modelling on a global scale. The functions of the SDM, the calibration/validation process, sensitivity and limitations of this model are presented using the results of the sampling points presented in Chapter III. The results show that the SDM has a good fit with the observed values (PBIAS=4.5) at the local scale at static validation.

A dynamic first extrapolation of the model to basin scale in the same basin (i.e., the Amazon) was performed from 2011-2019 at daily time step. Total annual denitrification ( $N_2 + N_2O$ ) in the three wetland typologies was  $11.8 \pm 1.36 \text{ TgN.yr}^{-1}$  (Tg = Teragram =  $10^{12} \text{ g}$ ). Flooded forests contributed the most (85%) with  $10.1 \pm 1.21 \text{ TgN.yr}^{-1}$ , followed by freshwater marshes (15%) with  $1.7 \pm 0.23 \text{ TgN.yr}^{-1}$ , and then brackish wetlands (0.001%) with  $8.99 \pm 3.73E+05 \text{ kgN.yr}^{-1}$ . The annual specific fluxes calculated for flooded forests were  $169.26 \pm 21.55 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ , freshwater marshes  $153.64 \pm 21.08 \text{ kg ha}^{-1} \text{ yr}^{-1}$  and brackish wetlands =  $46.56 \pm 19.30 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ . Denitrification peak for freshwater marshes is the highest and occurs in February (Max =  $0.29 \text{ TgN.month}^{-1}$ ), as well as brackish wetlands (max =  $24.5 \text{ MgN.month}^{-1}$ ). This peak corresponds to the beginning of the flooding season of the floodplains of the main streams. While the peak of the flooded forests (max =  $0.21 \text{ TgN.month}^{-1}$ ), is reached one month later (March) when the tributary floodplains also increase their inundation area. Flooded forests are active for a longer period (December to June), therefore they are the main contributors to denitrification of the basin. The most relevant wetlands in terms of denitrification; are located in the western part of the basin, corresponding to the largest extent of flooded forests.

Three different  $N_2O/N_2$  emission ratios were applied and the mean estimate of annual  $N_2O$  emission corresponding to the natural wetlands of the Amazon basin was  $0.79 \pm 0.49 \text{ Tg N-N}_2\text{O.yr}^{-1}$ . Guilhen et al., (2020) estimated a mean of  $1.03 \pm 0.02 \text{ TgN-N}_2\text{O.yr}^{-1}$  in the Amazon basin between 2011 and 2015, which estimation compared to our mean value between 2012 and 2019, is  $0.23 \text{ Tg N-N}_2\text{O.yr}^{-1}$  (+23%) higher than what we obtained with the SDM. Comparing the present results with the South American estimation of  $\sim 1.8 \text{ TgN-N}_2\text{O.yr}^{-1}$  from natural sources calculated by Tian et al., (2020), the Amazon basin wetlands contribute with  $44 \pm 27\%$  of the total natural source emissions for this region. Bouwman et al., (2013) calculated a global average riparian zone denitrification ( $N_2O + N_2$ ) of  $6 \text{ (5-9) TgN.yr}^{-1}$  for the year 2000. The estimate for freshwater marshes in the Amazon basin from the SDM of this study corresponds to  $1.74 \pm 0.23 \text{ TgN.yr}^{-1}$ , being 28 % of the total estimated by Bouwman et al., (2013).

To conclude, the SDM is suitable for the identification of key triggering moments, as well as identification of important zones. In addition to providing a first estimate of denitrification in areas where there is no in situ information. Despite the high uncertainties involved in the modelling, the results obtained for denitrification rates and  $N_2O$  emissions in natural wetlands are congruent with previous studies. In addition, the time series show the interannual evolution and the influence of climatic anomalies such as ENSO (El Niño - Southern Oscillation). These results may be indicators of possible future scenarios in which anomalies are repeated or intensified.

## RÉSUMÉ

Ce chapitre présente le modèle de dénitrification par l'humidité du sol (SDM). Ce modèle a été développé dans le cadre de la présente thèse. Il est basé sur un modèle initialement développé pour décrire les échanges hydrobiochimiques entre les eaux de surface et la zone hyporhéique des plaines inondables (Peyrard et al., 2011). Les améliorations apportées dans la présente étude correspondent à : (i) l'inclusion de l'humidité et de la température du sol à partir d'observations satellitaires au sol avec une résolution temporelle quotidienne et une résolution spatiale de 1 km. (ii) la distinction des différents types de zones humides (c'est-à-dire les forêts inondées, les marais d'eau douce, les zones humides saumâtres, les tourbières et les zones humides complexes). Ces deux changements sont essentiels pour étendre la modélisation des zones humides à l'échelle mondiale. Les fonctions du SDM, le processus de calibration/validation, sensibilité et limitations de ce modèle sont présentés.

Les points d'échantillonnage des résultats du chapitre III sont les valeurs de référence. Les résultats montrent que le SDM a un bon ajustement avec les valeurs observées (PBIAS = 4.5) à l'échelle locale. Une première extrapolation du modèle à l'échelle du bassin dans le même bassin (c'est-à-dire l'Amazonie) est effectuée. La dénitrification annuelle totale ( $N_2 + N_2O$ ) dans les trois typologies de zones humides était de  $11,8 \pm 1,36 \text{ TgN.an}^{-1}$  ( $Tg = 10^{12} \text{ g}$ ). Les forêts inondées ont contribué le plus (85 %) avec  $10,1 \pm 1,21 \text{ TgN.an}^{-1}$ , suivies des marais d'eau douce (15 %) avec  $1,7 \pm 0,23 \text{ TgN.an}^{-1}$ , puis des zones humides saumâtres (0,001 %) avec  $8,99 \pm 3,73 \cdot 10^5 \text{ kgN.an}^{-1}$ . Les flux spécifiques annuels calculés pour les forêts inondées étaient de  $169,26 \pm 21,55 \text{ kg.ha}^{-1}.\text{an}^{-1}$ , les marais d'eau douce  $153,64 \pm 21,08 \text{ kg.ha}^{-1}.\text{an}^{-1}$  et les zones humides saumâtres =  $46,56 \pm 19,30 \text{ kg.ha}^{-1}.\text{an}^{-1}$ . Le pic de dénitrification pour les marais d'eau douce est le plus élevé et se produit en février (Max =  $0,29 \text{ TgN.mois}^{-1}$ ), ainsi que pour les zones humides saumâtres (Max =  $24,5 \text{ MgN.mois}^{-1}$ ). Ce pic correspond au début de la saison d'inondation des plaines inondables des principaux cours d'eau. Alors que le pic des forêts inondées (Max =  $0,21 \text{ TgN.mois}^{-1}$ ) est atteint un mois plus tard (mars) lorsque les plaines inondables des affluents augmentent également leur zone d'inondation. Les forêts inondées sont actives pendant une période plus longue (décembre à juin), elles sont donc les principales contributrices à la dénitrification du bassin. Les zones humides les plus pertinentes en termes de dénitrification sont situées dans la partie orientale du bassin, correspondant à la plus grande étendue de forêts inondées.

Trois différents rapports d'émission  $N_2O/N_2$  ont été appliqués et l'estimation moyenne de l'émission annuelle de  $N_2O$  correspondant aux zones humides naturelles du bassin de l'Amazonie était de  $0,79 \pm 0,49 \text{ TgN-N}_2\text{O.an}^{-1}$ . Si l'on compare les présents résultats à l'estimation sud-américaine de  $\sim 1,8 \text{ TgN-N}_2\text{O.an}^{-1}$  provenant de sources naturelles, calculée par Tian et al. (2020), les zones humides du bassin de l'Amazonie contribuent à  $44 \pm 27 \%$  des émissions totales de sources naturelles pour cette région. Bouwman et al. (2013) ont calculé une dénitrification moyenne mondiale des zones riveraines ( $N_2O + N_2$ ) de 6 (5-9)  $\text{Tg.N.an}^{-1}$  pour l'année 2000. L'estimation pour les marais d'eau douce du bassin de l'Amazonie à partir du SDM de cette étude correspond à  $1,74 \pm 0,23 \text{ Tg.N.an}^{-1}$ , soit 28 % du total estimé par Bouwman et al. (2013). Enfin, Guilhen et al. (2020) ont estimé une moyenne de  $1,03 \pm 0,02 \text{ TgN-N}_2\text{O.an}^{-1}$  dans le bassin de l'Amazonie entre 2011 et 2015, ce qui, comparé à notre valeur moyenne entre 2012 et 2019, est  $0,23 \text{ TgN-N}_2\text{O.an}^{-1}$  (+23%) plus élevé que ce que nous avons obtenu avec le SDM.

En conclusion, le SDM est approprié pour l'identification des moments clés de déclenchement, ainsi que pour l'identification des zones importantes. En plus de fournir une première estimation de la dénitrification dans les zones où il n'y a pas d'informations in situ. Malgré les incertitudes élevées liées à la modélisation, les résultats obtenus pour les taux de dénitrification et les émissions de  $N_2O$  dans les zones humides naturelles sont conformes aux études précédentes. De plus, les séries temporelles montrent l'évolution interannuelle et l'influence des anomalies climatiques telles que l'ENSO (El Niño - Southern Oscillation). Ces résultats peuvent être des indicateurs de scénarios futurs possibles dans lesquels les anomalies se répètent ou s'intensifient.

## RESUMEN

Este capítulo presenta el modelo de desnitrificación de la humedad del suelo (por sus siglas en inglés = SDM). Este modelo fue desarrollado en el marco de la presente tesis. Se basa en un modelo originalmente desarrollado para describir los intercambios hidrobioquímicos entre las aguas superficiales y la zona hiporreica de las llanuras de inundación (Peyrard et al., 2011). Las mejoras realizadas en el presente estudio corresponden a: (i) la inclusión de la humedad y la temperatura del suelo a partir de observaciones terrestres por satélite con una resolución temporal diaria y una resolución espacial de 1 km y (ii) la distinción de los distintos tipos de humedales (es decir, bosques inundados, pantanos de agua dulce, humedales salobres, turberas y humedales complejos). Estos dos cambios son fundamentales para ampliar la modelización de los humedales a escala mundial.

Las funciones del SDM, el proceso de calibración/validación y sensibilidad de este modelo son presentados. Los puntos de muestreo de los resultados del capítulo III son los valores de referencia. Los resultados muestran que el SDM tiene un buen ajuste con los valores observados (PBIAS=4,5) a escala local. Después, una primera extrapolación del modelo a escala de cuenca, en la misma cuenca (es decir, la Amazonia) El modelo estimó una desnitrificación total anual ( $N_2 + N_2O$ ) en las tres tipologías de humedales fue de  $11,8 \pm 1,36 \text{ Tg N año}^{-1}$  (Tg = teragramo;  $Tg = 10^{12} \text{ g}$ ). Los bosques inundados fueron los que más contribuyeron (85%) con  $10,1 \pm 1,21 \text{ Tg N año}^{-1}$ , seguidos por los pantanos de agua dulce (15%) con  $1,7 \pm 0,23 \text{ Tg N año}^{-1}$ , y luego los humedales salobres (0,001%)  $8,99 \pm 3,73E+05 \text{ kg N año}^{-1}$ . Los flujos específicos anuales calculados para los bosques inundados fueron de  $169,26 \pm 21,55 \text{ kg ha}^{-1} \text{ año}^{-1}$ , los pantanos de agua dulce  $153,64 \pm 21,08 \text{ kg ha}^{-1} \text{ año}^{-1}$  y los humedales salobres  $46,56 \pm 19,30 \text{ kg ha}^{-1} \text{ año}^{-1}$ .

El pico de desnitrificación para los pantanos de agua dulce es el más alto y ocurre en febrero (Max =  $0,29 \text{ Tg N mes}^{-1}$ ), así como los humedales salobres (Max =  $24,5 \text{ Mg N mes}^{-1}$ ). Este momento corresponde al inicio de la temporada de inundación de las llanuras de inundación de los arroyos principales. Mientras que el pico de los bosques inundados (Max =  $0,21 \text{ Tg N mes}^{-1}$ ), se alcanza un mes después (marzo) cuando las llanuras de inundación de los afluentes también aumentan su superficie de inundación. Los bosques inundados están activos durante un periodo más largo (de diciembre a junio) también la causa de su importante influencia en la desnitrificación de la cuenca. Los humedales más relevantes en cuanto a desnitrificación; se encuentran en la parte oriental de la cuenca, que corresponden a la mayor extensión de bosques inundados.

Se aplicaron tres tasas de emisión de  $N_2O/N_2$ , la estimación media de la emisión anual de  $N_2O$  correspondiente a los humedales naturales de la cuenca del Amazonas fue de  $0,79 \pm 0,49 \text{ Tg N-N}_2\text{O año}^{-1}$ . Comparando los presentes resultados con la estimación de América del Sur  $1,8 \text{ Tg N-N}_2\text{O año}^{-1}$  de fuentes naturales calculada por Tian et al., (2020), los humedales de la cuenca del Amazonas contribuyen con el  $44 \pm 27\%$  del total de las emisiones de fuentes naturales para esta región. Bouwman et al., (2013) calculó un promedio global de desnitrificación de la zona ribereña ( $N_2O + N_2$ ) de 6 (5-9)  $\text{Tg N año}^{-1}$  para el año 2000. La estimación de los humedales de agua dulce en la cuenca amazónica a partir del SDM de este estudio corresponde a  $1,74 \pm 0,23 \text{ Tg N año}^{-1}$ , siendo el 28 % del total estimado por Bouwman et al., (2013). Por último, Guilhen et al., (2020) estimaron una media de  $1,03 \pm 0,02 \text{ Tg N-N}_2\text{O año}^{-1}$  en la cuenca del Amazonas entre 2011 y 2015 que, comparada con nuestro valor medio entre 2012 y 2019, es  $0,23 \text{ Tg N-N}_2\text{O año}^{-1}$  (+23%) superior a la que obtuvimos con el SDM.

Para concluir, el SDM es adecuado para la identificación de momentos claves de activación, así como identificación de las zonas importantes. Además de proporcionar una primera estimación de la desnitrificación en áreas donde no hay información in situ. A pesar de las altas incertidumbres que implica la modelización, los resultados obtenidos de las tasas de desnitrificación y las emisiones de  $N_2O$  en los humedales naturales son congruentes con estudios anteriores. Además, las series temporales muestran la evolución interanual y la influencia de anomalías climáticas como ENSO (El Niño - Oscilación del Sur). Estos resultados pueden ser indicadores de posibles escenarios futuros en los que las anomalías se repitan o intensifiquen.

## INTRODUCTION

Transformation of inorganic N species in soils occurs mainly through two microbial metabolic pathways, named nitrification and denitrification (Parton et al., 1996). These pathways are energy-yielding electron transfer processes, which are regulated by the presence or absence of oxygen (Schmidt et al., 2004). Nitrification is an aerobic process carried out primarily by autotrophic bacteria. Heterotrophic nitrification may be important in some conditions, especially acidic forest soils (Prosser, 2011). The net result of the complete nitrification pathway is oxidation of  $\text{NH}_4$  to  $\text{NO}_3$ , by products via incomplete pathways producing volatile species  $\text{NO}$  and  $\text{N}_2\text{O}$ . The major factors that control nitrification rates include soil temperature, soil water and organic substrates (Chen et al., 2018). Denitrification is an anaerobic pathway in which  $\text{NO}_3$  is used as the terminal acceptor for electrons generated during anaerobic nitrification. The complete denitrification pathway reduce  $\text{NO}_3$  to  $\text{N}_2$  in four stages (Canfield et al., 2010). In addition to the terminal product  $\text{N}_2$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$  are generated as obligatory free intermediates. The relative yield of the intermediates ( $\text{N}_2\text{O}$  and  $\text{NO}$ ) is a function of the soil moisture content. Less gas loss and more complete reaction in diffusion limiting wet conditions. Soil texture also moderates the  $\text{N}_2\text{O}$  efflux. Total denitrification N loss is positively correlated to available C, soil  $\text{NO}_3$ , and water-filled pore space (WFPS) and that the  $\text{N}_2/\text{N}_2\text{O}$  ratio is positively correlated to WFPS and available C and negatively correlated to soil  $\text{NO}_3$  level (Butterbach-Bahl et al., 2013; Huang and Gerber, 2015; Hunter et al., 1998).

Denitrification and nitrification pathways are well understood and a number of different approaches have been used to develop N cycling models of which are drawn to varying degrees on field and laboratory data. Quantifying where, when and how much nitrification and denitrification occurs on the basis of measurements alone at larger scale remains particularly costly and problematic. Therefore, models have become essential tools for integrating current knowledge and available data to develop a model with rate-controlling properties so then the losses of N within landscape can be quantified at watershed, regional and global scale (Boyer et al., 2006).

The interest towards this process has been enhanced due to the perturbation of the global N cycle by human activities (e.g. industrial fertilizer production by Haber–Bosch process, fossil fuel combustion and manure nitrogen (N) application). These activities are increasing  $\text{N}_2\text{O}$  concentrations by ~21%, from 271 ppb at pre-industrial level to 329 ppb in 2015 (Prather et al., 2015; Thompson et al., 2019; Tian et al., 2018). However, our capacity of modelling the

mechanisms responsible for terrestrial N<sub>2</sub>O emission is still limited. Estimates of global terrestrial N<sub>2</sub>O emissions from natural sources vary up to a factor 3 and range between 3.3 and 9.0 TgN.yr<sup>-1</sup> (Ciais et al., 2014)

Many models have been developed to understand nitrification and denitrification processes, making a distinction between soils and water, and having different scope of natural and agricultural soils at various spatiotemporal scales. In order to better understand natural and human –induced biogenic N<sub>2</sub>O that have large ranges of uncertainties, Tian et al., (2018) had established The Global N<sub>2</sub>O Model Intercomparison Project, that aims to investigate the uncertainty sources in N<sub>2</sub>O estimates and provide multimodel N<sub>2</sub>O emission estimates from natural and agricultural soils. The participating models in this project are ten and they simulate the major N cycling process as shown in Table 7. For soil N processes, all 10 models simulated N leaching according to water runoff rate; however, the models differ in representing nitrification and denitrification processes and the impacts of soil chemical and physical factors. The differences in simulating nitrification and denitrification processes are one of the major uncertainties in estimating N<sub>2</sub>O emissions (Tian et al., 2018). Besides the differences among them, these ten models are process-based models and consider temperature, soil water content, and C<sub>NO3</sub> when calculating denitrification. Nine of the ten models are capable of simulating natural and agricultural ecosystems, while CLM-CN, only simulates N<sub>2</sub>O emissions from natural vegetation.

The global N<sub>2</sub>O budgets for 2007-2016 is first divided by 18 sources and various different chemical sinks. Natural sources average N<sub>2</sub>O emissions are calculated as 9.7 Tg N.yr<sup>-1</sup> ranging from (8-12 Tg N.yr<sup>-1</sup>). The natural emissions are divided in four compartments (i) natural soils calculated 5.6 Tg N.yr<sup>-1</sup>, with a range of 4.9-6.5 Tg N.yr<sup>-1</sup>, followed by (ii) oceans (3.4 Tg N.yr<sup>-1</sup>, in a range of 2.5-4.3 Tg N.yr<sup>-1</sup>), (iii) lightning and atmospheric production contribute with 0.4 Tg N yr<sup>-1</sup> with a range of 0.2-1.2 Tg N.yr<sup>-1</sup>, and lastly (iv) inland waters, estuaries and coastal zones are estimated to contribute with 0.3 Tg N.yr<sup>-1</sup> (0.3-0.4 Tg N.yr<sup>-1</sup>) (Tian et al., 2020). It's already remarkable that this project has a compartment exclusively dedicated to inland waters and estuaries, acknowledging and being in line regarding the importance of wetlands in the global nitrogen cycle.

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**Table 7.** Model characteristics in simulating major N cycling processes at global scale used in the Global N<sub>2</sub>O Model Intercomparison Project.

	CLM-CN	DLEM	LM3V-N	LPJ-GUESS	LPX-Bern	O-CN	ORCHIDEE	ORCHIDEE- CNP	TRIPLEX- GHG	VISIT
Open N cycle <sup>a</sup>	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
C–N coupling	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
N pools <sup>b</sup>	(13, 3, 4)	(6, 6, 8)	(6, 4, 3)	(5, 6, 11)	(4,3,8)	(9, 6, 9)	(9, 6, 9)	(9, 6, 9)	(3, 9, 4)	(4, 1, 4)
Demand and supply-driven plant N uptake	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
N allocation <sup>c</sup>	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic
Nitrification	$f(T, SWC)$	$f(T, SWC, C_{NH_4})$	$f(T, SWC, C_{NH_4})$	$f(T, SWC, C_{NH_4})$	$f(T, SWC, C_{NH_4})$	$f(T, SWC, pH, C_{NH_4})$	$f(T, SWC, pH, C_{NH_4})$	$f(T, SWC, pH, C_{NH_4})$	$f(pH, C_{NH_4}, T, SWC)$	$f(T, SWC, pH, C_{NH_4})$
Denitrification	$f(T, SWC, C_{NO_3})$	$f(T, clay, rh, C_{NO_3})$	$f(T_{soil}, rh, SWC, C_{NH_4}, C_{NO_3})$	$f(T, rh, SWC, C_{NO_3})$	$f(T, SWC, R_{mb}, C_{NO_3})$	$f(T, SWC, pH, R_{mb}, C_{NO_3})$	$f(T, SWC, pH, denitrifier, C_{NO_3})$	$f(T, SWC, pH, R_{mb}, C_{NO_3})$	$f(DOC, C_{NO_3}, pH, T_{soil})$	$f(SWC, rh, C_{NO_3})$
Mineralization, immobilization	$f(C:N)$	$f(C:N)$	$f(C_{NO_3}, C_{NH_4})$	$f(C:N)$	$f(C:N)$	$f(C:N)$	$f(C:N)$	$f(C:N)$	$f(C:N)$	$f(C:N)$
N leaching	$f(runoff)$	$f(runoff)$	$f(runoff)$	$f(runoff)$	$f(runoff)$	$f(runoff, clay)$	$f(runoff)$	$f(runoff)$	$f(runoff)$	$f(runoff)$
NH <sub>2</sub> volatilization	$f(C_{NH_4})$	$f(pH, T, SWC, C_{NH_4})$	$f(pH, T, SWC, C_{NH_4})$	$f(pH, T, SWC, C_{NH_4})$	$f(pH, T, SWC, C_{NH_4})$	$f(pH, C_{NH_4})$	$f(pH, C_{NH_4})$	$f(pH, C_{NH_4})$	$f(pH, C_{NH_4})$	$f(pH, T, SWC, C_{NH_4})$
Plant N turnover <sup>d</sup>	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic
N resorption	$f(C:N)$	$f(C:N)$	Fixed	Crop: dynamic, the rest: fixed	$f(N_{leaf})$	Fixed	$f(N_{leaf})$	Fixed	$f(C:N)$	Fixed
N fixation	$f(NPP)$	Fixed	$f(C_{NH_4}, C_{NO_3}, light, plant demand)$	$f(ET)$	Implied by mass balance	$f(C_{cost}, C_{root})$	$f(ET)$	$f(NPP)$	$f(biomass)$	$f(ET)$
N fertilizer use	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Manure N use	No	Yes	Yes	Yes	No	No	Yes	Yes	No	Yes
N deposition	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

<sup>a</sup> “Open” denotes that excess N can be leached from the system. <sup>b</sup> Numbers of N pools (vegetation pools, litter pools, soil pools).

<sup>c</sup> Dynamic denotes time-varied N allocation ratio to different N pools.

<sup>d</sup> Turnover time for various vegetation nitrogen pools: soil temperature ( $T$ ); soil clay fraction (denoted as clay); evapotranspiration (ET); vegetation carbon (denoted as biomass); NPP; leaf N concentration ( $N_{leaf}$ ); soil surface and drainage runoff (denoted as runoff); carbon cost during N<sub>2</sub> fixation ( $C_{cost}$ ); SWC; denitrifier: soil denitrifier biomass; soil heterogeneous respiration (rh) from Tian et al., (2018)

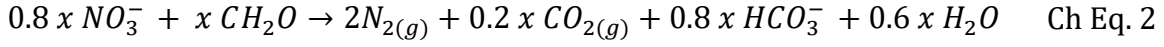
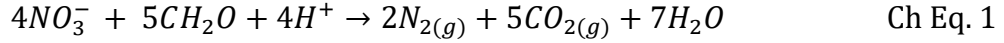
Inspired by this project and the different ways of modelling denitrification. The present model was developed with the particular aim of investigating denitrification exclusively in wetlands. Based on the precise hypothesis that wetlands play a key role in the global nitrogen cycle (Martínez-Espinosa et al., 2021). This model aims to take into account diversity of natural wetlands ecosystems, and its sensibility to daily soil moisture and temperature changes. The development of this model was motivated by the previous restriction to watershed approach and the lack of field data in many important natural wetlands at global scale, especially in the tropical areas. The present model is not linked to a watershed modelling; instead, it could be applied at different spatiotemporal scales, by using satellite earth observation. It aims to be a useful tool for estimating natural wetlands dynamics in the last ten years, and their sensibility to global changes. It also represents an interesting tool to identify hot moments and hot places in different spatiotemporal scales.

## SOIL DENITRIFICATION MODEL FOR WETLANDS

The development of the present model is motivated by the fact that the models to date are mainly developed for agricultural purposes. Unlimited supplies or external imposed loads of organic N can be applied with relative short periods of records for representing the rate-controlling variables. They are targeted to be used at local scale (field or watershed), and they need long-term available data for calibration/validation. The adoption of any of these models will demand data that is not available at global scale. Therefore, these models serve as a guideline to understand how the process is approached, as well as to identify the key parameters. Taking into account the pros and cons of the existing models and following the principle of parsimony, a simplified view of the denitrification process was adopted by making several assumptions.

### DENITRIFICATION REACTION

The classic chemical process (Ch Eq. 1) that produced  $N_2$  is the denitrification. However, the alkalinity plays an important role of denitrification therefore, the chemical reaction used in the present study was (Ch Eq. 2), by using  $x=5$  in (Ch Eq.2) to compare the use of organic carbon and the consumption or the production of the other molecules. This equation indicates the need of organic compounds as the source of energy for soil bacteria, and the need of oxygen in anoxic conditions, which is obtained from the nitrates.



## PRECEDING DENITRIFICATION MODELS

In this study, denitrification was modelled using a modified version of the equation applied by Peyrard et al., 2011 on the hyporheic zone (Eq. 1) and later on by Sun, 2015 in the river water and groundwater exchange in an alluvial plain in two particular study cases. Then applied in floodplains in different watershed under tropical, temperate and arctic conditions, proving that it can be suitable for global studies (Fabre et al., 2020) (Eq. 2), and that can be adapted to include satellite data (Guilhen et al., 2020) (Eq. 3).

$$R_{NO_3^-} = 0.8 x \cdot \left( \rho_b \frac{1-\varphi}{\varphi} \cdot k_{POC} POC + k_{DOC} DOC \right) \cdot \frac{[NO_3^-]_i}{[NO_3^-]_i + K_{NO_3^-}} \left( 1 - \frac{[O_2^-]}{K'_{O_2} + [O_2^-]} \right) \cdot k_{NH_4^+} [NH_4^+] \frac{[O_2^-]}{K_{O_2} + [O_2^-]} \quad \text{Eq. 1}$$

$$R_{NO_3^-} = 0.8 x \cdot \left( \rho_b \frac{1-\varphi}{\varphi} \cdot k_{POC} POC \cdot \frac{10^6}{M_c} + k_{DOC} [DOC]_i \right) \cdot \frac{[NO_3^-]_i}{[NO_3^-]_i + K_{NO_3^-}} \cdot \frac{Q_i}{Qbnk} \cdot e^{-\frac{(T_i - T_{opt})^2}{100}} \quad \text{Eq. 2}$$

$$R_{NO_3^-} = 0.8 x \cdot \left( \rho_b \frac{1-\varphi}{\varphi} \cdot k_{POC} POC \cdot \frac{10^6}{M_c} + k_{DOC} [DOC]_i \right) \cdot \frac{[NO_3^-]_i}{[NO_3^-]_i + K_{NO_3^-}} \cdot SWAF \cdot Q_{wa} \quad \text{Eq. 3}$$

where  $R_{NO_3^-}$  is the denitrification rate ( $\mu\text{mol.L}^{-1}.\text{d}^{-1}$ ),  $0.8 \cdot \alpha$  represents the stoichiometric proportion of  $NO_3^-$  consumed in denitrification compared to the organic matter used with  $\alpha=5$  as mentioned in Peyrard et al., (2011),  $\rho$  is the dry sediment density ( $\text{kg.dm}^{-3}$ ),  $\varphi$  is the sediment porosity,  $k_{POC}$  is the mineralization rate constant of particulate organic carbon (POC) ( $\text{d}^{-1}$ ), POC refers to the POC in the soil and the aquifer sediment (%),  $M_c$  is the carbon molar mass ( $\text{g mol}^{-1}$ ), DOC refers to the dissolved organic carbon in the aquifer water ( $\mu\text{mol L}^{-1}$ ),  $k_{DOC}$  is the mineralization rate constant of DOC ( $\text{d}^{-1}$ ),  $K_{NO_3^-}$  is the half-saturation constant for  $NO_3^-$  limitation ( $\mu\text{mol.L}^{-1}$ ), and  $NO_3^-$  is the nitrate concentration in the aquifer ( $\mu\text{mol.L}^{-1}$ ),  $K'_{O_2}$  is the half saturation for oxygen inhibition  $K_{O_2}$  half-saturation for oxygen limitation in oxic mineralization,  $k_{NH_4^+}$  nitrification rate constant. In equation 2 and 3 the nitrification rate was eliminated and the half-saturation for oxygen inhibition was replaced by  $Q_i$  and  $Qbnk$  are the discharge on day  $i$  and the discharge at bank full depth,  $T_i$  and  $T_{opt}$  are the temperature in the subbasin on day  $i$  and the optimal temperature for denitrification. Lastly, for the last modification, SWAF corresponds to the fraction of land covered with open waters from satellite



data (Al Bitar et al., 2017; Parrens et al., 2019), and  $Q_{wa}$  is the water storage capacity for each type of soil. All these approaches are still limited to a watershed scale and are coupled to a numerical model. Therefore, the original equation was once again modified and included to a nitrification-denitrification model explained in the next section.

## MODEL COMPONENTS

### DENITRIFICATION

Wetlands denitrification rate adopted has been structured as NEMIS model (Eq.4) (Hénault and Germon, 2000), adapting the multi-component method (Berner, 1980) where the potential denitrification is calculated from the first order kinetic model (Hunter et al., 1998) presented above (Eq. 1-3) adapted as follows,

$$D_w = Dp \cdot f_N \cdot f_{SM} \cdot f_T \quad \text{Eq. 4}$$

with

$$Dp = 0.8 x \cdot \rho_b \frac{1 - \varphi}{\varphi} \cdot k_{oc} [OrgC] \quad \text{Eq. 4.1}$$

$$f_N = \frac{[NO_3^-]_i}{[NO_3^-]_i + K_{NO_3^-}} \quad \text{Eq. 4.2}$$

$$f_T = e^{-\frac{(T_i - T_{opt})^2}{(T_i * T_{opt})}} \quad \text{Eq. 4.3}$$

$$f_{SM} = \frac{SM_i - SM_{res}}{SM_{sat} - SM_{res}} \quad \text{Eq. 4.4}$$

$$\text{If } f_{SM} \leq 0.7, NO_3 \text{ denit} = 0$$

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  $x = 5$  presented in the stoichiometry equation (Ch Eq. 2),  $\rho_b$  is the bulk density ( $kg.dm^{-3}$ ),  $\varphi$  is the porosity, calculated for each soil type,  $k_{oc}$  ( $d^{-1}$ ) is organic carbon mineralization rate,  $[OrgC]$  ( $mole.kg^{-1}$ ) is the carbon,  $f_N$  is the unitless function explained in Eq. 4.2, that is the general form for the limitation term, depending of nitrates concentration  $[NO_3^-]_i$  ( $\mu g.g^{-1}$ ) and  $K_{NO_3^-}$  is the limiting constant for the electron acceptor. It generates a decrease in the association degradation process when the electron acceptor concentration

decreases,  $f_T$  is the unitless function explaining the temperature limitation (Eq. 4.3), 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). The last term  $f_{SM}$  is the unitless function (Eq. 4.4) depending on soil saturation,  $SM_i$  is the soil moisture ( $m^3 \cdot m^{-3}$ ),  $SM_{res}$  the minimum soil moisture that allows the reaction to happen, and  $SM_{sat}$  the maximum saturation of the soil ( $m^3 \cdot m^{-3}$ ). If WFPS (water-filled pore space) is higher than 70% anoxic conditions are guaranteed (Bateman and Baggs, 2005). Consequently, a threshold that indicates soil anoxic conditions that activate denitrification was set at  $f_{SM} = 0.7$ .

## NITRATES PRODUCTION

In order to calculate dynamically the denitrification, process a budget of nitrates have to also be modelled, the present model aims to simulate the production in natural conditions. With no addition of fertilizers or any other source besides the local production. Nitrification production rate ( $kg \cdot ha^{-1} \cdot yr^{-1}$ ) (Girard et al., 2011) is calculated as follows,

$$NO_3_{nit} = N_{org} \cdot k_2 \cdot f_{SM} \quad \text{Eq. 5}$$

with

$$N_{org} = \frac{C_{org}}{C:N} \quad \text{Eq. 5.1}$$

$$k_2 = \frac{1200}{(C + 200) \cdot (0.3[CaCO_3] + 200)} \cdot \rho_b \cdot (0.2 * MAT - 10) \quad \text{Eq. 5.2}$$

$$f_{SM} = \frac{SM_i - SM_{res}}{SM_{sat} - SM_{res}} \quad \text{Eq. 5.3}$$

$$\text{If } f_{SM} \geq 0.7, NO_3_{nit} = 0$$

where  $N_{org}$  is the organic nitrogen in soil calculated as Eq 5.1, where  $OrgC$  is the organic carbon in soil ( $gC \cdot kg^{-1}$ ), and C:N is the ratio of carbon and nitrogen.  $k_2$  is the mineralization rate of  $NO_3$ , calculated as Eq. 5.2, where C and  $[CaCO_3]$  correspond to the clay (%) and carbonate content ( $gC \cdot kg^{-1}$ ),  $\rho_b$  is the bulk density ( $kg \cdot dm^{-3}$ ), and MAT (Mean Annual Temperature) ( $^{\circ}C$ ).  $f_{SM}$  is the unitless function of soil moisture calculated as Eq. 5.3, where SM is the soil moisture in a given day ( $H_2O \ m^3 \cdot m^{-3}$  soil),  $SM_{res}$  ( $H_2O \ m^3 \cdot m^{-3}$  soil), is the minimum soil moisture where the plants are still able to extract water, this can be also be called wilting point, and the  $SM_{sat}$  ( $H_2O \ m^3 \cdot m^{-3}$  soil), is the maximum water capacity specific for each soil type.

## NITRIFICATION-DENITRIFICATION COUPLING

Nitrification and denitrification are complementary and depend on the disposition of oxygen in soil. The complementary of the processes is represented with the soil moisture factor, which has a threshold (0.7) (same for both), but that acts inversely and does not allow the overlapping of both processes. This threshold was defined, considering that water-filled pore space is optimal at 0.6 of nitrification and 0.8 for denitrification (Parton et al., 1996). However, in order to have a transition between nitrification and denitrification, 0.7 was supposed to be a good compromise. Saturated soils extension and its dynamics is crucial to improve the estimation of biogeochemical processes and respond with more accuracy questions like when and how much as indicator at global scale (Bateman and Baggs, 2005; Dorigo et al., 2017; Yin et al., 2019). Excluding management practices, in natural conditions, wetlands represent the ecosystems where the soil is saturated more often, yet the area of the wetlands is not always constant, they can shrink or expand as an effect of season weather (Mitsch et al., 2013). Given that  $NO_3^-$  concentration in soil vary in time and they are the main limiting factor for denitrification in natural wetlands a budget of nitrates in soil was calculated as follows,

$$NO_{3i}^- = NO_{3i-1}^- + [NO_{3i}^-]_{nit} \cdot \delta t - [NO_{3i}^-]_{denit} \cdot \delta t \quad \text{Eq. 6}$$

where  $NO_{3i-1}^-$  is the budget of nitrates in the previous time,  $NO_{3i}^-$  ( $\mu\text{g g}^{-1}$ ) is the nitrates produced by nitrification on a given day and  $NO_{3i}^-$  is the nitrates denitrified on the same day and  $\delta t$ , to denote the change in time. The model is built up by variables and constants summarised in Table 8. Values for some parameters are determined from data or literature. The parameter left for calibration is  $K_{NO_3^-}$  that will be explained in the next section.

Denitrification rate in the SDM is obtained in  $\mu\text{g g}^{-1}$ , in order to compare and to spatialize; the results were converted to  $\text{kg}\cdot\text{ha}^{-1}$  as follows,

$$Denit_{\text{kg}\cdot\text{ha}} = [NO_{3i}^-]_{denit} * \rho_b * depth$$

where  $\rho_b$  is the bulk density ( $\text{kg}\cdot\text{dm}^{-3}$ ),  $depth$  was considered to be 3 dm.

**Table 8.** Variables and constants for wetlands denitrification model

Variable	Units	Description
$\varphi$	-	Porosity
$\rho_b$	kg dm <sup>-3</sup>	Dry sediment density
$T_i$	°C	Temperature
$SM_i$	m <sup>3</sup> m <sup>-3</sup>	Soil saturation
$SM_{res}$	m <sup>3</sup> m <sup>-3</sup>	Minimal soil saturation capacity
$SMSat$	m <sup>3</sup> m <sup>-3</sup>	Maximal soil saturation capacity
$[OrgC]$	mole kg <sup>-1</sup>	Organic carbon content
$C_{org}$	g C kg <sup>-1</sup>	Organic carbon content
$[NO_3^-]_i$	µg g <sup>-1</sup>	Nitrates concentration
$k_{oc}$	d <sup>-1</sup>	Mineralization rate
$\delta t$	day	Time step
$[NO_3^-]_{nit}$	µg g <sup>-1</sup>	Nitrates in soil
$[NO_3^-]_{denit}$	µg g <sup>-1</sup>	Nitrates denitrified
$k_2$	-	Mineralization rate
$MAT$	°C	Mean annual temperature
$C:N$	-	N/C ratio
$N_{org}$	g N kg <sup>-1</sup>	Organic nitrogen
<b>Constant</b>	<b>Units</b>	<b>Description</b>
$T_{opt}$	°C	Optimal temperature
$K_{NO_3^-}$	µg g <sup>-1</sup>	Nitrate limitation constant

## N<sub>2</sub>O-N<sub>2</sub> RATIO OUTGASSING

The most common bottom-up method used to quantify terrestrial N<sub>2</sub>O emissions is based on emissions factors (EFs) that estimates N<sub>2</sub>O emissions as a percentage of soil N inputs. The standard Tier 1 IPCC methodologies used a default emissions factor (1% of N input). However, this assumption had been questioned as it assumes a linear relationship between N input and N<sub>2</sub>O emissions, whereas for many ecosystems or fertilized cropping system the relationship is non-linear. Different methodologies had been used to calculate N<sub>2</sub>O emissions in bottom-up approaches. In agricultural soils, Grosso et al., (2008) had combined field-scale estimates and a DAYCENT (daily century) ecosystem model estimating direct N<sub>2</sub>O emissions to adjust the default IPCC ratio value. Other studies had also calculated ratio based on bottom-up approaches (Table 9). N<sub>2</sub>O emissions are highly variable in space and time, and there has not been a consensus of 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 N<sub>2</sub>O (top-down approach) (Grosso et al., 2008). The present model aims to estimate global natural

denitrification, the results will be presented in  $\text{TgN.yr}^{-1}$  ( $\text{N}_2\text{O} + \text{N}_2$ ) as the complete denitrification in anoxic conditions produce mainly  $\text{N}_2$ .

IPCC  $R_{\text{N}_2\text{O}}$  (0.1) could overestimate the natural emissions, to give an estimation of the possible  $\text{N}_2\text{O}$  emissions, three different ratio from the literature proposed by Scheer et al., 2020 for freshwater wetlands (0.02), ratio proposed by Schlesinger, 2009 (0.082).

**Table 9.** Mean  $\text{N}_2\text{O}$ -yield values from various laboratory and field studies of denitrification

Systems	$R_{\text{N}_2\text{O}}^{\text{a}}$	$R_{\text{N}_2\text{O}}^{\text{b}}$
	$\text{N}_2\text{O-N}/(\text{N-N}_2+\text{N}_2\text{O})$	$\text{N}_2\text{O-N}/(\text{N-N}_2+\text{N}_2\text{O})$
Agricultural soils	$0.375 \pm 0.035$ (SE)	$0.109 \pm 0.020$ (SE)
Soils under natural or recovering vegetation	$0.492 \pm 0.066$ (SE)	$0.124 \pm 0.031$ (SE)
Freshwater wetlands and flooded soils	$0.082 \pm 0.024$ (SE)	$0.020 \pm 0.009$ (SE)

<sup>a</sup> (Schlesinger, 2009)  
<sup>b</sup> (Scheer et al., 2020)

## SENSITIVITY ANALYSIS

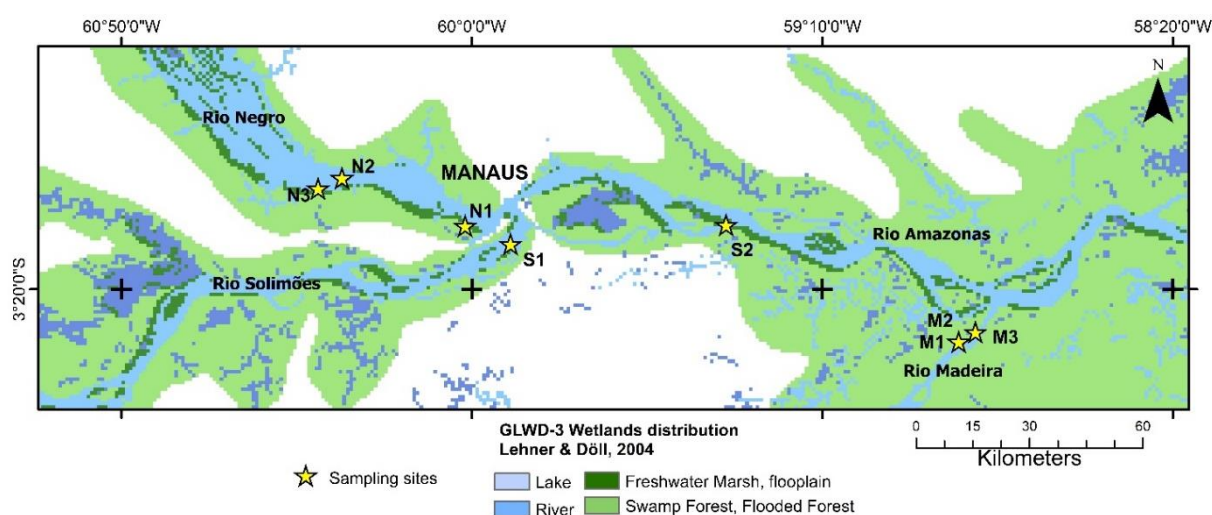
The model sensitivity analysis was carried out in two parts, presented as follows. Part I is based on the validation of the model. The model results are compared to the laboratory results (Chapter III) at three different steps: (i) a static validation (comparison of denitrification rates produced with the soil characteristics and nitrates concentrations of the laboratory conditions). (ii) a dynamic validation (nitrate concentration was replaced by the modeled budget and its sensibility to soil moisture activation and consumption of nitrates is tested) (iii) a spatialized and the dynamic validation (the model was applied using global databases, in the punctual sampling sites, obtaining denitrification and soil moisture time series from 2011-2019). Part II, corresponds to the first attempt of extrapolation on a larger scale (basin scale), where the model assumptions are being tested at the Amazon basin. The identified hot spots, hot moments and denitrification rates were assessed with previous studies. Then, limitations of the present model were identified.

# PART I

## LOCAL VALIDATION

### INPUT DATA

The validation of the model was carried out using the soil data from collected samples of the field campaign and the materials, methods and results of the observations in laboratory-controlled conditions presented previously in chapter III. These sites are distributed in the central Amazonian floodplain and the two main wetlands types (freshwater marsh, and flooded forest) from this watershed are represented (Figure 22).



**Figure 22.** Sampling sites distributed in the central Amazonian floodplain, constituted by two main non-permanent wetland types: floodplain (light green) and flooded forest (dark green), and two permanent wetlands: lakes (dark blue) and river (light blue). Wetlands classification from Lehner and Doll, (2004).

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

The first order kinetics are involved in the multi-component method. However, since the study is based on a combination of redox reactions, this kinetics are put in factor with "limiting" terms. The half saturation constant is integrated in the denitrification model in a Michaelien type function that limits the denitrification capacity, and is related to nitrates quantity (Peyrard et al., 2011). In previous studies the  $K_{NO_3^-}$  was fixed as  $22 \text{ g kg}^{-1}$  for agricultural fields, (Oehler et al., 2007), which is a high value that does not correspond to our results of chapter III, where the saturation was reached before. To adjust this value to wetlands ecosystems, the constant (Eq. 8) was calculated based on observations recorded in the present study (Eq. 7) as follows,

$$A = \frac{Di}{Dp} \quad \text{Eq. 7}$$

$$K_{NO_3^-} = \frac{[NO_3^-]_i}{A} - [NO_3^-]_i \quad \text{Eq. 8}$$

where  $A$  is relation factor between  $Dp$  potential denitrification in no limiting nitrates and  $Di$  is the observed denitrification with no addition of nutritive solution with  $i$  concentration =  $[NO_3^-]_i$ . The resulting mean value used as wetlands ecosystems constant; fixed as  $k_{NO_3^-} = 605 \mu\text{gN.g}^{-1}$ .

### CARBON MINERALIZATION RATES $k_{OC}$

This parameter refers to the mineralization rate of the organic carbon in the soil studied. This rate depends on the lability of the organic matter. In the previous denitrification model application (Fabre et al., 2020; Guilhen et al., 2020; Peyrard et al., 2011; Sun, 2015), organic carbon was divided in two components: (i) Particulate organic carbon (POC) and (ii) Dissolved organic carbon (DOC), due to its application mainly in the aquatic environment. In this study, organic carbon is calculated from the soil, so only one term is referred to the organic carbon that intervenes in the denitrification reaction. In this study, different  $k_{OC}$  rates were determined by wetland typology based on literature values. These constants can be modified if local data or in situ measurements are available. In the present study, mineralization rates used were reported by other studies on diverse study cases in different wetlands types and in different latitudes, these rates are shown in Table 10.

**Table 10.**  $K_{OC}$  for different wetlands typologies

<b>Land use classes</b>	<b><math>K_{OC}</math> (d<sup>-1</sup>)</b>	<b>References</b>
Freshwater marsh	0.062	(Yin et al., 2019)
Flooded forest	0.016	(Bridgham et al., 1998)
Brackish wetlands	0.076	(Mou et al., 2018)

## VALIDATION

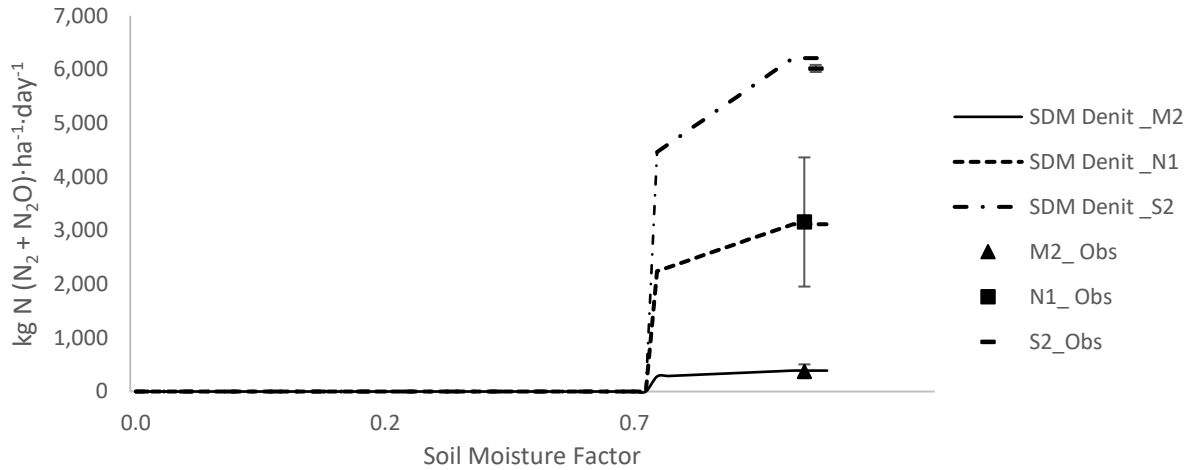
A review of literature values of wetlands denitrification rates has been done in order to compare the results of the present study, most of the values correspond to temperate areas, and few correspond to tropical areas. The Amazon basin is an important watershed worldwide therefore data has been recorded in some wetlands. The reference values are presented in Appendix. However, a lack of data specific for natural wetlands soils in tropical ecosystems was encountered. Each study presents their results in different units, with not all the soil properties parameters needed to model the same soil with the present model. Yet, as part of this thesis, a fieldwork was carried out in the Amazonian floodplain, with two main different wetland typologies (flooded forest and freshwater marsh). The results and data obtained during this experience are presented in chapter III. Those values are used for validation of the present model. Percent Bias (PBIAS) (Moriassi et al., 2007) and linear correlation was applied, if  $p$ -value  $< 0.05$ , then is considered a good fit. The nitrification budget is tested, coupling denitrification and nitrification functions. Soil moisture and temperature satellite diurnal data from (2011-2019) was extracted at the eight sampling points presented in chapter III. Because two of the sites are closer than  $1 \text{ km}^2$  (soil moisture satellite data spatial resolution) seven different soil moisture dynamics are applied to the sampling points (M1 and M2 had the same soil moisture dynamics). The kOC from the laboratory data was replaced for the literature kOC values corresponding to freshwater marshes and flooded forest, according to the wetland's typology of each site. Diurnal time series of denitrification are calculated for each sample, the punctual observed values in laboratory conditions (with no addition of nutrient solution) (chapter III, treatment=N) are added to the graphic, to estimate at which moment of the nitrogen cycle the samples were taken.

### STATIC VALIDATION

The SDM in optimal conditions (temperature, moisture and unlimited nitrates), gives the potential denitrification rate based on soil characteristics and organic carbon decomposition rate. That is the maximum rate the SDM will calculate, and changes from soil to soil. The model integrates three limiting factors that affect equally and that had been normalized in a range of 0-1. If one of these factors is zero then denitrification is null. In order to illustrate the model limiting functions, three samples were selected (N1, S2, M2), and their different reactions to the three limiting factors. Soil moisture factor ( $f_{SM}$ ) has a threshold of 0.7, meaning that if  $f_{SM}$

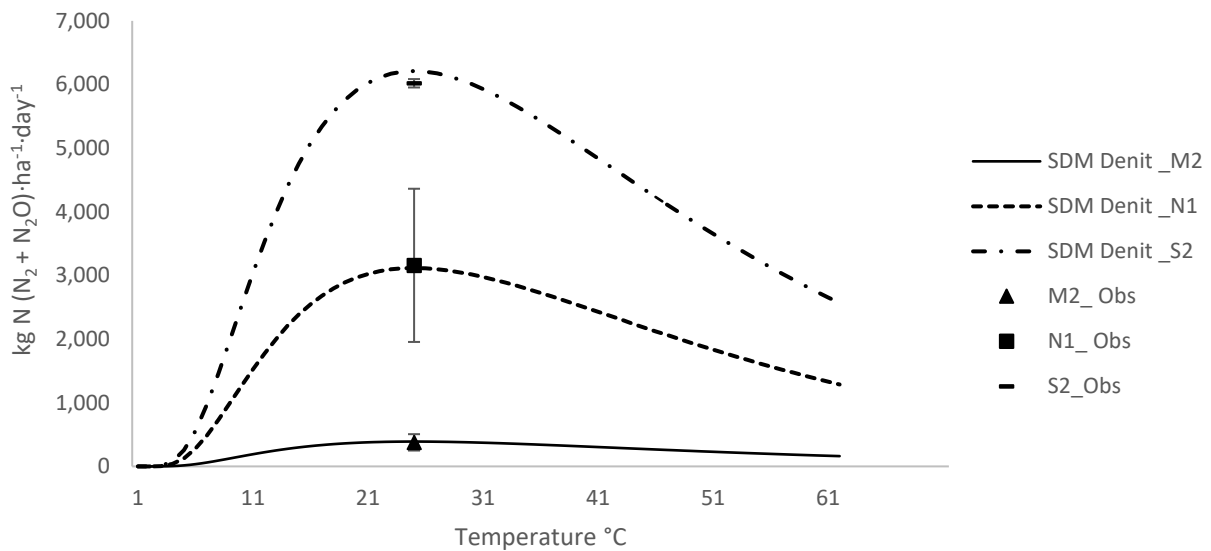


is below 0.7 denitrification is automatically zero. When  $f_{SM}$  is above 0.7 denitrification production begins, and the maximum is reached when soil is completely saturated (soil moisture factor = 1) (Figure 23).



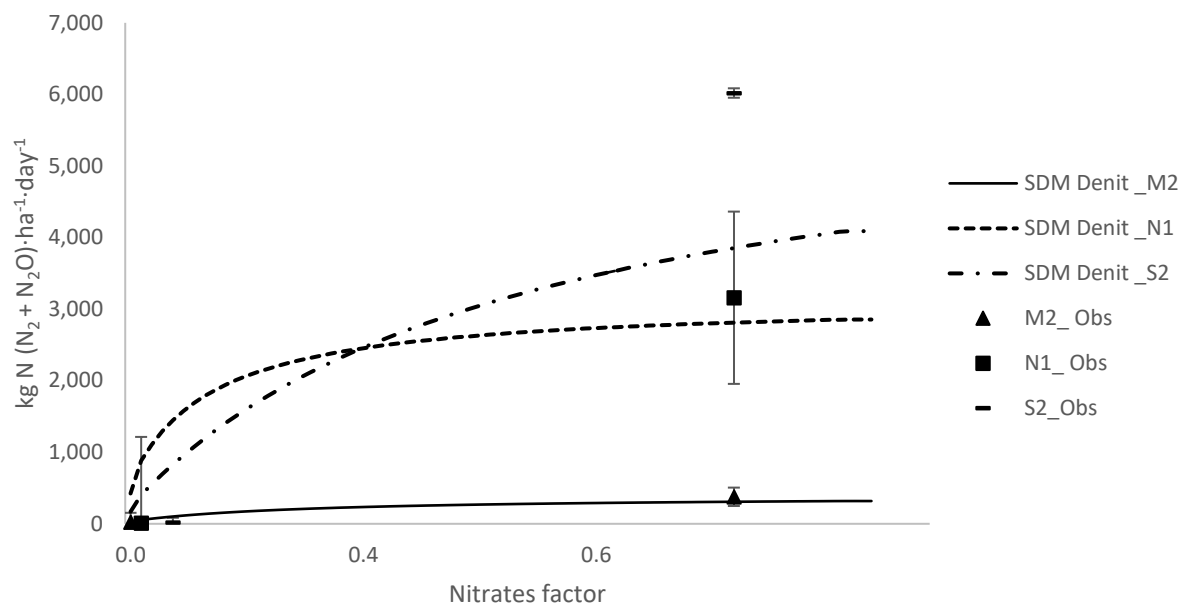
**Figure 23.** Modelled denitrification with Soil moisture factor as only limiting factor.

Denitrification is also sensitive to temperature (Figure 24), the SDM considered that below 4°C no denitrification is possible, and it increases until the optimal temperature, set at 25°C, after there is a decline of denitrification if temperature still rises.



**Figure 24.** Modelled denitrification with temperature as only limiting factor.

The third limiting factor is  $f_N$  that refers to nitrate saturation function (Figure 25). In a system where nitrates are unlimited, optimal temperature and soil moisture, denitrification increases very rapidly and then it stabilizes, reaching its potential denitrification capacity.

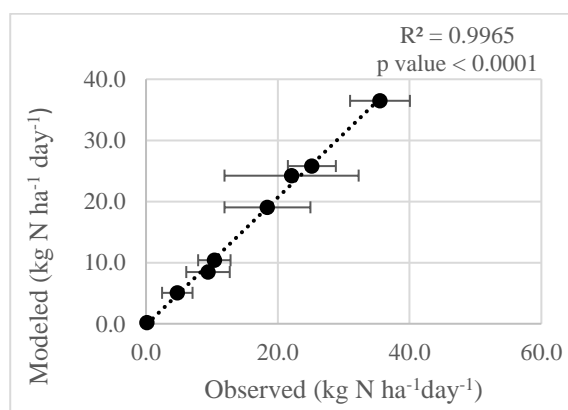


**Figure 25.** Modelled denitrification with nitrate as only limiting factor.

Modelled results for each sampling soil are compared to laboratory-controlled conditions (Table 11). The observations and the model have a very good fit ( $p$ -value < 0.001) regarding natural and potential emissions as shown in Figure 26 a-b. PBIAS=4.15 for limiting conditions.

**Table 11.** Denitrification rates from the amazon wetlands (observed and modelled)

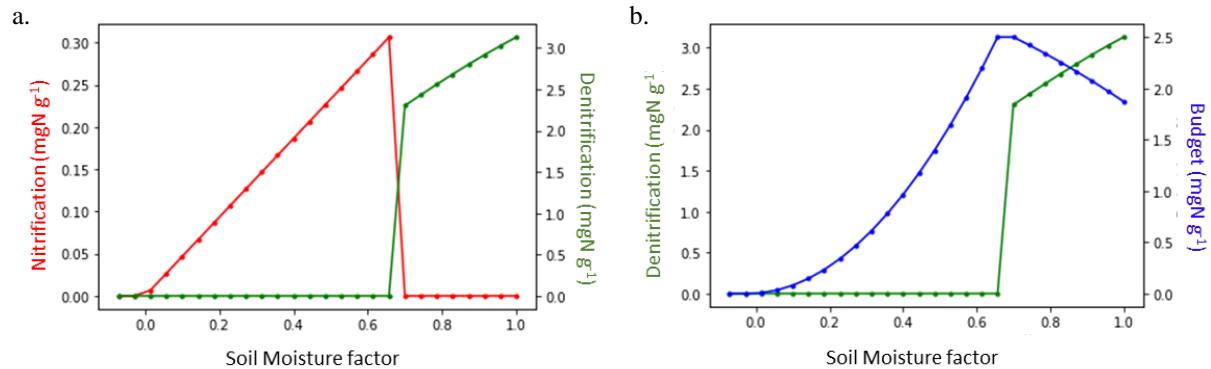
Site	[NO <sub>3</sub> <sup>-</sup> ] μg.g <sup>-1</sup>	[OrgC] g.kg <sup>-1</sup>	Observed denitrification kgN.ha <sup>-1</sup> .day <sup>-1</sup>	Standard Error (±)	Potential denitrification kgN.ha <sup>-1</sup> .day <sup>-1</sup>	K <sub>OC</sub> (d <sup>-1</sup> )	Model natural denitrification kgN.ha <sup>-1</sup> .day <sup>-1</sup>	Model potential denitrification kgN.ha <sup>-1</sup> .day <sup>-1</sup>
N1	0.45	190.28	10.37	2.46	3158.64	0.006	10.39	3177.72
N2	0.04	0.18	0.12	0	188.86	0.122	0.16	258.25
N3	0.05	17.14	35.51	4.54	10355.91	0.066	36.46	10690.22
S1	0.10	89.16	9.41	3.3	1593.15	0.003	8.46	1441.72
S2	0.08	6.37	18.43	6.52	6019.25	0.109	19.05	6211.43
M1	0.13	4.42	22.09	10.18	9744.47	0.271	24.24	10648.62
M2	0.19	12.66	25.17	3.64	377.42	0.004	25.8	389.93
M3	0.06	0.64	4.75	2.31	1380.42	0.204	5.06	1480.55



**Figure 26 a.** Correlation between observed and modelled denitrification results of the eight sample sites in limiting [NO<sub>3</sub><sup>-</sup>] and [OrgC].

## DYNAMIC VALIDATION

When applying the model dynamically, nitrification function is also affected by temperature and soil moisture. Nitrification will be active when soil moisture factor is below 0.7 (Figure 27a.), and then when soil moisture increases nitrate budget will began to be consumed by denitrification (Figure 27b).

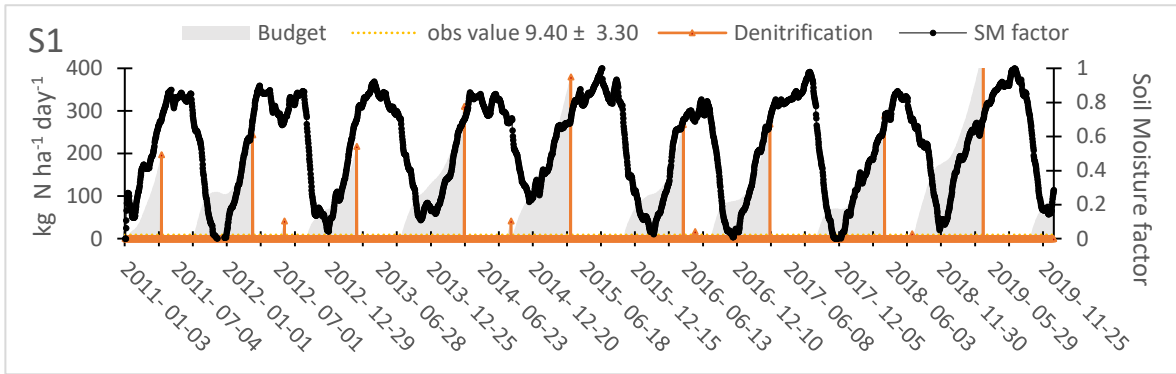


**Figure 27 a.** Dynamic nitrification and denitrification activation and deactivation when the soil moisture changes in time. **b.** Nitrates budget consumption when denitrification is activated

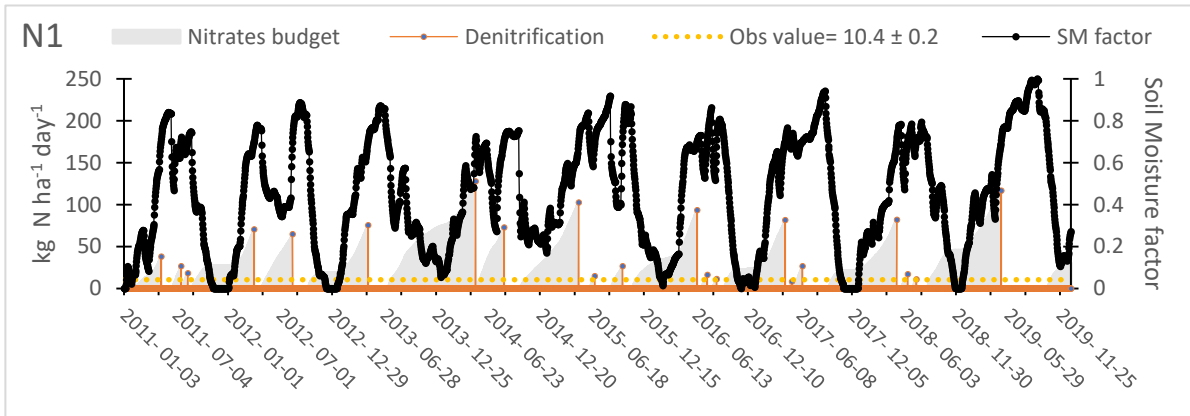
## SPATIALIZED VALIDATION

Denitrification and nitrate budget time series are compared to soil moisture dynamics of each site (Figure 28 a-g). They are presented from the highest production observed in the flooded forest Solimões 1 (S1), followed by the two flooded forest of Negro river (N1 and N3), then freshwater bush marsh of Madeira (M2), and at the end the herbaceous freshwater marshes of Solimões and Madeira (M1 and M3). The sandy beach was excluded as there was no clear wetland vegetation typology. The laboratory measurements are punctual and from controlled condition, therefore they cannot be place as a moment in time. However, those values are our reference of observed denitrification in each soil sampled. Therefore, they are added to the graphics as continues line. Table 12 presents the modelled denitrification summary, where the maximum-modelled diurnal denitrification value is presented, followed by interannual rates, and identification of the peak denitrification year. These time series are dictated by soil moisture dynamics, a correlation of soil moisture and modelled denitrification rates of each sampling site is compiled in Figure 29a-b, to illustrate model denitrification law.

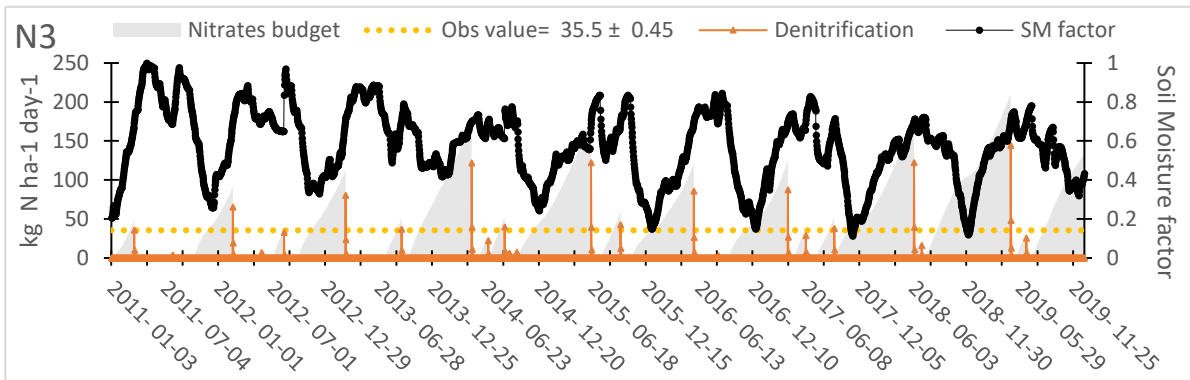
a.  $k_{OC} = 0.016$  Flooded forest



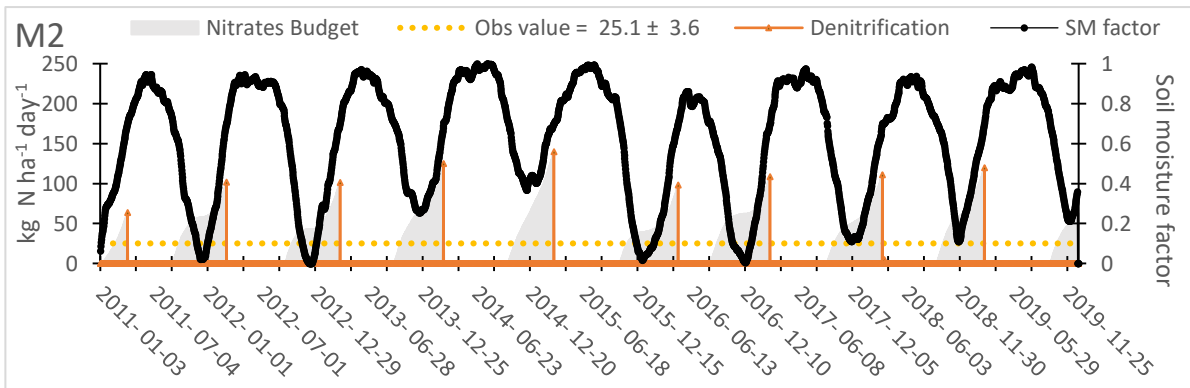
b.  $k_{OC}=0.16$  Flooded forest



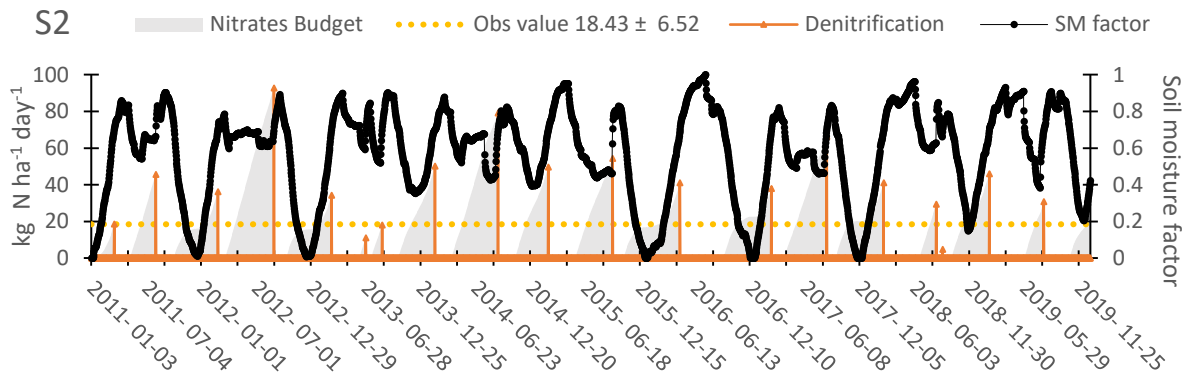
c.  $k_{OC}=0.16$  Flooded forest



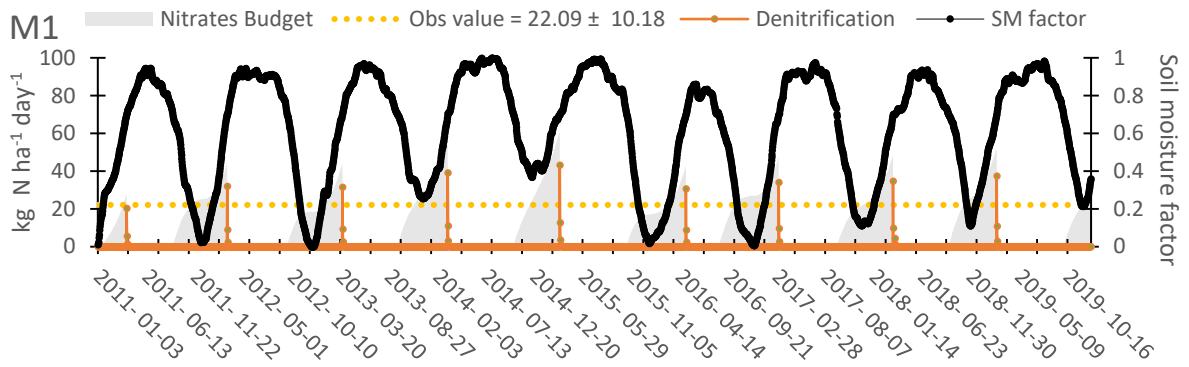
d.  $k_{OC}=0.062$  Freshwater marsh.



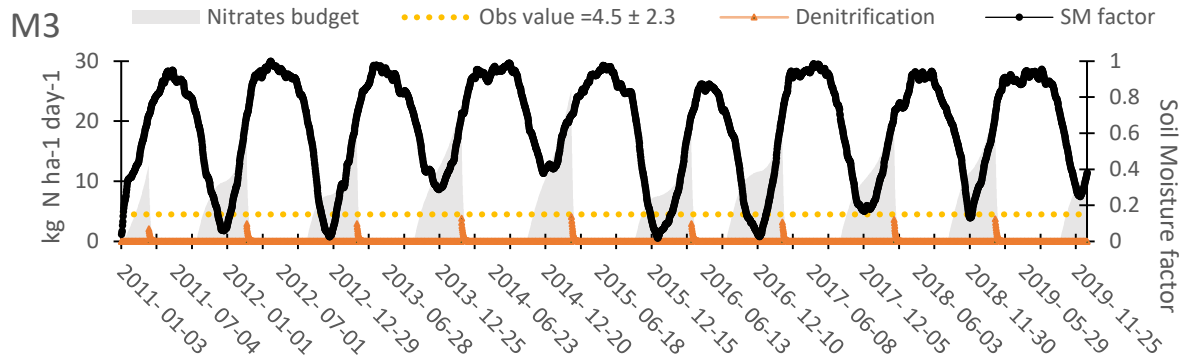
e.  $k_{OC}=0.062$  Freshwater marsh



f.  $k_{OC}=0.062$  Freshwater marsh



g.  $k_{OC}=0.062$  Freshwater marsh

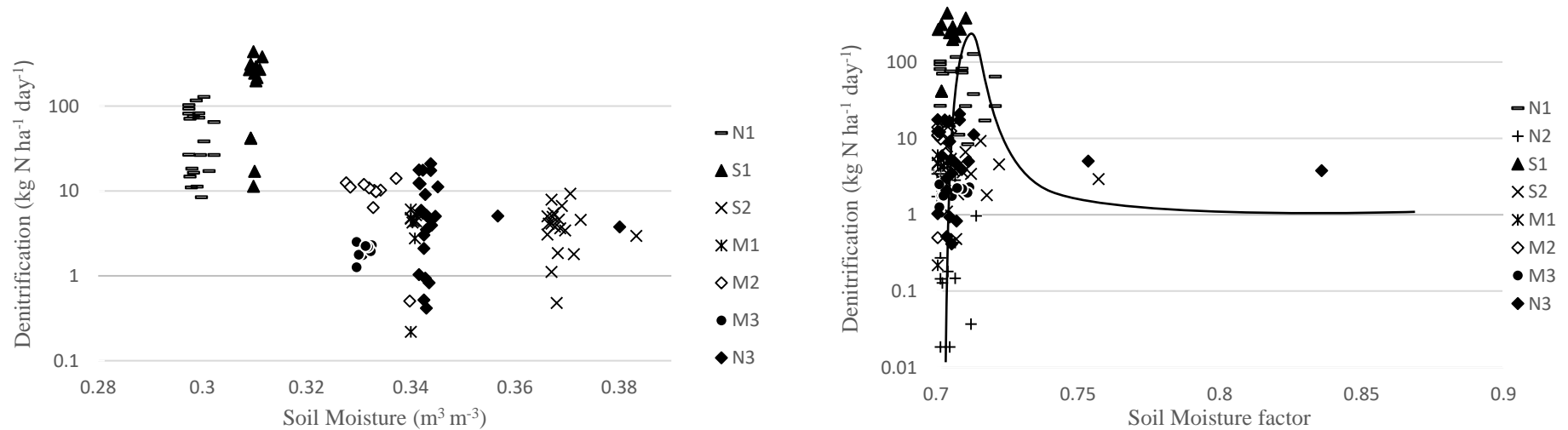


**Figure 28a-g.** Diurnal time series from 2011-2019 of nitrate budget, denitrification and soil moisture dynamics of soils samples, with  $k_{OC}$  corresponding to their wetland typology. Left axis corresponds to modelled denitrification, reference value of denitrification ( $\text{kgN} \cdot \text{ha}^{-1} \cdot \text{day}^{-1}$ ) from laboratory conditions with limiting nitrates, and nitrification budget ( $\text{kgN} \cdot \text{ha}^{-1} \cdot \text{day}^{-1}$ ). Right axis corresponds to soil moisture values ( $\text{m}^3 \cdot \text{m}^{-3}$ ).

**Table 12.** Summary of observed and modelled results.

Soil	C/N	Org Carbon g kg <sup>-1</sup>	Mean Interannual Temperature °C 2011-2019	Interannual max soil moisture	Interannual residual soil moisture	Reference Nitrate limited kg N ha <sup>-1</sup> day <sup>-1</sup>	standard error kg N ha <sup>-1</sup> day <sup>-1</sup>	Reference Potential kg N ha <sup>-1</sup> day <sup>-1</sup>	Model max kg N ha <sup>-1</sup> day <sup>-1</sup>	Model inter-annual nitrification* kg N ha <sup>-1</sup> year <sup>-1</sup>	Model inter-annual denitrification* kg N ha <sup>-1</sup> year <sup>-1</sup>	year	Max*	year	Min*
N1	16.17	190.28	27.46	0.37	0.12	10.41	2.46	3177.72	128.64	128.03	127.57	2014	200.81	2013	75.69
N2	1.42	0.18	27.57	0.40	0.13	0.16	0	258.25	0.18	28.91	25.92	2019	38.88	2012	17.40
N3	15.43	17.14	27.59	0.43	0.14	36.56	4.54	10690.22	144.26	198.74	198.80	2014	275.71	2016	125.57
S1	11.08	89.16	27.76	0.39	0.13	8.45	3.3	1441.72	436.94	315.12	315.90	2018	436.94	2013	216.59
S2	10.24	6.37	27.71	0.46	0.15	19.12	6.52	6211.43	92.77	90.96	90.34	2014	129.23	2016	41.00
M1	7.99	4.42	28.19	0.42	0.14	24.28	10.18	10648.62	43.25	49.49	49.33	2015	60.62	2016	42.50
M2	7.44	12.66	28.19	0.42	0.14	25.78	3.64	389.93	139.89	114.20	113.83	2015	139.89	2016	98.07
M3	4.52	0.64	28.21	0.41	0.14	5.05	2.31	1480.55	4.13	20.88	20.36	2018	25.12	2018	15.71

\* 2011 was excluded, as it is the first year of the model and the nitrate pool is building up, the mean value refers to 2012-2019.



**Figure 29a.** Relation of denitrification moments from (2011-2019) and the corresponding soil moisture value of the sampling sites. **b.** denitrification rate vs. soil moisture factor.

## SDM LOCAL VALIDATION

The SDM here presented shows that simulated denitrification has a good fit (PBIAS:4.15) compared with reference values of denitrification in controlled laboratory conditions (i.e. optimal temperature, saturated soil) with limited nitrates. The functions of each limiting factor of the model was built up in order to represent denitrification changes when one of those factors are under the optimal conditions, the more abrupt effect is produced by soil moisture, then depending the quantity of nitrates available in the system, and the capacity of each soil, the consumption will be effectuated shortly. SDM aims to calculate the denitrification rate of natural wetlands ecosystems, under the hypothesis that nitrates are limited. In the case of the Amazon, considered a low disturbed watershed, time series results showed that denitrification events are short (Figure 30b). Koschorreck, 2005 reports that nitrates content of the sediments of an amazon floodplain lake were always low (below  $0.04 \mu\text{mol.g}^{-1}$ ), so nitrates limited denitrification. Bowden, 1987, reported that nitrates formed by nitrification in freshwater wetland goes from  $< 0.1$  to  $10 \text{ gN.m}^{-2}.\text{yr}^{-1}$ . SDM simulates a nitrate annual budget of the eight different sites that goes from 2.09 to  $11.83 \text{ gN.m}^{-2}.\text{yr}^{-1}$ , with a maximum of  $31.51 \text{ gN.m}^{-2}.\text{yr}^{-1}$  which value corresponds to a flooded forest (S1). Modelled nitrates budget, are within the range of previous results reported. The two sites that show the highest modelled denitrification peak were (S1 and N1), as observed in lab conditions and reported in chapter III.

Besides the lack of in situ data of  $\text{N}_2\text{O}$  emission, controlled conditions in the laboratory isolate the limiting factor (nitrates) and ensure optimal temperature and saturation. Acknowledging the benefits of laboratory conditions, the present model was calibrated and validated with this data. The eight soil samples had a large range of soils properties; from low organic carbon content, mineral soils to rich organic soils. These soils gave a hint of the heterogeneity of wetlands, in terms of soil characteristics. Even though the study area is small compared with the Amazon watershed size, and that sampling sites were all located at the river edge, the time series of soil moisture shows that each site has their own dynamics, and their maximum soil moisture range (8a).

SDM does not simulate plant uptake or dissimilatory reduction to ammonium as it is considered to be conservative processes (which products stay in the ecosystem), assuming steady-state conditions. SDM also does not simulate carbon budget; as it is assumed that annual flux of carbon is greater than losses (respiration; harvesting, export, burial). So organic carbon content was taken as constant for each soil type. In the case of Amazon, this assumption is based on literature; that report that plant biomass accumulated during rising water stage of the annual

flood cycle; has a peak at 23000 to 6100  $\text{g.m}^{-2}$  and decreased later in the year. Annual net primary production was estimated to range from 2400 to 3500  $\text{g m}^{-2} \text{ yr}^{-1}$ , with above water production between 650 and 1100  $\text{g.m}^{-2}.\text{yr}^{-1}$ , and below water production between 1700 and 2600  $\text{g.m}^{-2}.\text{yr}^{-1}$  (Silva et al., 2009). This assumption has been observed in other tropical wetlands. Alongi et al., (2004) reported that in a tropical mangrove forest in Malaysia accumulate sediment and organic carbon, with a net ecosystem production (+21). They also reported that N mineralization is greatest at the old-growth forest, and denitrification has a rapid turnover (hours to 1-2 days). They also noted that sediment-water exchange of nitrogen was minor. In these mangrove forests, the average denitrification was the largest loss in relation to N loading ranging from (39-93%). This evidence supports the assumption of considering denitrification as main system loss, and carbon content no limited, therefore no need to calculate a budget, but its available quantity is different from soil to soil.

Denitrification instead is only observed as a peak event at the beginning of the saturation phase. Yet if nitrates become unlimited then the peak will be longer and incomplete, producing  $\text{N}_2\text{O}$  (Blackmer and Bremner, 1978). The intensity magnitude of denitrification peak could be explained due to the bimodal flooding dynamics of this particular watershed and the large extent of floodplains that expands and reduces by hundreds of kilometres (Hess et al., 2003). If there is a frequent exchange of saturation-no saturation denitrification occurs more often but the intensity of events is lower, as there is less nitrates available in soil. This response may be valid in a natural scenario, but when integrating anthropogenic nitrogen input, the dynamic saturation, no saturation will bring or leach nitrogen. At local scale, denitrification –nitrification could happens during the whole inundation period, as soils are a heterogeneous environment, where there is an efficient interaction of soil bacteria and plants roots creating areas where the oxygen is available all year long (Reddy et al., 1989a). Nonetheless, SDM was not designed for a local scale, but for a large scale, therefore denitrification events may only happen at the beginning of the phase change. The second part of the present chapter presents the results of the model extrapolation.



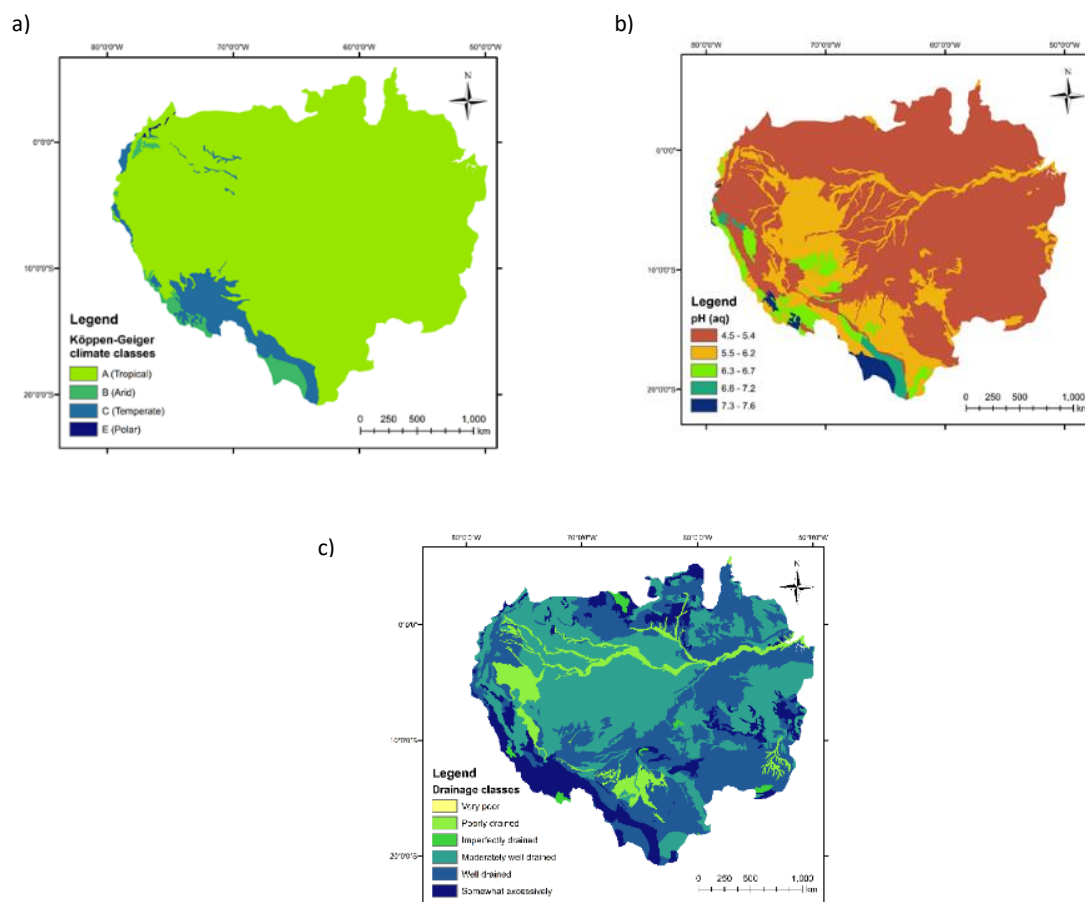
## PART II

# MODEL EXTRAPOLATION AT BASIN SCALE

## STUDY SITE

Later on, in order to upscale the methodology, the present model was tested in the Amazonian basin. This basin was chosen as a previous denitrification model approach was applied there (Guilhen et al., 2020), and the SDM results can be then compared with those previously obtained.

The Amazonian basin is the biggest basin worldwide with a total surface of 7 184 749 km<sup>2</sup>, which has 11 -13 % of its total surface covered by natural wetlands (permanent and non-permanent). Dominated by tropical climate and acid pH and poorly to moderate drainage soils (Figure 31a-c).



**Figure 30a.** Amazonian basin climate classes, **b.** pH range, and **c.** soil drainage classes data from WISE-30sec (Batjes, 2015).

## INPUT DATA

The databases for this study were selected under the criteria of global availability, free access, and sound sources. Because the aim of the present model is to be able to be applied at global scale and where field data is not available. The databases selected are presented in Table 13 and explained in detail further on.

**Table 13.** Global scale input data

Parameter	Variable	Temporal resolution	Spatial resolution	Time series	Database
- Bulk density - Org Carbon - C:N ratio	- Clay perc - [CaCO <sub>3</sub> ]	Soil properties	- 1 km <sup>2</sup>	-	WISE 30sec (Batjes, 2015)
Wetlands typology	Land Use	-	1 km <sup>2</sup>	-	(Arino et al., 2011; Lehner and Doll, 2004)
Sub-oxic or anoxic conditions	Soil Moisture	Daily	1 km <sup>2</sup>	2010-2019	(Al Bitar et al., 2017)
Denitrifies activity	Temperature	Daily	1 km <sup>2</sup>	2010-2019	(Al Bitar et al., 2017)

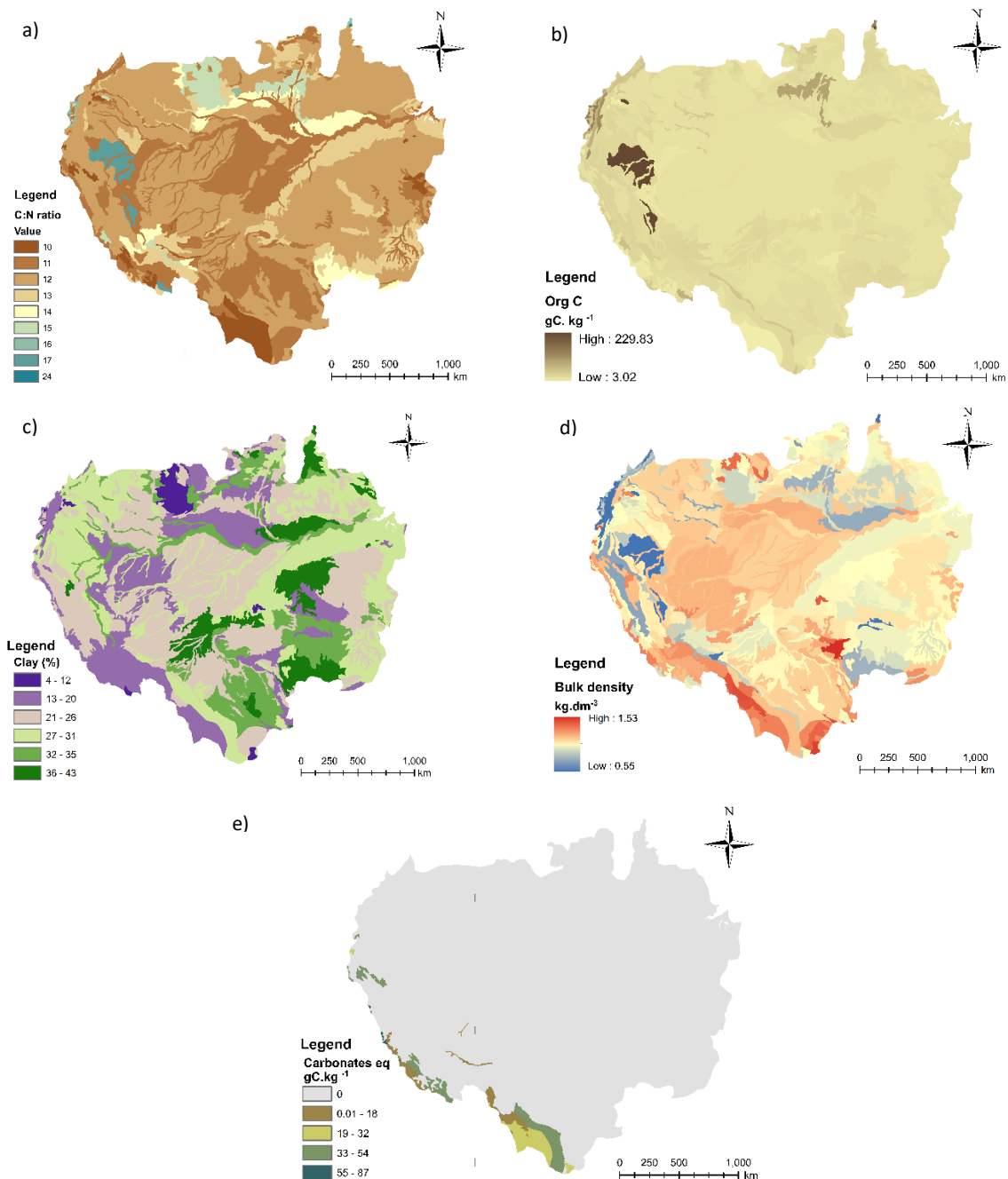
### SOIL PROPERTIES

Soil properties needed for the model were extracted from the same database, WISE-30 sec (Batjes, 2015), this database is a spatialized dataset compiled using traditional mapping approaches. A short summary of the main features of this database is presented here and a detailed description can be found in Batjes, 2015. WISE-30 sec is composed of a soil-geographic and soil attribute component. The former was derived from a geographic information system (GIS) overlay of the Harmonised World Soil Database (HWSD) (Nachtergaele et al., 2010) and the Köppen-Geiger climate class map (Peel et al., 2007) as a covariate, while soil property estimates attribute data for these compound map units were derived using taxotransfer (TTR) procedures. The spatial resolution (30 by 30 sec) of this dataset is aimed for exploratory assessments at the global level. Studies at (sub national level should be based on regionally more detailed soil data sets (Batjes, 2015). This dataset considers 20 soil properties that are commonly required for global agro-ecological zoning, land evaluation, modelling of soil gaseous emissions, and analyses of global environmental change (Batjes, 2015).

These estimates were derived from statistical analyses of data for 21,000 soil profiles of the ISRIC-WISE database (Batjes, 2012). The best estimates are presented for fixed depth intervals of 20 cm up to a depth of 100 cm, and 50 cm between 100 cm and 200 cm (or less when appropriate) for so-called ‘synthetic’ profiles (as defined by their ‘soil/climate’ class).

For each attribute, a mean value associated statistical uncertainties is provided. This data set can be linked to the spatial data through their unique map unit, which is a combination of the soil unit and climate class code (Batjes, 2015).

The present model used the following soil characteristics: C/N ratio, organic carbon, bulk density, carbonates equivalents, and clay percentage (Figure 32. a-e).



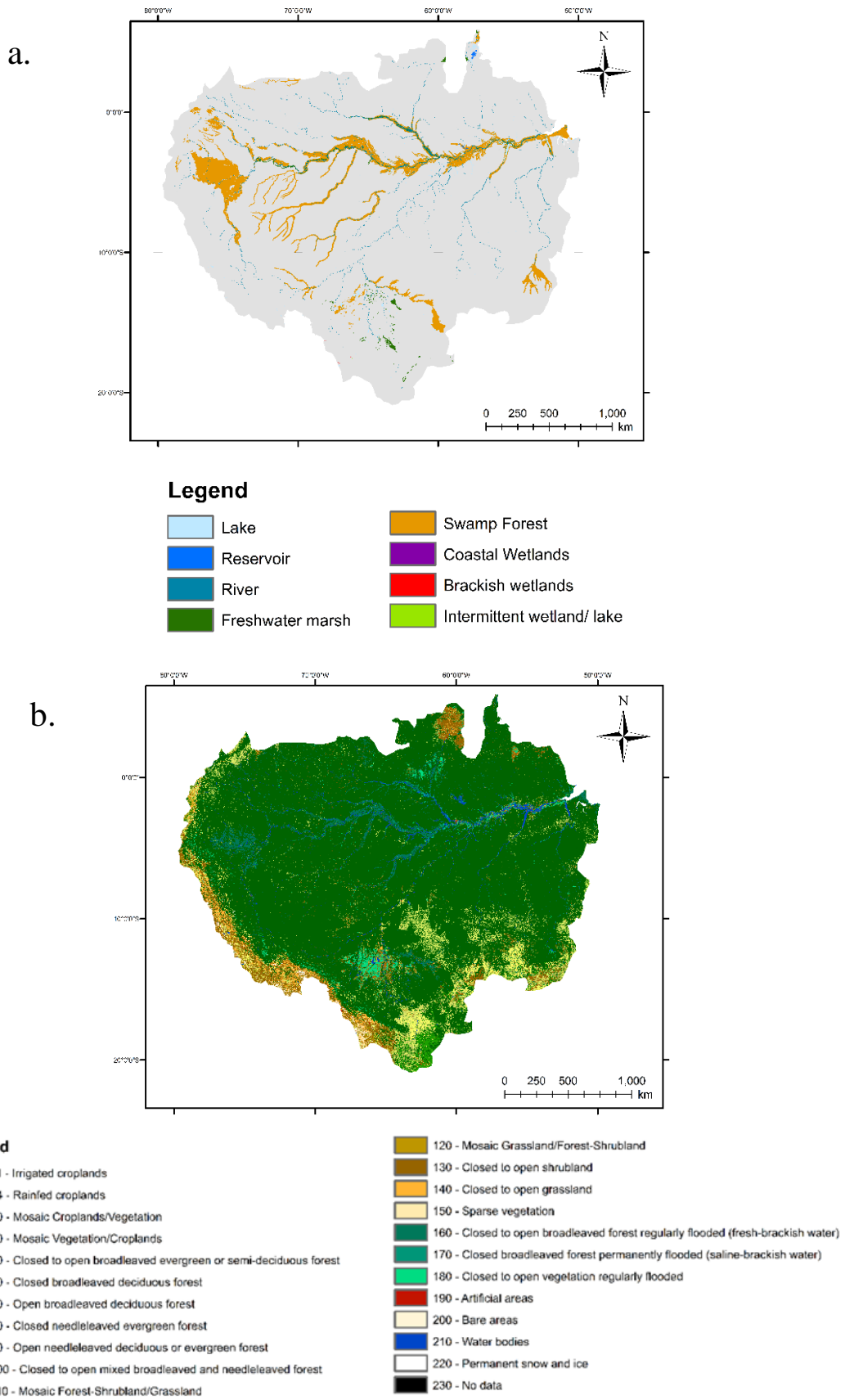
**Figure 31.** Spatialization of soil properties (i.e. input data) needed for the model **a)** C:N ratio, **b)** organic carbon (Org C kg<sup>-1</sup>), **c)** clay (%), **d)** bulk density (kg.dm<sup>-3</sup>), **e)** carbonate equivalent (gC.kg<sup>-1</sup>) data from WISE-30sec (Batjes, 2015).

## NATURAL WETLANDS TYPOLOGY AND DISTRIBUTION

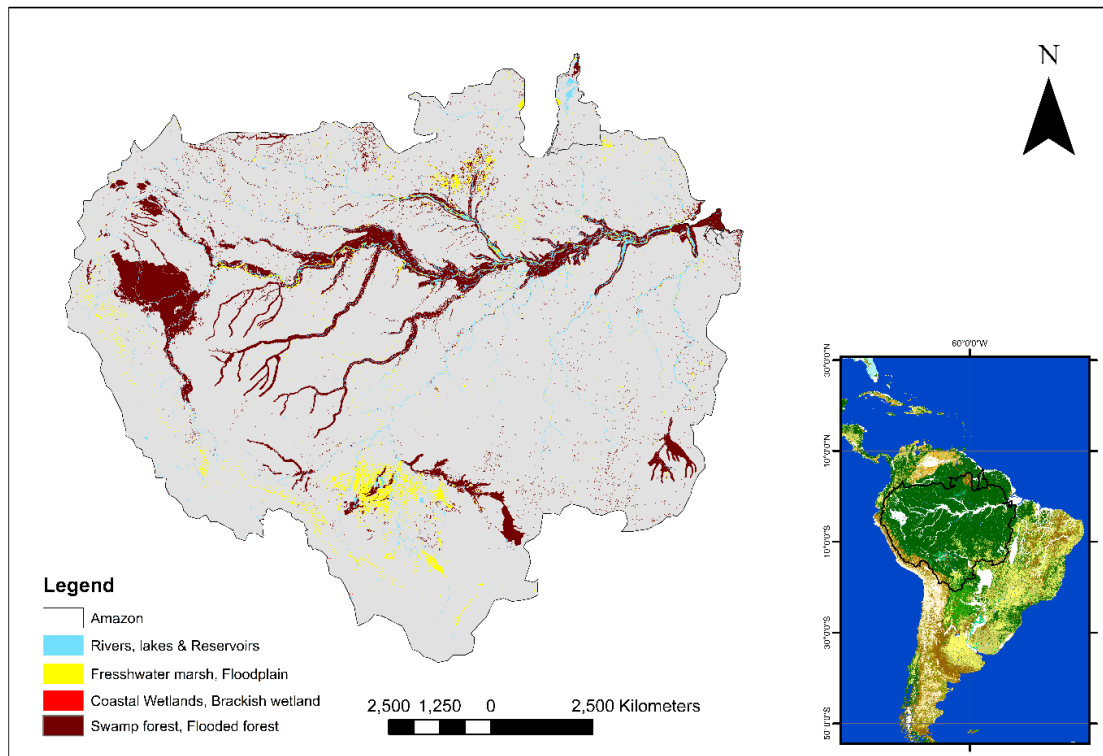
In the present study, the global lakes and wetlands database level 3 (GLWD-3) provide by Lehner and Doll, (2004) (Figure 33a) and the Global Cover 2009 (Friedl et al., 2010) (Figure 33b), were combined and used as the potential maximal area of natural wetlands distribution (Figure 34). The combination of these two databases was done to avoid missing out some potential natural wetlands because GLWD-3 has not been updated since, and comparing it with Global Cover 2009, some wetlands areas were not taken into account. The resulting area is considered as the potential maximal extension of natural wetlands distribution, and is therefore where the present model was applied.

Wetland typology for the present study was simplified in seven classes, following the Ramsar main classification. Rivers, lakes and reservoirs (not considered for the denitrification model in the present study) and, the temporal wetlands divided as: (i) Freshwater marsh/floodplain; (ii) swamp/flooded forest; (iii) coastal wetlands/brackish salt water, and refers to a mosaic of different small wetlands, not defined by vegetation characteristics. This static distribution of wetlands is the delineation where the model was applied. Yet, this wetland distribution is just a mask of the potential distribution, as it does not inform about wetlands dynamics (i.e. terrestrial and aquatic phase).

CHAPTER IV-PART II



**Figure 32.**Wetlands distribution and typology by a) Global wetlands map GLWD-3, spatial resolution of 1km<sup>2</sup> from Lehner & Döll (2004) & b) Land use by Global land cover of 2009 (Friedl et al., 2010).



**Figure 33.** Amazonian wetlands typology used as the maximal area of wetlands distribution for the present study, as a result of GLWD-3 and Global land cover of 2009

### SOIL MOISTURE AND TEMPERATURE

Due to the importance of soil moisture and temperature for activate or deactivate denitrification and nitrification reactions it has been reported that satellite data is the most accurate data for asses these processes as they can record diurnal changes and are able to observe difficult access areas all over the planet (Martínez-Espinosa et al., 2021). The present model will use soil moisture and temperature product from SMOS satellite (Kerr et al., 2010).

A summary of the product processor is presented here and a detailed description can be found in Al Bitar et al., 2017 & Kerr et al., 2010. The global SMOS level 3 daily soil moisture (L3SM) and brightness temperature (TB) satellite products consist in a multi-orbit algorithm (MO). This MO methodology enhances the robustness and quality of SM estimations. TB and L3SM was compare to the soil moisture Active Passive (SMAP) mission, launched by NASA in January 2015. Regarding the mean TB, there are small differences between products, yet SMAP has a wider coverage due to the RFI filtering. SM retrievals on a global scale were compared with L2SM- SO (previous version), and L3SM –MO had improved the coverage and the number of successful retrievals (Al Bitar et al., 2017).

## SDM PYTHON MODULE MODEL

It was necessary to develop a software-based model to harmonize the different databases. The module model was buildup in Python programming language, which allows optimizing the work and integrating systems mode effectively with an open-source license.

The SDM Python Module Model (Figure 35) was developed in collaboration with Dr. Ahmad Al bitar from the Centre d'Etudes Spatiales de la Biosphère, Toulouse France. Different fix modules that interact to each other constitute SDM-PMM. A brief description of each module is presented below. The scripts for each module are presented in appendix of chapter IV.

**IN-OUT:** This module is constituted by fifteen functions that reads input data and that write the outputs files. The readable parameters are latitude, longitude, date and in converts all the input data in arrays.

**MODEL:** This module contains the equations of the SDM. (Nitrification, Denitrification, Nitrates budget).

**TOOLS:** This module is constituted by functions that help cut the global data to the region of interest, and to homogenize the grid using the soil database as the reference grid. It also assigned the mineralization rates (Koc) to each pixel according to their land class.

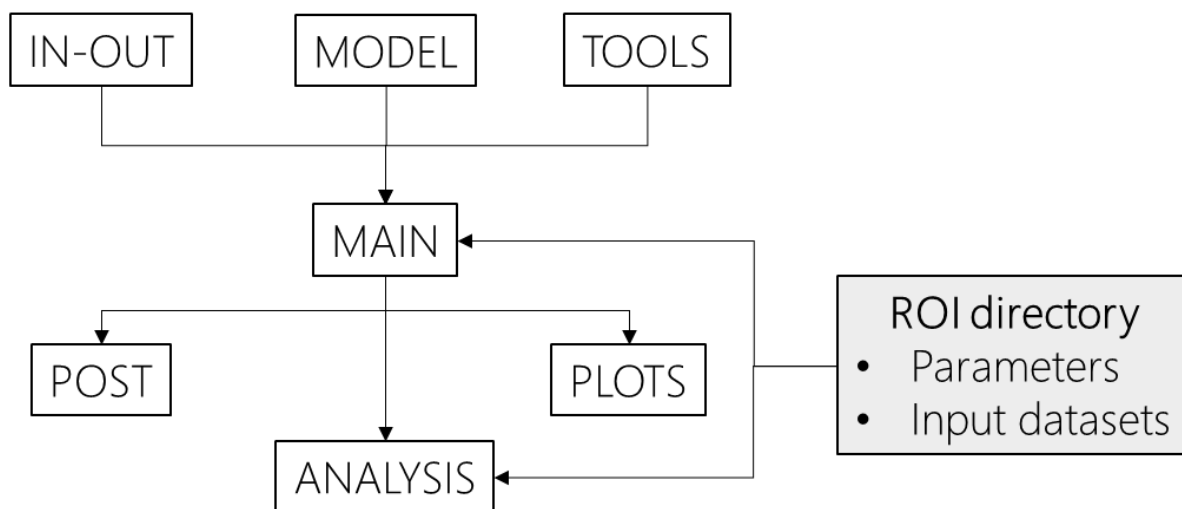
**POST:** This module allows the extraction of punctual time series of denitrification, nitrification, as well as forcing data (temperature, soil moisture). It is possible to extract a specific period, or the whole time series.

**PLOTS:** This module has the functions to be able to map the results, geographically projected, converting indexes to latitude and longitude.

**MAIN:** This module is where the simulation is being run. First, the modules are being called. Then, it generates the output folders where data will be storage. Reads data directories of dynamic data, and static data. As all input data is global, if the simulation wants to be run on a specific area, the data is being extracted for a region of interest defined by the user, in latitude and longitude polygon. Then Koc is assigned and the simulation is carried out only in the terrestrial territories where Koc is given (i.e. wetlands). Once the data is homogenized, then denitrification model loop run at daily scale. Each loop, denitrification, nitrification, and budget, are stored as fluxes in  $\text{mgN g}^{-1}$ .

**ANALYSIS:** This module is where data produced in the main loop will be called as input data, and spatialized analysis are carried out. First, a unit transformation from  $\text{mgN g}^{-1}$  to  $\text{kgN ha}^{-1}$  is performed, interannual denitrification mean; annual and monthly mean are calculated by area, and by ecosystem. Total denitrification ( $\text{N}_2 + \text{N}_2\text{O}$ ) by area ( $\text{kg N ha}^{-1}$ ), daily, weekly, monthly and annual can be also calculated. These functions; are a first exploratory exploitation of SDM, but the algorithms can be improved in addition to adapted to specific objectives, for more in-depth analysis.

The **MAIN** and **ANALYSIS** modules are the only ones that needs to be updated, specific directory to use for the region of interest (ROI). The ROI directory file is constructed as an eXtensible Markup Language, (XML). This format is easy to use, and can be open as text file; it is used to structure data for storage and transport. This file contains the tag names that clearly define and explain the data.



**Figure 34.** Conceptual diagram of the modules of SDM coded in Python and their interactions. The Main module is where de user interacts with the model. The preliminary results are saved and later called in the analysis module.

### SPATIALIZE DYNAMIC APPLICATION

In order to extrapolate the use of this model a larger scale,  $K_{OC}$  values from (Table 10) and soil properties at global scale presented above (Table 13) were used. The model was applied in the wetlands of the whole Amazon basin from 2011-2019. At basin scale, an interannual and monthly mean denitrification ( $\text{N}_2 + \text{N}_2\text{O}$ ) by area ( $\text{kgN.ha}^{-1}.\text{yr}^{-1}$ ) or ( $\text{kgN.ha}^{-1}.\text{month}^{-1}$ ) was calculated. Denitrification hot spots and hot moments at basin scale were identified. Subsequently eight points in different locations that resulted “hot areas” were selected and time series of denitrification and soil moisture of these sites is presented. Annual denitrification was

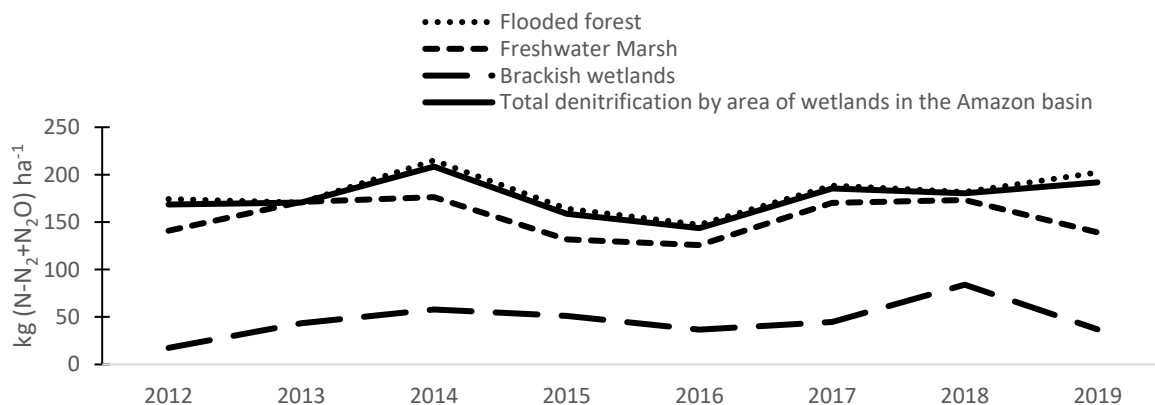


then partitioned by wetland typology (kgN by total area of each wetland type). Percentage, ecosystem efficiency by area ( $\text{kgN}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ),  $\text{N}_2\text{O-N}$   $\text{kg}\cdot\text{yr}^{-1}$  contribution to annual denitrification by each wetland type were estimated with different ratios. Results were compared with other studies (model-based and field-based). The first year of the simulation (i.e. 2011) was excluded from average calculations as nitrogen budget is under construction and the model has not yet stabilized.

## RESULTS

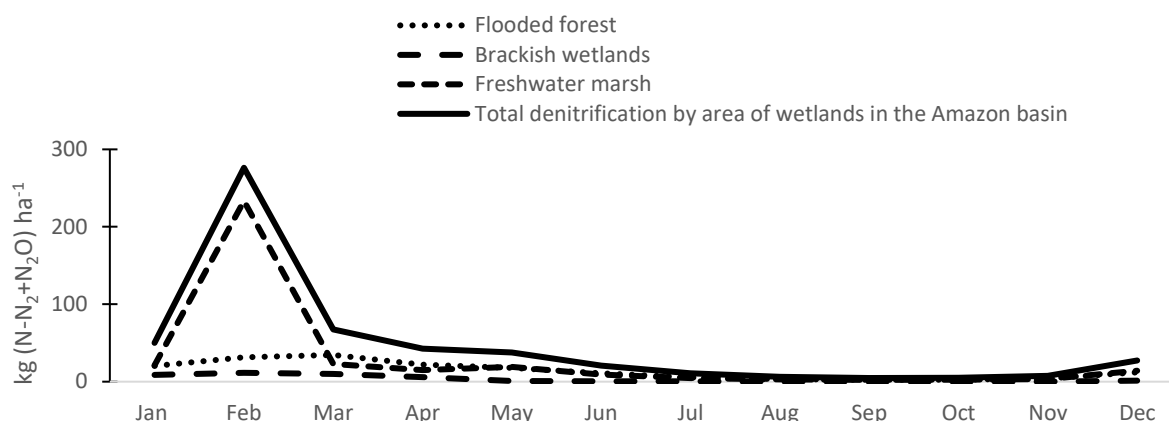
### DYNAMIC RESULTS- AT BASIN SCALE

Annual and monthly denitrification specific flux for 2012-2019 (Figure 36 and 37) by wetlands typology. Flooded forest yearly specific flux is constantly high. Yet in 2013 and 2018 freshwater marshes specific flux are approaching flooded forests. Both rates have an overlapping range, flooded forest ( $215.06\text{-}147.26 \text{ kgN}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ) and freshwater marshes ( $176.32 \text{ -}125.79 \text{ kgN}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ). This is not the case with brackish wetlands, which range oscillates in lower values ( $46.56\text{-}17.43 \text{ kgN}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ).



**Figure 35.** Annual Amazonian wetlands efficiency rates by wetlands typology in  $\text{kg}(\text{N-N}_2\text{O} + \text{N-N}_2)\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ .

The monthly dynamics (Figure 37) shows that freshwater marsh has a clear hot moment in the year that corresponds to February. On the other hand, flooded forest had a less abrupt behavior, and a longer peak (Nov-April). The total denitrification observed at basin scale reach its peak in February when the three wetlands are highly active, then the rest of the season, only flooded forest lead denitrification activity.



**Figure 36.** Monthly interannual denitrification by wetland typology in kg N (N<sub>2</sub>+N<sub>2</sub>O) ha<sup>-1</sup> month<sup>-1</sup>.

The total contribution by wetland typology is presented in Table 14. Flooded forest wetlands are the dominant wetlands in this watershed contributing with (~10 TgN.yr<sup>-1</sup>) that corresponds to 83-88% of the total annual denitrification. However, the freshwater marshes that represent only the 1.5% of the total watershed area contribute with (~1.74 TgN.yr<sup>-1</sup>), 12-17% of the total denitrification registered annually, proving a high ecosystem denitrification efficiency. Contribution of brackish wetlands is (0.01%). The maximum denitrification registered in flooded forest and freshwater marshes was in 2014, while the brackish wetlands peak is in 2018.

N<sub>2</sub>O and N<sub>2</sub> emissions from each wetland type and total basin are calculated with three different ratios (Table 15). Total annual emissions range from 0.24 to 1.18 TgN-N<sub>2</sub>O.yr<sup>-1</sup> depending on the ratio used.

Our results were compared to the only other estimation of denitrification outgassing in the watershed, 1.03 TgN-N<sub>2</sub>O.yr<sup>-1</sup> (Guilhen et al., 2020). Using the same ratio, SDM estimates an outgassing of 1.18± 0.13 TgN-N<sub>2</sub>O.yr<sup>-1</sup>, 12.7 % higher than them. Using a ratio specifically for freshwater wetlands, proposed by Scheer et al (2020). SDM calculates 0.24 TgN-N<sub>2</sub>O.yr<sup>-1</sup> (77% less than what has been reported by Guilhem et al (2020), this ratio could be more accurate at what had been observed as natural emissions. In this study, two ratios are proposed based on the DEA and correlation to organic carbon content. Considering that freshwater marshes have less organic carbon available compared to brackish wetlands and flooded forests, two different emission ratios were observed, which are being applied to our results (0.61 TgN-N<sub>2</sub>O.yr<sup>-1</sup>), this estimation is 60% lower than Guilhen et al., (2020)

**Table 14.** Annual contribution and efficiency of each wetland type present in the amazon basin.

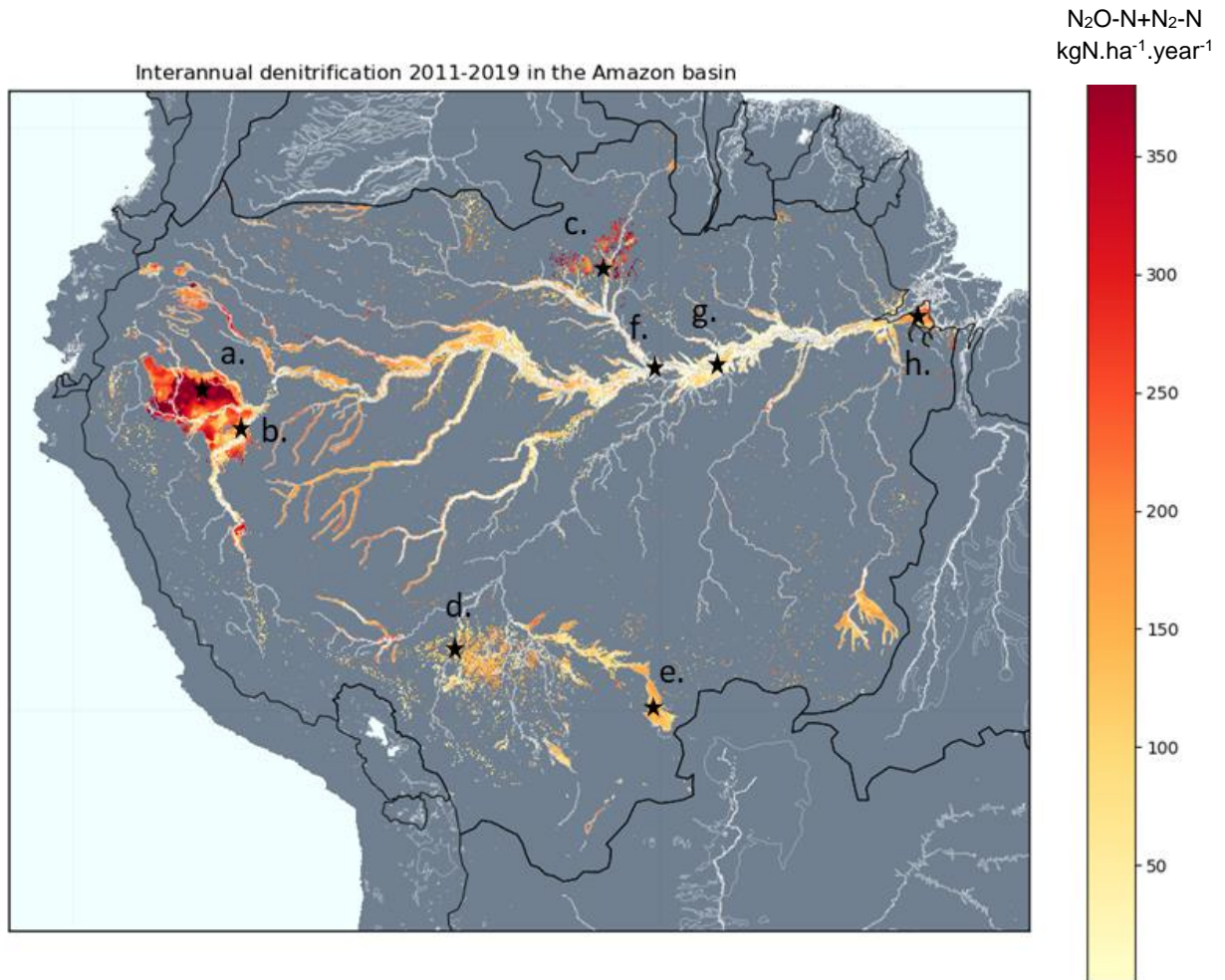
year	Flooded forest (Tg N yr <sup>-1</sup> )	Percentage of contribution	Efficiency kg ha yr <sup>-1</sup>	Freshwater Marsh (Tg N yr <sup>-1</sup> )	Percentage of contribution	Production rate kg N·ha yr <sup>-1</sup>	Brackish wetlands (10 <sup>3</sup> kg N yr <sup>-1</sup> )	Percentage of contribution	Production rate kgN·ha yr <sup>-1</sup>	Total denitrification by wetlands in the Amazon basin (Tg N yr <sup>-1</sup> )	Production rate kgN ha <sup>-1</sup> yr <sup>-1</sup>
2012	9.7	86%	174.30	1.59	14%	140.92	336	0.00%	17.43	11.3	15.88
2013	9.5	83%	170.53	1.94	17%	171.32	838	0.01%	43.41	11.5	16.07
2014	12.0	86%	215.06	1.99	14%	176.32	1120	0.01%	58.05	14.0	19.64
2015	9.1	86%	164.14	1.49	14%	131.90	988	0.01%	51.17	10.7	14.94
2016	8.2	85%	147.26	1.42	15%	125.79	706	0.01%	36.57	9.6	13.53
2017	10.5	84%	188.45	1.93	15%	170.42	865	0.01%	44.80	12.5	17.46
2018	10.2	84%	181.77	1.96	16%	173.22	1620	0.01%	84.02	12.1	16.98
2019	11.3	88%	202.43	1.57	12%	139.26	715	0.01%	37.06	12.9	18.06
Max	12.0	88%	215.06	1.99	17%	176.32	1620	0.01%	84.02	14.0	19.64
Interannual mean ± SD	10.1 ± 1	85%	169 ± 21	1.74 ± 0.2	15%	153 ± 21	899 ± 373	0.01%	46 ± 19	11 ± 1.3	16.5 ± 1.9
Total	80.8	85%	1523.33	13.9	15%	1298.41	7190	0.01%	372.51	94.7	132.55

**Table 15.** Annual N-N<sub>2</sub>O emissions from denitrification by wetland typology in the Amazon watershed

Wetland typology	R <sub>N2O</sub> IPCC (0.1) Tg N <sub>2</sub> O-N· yr <sup>-1</sup>	R <sub>N2O</sub> (0.082) Tg N <sub>2</sub> O-N· yr <sup>-1</sup>	R <sub>N2O</sub> (0.02) Tg N <sub>2</sub> O-N· yr <sup>-1</sup>	Mean R <sub>N2O</sub> (0.055) Tg N <sub>2</sub> O-N· yr <sup>-1</sup>	Mean R <sub>N2O</sub> (0.035) Tg N <sub>2</sub> O-N· yr <sup>-1</sup>
<b>Flooded forest</b>	1.01	0.83	0.20	0.55	
<b>Freshwater Marshes</b>	0.17	0.14	0.03		0.05
<b>Brackish wetlands</b>	8.9E-05	7.3E-05	1.8 E-05	4.9 E-05	
<b>Total</b>	1.18	0.97	0.24		0.61
Guilhen et al., (2020)	1.03				

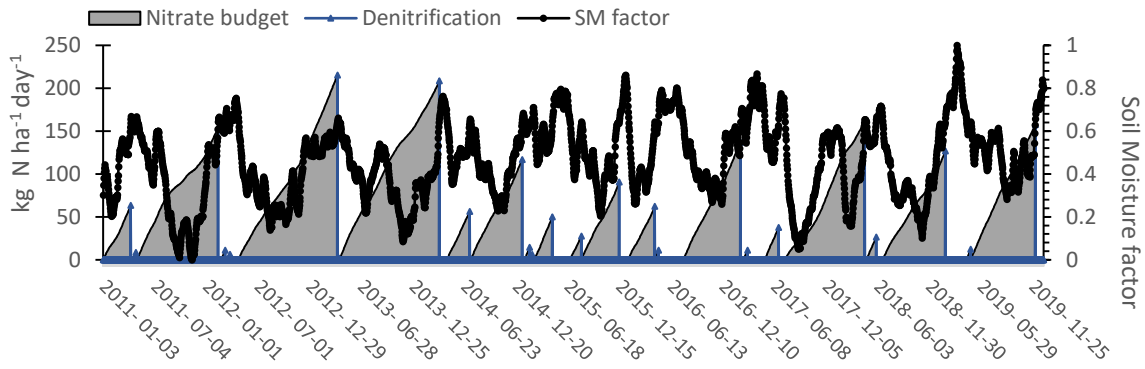
## SPATIALIZED RESULTS- AT BASIN SCALE

The SDM is a spatialized model. Here the denitrification results presented only in the Amazon basin (Figure 38). Eight points within the basin were selected in order to perform punctual time series at daily basis (Figure 39 a-h), to identify the different dynamics, peaks and its relation to soil moisture pulses.

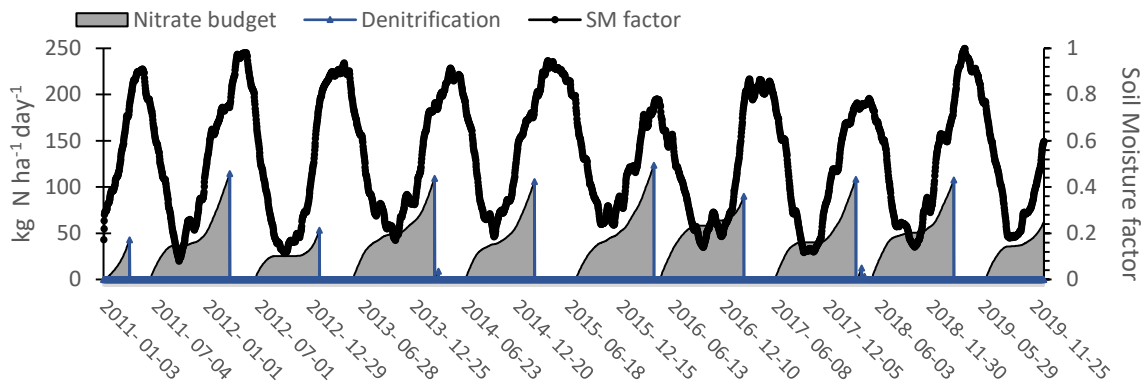


**Figure 37.** Interannual denitrification in natural wetlands estimated with SDM for 2012-2019. The main hot spot of denitrification ( $N_2+N_2O$ ) is identified in the western part of basin, with maximum values that range ( $\sim 400-250$   $kg N ha^{-1} yr^{-1}$ ).

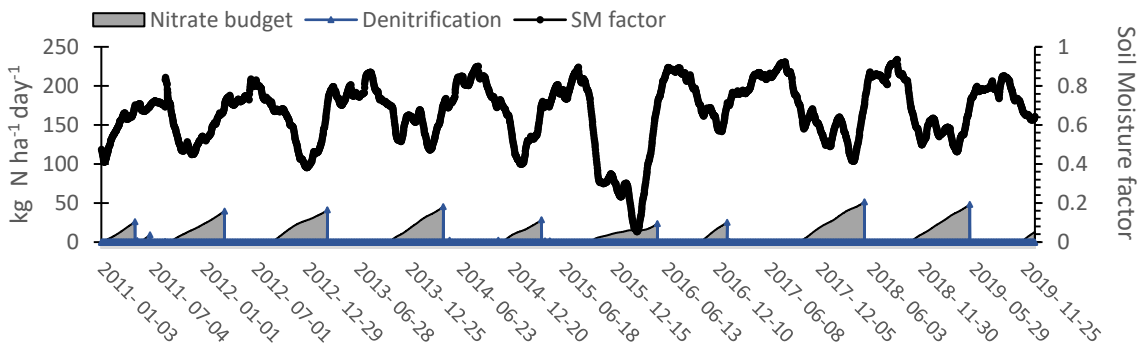
**a. Marañón 4.11, °S 75.48 °W**



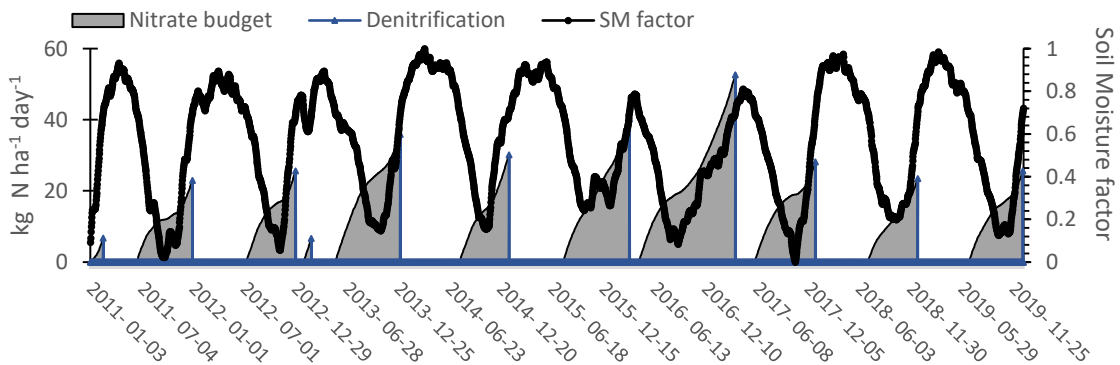
**b. Ucayali 4.99 °S, 74.21 °W**

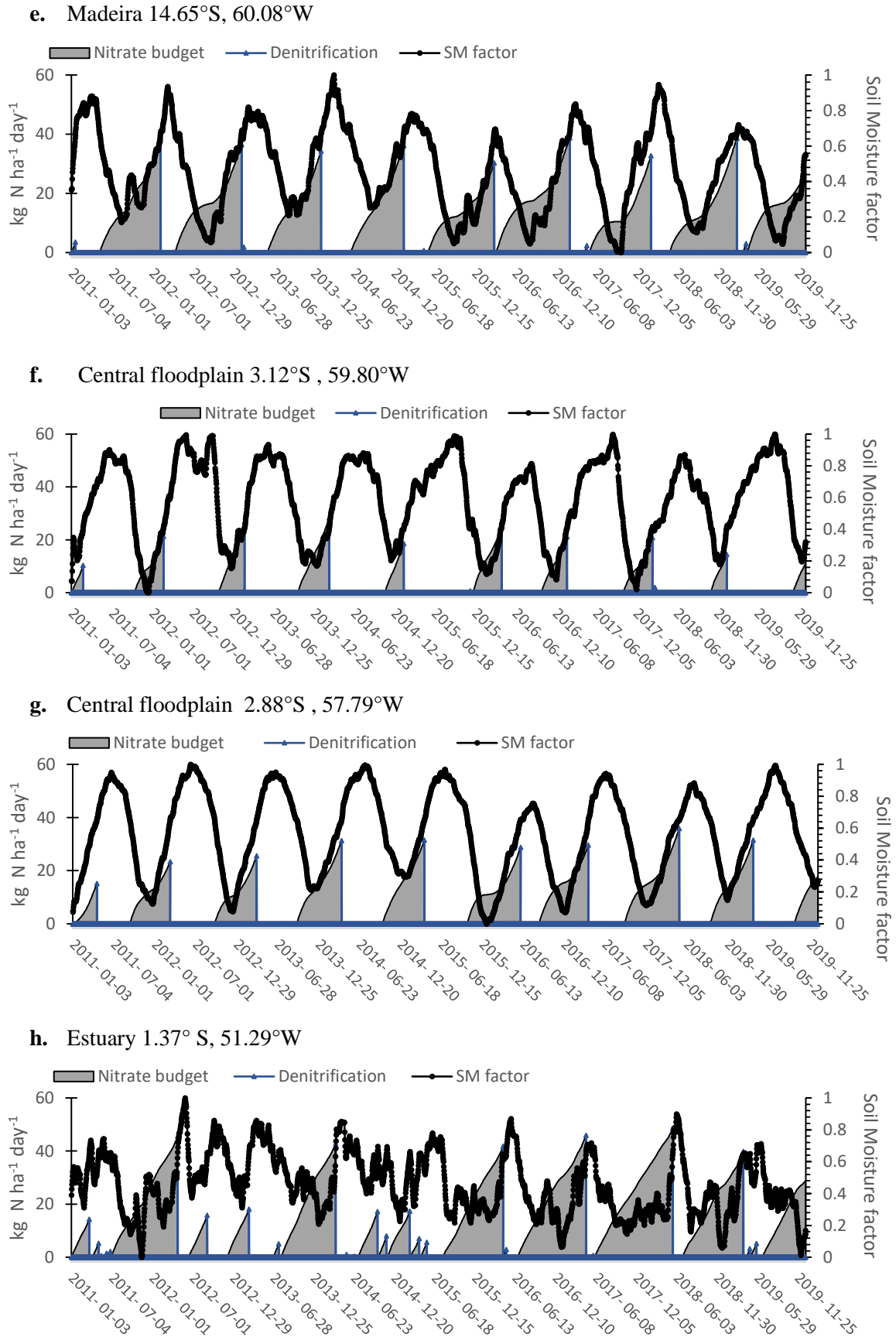


**c. Branco 1.141°S, 61.77 °W**



**d. Beni 13.20 °S, 65.99° W**

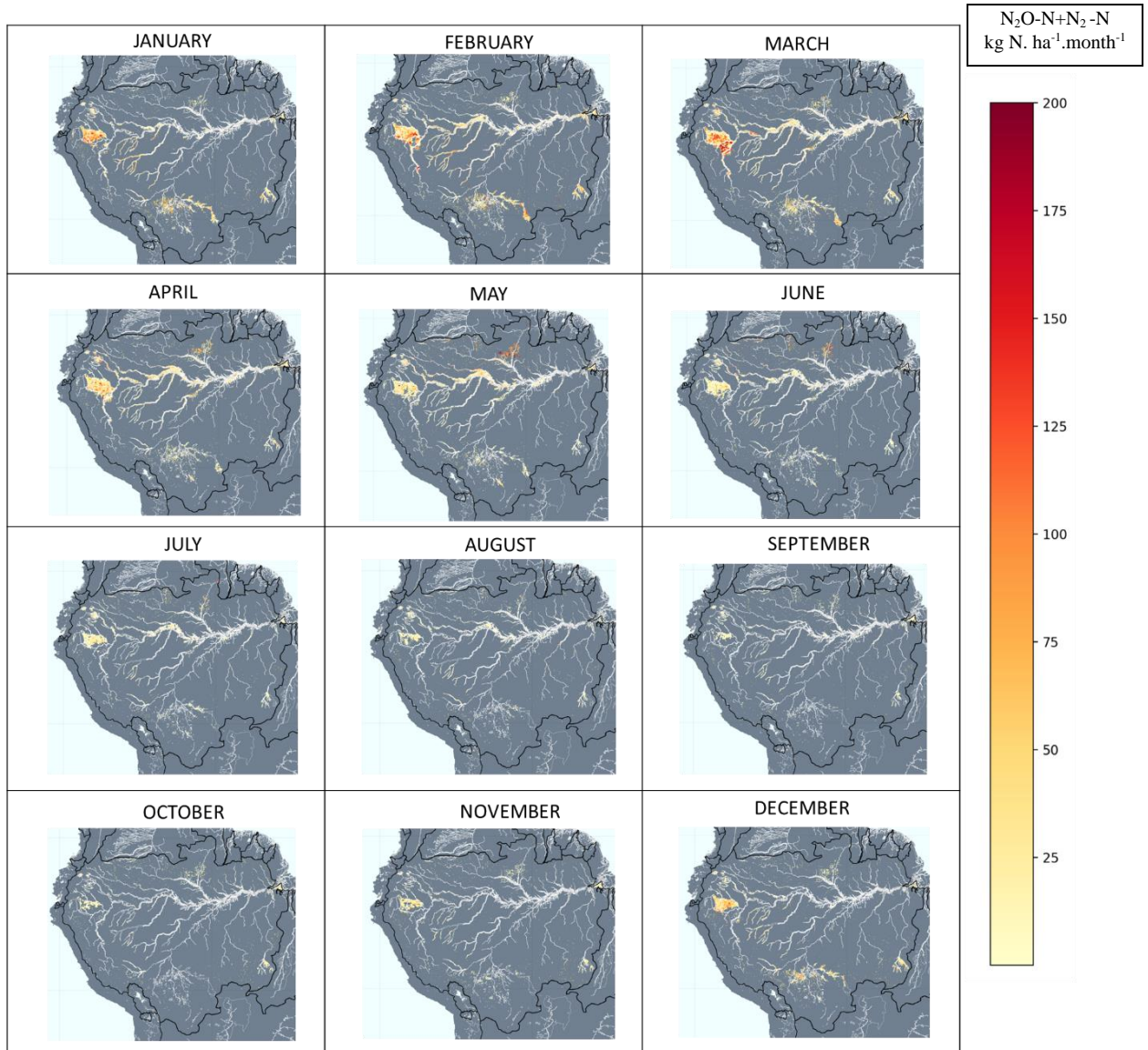




**Figure 38. a-h** Time series of denitrification ( $N_2O + N_2$ ) events from 2011-2019 in different points in the watershed that are located in the main wetland's areas. From highlands to lowlands, expressed in  $kg\ N\ ha^{-1}\ day^{-1}$ .

Previous analysis shows that peaks have a periodicity (Figure 39 a-h). However, the peaks of the different sites are not always at the same time. Activation of each wetlands within the watershed is different at monthly scale. Interannual mean graphical representation was produced (Table 16). The model is build up at diurnal time step, as denitrification peaks are shorter than a month. However, due to the high variability of denitrification and the short duration of peaks, the monthly approach seems to be more informative in the first term.

**Table 16.** Interannual Monthly denitrification dynamics from 2012-2019



## DISCUSSION

The present model has its basis on the soil properties and it assumes anoxia via soil saturation. The results show that SDM is able to model the flood pulse that in turn, activates denitrification. Denitrification in wetlands, especially in floodplains, has been correlated with redox potential and organic matter (Brettar et al., 2002). Even though redox potential is not taken (explicitly) as a parameter. The activation of denitrification just after a saturation implies soil physical and chemical changes directly caused by the flood pulse. Which dynamics have a great impact on microbial nitrogen turnover.(Neill, 1995; Robertson et al., 1988).

Once the O<sub>2</sub> is exhausted, facultative anaerobic bacteria will be forced to use nitrates, which provide the next highest amount of energy (+280 to +220 mV) (Canfield et al., 2010). This succession process will continue as each electron acceptor supply is used. As nitrates are limited in natural conditions, the reduction continues. Each step means a change in the environment (pH and redox potential). Amazonian wetlands soils are recognized for their close nutrient cycle, long periods of saturation with low redox potential (-200 to -280 mV) being mainly methanogens environments, contributing with 110 TgC-CH<sub>4</sub> yr<sup>-1</sup> (Potter, 1997).

Diurnal information of soil moisture allows the present model to be more precise in terms of activation/deactivation of denitrification, as well as nitrogen poll recharge. The soil moisture dynamics are different from sampling points from river to river, while Madeira sampling points have a very regular periodicity, Negro river sampling points do not show a clear saturation pattern.

The SDM model identified Marañón wetlands as the main denitrification hotspot of the basin, with a range of 150-400 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Figure 23). This wetland is dominated by flooded forest typology (Figure 19).

This result is aligned to previous studies carried out in the Amazonian basin, that identified the N<sub>2</sub>O hot spot in this area (Pärn et al., 2021; Ricaud et al., 2009; van Lent et al., 2015). The global hotspot of N<sub>2</sub>O emissions measured in upper troposphere by IASI satellite, show that Amazonian rainforest is the biggest hotspot of N<sub>2</sub>O in the world and that within the Amazon basin, Marañón basin has a daily average N<sub>2</sub>O emission > 2.5\*10<sup>-10</sup> mole s<sup>-1</sup> (Ricaud et al., 2009).

Correlating this result to the landscape, this wetland area corresponds to the *Abanico del Pastaza*, which is the largest Ramsar site in the Peruvian Amazon, covering (3 827329 hectares)



designated the 5<sup>th</sup> June, 2002. This reserve is also a hot spot for biodiversity, as it is home of 300 fish species, 261 birds, 66 mammal species, 57 amphibians and 38 reptile species. Moreover is food source for indigenous communities, from five different ethnic groups (i.e. Achuar, Kandozi, Quechua, Cocama and Urarina) (WWF, 2012). This wetland is also the largest protected floodplain in the Amazon Basin, and human occupation is largely restricted (Ramsar Site 1174.). Our denitrification results add to the list of benefits that *Abanico del Pastaza* provides. The high denitrification rate of this area is a consequence of the pedo-climatic and hydrological configuration of Marañón basin. The main river, Marañón, has its source at 5800 masl (Meters above sea level), from the *Nevado de Yapura* glacier in the Andes Mountain range (only 110 km from the Pacific Ocean). Then it follows a north-northwest direction. This part of the watershed is narrow and precipitation is not abundant. Then in its eastward bed, it receives on the left bank a much more abundant tributary (Santiago River), which increases the volume of its water by more than a third. This river flows through varying hydro-climatology regimes related to elevation gradients and river distance from headwaters. After crossing large defiles. Marañón river enters with a flow of  $5\,000\text{ m}^3\cdot\text{s}^{-1}$  in the immense plain that define the main course of the Amazonian system, and will cross until the Atlantic. Three tributaries born in Ecuador (Morona River (530 km,  $1,000\text{ m}^3\cdot\text{s}^{-1}$ , the Pastaza River (740 km,  $2,800\text{ m}^3\cdot\text{s}^{-1}$ ), and the Tigre River (940 km, very winding,  $2,700\text{ m}^3\cdot\text{s}^{-1}$ ) join the river at the Abanico del Pastaza, contributing with volcanic sediments brought down from Ecuadorian Andes and increasing its flow by four (Amazon Waters, 2021). At this point, the river's appearance changes, becoming much wider, cluttered with islands, the banks are low, flat and frequently flooded. This scenario provides optimal conditions for efficient complete denitrification, and removal of large amounts of carbon dioxide. Yet, disturbance of this ecosystem could mean an increase in  $\text{N}_2\text{O}$  emissions, creating a devastating feedback on climate change (Pärn et al., 2021).

### SEASONAL DYNAMICS

The time series executed for validation (central Amazonian floodplain sampling points) and samples (points from the hotspots of the watershed), showed that denitrification events length is 1-2 days (scenario where nitrates' only source is the local production) in the same place. The reason why the events are short is due to the nitrate limitation. This result is in line with stimulation experiments reported in chapter III and by other previous studies (Kern et al., 1996; Koschorreck, 2005), where the DEA of soils is much higher than what is observed in undisturbed samples. Amazon basin is a tropical watershed, with a clear flooding season, that has a great impact on the nitrogen pools, showing clear nitrogen patterns, that is similar to

northern ecosystems where season is dictated by temperature (Neill, 1995). Different vegetation did not alter the general patterns of nitrogen dynamics but the absolute extent of fluctuations (Figure 21-22).

At watershed monthly denitrification (Table 16) it is possible to observe a transition of active areas within a year. In March, hot areas are mainly located in the inland wetlands (west part of the basin) and then high active wetlands areas are transferred downstream to the east. Freshwater marshes' denitrification peak is the highest and occurs in February (Max= 0.29 Tg N month<sup>-1</sup>), as well as brackish wetlands (max=24.5 Mg N month<sup>-1</sup>). This peak corresponds to the beginning of the flooding season of the floodplains of the main streams. While the peak of the flooded forests (max= 0.21Tg N month<sup>-1</sup>), is reached one month later (March) when the tributary floodplains also increase their inundation area. Flooded forests are active for a longer period (December to June), therefore they are the main contributors to denitrification of the basin. These results are aligned to the hydrographic dynamics of surface water, and flooding seasonality (Richey et al., 2002). Indicating that SDM, which does not calculate discharge or river flooding dynamics, is able to obtain the same seasonal behaviour by Soil Moisture satellite observations.

#### ANNUAL CONTRIBUTION

Total annual denitrification (N<sub>2</sub> + N<sub>2</sub>O) in the three wetlands' typologies was 11.8 ± 1.36 Tg N yr<sup>-1</sup>. Flooded forests contributed the most (85%) with 10.1±1.21 Tg N yr<sup>-1</sup>, followed by freshwater marshes (15%) with 1.7±0.23 Tg N yr<sup>-1</sup>, and then brackish wetlands (0.001%) with 8.99±3.73E+05 kg N yr<sup>-1</sup>. The annual specific fluxes calculated for flooded forests were 169.26±21.55 kg N<sub>2</sub>O+N<sub>2</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>, freshwater marshes 153.64 ± 21.08 kg N<sub>2</sub>O+N<sub>2</sub>-N ha<sup>-1</sup> yr<sup>-1</sup> and brackish wetlands= 46.56±19.30 kg N<sub>2</sub>O+N<sub>2</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>.

van Lent et al., (2015) reported that 0.5 to 2.6 kg N<sub>2</sub>O-N ha yr<sup>-1</sup> are produced in the palm swamp peat by in situ observations. If to our SMD flooded forest specific flux (169.26±21.55 kg N<sub>2</sub>O+N<sub>2</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>), we applied the ratio (0.02) for flooded soils proposed by Scheer et al., (2020) the emissions of flooded forest will be 3.38 ± 0.43 kg N<sub>2</sub>O-N ha yr<sup>-1</sup> which estimation is closer to van Lent et al., (2015). 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 changes regarding the season. They reported that March (the main peak) has low N<sub>2</sub>O emissions, and very high N<sub>2</sub> potential. Instead, in September the emission rate had a higher N<sub>2</sub>O production ratio.

From the literature three different N<sub>2</sub>O/N<sub>2</sub> emission ratios were applied and a specific ratio based on the gave an annual N<sub>2</sub>O outgassing of 0.79 ± 0.49 Tg N-N<sub>2</sub>O yr<sup>-1</sup> corresponding to the interannual average of natural wetlands of the Amazon basin for a period corresponding 2012 and 2019,

calculated with SDM. Guilhen et al., (2020) estimated a mean of  $1.03 \pm 0.02$  Tg N-N<sub>2</sub>O yr<sup>-1</sup> in the Amazon basin between 2011 and 2015, which estimation is 0.23 Tg N-N<sub>2</sub>O.yr<sup>-1</sup> less than what we obtained with the SDM. Melillo et al., (2001) estimated 1.3 Tg N-N<sub>2</sub>O.yr<sup>-1</sup> for the whole forests in the Amazon Basin over the period 1978-1995. Melillo et al., (2001) value is higher than what SDM had estimated. Their estimation refers to forest in general, but do not specified if they include flooded forest. Nonetheless, our estimation regarding natural wetlands in the Amazonian basin is the same range as their estimation, and it represents (60%) of the forest contribution.

Comparing the present results with the South American estimation of  $\sim 1.8$  Tg N-N<sub>2</sub>O yr<sup>-1</sup> from natural sources calculated by Tian et al., (2020), the Amazon basin wetlands contribute with 17-71% of the total natural source emissions for this region. Bouwman et al., (2013) calculated a global average riparian zone denitrification (N<sub>2</sub>O+ N<sub>2</sub>) of 6 (5-9) TgN.yr<sup>-1</sup> for the year 2000. The estimate for freshwater marshes in the Amazon basin from the SDM of this study corresponds to  $1.74 \pm 0.23$  Tg N yr<sup>-1</sup>, being 28 % of the total estimated by Bouwman et al., (2013).

## INTERANNUAL TRENDS

The Amazon is a tropical basin where temperature variation throughout the year is mild and it never compromises the nitrification or denitrification. So, temperature limiting functions of SDM do not have an important impact on denitrification in this scenario. This will not be the case when applying the model to the temperate or boreal wetlands. However, climatic anomalies had an effect on denitrification peaks observed. Furthermore, when comparing long-term tendency there are some points (i.e. N2-N3) where there is a decrease of soil moisture maximal value, that may be linked to climate change. The maximal annual denitrification simulated was registered in 2014 for flooded forests and freshwater marshes. Hydrological monitoring during 2014, registered a significant accumulation of rainfall in the west and south of the Amazon basin in the states of Acre, Rondônia and Amazonas. In January 2015, a frontal system occurred in the southeast of Brazil. The highest rainfall accumulation was in the Upper Solimoes basin. It has been reported that the Amazon river had a dry warm season in 2016, as a consequence of prolonged ENSO (2014-2015 and part of 2016) (Lima et al., 2019; Santoso et al., 2017).

## LIMITATIONS

The present model is based on some assumptions that help to explain a complex process as denitrification. These assumptions are also the limitations. The model's main uncertainties are related to the lack of in-situ data. However, SDM is a process-based model and only one

parameter ( $k_{\text{NO}_3}$ ) is calibrated, which can be improved if there is data available that explains the particular conditions of the region of interest, and ecosystem to study. A great improvement to the model will be to include the pH effect as an inhibitor.

This model considered carbon budget as constant, assuming that there is not an input or output of organic carbon from any source but local carbon source. 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. Moreover, the organic carbon pool is not partitioned (i.e. particulate organic carbon and dissolved organic carbon). These two main changes are compensated for in the mineralization rate of organic carbon ( $K_{\text{OC}}$ ), which is particular for each kind of simplified wetland ecosystem typology. The values adopted aimed to be used at global scale, they are on the range of what was observed in the laboratory conditions. As those values were obtained in controlled conditions, not necessarily showing the natural in situ conditions, data from literature in different sites was assigned to define a  $K_{\text{OC}}$  by wetland typology.

The model is built up in a binary assumption, which does not allow nitrification to happen at the same time as denitrification in the same point. Fixing a soil moisture threshold. This may not be true when looking in detail, as the soil structure and the root zone has most of the time some oxygen available, but this binary function indicates the portion outgassed.

The nitrogen budget calculated in the present study considers only the natural in situ production and does not take into account anthropogenic contribution. Other processes such as plant uptake and dissimilatory reduction to ammonium had been neglected, as it is considered a closed system. If data is available, the model has the capacity for being adapted to partitione the nitrogen budget to different ends (i.e. plant uptake, annamox, DRNA, leaching). The model is highly sensitive to nitrates concentration, as the DEA of these soils is much higher than what is reported in the present study. If nitrates are set as unlimited, meaning a high disturbance on the natural wetlands, the denitrification rates increase fold-4. This increase on the result may be analysed carefully, as high nitrate concentration in soils causes incomplete denitrification and  $\text{N}_2\text{O}$ - $\text{N}_2$  outgassing ratio enhances  $\text{N}_2\text{O}$  emissions (Weier et al., 1993). A surplus of nitrates also affects ecosystem functionality and biodiversity may be threatened (Huang et al., 2017; Smith, 2003).

Denitrification emission ratio depends from many local variables and it changes drastically as the time passes; at the beginning of the inundation or wetting event, its expected to have a peak

of  $N_2O$  emission, but later on it have been observed that the  $N_2$  emissions (complete denitrification) is what its observed the most. Therefore, a further step is to develop a module that could calculate different  $N_2O/N_2$  ratio according to the soil properties, the water quality and the time from the wetting event, to propose a more suitable  $N_2O/ N_2$  ratio.

The SMD adopted a mean value from three ratios reported in the literature. This ratio should be taken as an indicator, but measurements of  $N_2$  and  $N_2O$  emissions in the field with new methodologies or tools will be more accurate, as well as long term monitoring efforts could be interesting to be avle to better understand the  $N_2 N_2O$  periodicity (if that exists) and to have data to calibrate the model. .

## CONCLUSION AND FURTHER RESEARCH

The SDM main contribution is the identification of hot moments and hot spots. As it has the capacity to simulate denitrification on a diurnal basis, in places where field data is not available, due to satellite data inclusion. The development of the SDM python module model pretends to be an open platform, user friendly that can be improved and that may allow to perform more analysis. In the context of presenting the model and its application, a demonstration of the capacities of the model are shown, as an exploratory example.

The principal component of this model is the soil moisture and temperature, which is the input data that is dynamic. These input data are key for modelling of nitrate budget, and denitrification activation- deactivation. Despite uncertainties at local scale, the range of denitrification modelled annually is comparable with observations and previous studies.

Time series showed the interannual evolution and the influence of climate anomalies as the ENSO in previous years, where field data is not available. These results may be indicators of possible future scenarios when the anomalies will repeat and or intensify. As further research, this model could be tested at different scales (continents or regions) as well as in different watersheds at different climatic regimes (i.e. boreal or temperate). This may help to identify further limitations and to identify the different hot moments and priority wetland areas. This model also elucidates the role of forested wetlands in a watershed basis, and may be tested in other basins dominated by another wetland typology in order to identify if significant changes of contribution are linked to wetland typology.

# CHAPTER V

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## GLOBAL DYNAMIC ASSESSMENT OF NATURAL WETLANDS SOILS' DENITRIFICATION USING SDM



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## ABSTRACT

This chapter presents the main results of the PhD thesis, whose objective is to elucidate the role of wetlands in the global nitrogen cycle. Here the Soil Denitrification Model (SDM) was applied at global scale in natural wetlands ecosystems. The natural wetlands were classified in five different typologies (freshwater marshes, flooded forest, brackish wetlands, peatlands and complex wetlands). The world was divided into seven regions and the simulation period was from 2011 to 2019 on a daily basis. Denitrification rates were calculated on a yearly and monthly basis.

The freshwater marshes are the wetland typology that contribute the most to the annual budget with  $85 \text{ TgN}(\text{N}_2\text{O} + \text{N}_2).\text{year}^{-1}$ , as they are the most abundant wetland typology. The most efficient wetlands for denitrification were the flooded forest ( $456 \text{ kgN}(\text{N}_2\text{O} + \text{N}_2)\text{ha}^{-1}.\text{year}^{-1}$ ) registered in Southeast Asia Oceania region. This region also resulted to be the most efficient region with an interannual denitrification efficiency of  $282 \text{ kgN}(\text{N}_2\text{O} + \text{N}_2).\text{ha}^{-1}.\text{year}^{-1}$ . The main hot moment for freshwater marshes and complex wetlands was registered in May. The interannual denitrification in natural wetlands was estimated to be  $169 \pm 18 \text{ TgN}(\text{N}_2\text{O} + \text{N}_2).\text{year}^{-1}$ , to our knowledge, no other denitrification estimation has been done in natural wetlands at global scale. Comparing our results with global budgets, our denitrification estimations are higher than the latest assessment of denitrification in natural soils calculated by Bouwman et al., (2013) for the year 2000,  $79 \text{ TgN}(\text{N}_2\text{O} + \text{N}_2).\text{year}^{-1}$ . However, denitrification rates are in line with field studies.

This model gives the first denitrification global estimation in natural wetlands in the last decade, based on a daily analysis. The results presented here are a synthesis that aims to highlight the main hot spots and hot moments at global scale. The SDM global application is one step towards the understanding of denitrification dynamics in wetlands and intends to contribute with valorisation of wetlands in the global nitrogen cycle. The analysis carried out here may be taken as a general introduction of the potential of the SDM and that can lead to many other in-depth studies. Moreover, the lack of field data in many of the identified hot spots, it is an opportunity for future research.

## RÉSUMÉ

Ce chapitre présente les principaux résultats de la thèse de doctorat, dont l'objectif est d'élucider le rôle des zones humides dans le cycle global de l'azote. Le modèle de dénitrification des sols (SDM) a été appliqué à l'échelle mondiale dans des écosystèmes de zones humides naturelles. Les zones humides naturelles ont été classées en cinq typologies différentes (marais d'eau douce, forêt inondée, zones humides saumâtres, tourbières et zones humides complexes). Le monde a été divisé en sept régions et la période de simulation s'est étendue de 2011 à 2019 sur un pas de temps quotidien. Les taux de dénitrification ont été calculés sur une base annuelle et mensuelle.

Les marais d'eau douce sont la typologie de zone humide qui contribue le plus au budget annuel avec 85 TgN(N<sub>2</sub>O+N<sub>2</sub>), car ils sont la typologie de zone humide la plus abondante. Les zones humides les plus efficaces pour la dénitrification sont les forêts inondées (456 kgN(N<sub>2</sub>O+N<sub>2</sub>).ha<sup>-1</sup>.an<sup>-1</sup>) enregistrées dans la région Asie du Sud-Est-Océanie. Cette région s'est également avérée être la plus efficace avec une efficacité de dénitrification interannuelle de 282 kgN(N<sub>2</sub>O+N<sub>2</sub>).ha<sup>-1</sup>.an<sup>-1</sup>. Le principal moment chaud pour les marais d'eau douce et les zones humides complexes a été enregistré en mai. La dénitrification interannuelle dans les zones humides naturelles a été estimée à 169± 18 TgN(N<sub>2</sub>O+N<sub>2</sub>).an<sup>-1</sup>, à notre connaissance, aucune autre estimation de dénitrification n'a été faite dans les zones humides naturelles à l'échelle mondiale. En comparant nos résultats avec les budgets mondiaux, nos estimations de dénitrification sont plus élevées que la dernière évaluation de la dénitrification dans les sols naturels calculée par Bouwman et al. (2013) pour l'année 2000, soit 79 TgN (N<sub>2</sub>O +N<sub>2</sub>).an<sup>-1</sup>. Cependant, les taux de dénitrification sont en accord avec les études de terrain.

Ce modèle donne la première estimation globale de dénitrification dans les zones humides naturelles au cours de la dernière décennie, basée sur une analyse quotidienne. Les résultats présentés ici sont une synthèse qui vise à mettre en évidence les principaux points chauds et moments chauds à l'échelle mondiale. Les résultats du SDM présentés ici ne sont qu'un premier pas vers la compréhension de la dynamique de la dénitrification dans les zones humides et visent à contribuer à la valorisation des zones humides dans le cycle global de l'azote. L'analyse réalisée ici peut être considérée comme une introduction générale du potentiel du SDM et peut conduire à de nombreuses autres études approfondies. De plus, le manque de données de terrain dans de nombreux hot spots identifiés constitue une opportunité pour des recherches futures.



## RESUMEN

Este capítulo presenta los principales resultados de la tesis doctoral, cuyo objetivo es dilucidar el papel de los humedales en el ciclo global del nitrógeno. Para ello se aplicó el Modelo de Desnitrificación del Suelo (SDM) a escala global en ecosistemas de humedales naturales. Los humedales naturales se clasificaron en cinco tipologías diferentes (marismas de agua dulce, bosques inundados, humedales salobres, turberas y humedales complejos). El mundo se dividió en siete regiones y el periodo de simulación fue de 2011 a 2019 en base diaria. Las tasas de desnitrificación se calcularon a tasa anual y mensual.

Las marismas de agua dulce, son la tipología más abundante y son las que más contribuye al balance anual con 85 Tg N ( $\text{N}_2\text{O} + \text{N}_2$ ). Los humedales más eficientes para la desnitrificación fueron los bosques inundados ( $456 \text{ kg N } (\text{N}_2\text{O} + \text{N}_2) \cdot \text{ha}^{-1} \cdot \text{año}^{-1}$ ). La región del Sudeste Asiático de Oceanía resultó ser la más eficiente con una eficiencia de desnitrificación interanual de  $282 \text{ kg N } (\text{N}_2\text{O} + \text{N}_2) \cdot \text{ha}^{-1} \cdot \text{año}^{-1}$ . El principal pico de desnitrificación para las marismas de agua dulce y los humedales complejos se registró en mayo. La desnitrificación interanual en los humedales naturales se estimó en  $169 \pm 18 \text{ Tg N } (\text{N}_2\text{O} + \text{N}_2) \cdot \text{año}^{-1}$ , hasta donde se sabe, no se ha realizado ninguna otra estimación de desnitrificación en humedales naturales a escala global. Comparando nuestros resultados con los balances globales, nuestras estimaciones de desnitrificación son más altas que la última evaluación de desnitrificación en suelos naturales calculada por Bouwman et al., (2013) para el año 2000 ( $79 \text{ TgN } (\text{N}_2\text{O} + \text{N}_2) \cdot \text{año}^{-1}$ ). Sin embargo, las tasas de desnitrificación están en línea con los estudios de campo.

Este modelo ofrece la primera estimación global de desnitrificación en humedales naturales de la última década, basada en un análisis diario. Los resultados presentados aquí son una síntesis que pretende destacar los principales puntos y momentos calientes a escala global. Los resultados del SDM aquí presentados son sólo un primer paso hacia la comprensión de la dinámica de la desnitrificación en los humedales y pretende contribuir con la valorización de los humedales en el ciclo global del nitrógeno. El análisis realizado aquí puede tomarse como una introducción general del potencial del SDM y que puede conducir a muchos otros estudios en profundidad. Además, la falta de datos de campo en muchos de los focos de desnitrificación identificados, es una oportunidad para futuras investigaciones.

# INTRODUCTION

In all living organisms, nitrogen is present in different chemical forms (Galloway et al., 2004). The transformation of these elements depends on the interaction of abiotic factors and living organisms i.e. biogeochemical cycles. The understanding of these exchanges are the basis to identify the turning points at global scale i.e. climate change, carbon sequestration and eutrophication (Melillo et al., 2003).

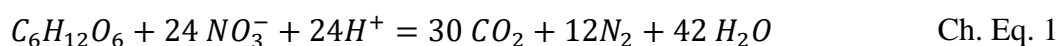
## FROM THE ATMOSPHERE TO THE BIOSPHERE

Dinitrogen ( $N_2$ ) is the most abundant gas of Earth's atmosphere (80%), however in this chemical form is not available for the majority of living organisms (99%) (Galloway et al., 2003). The conversion of  $N_2$  (nonreactive N), into reactive N (Nr) or biologically available forms e.g., ammonia [ $NH_3$ ] and ammonium [ $NH_4^+$ ], inorganic oxidized forms (e.g., nitrogen oxide [ $NO_x$ ], nitric acid [ $HNO_3$ ], nitrous oxide [ $N_2O$ ], and nitrate [ $NO_3^-$ ]), and organic compounds (e.g., urea, amines, proteins, and nucleic acids) is a process that naturally (undisturbed scenario) was carried out by lightning and by nitrogen-fixing bacteria. Lightning contribution has been estimated as  $< 10 \text{ Tg Nyr}^{-1}$  (Galloway et al., 1995) and has not been affected by human activities. Estimation of biological nitrogen fixation is uncertain and variable according to environmental dynamics, and it represents a regulatory factor on the availability of nutrients for primary production in every ecosystem. Globally has been calculated as  $\sim 128 \text{ Tg N yr}^{-1}$  (Galloway et al., 2004). Nevertheless, N global cycle has been altered mainly by three anthropogenic activities: (i) nitrogen fertilizers production, (ii) nitrogen-fixing crops, and (iii) fossil fuel combustion (Vitousek et al., 1997a). The ensemble of these activities significantly increased N natural availability by over an order of magnitude in a period of 140 years, from 1860 to 2000 it passed from 15-165  $\text{Tg N yr}^{-1}$  (Galloway et al., 2003). Enhancing crops yields hastened food production, solving one key constraint to feeding greater than half of the world's human population (Erismann et al., 2008b; Houlton et al., 2019). Yet, the input of fertilizers, brought along disadvantages associated with public health (Townsend et al., 2003), economy (Rockström et al., 2009) and environment (Vitousek et al., 1997a). Fertilizer input exceeds the rate of plant nutrient assimilation in targets (Zhang, 2017). Consequently, leaching of significant amounts of nitrogen and other soil nutrients to the groundwater, transported by surface water to other terrestrial ecosystems, and later on discharged to the ocean cause in turn, long term soil fertility losses (Ayoub, 1999). In addition to contributing substantially to the acidification of soils, streams and lakes (Grennfelt and Hultberg, 1986) and an unbalance of

primary production (eutrophication) in a vary range of terrestrial and coastal ecosystems worldwide (Huang et al., 2017; Weldeslassie et al., 2018). The most notorious influence is observed in coastal areas with algal blooms and hypoxic “dead zones” (Diaz and Rosenberg, 2008; Glibert and Burkholder, 2006). The alteration in N cycle, is another example of the accumulative human impact contributing to the global change and represents a challenge to the policy makers and IPCC-type organization to achieve efficient public-private partnerships to scale solutions (Houlton et al., 2019).

#### FROM THE BIOSPHERE TO THE ATMOSPHERE

Thinking a world without fertilizers is not feasible, as the human population keeps increasing, food demand follows the path. Imperative changes in policies are needed to improve the use of fertilizers, human consumption, and food waste to be able to decrease the impact (Houlton et al., 2019; Mosier et al., 2004). Besides the policies and technologies that could solve the issue, there is a natural process called denitrification that returns reactive N (Nr) to N<sub>2</sub> (Ch. Eq. 1) (DeLaune and Reddy, 2008).



$$G_{298}^\circ = 2\,202 \text{ kJ mol}^{-1}$$

At global scale, denitrification occurs mainly in the open ocean with a rate of  $17.0 \times 10^{12}$  mol year<sup>-1</sup>. In the terrestrial ecosystems when the previous conditions are met, a rate of  $7.1 \times 10^{12}$  mol year<sup>-1</sup> is reached (Canfield et al., 2010). The total nitrogen fluxes calculated for the biosphere in the 1990s was 239 (continents) + 121 (oceans) = 360 of Tg N<sub>2</sub> fixation, and 115 (continents) + 129 (oceans) =244 of denitrification Tg N<sub>2</sub>. Biosphere net budget of 116 Tg N fixed year<sup>-1</sup> (Galloway et al., 2004). The terrestrial denitrification is consequently an important factor to understand and to return the Nr to the atmosphere before it arrives to the coastal areas (Galloway et al., 2003).

Once the nitrogen becomes reactive (Nr), the N cycling is closely related to the other biogeochemical cycles of the essential elements, particularly that of carbon and oxygen (Burgin et al., 2011). To activate this process and to be completed a series of environmental conditions must be met, which are: (i) ability to synthesis nitrogen oxide reductases, (ii) availability of nitrates and organic carbon; (iii) environmental factors such as specific range of pH, redox potential and temperature; and (iv) anoxic conditions (Canfield et al., 2010). More than 60 genera of microorganisms have been identified capable of using nitrogen oxides as electron

acceptors (denitrifies) and carry out the entire reduction pathway (Philippot et al., 2007). Denitrifiers represent up to 5% of the total soil microbial community, incomplete denitrification may be due to a lack or changes of the previous conditions, when the reaction is not completed, N<sub>2</sub>O (greenhouse gas) is emitted (Philippot et al., 2013).

Denitrification is a process that occurs in the soil and is carried out by facultative bacteria in anoxic soils, widely common state in saturated soils (Reddy and Patrick, 1984), as water level fluctuate, soils alternate between saturated or unsaturated, affecting the chemical soil environment i.e. redox potential, pH and salinity (Vepraskas et al., 2000). Soils' water content directly influences inorganic and biological reactions as in saturated soils, oxygen is a limiting factor and it is absent as the trigger for denitrification (Mitsch et al., 2009; Seitzinger et al., 2006).

If WFPS (water-filled pore space) is higher than 70% anoxic conditions are guaranteed (Bateman and Baggs, 2005). These changes in the soil moisture are often due to natural occurrence or with intended purpose for agricultural reasons. Permanent or long term-saturated soils are found in natural wetlands (Matthews, 1993). Microbiota activity in wetlands soils is key to understanding organic matter accumulation and decomposition, this process occurs in aerobic and anaerobic conditions and increases with increasing temperature up to approximately 35-40°C (Benoit et al., 2015).

The organisms in the scale of minutes and hours regulate the transformation of NO<sub>3</sub><sup>-</sup> by denitrification. When scaling the process to a global scale the focus may be on rainfall events (daily), seasonal weather patterns (months), management activities, and annual and decadal climate variations as regulators at monthly, seasonal, annual and longer time scales (Groffman, 2012; Shumilova et al., 2019).

#### SOIL AND TEMPERATURE DYNAMICS RELEVANCE

Better understanding of saturated soils extension and its dynamics is crucial to improve the estimation of biogeochemical processes and respond with more accuracy questions like when and how much as indicator at global scale (Bateman and Baggs, 2005; Dorigo et al., 2017; Fabre et al., 2020; Martínez-Espinosa et al., 2021; Yin et al., 2019). Excluding management practices, in natural conditions, wetlands represent the ecosystems where the soil is saturated more often, yet the area of the wetlands is not always constant, they can shrink or expand as an effect of season weather (Mitsch et al., 2013a). Wetlands represent 1-9% of Earth's surface, they are transitional ecosystems that connect terrestrial and aquatic environments. In particular,

estimates of global wetland area range from 0.54 to 29.83 million km<sup>2</sup> and the class-specific spatial consistency of wetlands is less than 1% (Hu et al., 2017b). An extended research to estimate the area has been done at global scale, some of the estimations are shown in Table 17.

The most recent static estimation that combines remote sensing data but still in agreement with regional estimates as documented in literature is the GLWD-3, and could serve as an estimation of permanent wetland extent for global hydrology and climatology models (Lehner and Doll, 2004).

**Table 17.** Global wetlands area estimates

Source	Region	Wetland Classification	Area (10 <sup>3</sup> ) km <sup>2</sup>	Global terrestrial surface (%)
Topographic Wetness Index (PTWI) (Hu et al., 2017b)	Global	Potential area	29 830	19
Global databases compilation (Hu et al., 2017b)	Global	Total natural wetlands	1 530 – 14 860	1-10
Global Lake and Wetlands distribution (GLWD-3) (Lehner and Döll, 2004)	Global 12 classes	Total lakes and reservoirs (Classes 1-2)	2679	2.0
		Total wetlands (classes 3-12)	8 219-10 119	6.2-7.6
(Matthews and Fung, 1987)	Global	Total natural wetlands (excl. irrigated rice fields)	5 300	3.95
(Aselmann and Crutzen, 1989)	Global	Total natural freshwater wetlands (including lakes)	5 700	4.25
(Dugan, 1993)	Global	Wetlands (assumedly freshwater only)	5 600	4.18
(Finlayson et al., 1999)	Global	All wetlands	12 758. 470 – 12 792. 110	9.52-9.54

Currently the tools to calculate the extent of wetlands had improved and the remote sensing products and new detection techniques led to more accurate and dynamic area calculations (Martínez-Espinosa et al., 2021). Therefore, these static estimations were considered as maximal extension and diversity of natural wetlands. Denitrification is also sensitive to temperature, and has an optimum temperature range of 25-30°C (Saad and Conrad, 1993).

In this study, we aim to contribute to the understanding of denitrification patterns at global scale. This study will be the first estimation at diurnal time step that would estimate the natural denitrification in natural wetlands ecosystems based on a parsimonious denitrification model based on diurnal soil moisture and temperature from satellite data, and soil properties i.e. (bulk density, porosity, texture, organic carbon, carbon nitrogen ratio) from a global database. This model aims to improve our capacity of observation of dynamic processes, as denitrification. It

will be possible to identify the large-scale hot spots and estimate denitrification hot moments worldwide at a spatial resolution of 1km<sup>2</sup>, from 2011-2019. Providing a simplified approach about nitrate natural retention patterns.

## METHODOLOGY

### INPUT DATA

In order to apply the Soil Denitrification Model (hereafter SDM). Several global databases are required Table 18. The detailed description of the selection of these databases and the characteristics of each one is explained in detail in chapter IV.

**Table 18.** Global scale input data

Parameter	Variable	Temporal resolution	Spatial resolution	Time series	Database
- Bulk density - Org Carbon - C:N ratio	- Clay perc - [CaCO <sub>3</sub> ]	Soil properties	- 1 km <sup>2</sup>	-	WISE 30sec (Batjes, 2015)
Wetlands typology	Land Use	-	1 km <sup>2</sup>	-	(Arino et al., 2011; Lehner and Doll, 2004)
Sub-oxic or anoxic conditions	Soil Moisture	Daily	1 km <sup>2</sup>	2010-2019	(Al Bitar et al., 2017)
Denitrifies activity	Temperature	Daily	1 km <sup>2</sup>	2010-2019	(Al Bitar et al., 2017)

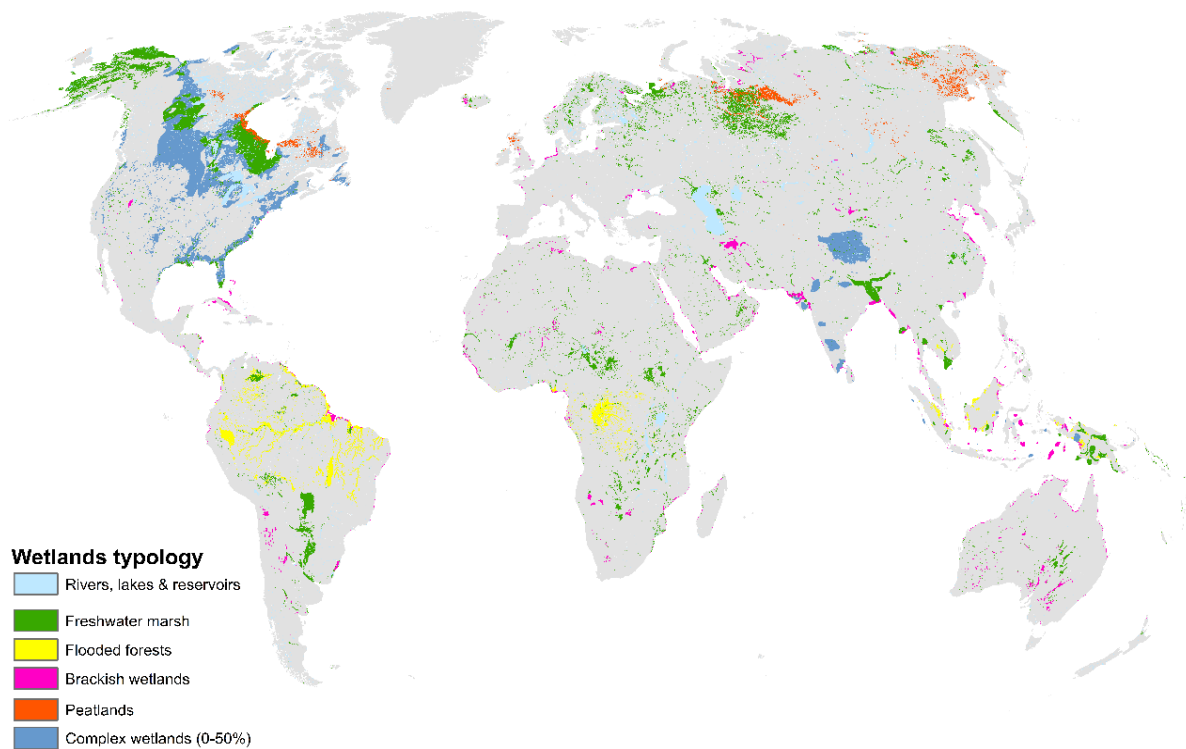
Mineralization rates ( $k_{OC}$ ) for the global denitrification assessment are determined by wetland typology based on literature values. Detailed description of  $k_{OC}$  is presented in chapter IV. Three of these values were already used. Yet, Peatlands and Wetlands complex were not present in the Amazon basin. Table 19 presents the five values that will be used for the five wetlands typologies.

**Table 19.**  $K_{OC}$  for different wetlands typologies

Land use classes	$K_{OC}$ (d <sup>-1</sup> )	References
Freshwater marsh	0.062	(Yin et al., 2019)
Flooded forest	0.016	(Bridgham et al., 1998)
Brackish wetlands	0.076	(Mou et al., 2018)
Peatlands	0.022	(Bridgham et al., 1998)
Wetlands complex	0.072	(Kumar et al., 2018)

As explained in chapter IV, wetland typology for the present study was simplified in seven classes, following the Ramsar main classification (Figure 39). Combining the global lakes and

wetlands database level 3 (GLWD-3) provided by Lehner & Döll (2004) and the Global Cover 2009 (Friedl et al., 2010). The permanent wetlands (not considered for the denitrification model in the present study) and the temporal wetlands divided as: (i) Freshwater marsh/floodplain; (ii) swamp/flooded forest; (iii) bog, fens, mire. As well as (iv) coastal wetlands/brackish salt water; and (v) wetlands complex (0-50%). The latter class is the union of two classes from GLWD-3, and it indicates only fractional wetland areas. This class is a mix of different wetland types, for which there is no clear spatial coverage ratio and suggests ‘0–50% wetland’ (Lehner and Doll, 2004). This static distribution of wetlands is the delineation where the model was applied. Yet, this wetland distribution is just a mask of the potential distribution, as it does not inform about wetlands dynamics. The final surface for each wetland typology considered as potential maximal area in this study is presented in Table 20.



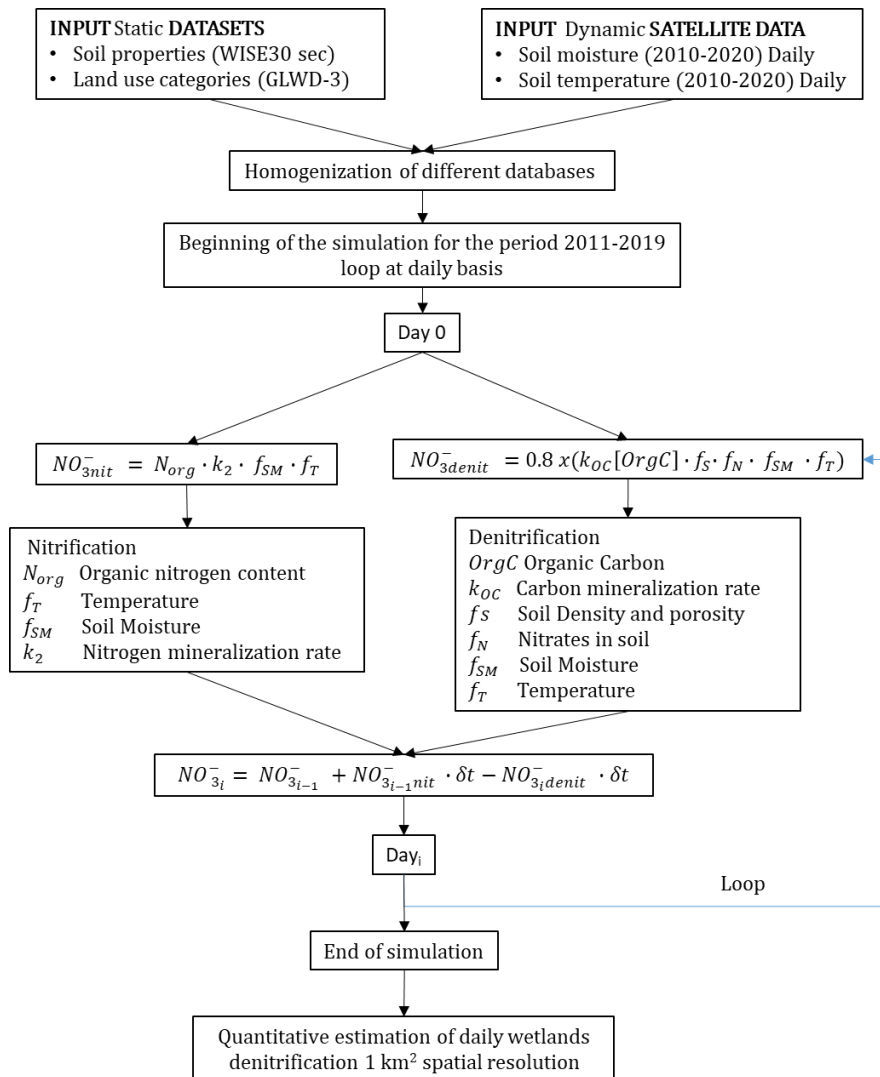
**Figure 39** Global wetlands typologies used as the maximal area of wetlands distribution for the present study.

**Table 20.** World wetland's potential area

	<b>GLWD_3 Wetlands typology potential area (10<sup>3</sup> km<sup>2</sup>)</b>	<b>Global Cover 2009 Typology potential area (10<sup>3</sup> km<sup>2</sup>)</b>	<b>Present Study potential area (10<sup>3</sup> km<sup>2</sup>)</b>
Rivers, Lakes & Reservoirs	5680.82		5680.82
Freshwater floodplain	8929.65	1278.64	10208.3
Flooded forest	1 367.18	577.25	1944.43
Brackish wetlands	1523.17	51.91	1575.08
Peatlands	1778.71		1778.71
0-50% wetlands	9767.67		9767.67
Total natural wetlands potential area	29047.23		30955.04
Total non-permanent wetlands potential area	23366.40	1907.81	25274.22

### MODEL APPLICATION AND DATA ANALYSIS

Here the simplified workflow (Figure 40) representing the main steps of the SDM.



**Figure 40.** Workflow of the simulation loop of the SDM.



The world was divided by regions as shown in Figure 41. Globally the most abundant wetlands are freshwater marshes, which are mainly located in the floodplains, followed by complex wetlands, which term refers to a wetlands mosaic, and the rest corresponds to flooded forests, peatlands and brackish wetlands (Figure 42a-b).

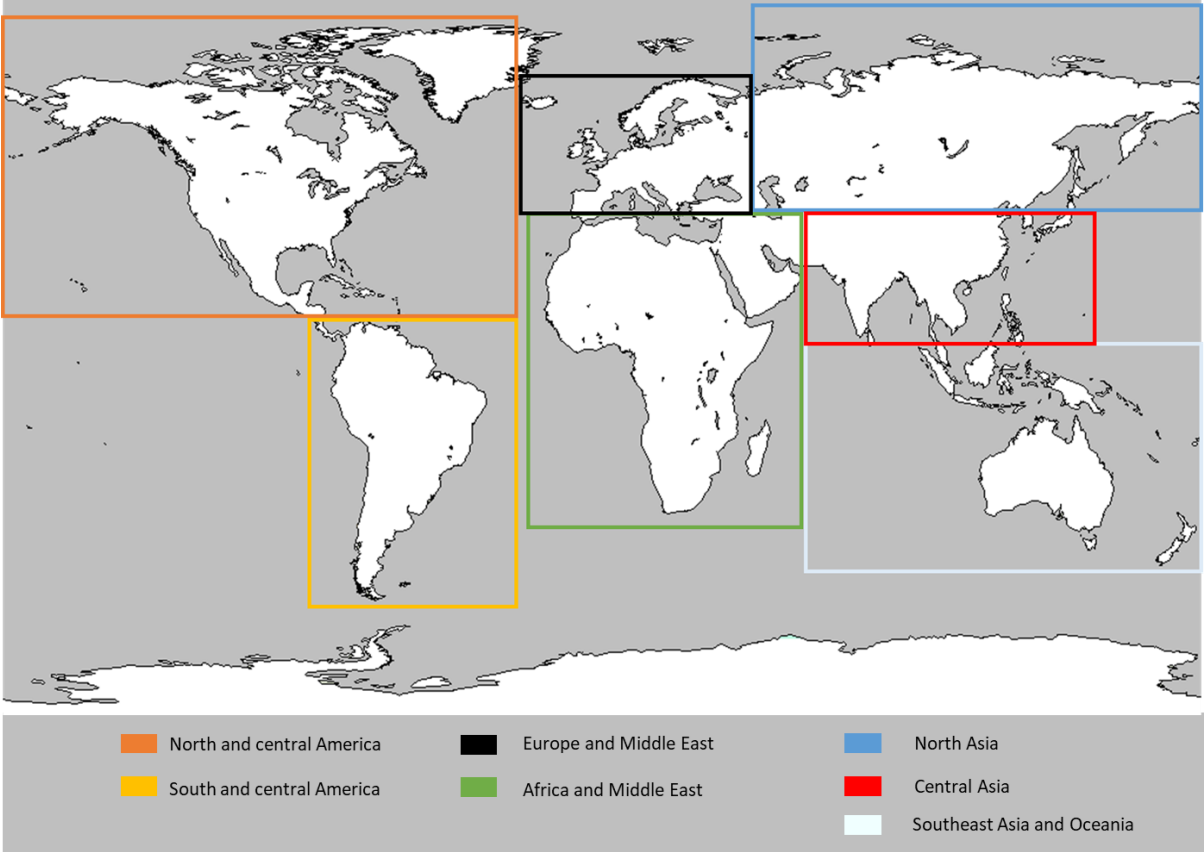


Figure 41. Seven regions designated for the present study.

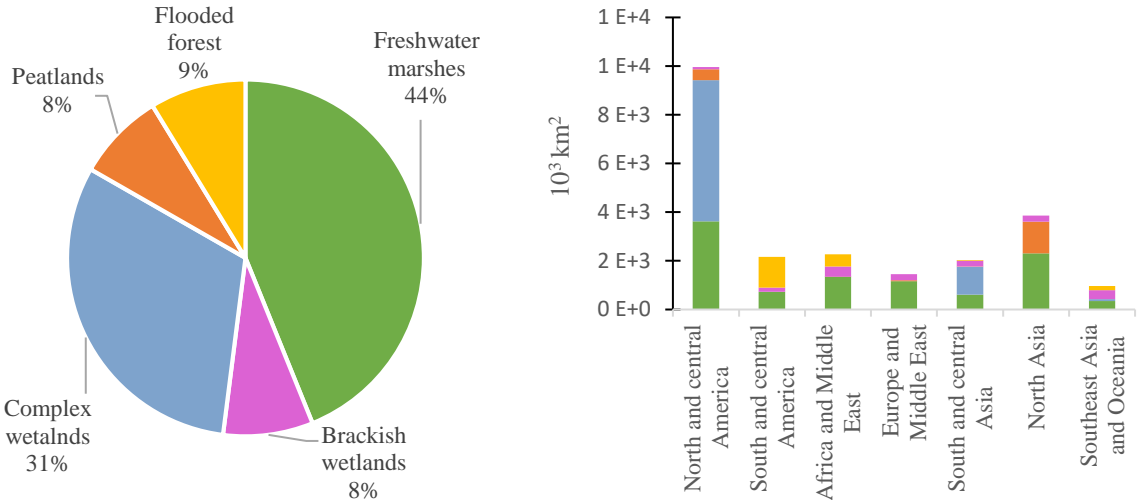
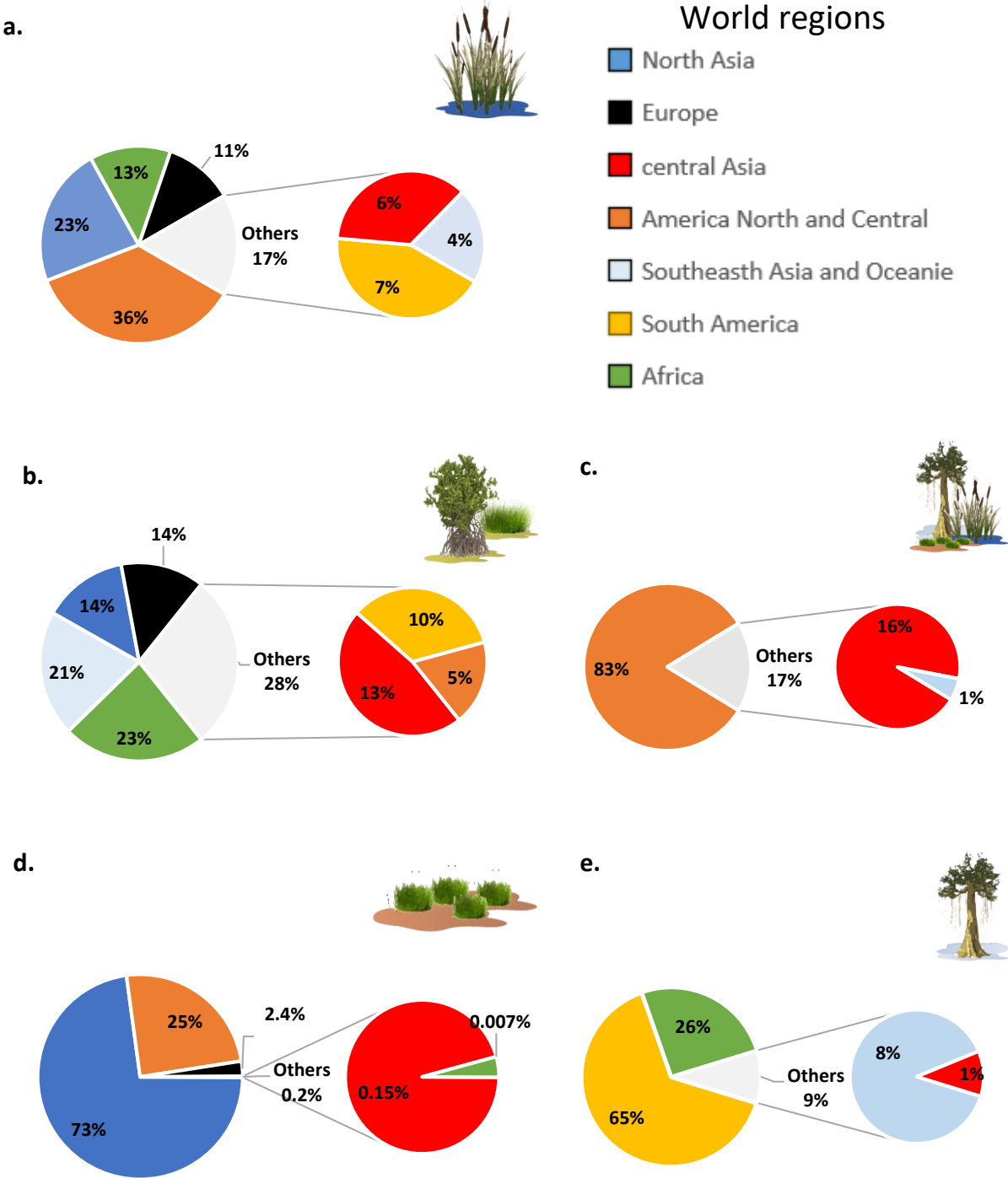


Figure 42. a. Pie chart with percentage of wetlands abundance by typology and b. histogram representing the maximal wetlands area by region of interest

Within the designated regions, the distribution of wetlands is heterogeneous and not all the typologies are distributed in all regions, the percentage of presence of each wetland typology by region is shown in Figure 43a-e.



**Figure 43.** Wetlands typology abundance (%) by world regions. a. freshwater marsh, b. brackish wetlands, c. complex wetlands, d. peatlands, e. flooded forests)

Once the regions were designated, the model was run at daily basis, from 01/01/2011-01/01/2020, for each region. The first year of the simulation was excluded from the interannual mean calculations as it was considered a calibration period, as the nitrates budget is being stabilized.

The total interannual mean and standard deviation of denitrification ( $N-N_2+N-N_2O$ ) by region and by wetland typology was calculated and presented in Tg N. yr<sup>-1</sup>. Identification of the yearly main denitrification by wetland type by region. Then annual denitrification by wetland typology was calculated as specific flux yearly (kg N. ha<sup>-1</sup>. yr<sup>-1</sup>), monthly (kg N. ha<sup>-1</sup>. month<sup>-1</sup>). Finally, the hot moments and hot spots at global scale are identified. Quantitative estimations are being compared with the only previous global estimation of terrestrial denitrification (Bouwman et al., 2013). Regional analysis, that shows the multi annual variability, and monthly dynamics by wetland typology are presented in the appendix of this chapter.

In natural wetlands, N<sub>2</sub> is expected to be the main denitrification product. Yet, there is always a low proportion of N<sub>2</sub>O emitted (Wang et al., 2011). A consensus N<sub>2</sub>O-N<sub>2</sub> ratio is not achieved. As it has been reported that there is a large ratio uncertainty that may be associated to the water table change, and aerated soil volume, which at the time could increase the proportion of N<sub>2</sub>O production in either of nitrification and denitrification (Yang et al., 2013). The ratio is also influenced by nitrate supply, in rich NO<sub>3</sub> conditions, nitrates inhibit the transformation of N<sub>2</sub>O to N<sub>2</sub> (Blackmer and Bremner, 1978). When there is nitrate deficiency in soils, N<sub>2</sub>O emissions increase at a low water table, possible due to nitrification of ammonium (Neill, 1995; van den Berg et al., 2017). In the present study, denitrification is expressed in Tg N yr<sup>-1</sup> (N<sub>2</sub>O+N<sub>2</sub>) and compared to previous denitrification estimations (Bouwman et al., 2013).

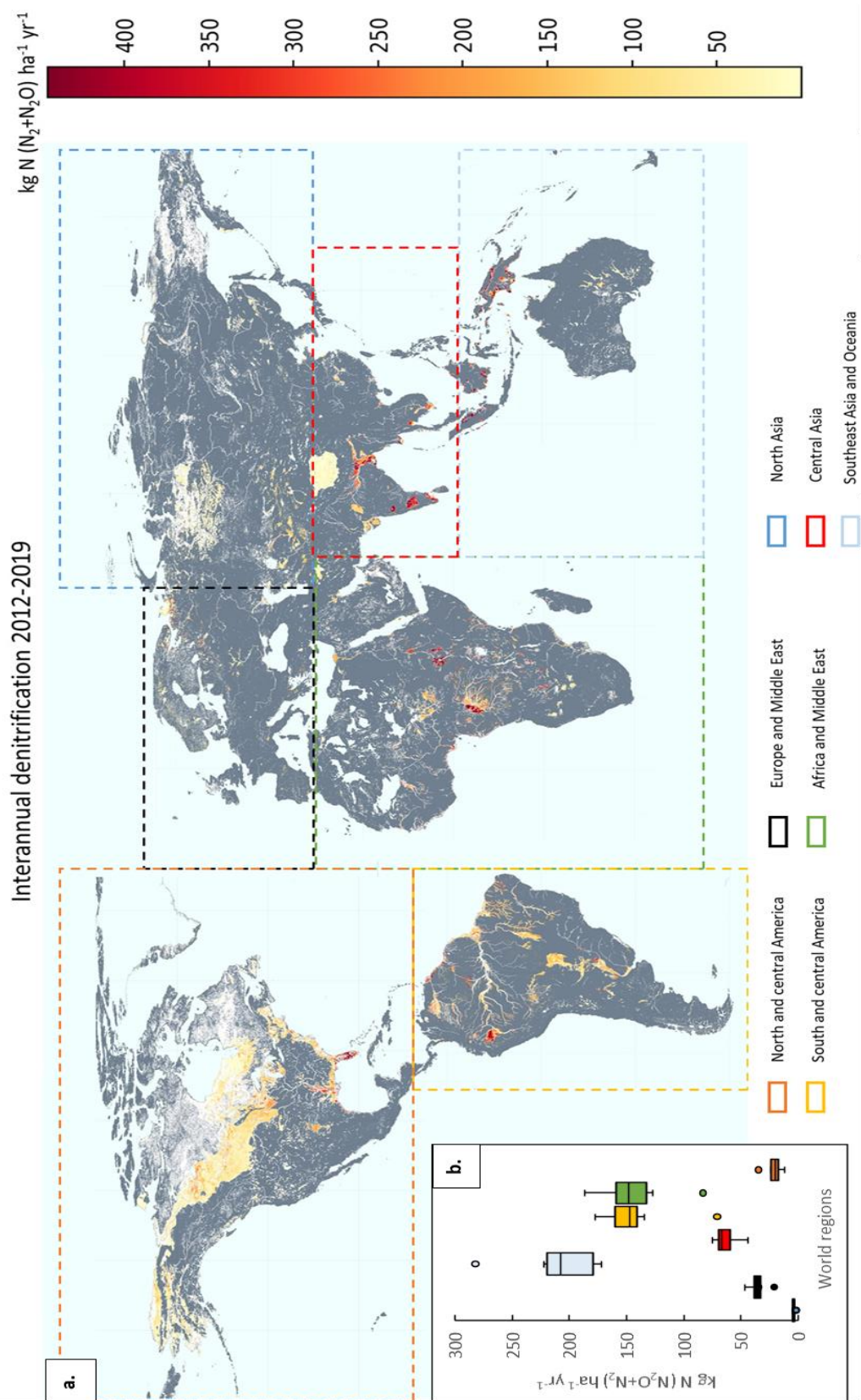
Besides the N<sub>2</sub>O N<sub>2</sub> ratio uncertainties, and due to the importance of N<sub>2</sub>O as greenhouse gas, an estimation of the N<sub>2</sub>O emissions from natural wetlands is also provided. For doing that, three different ratios were used: (i) IPCC R<sub>N<sub>2</sub>O</sub> (0.1) that is the most common ratio used but could overestimate the natural emissions (Bouwman et al., 2013), (ii) ratio proposed by Scheer et al., (2020) for freshwater wetlands (0.02), and (iii) ratio proposed by Schlesinger, 2009 for flooded soils (0.082). Due to the large range of ratio valuations, a mean ratio (0.06) from these three ratios is also applied. The annual range of N<sub>2</sub>O emission was then compared to global N<sub>2</sub>O previous estimations.

## RESULTS

Our study aims to contribute to the understanding of the natural emissions dynamics. It was specifically applied in wetland ecosystems as they represent the ideal conditions for complete denitrification. The results are divided by annual and monthly contributions.

The SDM calculated the annual denitrification from 2012 to 2019 as a result of a diurnal application at 1 km<sup>2</sup> spatial resolution. The spatialized interannual denitrification mean for the simulated period was obtained (Figure 44a.). Southeast Asia and Oceania region was the region with the highest specific flux by region, followed by South and Central America, and Africa (Figure 44b), the least active region was North Asia, all the results from SDM are expressed in kg N (N<sub>2</sub>O+N<sub>2</sub>).ha<sup>-1</sup>.yr<sup>-1</sup>.

Table 21 shows the summarized information regarding the interannual mean and standard deviation for the yearly estimation by region, as well as their minimal and maximal contributing year of each region. The same analysis was done by wetland typology at global scale was calculated (Table 22). Figure 45a -e identified and compare the variations of the wetland typology efficiency by region. North America, Africa and South America are the regions contributing the most, with the main contribution coming from freshwater marshes from Africa, complex wetlands from North America, followed by the flooded forest in South America.



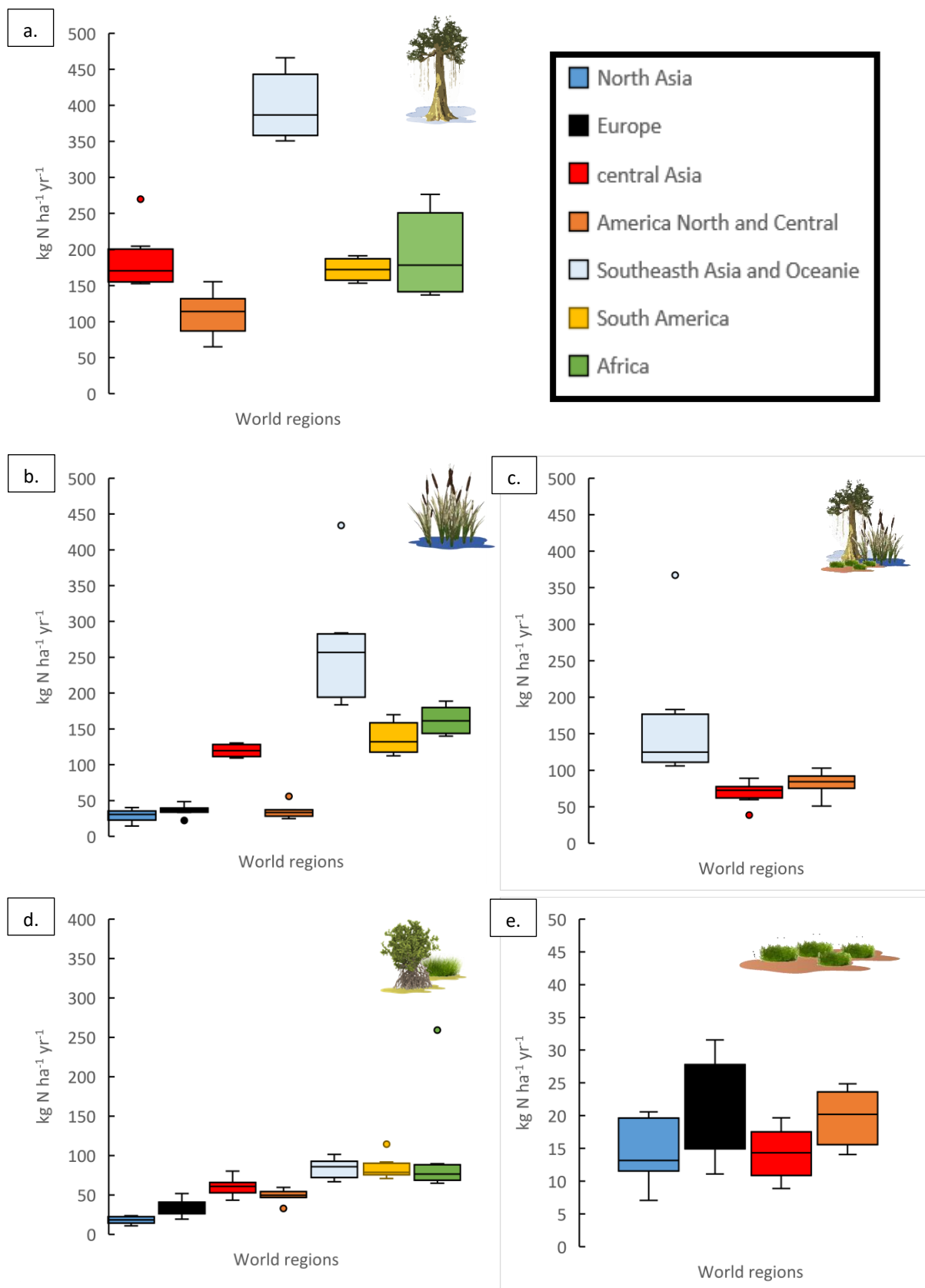
**Figure 44.a.** Interannual denitrification of the simulation period (2012-2019) at 1 km spatial resolution expressed in  $kg N (N_2O + N_2).ha^{-1}.yr^{-1}$ , indicating the annual hot spots and the seven regions of interest. **b.** Specific interannual flux variability by region of interest.

**Table 21.** Interannual yearly denitrification N-N<sub>2</sub>+N-N<sub>2</sub>O by ROI

<b>Region of interest</b>	<b>Average TgN.yr<sup>-1</sup></b>	<b>Standard Deviation</b>	<b>min TgN.yr<sup>-1</sup></b>	<b>max TgN.yr<sup>-1</sup></b>
Europe	5.12	1.02	3.08 → 2012	6.74 → 2018
North Asia	1.28	2.24	4.5 → 2012	11.48 → 2014
Southeast Asia and Oceania	19.97	3.34	16.53 → 2012	27.09 → 2016
South central Asia	5.83	2.8	18.30 → 2012	27.74 → 2019
South America	33.08	3.25	29.02 → 2012	38.47 → 2014
Africa	34.5	4.03	28.75 → 2012	42.38 → 2019
America North and Central	69.57	12.84	64.36 → 2017	93.92 → 2013
<b>TOTAL</b>	<b>169.36</b>	<b>18.31</b>		

**Table 22.** Interannual denitrification N-N<sub>2</sub>+N-N<sub>2</sub>O by wetlands typology

<b>Wetland typology</b>	<b>Average TgN.yr<sup>-1</sup></b>	<b>Standard Deviation</b>	<b>min TgN.yr<sup>-1</sup></b>	<b>max TgN.yr<sup>-1</sup></b>	<b>Region main contribution</b>
Peatlands	2.84	0.61	1.87 → 2012	3.64 → 2018	North Asia
Brackish wetlands	10.78	0.90	8.93 → 2012	11.9 → 2014	Southeast Asia and Oceania
Flooded forest	38.37	2.85	33.6 → 2012	42.7 → 2014	South America
Complex Wetlands	56.7	10.2	34.8 → 2012	69.5 → 2013	America North and Central
Freshwater marsh	85.03	9.92	67.1 → 2012	98.8 → 2013	Africa



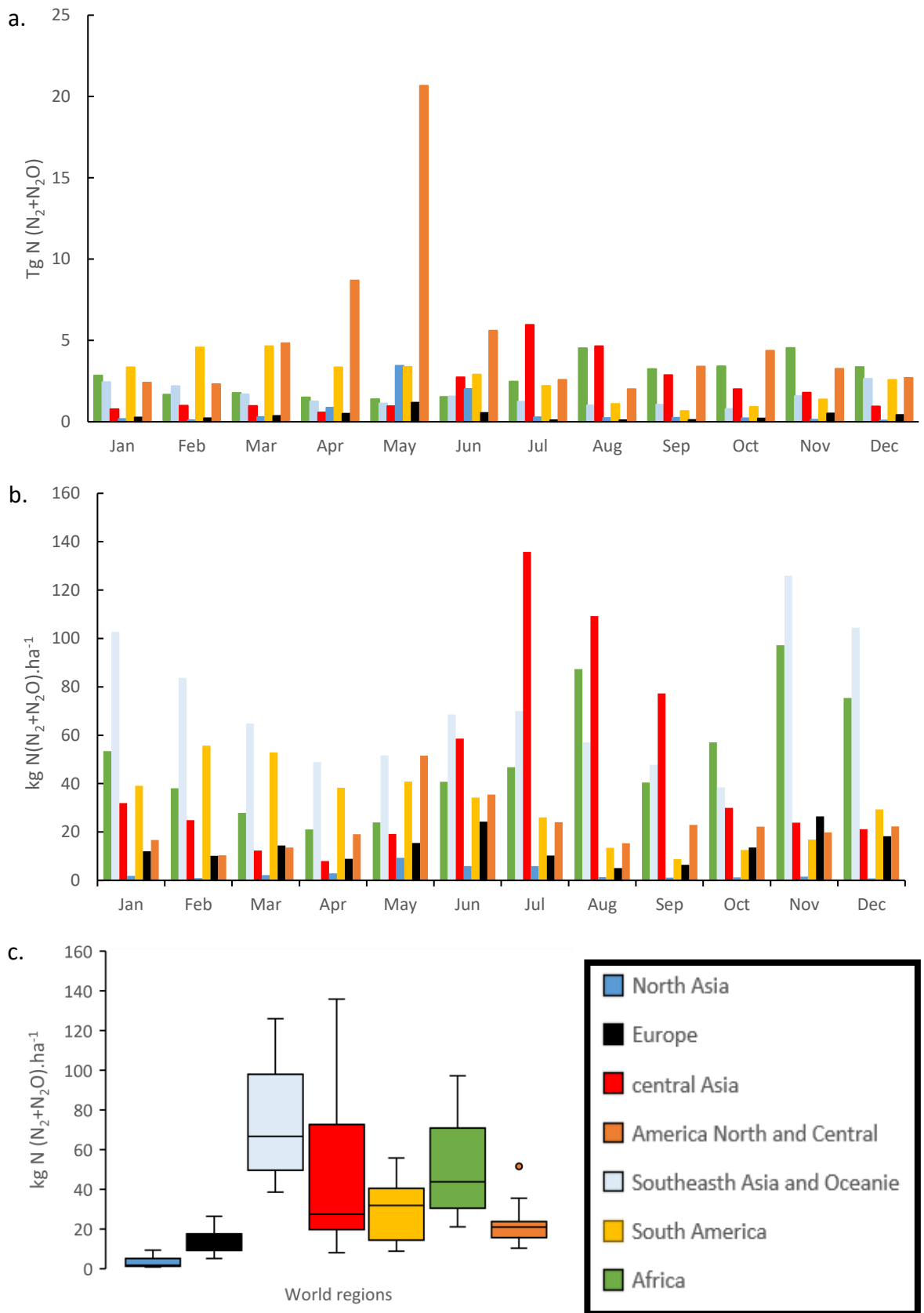
**Figure 45.** Annual denitrification ( $N_2-N + N_2O-N$ ) variation by region for each wetland's typology (**a.** flooded forests, **b.** freshwater marshes, **c.** complex wetlands, **d.** peatlands).

Once each region and wetland contribution and variations at annual basis were identified, a monthly analysis was carried out in order to identify the hot moments. First the mean contribution by region by month was calculated and aggregated (Figure 46a.), showing that May is the moment when denitrification is contributing the most (~ 33 TgN (N<sub>2</sub> +N<sub>2</sub>O) mainly by North American wetlands. When looking the specific fluxes (Figure 46b.) July is when the highest efficiency is achieved, and Central Asia is the most efficient region (~135 kgN.ha<sup>-1</sup> month). Monthly variation by region was also estimated, and Central Asia is the region with the highest variation (Figure 46c.).

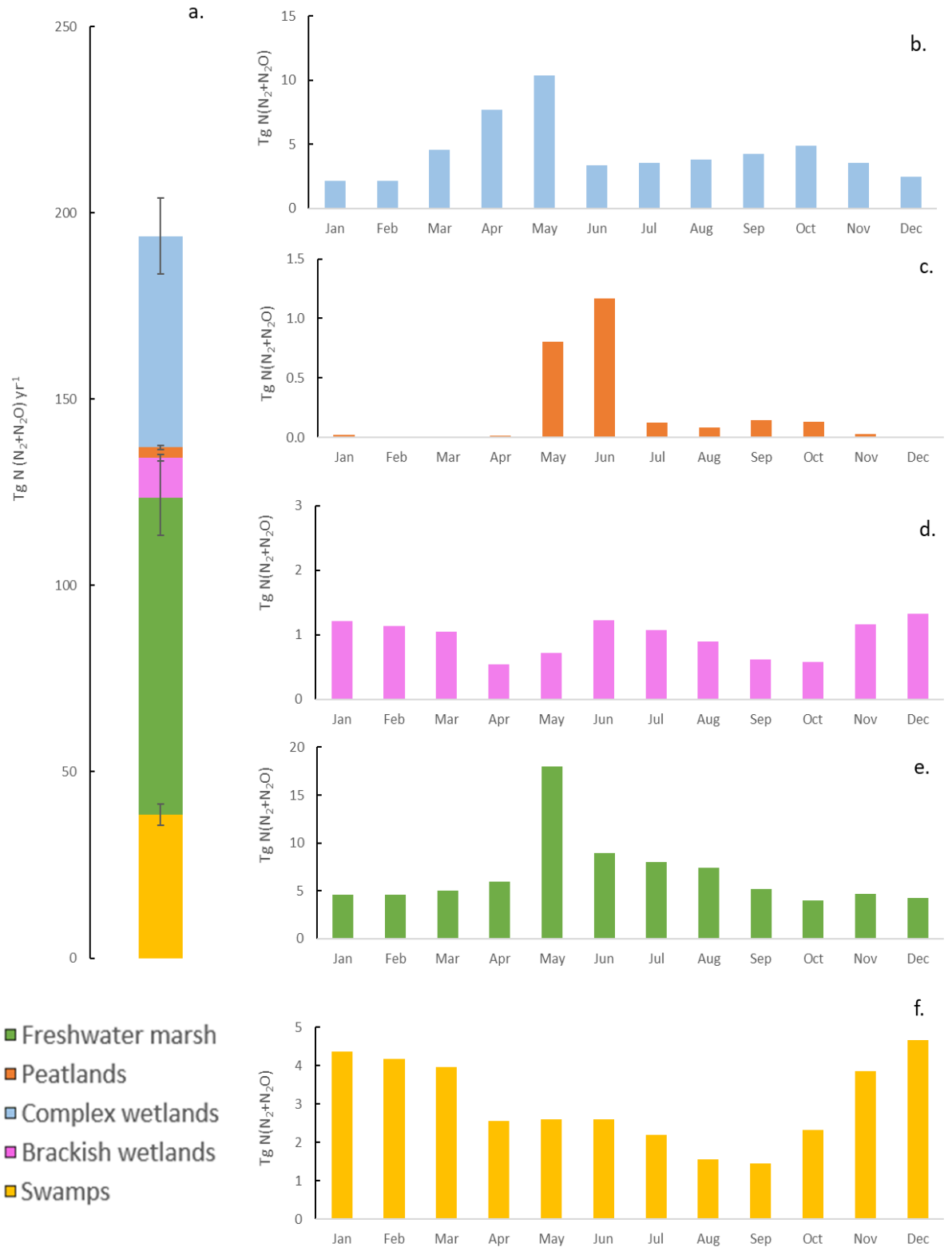
The global contribution by wetland typology is presented in Figure 47a, and then each wetland typology contribution was disaggregated by month (Figure 47b-f) in order to identify the hot moments. Freshwater marshes contributed the most, and they show a constant activity but in May, when their activity increases 3-fold. Complex wetlands are the second main contributors and their peak is also achieved in May, but they have an increasing curve the preceding months (Feb-Apr). In third place, the flooded forest is highly active half of the year from October to March. From April to June they are moderately active and September is the month with the least activity. Coastal wetlands contribute with 10.78 TgN (N<sub>2</sub>O + N<sub>2</sub>) and they have a rather constant contribution all year long, the months with the least contribution are April and October. Peatlands are the only typology that is not active all year long; they have an important activity in May and June, and then slight contribution the following months.

The monthly contribution and variation by wetlands are then being integrated by region (Figure 48). In the Northern regions (i.e. North American Europe and North Asia), the hot moment is always reached in May. Central Asia region, which is located in tropical latitudes, has its peak in July. In the southern regions, (i.e. South America, Africa, and Oceania) there is a less marked temporal variability in the case of South America the peak is reached in (Feb-Mar) while in Africa there are two separate peaks, one in August, with the marshes as main contributor and the second one in November which main contributor are the flooded forest. Southeast Asia and Oceania region have its peak in Dec-January with a higher contribution of flooded forest in December, and more contribution of Freshwater marshes in January. Freshwater marshes are the main contributors to all regional peaks, except for South America, which main contribution is coming from flooded forest. In the case of North America, May's peak is enhanced by complex wetlands. However, the most efficient wetland typology is the flooded forest.

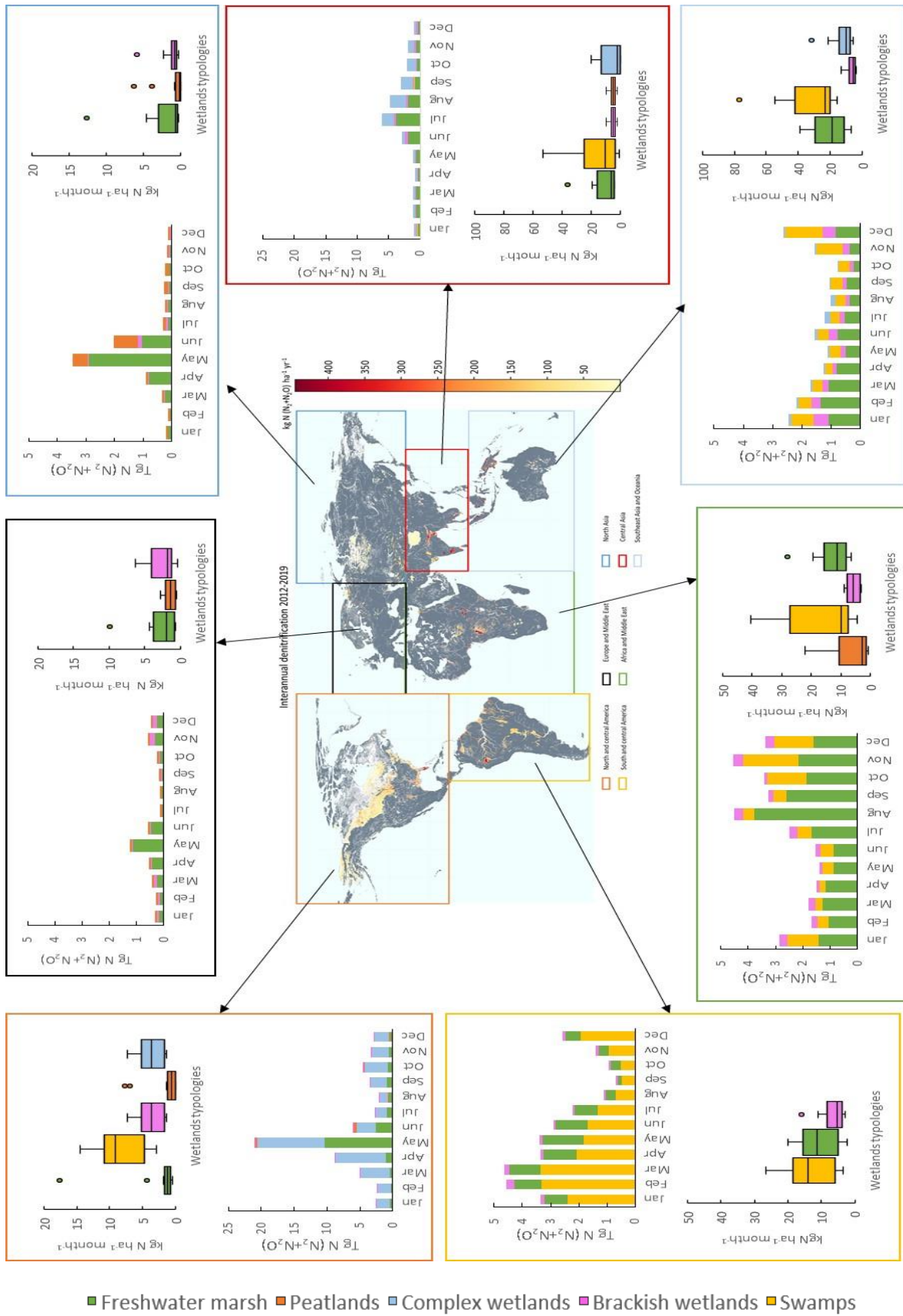




**Figure 46.** a. Cumulate monthly denitrification by region, b. specific monthly denitrification flux by region c. variation of monthly denitrification specific rate.



**Figure 47. a.** Contribution of each wetland typology to the interannual denitrification. **b-f** breakdown of the annual denitrification by wetland typologies by month.



**Figure 48.** Summary of spatialized denitrification by wetland typology by region monthly. Each region has its own histogram, which shows the cumulate denitrification monthly and the boxplots that shows the variability by month of each wetland typology

SDM interannual total denitrification was then compared with estimations of denitrification of other studies (Table 23). There are no estimations of denitrification by wetlands typology. Therefore, the only comparison here presented is with studies that calculate the denitrification based on other models, or mass balances.

**Table 23.** Different global estimations of denitrification by previous studies and the present results

	Total (Tg N)	Soils	Riparian areas	Total natural wetlands
(Söderlund and Svensson, 1977)		108-160		
(Tiedje, 1988)		105-185		
(Seitzinger et al., 2006)		124		
Galloway et al., (2004) (year 2000)	125			
Bouwman et al., (2013) (year 2000)	109 (101-118)	79 (72-85)	6(5-9)	
Canfield et al., (2010)	100			
Galloway et al., (2004) (year 2050)	173			
Bouwman et al., (2013) (year 2050)	110-158	80-119	6-8	
This study (interannual with Standard deviation of 2012-2019)				<b>169.36 ± 18.31</b>

Different  $R_{N_2O}$  were applied to SDM results by wetlands typology,  $N_2O$  probable emissions are shown in Table 24. These results are compared to the total estimation of  $N_2O$  emissions from soils under natural vegetation (Table 25)

**Table 24.** Denitrification annual  $N_2O$  emissions by wetland typologies applying different  $R_{N_2O}$ .

Wetland typology	$R_{N_2O}$ (0.1) <sup>1</sup>	$R_{N_2O}$ (0.082) <sup>2</sup>	$R_{N_2O}$ (0.02) <sup>3</sup>	$R_{N_2O}$ This study <sup>4,5</sup>
	Tg N- $N_2O$ yr <sup>-1</sup>			
<b>Flooded forest</b>	3.8	3.14	0.76	0.16
<b>Freshwater Marshes</b>	8.5	6.97	1.7	0.59
<b>Brackish wetlands</b>	1.0	0.88	0.21	2.11
<b>Peatlands</b>	0.2	0.23	0.05	1.98
<b>Complex wetlands</b>	5.6	4.59	1.12	2.98
<b>Total</b>	19.2	15.81	3.82	7.8

<sup>1</sup>IPCC, <sup>2</sup>Schlesinger et al., (2009) for flooded soils, <sup>3</sup>Scheer et al., (2020) for freshwater wetlands, <sup>4</sup>Organic soils (0.055), <sup>5</sup>Mineral soils (0.035)

**Table 25** Denitrification annual N<sub>2</sub>O emissions reported by previous studies at global scale.

References	Soils under natural vegetation N <sub>2</sub> O Tg N <sub>2</sub> O-N yr <sup>-1</sup>
Xu-Ri et al. (2012)*	9.3
Bouwman et al. (2013)*	4.9
Ciais et al. (2013)*	6.6
Tian et al. (2016)*	8.4
Tian et al. (2019)*	6.5
Tian et al. (2020)*	5.6
Crutzen et al. (2008)+	6.7
Saikawa et al. (2014)+	7.7
<b>Present study</b>	<b>7.8</b>
Mean	6.9

\* Bottom up +Top down

## DISCUSSION

### HOT SPOTS

The global interannual wetland denitrification budget calculated in the present study was 195 Tg N-N<sub>2</sub>+N<sub>2</sub>O per year, which production is homogeneous in time and space. Braking down this result, the main contribution is coming from tree main regions North America (69.57 Tg N-N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>), Africa (34.5 Tg N-N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>) and South America (~33.08 Tg N-N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>). Regarding wetland typology, freshwater marshes are the one contributing the most (85.03 Tg N -N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>). The largest area of marshes is situated in North America, however its contribution (20.55 Tg N -N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>) was ranked in second place of the annual freshwater marshes' denitrification budget. However, the main contribution is coming from African marshes (21.77 Tg N-N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>), which represents only 13% of the global freshwater marshes surface.

African hot spots, Nile basin wetlands (basin outlet and headwaters) pomp out as important hot spots. Historically the Nile basin and its floodplains had been the key for provisioning resources for millennia, sustaining one of the most important civilisations in history, the Egyptians, they had a close relation with the flooding fluctuations that included both geomorphology and the area cultivated (Hassan, 1997). But at the same time it represents a heavily disturbed area, yet it remains a livelihood for many millions of people (Baldassarre et al., 2011). Further on

McCartney, (2010) reported that Nile headwater wetlands, located in the sub Saharan region; play a vital role in the livelihoods of many millions of people. In addition, the entire wetland network in Uganda is thought to contribute to the hydrological regime of the Nile Basin and the ecohydrology of the region. At the same latitude towards west, the Inner Niger Delta is known to support approximately 1 million people, with livelihoods largely supported by fishing, livestock breeding and cultivation. From 1987 to 2003 rice production in this area has rapidly increased from 10,600 to 115,700 tonnes per year. The same had happened with livestock which total had increased reaching 2 and 3 million head of cattle and sheep, respectively, making these some of the highest-density livestock herds in Africa. In recent years, upstream dams and irrigation schemes have affected both the magnitude and timing of the annual flood. It has been estimated that average annual rice production has been reduced by a total of 15% (13,200 tonnes) and fish trade has been reduced by 18% (4,175 tonnes) as a consequence of these changes (Zwarts et al., 2005).

All above mentioned is evidence that African floodplain has been intensively exploited. If we relate this exploitation to denitrification, it would mean that there is many nitrates available, due to the rice fields. In addition, floodplains area had decreased due to land use change for livestock feed. All these impacts could be an indicator that the function of the freshwater marsh in this region has been degraded, including the complete denitrification function. Which could induce an increase of N<sub>2</sub>O emissions of the area Butterbach-Bahl et al., (2020) reported that Sub-Saharan is largely contributing with the N<sub>2</sub>O emissions of Africa.

On the other hand, the flooded forest of the central cuvette of the Congo basin is another evident hot spot. Congo cuvette dynamics is understudied, recent investigations reported the importance of these wetlands for the hydrology and sediment transport within the basin (Datok et al., 2021). At basin scale, Bauters et al., (2019) suggests that Congo basin has a large input of nitrogen (18.2 kg N ha<sup>-1</sup> year<sup>-1</sup>) coming from burning biomass. This input is partially balanced by hydrological dissolved nitrogen, and losses through soil leaching and streams (7.3 kg N ha<sup>-1</sup> year<sup>-1</sup>), which suggests a missing N sink of at least 11.9 kg N ha<sup>-1</sup> year<sup>-1</sup>, this missing nitrate can be associated to the wetlands denitrification function. Gallarotti et al., (2021) with N<sub>2</sub>O isotopic signatures and qPCR-derived gene abundance and expression data of nitrifying and denitrifying gene-bearing communities concluded that N<sub>2</sub>O emission in the Congo Basin are low (0.97 ± 0.79 kg N ha<sup>-1</sup> year<sup>-1</sup>). They associate this result to a complete denitrification, as they identify significant abundance and expression of the gene *nosZ* in soil samples from the lowlands forests study sites. This evidence could support that the cuvette has a high complete

denitrification ratio with low N<sub>2</sub>O emissions. In addition, this means that African wetlands are impacted differently. Freshwater marshes seem to be highly impacted and flooded forest could still be maintaining their pristine state. The wetlands' areas presented here are protected areas, meaning that the impact on these areas is supposed to be low, but due to the pressure of the area around this may not be completely true in all cases.

The largest flooded forest area is located South America (65%). In the Amazon basin, and as it has been explained in chapter IV, the “Abanico del rio Pastaza”(Ramsar Sites Information Service, 2002) is the most important hot spots of the basin. This area is relevant at regional scale and at global scale with a specific flux of ~400 kg N (N<sub>2</sub>O + N<sub>2</sub>).ha<sup>-1</sup>.yr<sup>-1</sup>. The flooded forest present in the Orinoco, Tocantins, Parnaiba and San Francisco contribute to the annual denitrification, showing hot spots with a gradient. These hot spots seem smaller, and information that is more relevant can be obtained about their importance when analysing them at basin scale than at global scale.

South America has 7% of the freshwater marshes worldwide, the largest freshwater marsh located of this region is located at the Parana basin with specific flux that at yearly basis has a large variability range from 170 kg N(N<sub>2</sub>+N<sub>2</sub>O) to 60 kg N (N<sub>2</sub>O + N<sub>2</sub>). This basin has a large hydrological alteration, due to reservoirs operations. However, these floodplains located between dams (Primavera and Itaipu) are reported to be important refuge for fish communities (Agostinho et al., 2008; Baumgartner et al., 2018 Santos and Souza, 2015).

Complex wetlands contribute with 56.7 Tg N -N<sub>2</sub>+N<sub>2</sub>O yr<sup>-1</sup>, North America is the region contributing the most, and where 83% of the complex wetlands are located. Comparing our results to the N<sub>2</sub>O emissions in North America region reported by Tian 2020, the wetlands present in Alaska, and Canada, are not shown as N<sub>2</sub>O emitting areas, which region has the largest area of complex wetlands worldwide. Meaning that our hot spots could be considered as complete denitrification hot spots. However, in the last ten years, and specifically in 2013, Alaska reported the third wettest year in the 96-year record for this state. In the same year, torrential downpours were registered in Canada, this year also represent the highest denitrification record of the region. On the contrary, in 2017, the least denitrification record was recorded, this matches with the severe precipitation deficits in 2017, that contribute to the development of the largest wildfires season) (*State of the Climate: Global Climate Report for Annual 2017*, 2018). British Columbia wetlands area corresponds to 16, 969 ha (Ministry of Forests, consulted 06/21), that may had been affected by the fires and the low precipitation.

Regarding the wetlands in United States, they mainly located in the East coast, and in the outlet of the Mississippi basin. This basin has been intensively harvested and high loads of fertilizers had been applied to the majority of the agricultural fields. Many efforts and research to restore the wetlands of the Mississippi in the last decades had have attracted attention to wetlands and have promoted many protection techniques and policies that are reducing the impact in the area and restoring some wetlands (Gomez-Velez et al., 2015; Mitsch and Day, 2006). However, there is still a high eutrophication problem leading to a persistent hypoxic zone that covers 20,000 km<sup>2</sup> (dissolved oxygen <2 mg/L) in the Gulf of Mexico, directly related to the strong effluence of fertilisers discharged into the river (Turner et al., 2012). Improvement of cultivation practices, reduction of fertiliser use and wetland restoration can be particularly important actions to reduce reactive nitrogen, eutrophication and coastal erosion (Olson and Suski, 2021; Rosenzweig et al., 2018). Our results show the high capacity of coastal wetlands located in the outlet of the basin to execute denitrification, this results are inline to the results of an experimental study in this area, that proof that denitrification is the dominant microbial respiration, and coastal wetlands represent an important Natural based Solution for the present hypoxia issue (Upreti et al., 2021). Successful stories are reported in Florida Everglades wetland (White and Reddy, 2003), which area has been a designated as national park, and long monitoring and research has been done, reporting some restauration efforts that may recover wetlands functionality (Diamond et al., 2021).

Central Asia (~5.8 Tg N -N<sub>2</sub>+N<sub>2</sub>O.yr<sup>-1</sup>), had its main hot spots in the south of the Indian peninsula, Ganges-Brahmaputra basin, and the exit of Mekong, Irrawaddy and Chao Praya basins. Even though the Tibetan plateau is the largest complex wetlands in the region it specific flux is lower. Central Asia is a region with the highest rice production worldwide, and which production is directly linked to floodplains and water supply. Most rice is consumed in the country where is grown, but increasing demand in Africa has leas to broader global trade (Elert, 2014) The rice production yields boom was due to the Green Revolution of the 1970s and 1980s. Rice yields were raised primarily by the introduction of new varieties and the use of more inputs. Investments in infrastructure to supply irrigation water and provide drainage raised both area and yields. The fertilizers used in Central Asia are very high and still increasing (Tan and Norhaizan, 2020). The wetlands hot spots in Central Asia in real context may be important refuge for local biodiversity, but they may also be some wetlands that are be threatened. Becoming hot spots of N<sub>2</sub>O emissions as unlimited nitrates are present.(Devkota et al., 2019).



Southeast Asia and Oceania ( $\sim 20 \text{ TgN-N}_2+\text{N}_2\text{O.yr}^{-1}$ ) is region constituted by islands. Looking the specific fluxes, Southeast Asia and Oceania region ( $\sim 220 \text{ kgN-N}_2+\text{N}_2\text{O.ha}^{-1}.\text{yr}^{-1}$ ) overcomes Africa and South America interannual mean ( $\sim 150 \text{ kgN-N}_2+\text{N}_2\text{O.ha}^{-1}.\text{yr}^{-1}$ ). The efficiency by region in SDM is dictated by the two main dynamic variables (temperature and soil moisture). The latitudinal gradient of the main wetlands in Southeast Asia and Oceania is concentrated in the tropical area, giving a constant an almost constant optimal temperature. While wetlands areas in South America and Africa had a larger latitudinal range, implying a temperature gradient. Moreover, wetland typology by region is different, South East Asia- Oceania region is dominated by brackish wetlands with the highest mineralization rates ( $K_{OC}$ ) is the highest, based on studies carried out in this region. Mangroves of the Southeast Asia had play an important role for costal protection and they represent the main source of livelihoods for many local populations (Alongi, 2008; Dahdouh-Guebas et al., 2005; Martínez-Espinosa et al., 2020), however deforestation (Otero et al., 2017) and sea level rise (Lovelock et al., 2015).represents the main threat. Our denitrification hot spots are showing that this region is the most efficient wetland denitrification hot spot worldwide.

The northern regions, North Asia ( $\sim 1.2 \text{ TgN -N}_2+\text{N}_2\text{O.yr}^{-1}$ ) and Europe ( $\sim 5.12 \text{ TgN -N}_2+\text{N}_2\text{O .yr}^{-1}$ ) contribute the least to the global budget, but their contribution still important. The northern peatlands represent the biggest area of carbon stock worldwide, and this stock is due to the permafrost layer (Hugelius et al., 2014). However, this permafrost has been reduced due to higher temperatures, activating the peat (Cohen et al., 2012), that in turn releases large amounts of dissolved carbon, needed for denitrification (Fabre et al., 2019). The relevance of this area can be better understood when looking the activation moments within the year.

## HOT MOMENTS

May is the principal denitrification hot moment at global scale, being the northern floodplains the main contributors (North America, Europe and North Asian floodplains). The South America freshwater marsh of the Parana basin also has its peak in May and the lowest. This floodplain hot moment is later than the peak by the flooded forest of the Amazonian basin (February- March). Peatlands that contribute less at global scale, they get active in May and they reach their peak in June. These peaks correspond to the snowmelt and the higher temperatures during the year.

Increased temperatures in arctic and temperate regions have a greater impact on the hydrological cycles and therefore in al biogeochemical cycles, included nitrogen. In the simulation period, we observed that the maximal denitrification in North Asia was registered in

2014, mainly boosted by freshwater marshes. That year, Russia had the warmest March-May since 1936, in addition, Japan had the wettest August since 1946, receiving nearly triple its monthly average. At global scale it was the warmest year across global land and ocean surface since 1880 (*State of the Climate: Global Climate Global Climate: Report for Annual 2014*, 2015). In 2014, the flooded forest of South America and the brackish wetlands of Southeast Asia and Oceania region also reported their maximal annual denitrification of the simulation period (2012-2019).

Annual temperatures since 2014 have only increased, European freshwater marshes and North Asia peatlands recorded their maximum denitrification two years later, 2018, that year is ranked as the sixth warmest year (1880-2020), with 2016 in first place (*State of the Climate: Global Climate Report for Annual 2020*, 2021). In 2016, South East Asia and Oceania reach it record annual denitrification contribution 27.09 TgN (N<sub>2</sub>O+N<sub>2</sub>).

The hot denitrification moments in the southern hemisphere correspond to the beginning of their rainy season: February, in the case of South America, November from Africa and December for Oceania. Nevertheless, southern hemisphere regions are active all year long. The ENSO and Monsoon intensity influence heavily these regions and the multi-annual denitrification records can elucidate their effect.

## SDM GLOBAL ESTIMATION COMPARED WITH OTHER STUDIES

As the SDM was exclusively applied in wetlands the estimations are based in local temperature, soil moisture and the soil N budget. No outflow or inflow is calculated. The majority of global model variables used similar inputs, but soil moisture. Hydrological dynamics are estimated with net precipitation and run off. Some models gave a total estimation with no disaggregation of the nitrogen pools; some others desegregate nitrogen pools, in soil, groundwater, riparian zone and exit to the surface water (Bouwman et al., 2013). In general, these models calculate the nitrogen balance and flows (vertical and horizontal) aiming to understand the contribution of agriculture the global nitrogen cycle in the last century.

In Table 23, the global results of SDM are compared to previous studies. The results are not integrated in any of the denitrification pools. The closest term could be, riparian zones a term that refers to the location of the soil, next to the river, but do not gave information about vegetation typology, that can be arboreous or herbaceous, which in SMD implies different denitrification efficiency. Therefore, our estimations are presented in another column. Our

global results indicate that natural wetlands are transforming 169 Tg N-N<sub>2</sub>+N<sub>2</sub>O per year, which value is higher than half the preceding models' total denitrification estimated in terrestrial ecosystems.

Nevertheless, within the range of uncertainty of various models. Each model estimation is obtained by different methodologies and input data which imply different uncertainties issues. The references shown were published from the earliest in 1977 and the latest in 2013. Only Bouwman et al., (2013) identified the riparian zones as separated pool and they remarked that riparian zones may be an important global source of denitrification and N<sub>2</sub>O emissions. However, their limitations towards spatial information with their low analysis resolution (0.5° x 0.5°) and lack of hydrogeological conditions information, made it impossible for them to locate the riparian zones. Nonetheless, these global estimations served as a reference for many local studies that quantify the impact of agricultural practices, riparian zones denitrification, and N<sub>2</sub>O emissions. To our knowledge no other global estimates of denitrification has been published lately. Therefore, the present model represents the first global denitrification estimation in wetlands.

In the last decades, more attention has been paid to greenhouse emissions, as the climate change effects are becoming more and more evident, and the IPCC had declared that we already passed the no return point. In this context global studies have been developed to quantify and spatialized CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O more accurately (Ciais et al., 2014; Kumar et al., 2018; Sauniois et al., 2016; Zhang et al., 2017). The time and space variations are key to improve policies and predict future evolution of emissions and the present impact. Tian et al., (2020) provided the latest global N<sub>2</sub>O annual budget estimation for the decade 2007-2016. They identified 18 different sources and sinks, of which natural emission sources are contributing with ~9.7 Tg N-N<sub>2</sub>O per year. This quantity calculated from the sum of different sources: (i) Natural soils (5.6 Tg N-N<sub>2</sub>O), (ii) Oceans (3.4 Tg N-N<sub>2</sub>O), (iii) Inland and coastal waters (0.3 Tg N-N<sub>2</sub>O), (iv) and lightning and atmosphere production (0.4 Tg N-N<sub>2</sub>O).

Denitrification results of SDM are obtained in (Tg N-N<sub>2</sub>+N<sub>2</sub>O), no specific R<sub>N<sub>2</sub>O</sub> is associated. Applying the different R<sub>N<sub>2</sub>O</sub> from the literature a large range of N<sub>2</sub>O emission is calculated (Table 24). The N-N<sub>2</sub>O interannual flux is ~19.2 Tg N-N<sub>2</sub>O, when using the IPCC ratio, which estimates a very high emission. This estimation could be interpret as the disturbed scenario, where reactive nitrogen is abundant and denitrification is incomplete (i.e. inhibition of *nosZ* enzyme, in charge of N<sub>2</sub>O to N<sub>2</sub> transformation), a common situation in agricultural fields,

where high emissions of N<sub>2</sub>O are reported worldwide (Butterbach-Bahl and Dannenmann, 2011).

If there may be a high disturbance in natural wetlands, the expected N<sub>2</sub>O outgassing could be critical and significant feedback to the global warming effect. However some studies had reported that IPCC ratio is over estimating natural emission (Bouwman et al., 2013; Scheer et al., 2020). When applying their alternative ratio for flooded soils and riparian areas based on field observations to our results, annual contribution decreases to 3.82 Tg N-N<sub>2</sub>O.

This annual emission is within the budget estimated by Tian et al., (2020) for natural soil emissions (5.6 Tg N-N<sub>2</sub>O). In that case, our estimation for natural wetlands (3.8 Tg N-N<sub>2</sub>O) would represents ~60% of their total natural soil emissions. Their estimation refers to a general natural soils pool, but they do not make any particular remark regarding the type of natural soils that may be contributing the most. Their contribution is relevant regarding the understanding of anthropogenic sources evolution, the imbalance and impact of these activities in the global nitrogen cycle, in the past, present and future. Their estimation pointed out that N<sub>2</sub>O main emission sources are associated to emerging economies, particularly Brazil, China and India. For example, they estimated that Brazilian N<sub>2</sub>O emissions were enhanced by 120% during 1980-2016. Their results estimate that present emission rates are tracking the highest Representative Concentration Pathway (RCP) of the five-assessment report of the IPCC, RCP 8.5. In this context, emissions from anthropogenic sources are more important and present a problem that needs to be addressed urgently. With this context in mind, the two N<sub>2</sub>O-N wetlands contribution are important to be considered. One as the worst-case scenario, if disturbance keep increasing maintaining the same emission rate, and the lower estimation as the best-case scenario where denitrification is completed and the main emissions correspond to N<sub>2</sub>.

## CONCLUSION AND PERSPECTIVES

Despite large uncertainties in our model approach, this study contributes with the first global identification of hot spots and hot moments with a spatial resolution of 1 km<sup>2</sup>. The SDM application at global scale indicates that natural wetlands play a key role on global nitrogen cycle, in an undisturbed and disturbed scenario. Being important reactive nitrogen sinks or possible N<sub>2</sub>O hot spots. Denitrification multi annual variation may serve as indicators of climatic anomalies and N<sub>2</sub>O emissions hot moments.

The SDM results here presented are just a first step towards the understanding of denitrification dynamics in wetlands and intends to contribute with valorisation of wetlands in the global nitrogen cycle. The analysis carried out here may be taken as a general introduction of the potential of the SDM and that can lead to many other in-depth studies.

It is the first model that gives spatial daily information considering wetland diversity, even though this typology has been simplified to make the model as parsimonious as possible. These five classes already shown that there is an important range of values regarding wetlands specific fluxes, which results match with values observed in the field if we applied the  $R_{N_2O}$  specific for flooded soils (Scheer et al., 2020). For example the SDM range results are inline to what has been observed in the flooded forest in the Amazon (Pärn et al., 2021) or the Congo lowlands forest (Gallarotti et al., 2021) and in coastal wetlands in USA (Upreti et al., 2021). The different wetland typology, the spatial and temporal information gave information that helps understand if the denitrification is completed or incompleted. Producing more  $N_2O$  emissions, highlighting the importance of denitrification as function or as risk.

The SDM, provide information of hot spots and hot moments that are understudied regarding denitrification activity. These hot spots may be in danger due to the anthropogenic activities around. The lack of field data represents an opportunity to future research to fill the gap regarding field measurements in these sites.

The SDM do not have a specific model that calculated the  $N_2O$  emissions, the ratios applied in the present study seems to be very ambiguous, the development of a module to calculate  $N_2O$  emissions based on a wetlands' typology, pH or  $NO_3^-$  saturation may be a worthy step forward.

# CHAPTER VI

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## CONCLUSION AND PERSPECTIVES



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The objective of the present PhD was to contribute to the knowledge and evidence regarding the role of natural wetlands in the global nitrogen cycle. This work focuses on the critical zone, aiming to relate the physical, biological and chemical processes involved in the nitrogen cycle occurring in soils. Wetlands were chosen as a model ecosystem, as they represent natural ecosystems where denitrification is frequently an active process.

Denitrification main regulators integrated in this modelling framework, allows simulating the functioning of natural wetlands, anticipating their evolution and identifying the fundamental processes involved in their functioning. Maintenance of water quality in aquatic ecosystems is directly related to wetlands. The effective functioning of wetlands is immediately reflected in the low transfer of nutrients from the surrounding aquatic ecosystems, avoiding eutrophication phenomena. Moreover, they are home and refuge for biodiversity and they play an important role in the hydrological cycle, regulating floods storage and recharging groundwater.

For millennia, humans benefited from the natural goods and services of these ecosystems, living in close relation with their hydrological dynamics, as an essential ingredient to their development. In the course of history different interests and “needs” of societies have changed and with them the value that human societies place on wetlands. The current economic development has led to major wetland loss, seeing wetlands as an opportunity as arable land. This change has meant that people have apparently become less directly dependent on wetland provisioning and functions. We now find ourselves in a scenario where a general detachment of humans from their natural environment has been the greatest cause of the vast environmental degradation and loss of biodiversity (Alongi et al., 2004; Ayoub, 1999; Bennett et al., 2015).

In this context, the present PhD research was developed looking for scientific arguments and quantitative proofs and tools that contribute to linking biodiversity, ecosystem services and human well-being. The contribution of this PhD is specifically towards denitrification dynamics at global scale in different typologies of natural wetlands ecosystems. This aim was addressed by three different means: (i) literature review, (ii) fieldwork, and (iii) modelling.

First, an exhaustive literature review (**Chapter II**) was useful to identify the development and broadening of research regarding the global nitrogen cycle and the latest recognition of wetlands' importance regulating terrestrial reactive nitrogen. In this chapter, a quantitative and qualitative literature analysis of wetlands' denitrification gave information about present gaps and trends of most sound research in the last fifty years. This review gave a solid base of the state of art of the research in this topic, a reinforcement that wetlands are acknowledged relevant



at global scale, yet global estimations of denitrification do not give any precise information of natural wetlands contribution. The conclusion of this research was a proposition of a conceptual way forward that introduces spatiotemporal dimension, to fill the gap related to the uncertainties related to wetlands dynamics and transfer of reactive nitrogen. This concept consists in a model-based methodology that allows estimating denitrification hot moments and hot spots in natural wetlands at global scale using satellite Earth Observations.

To transform this conceptual model to a sound process-based model, a fieldwork campaign (**Chapter III**) was carried out, in order to have field data that allow us to validate the model. It was expected to record  $N_2O$  emissions in situ with the acetylene inhibition in a chamber protocol experiment. Yet, this hypothesis had an unsuccessful outcome. Recording denitrification in situ in natural wetlands is still a difficult task with the current methods available, a longer campaign that allows the long-term monitoring of the wetland may help to catch the denitrification peaks, or ensure that  $N_2O$  emissions are low and therefore no records were found. Nevertheless, with our short fieldwork it is difficult to draw conclusions. The chamber protocol, in agricultural fields, reports successful outputs, as the nitrogen dynamic is well known, and as fertilizers based on nitrogen are added and reactive nitrogen is available. Besides no emissions recorded in the field, the campaign was very useful. A high wetland ecosystem diversity was observed and collected soil samples were later analysed in laboratory-controlled conditions, which gave valuable information of denitrification capacity of wetlands soils.

Literature, field and laboratory experimentations gave elements to propose specific changes to assess denitrification in wetlands ecosystems by modelling in a more specific way. The majority of the models are developed for being used in agricultural fields and at basin scale. Previous research in our group had already taken some steps forward. A denitrification equation has already been validated in riparian areas and satellite data was already used at basin scale. However, the application at global scale was still missing. Therefore, a development of a model specifically for wetlands was developed and named Soil Denitrification Model (SDM).

This model was presented, validated and tested in **Chapter IV**. The validation was done using the data collected and analysed in **Chapter III**. This step was important, as the main difficulty was to estimate the saturation capacity of wetlands soils. This constant was adapted for wetlands ecosystems using the soil diversity sampled. This chapter is divided into two parts. Part I, related to the numerical validation of SDM with soil samples, and Part II one focused on the development of the algorithms to be able to run the model at global scale, at daily time step for nine years. The main assumptions, limitations and uncertainties are presented here. They are

mainly related to the precision of the rates when analysing at local scale. Besides the uncertainties, it could provide a good indicator at global scale.

Chapter V was only possible with the integration of the main results of chapter II, III and IV. Each of these chapters were key to have a solid base to develop a model able to assess denitrification in wetlands at global scale. This chapter aimed to present a synthesis of the main functions of the model to understand the role of wetlands at global scale spatialized and dynamically. Annual and monthly analysis highlighted denitrification of main hot moments and main hot spots. Later on, the hot spots were identified in terms of their landscape and basin position, as well as human activity. SDM does not calculate the emission ratio  $R_{N_2O}$ , instead different ratios from the literature were applied and the discussion was placed at this point. The assessment of denitrification in wetland soils exclusively had never been proposed before at global scale. This model represents the first attempt of quantifying their activity, hoping to be the baseline for future studies that target to reduce the uncertainties of the present assessment.

Despite uncertainties, it proves that denitrification in wetlands is a significant function that may be underestimated. It highlights that efficient wetland functioning is sinking  $N_2O$  that could be potentially emitted, or transferred to the surrounding aquatic ecosystems, which in turn is contributing to maintaining good water quality. These ecosystems have an important denitrification capacity, which in a disturbed scenario is or will cause an important feedback of greenhouse emissions that contribute to global climate change.

The SDM in the actual form gives satisfactory results in the point of view of the identification and evolution in time of denitrification functionality in wetlands, as well as the identification of the hot moments and hot spots.

Many of the indicated hot spots are understudied in terms of denitrification capacity. These hot spots should be priority zones for the scientific community to develop more in-depth research. The precision of the SDM depends on the input data; if more precise wetlands classification and nitrates saturation capacity of the local ecosystems is known the model could provide information more accurately.

The creation of a module that calculates  $N_2O$  emissions with differentiated rates depending on anthropogenic impact could provide a more precise  $N_2O$  estimation than adopting the generic  $R_{N_2O}$  ratios. Later on, SMD could be correlated with climate anomalies and future climate scenarios, providing important information to reduce ecosystem degradation.

In turn, this study suggest some policies implications, first it advise further studies for the IPCC comprehending assessment.

Emphases denitrification process and spatial distribution by ecosystem type. Recognizing wetlands as the main actors in the denitrification process at a global scale.

Exploration of how factor human can control nitrogen deposition that in turn will improve the N<sub>2</sub>O emissions and reduce the ecosystems unbalance.

Articulate the potential co-benefits to wetlands denitrification towards already recognized wetlands ecosystem services (e.g. water quality and biodiversity).

Promote preservation of natural wetlands for N<sub>2</sub>O control, and return of N<sub>2</sub> to the atmosphere.

## CONCLUSION ET PERSPECTIVES

L'objectif du présent doctorat était de contribuer aux connaissances et aux preuves concernant le rôle des zones humides naturelles dans le cycle global de l'azote. Ce travail se concentre sur la zone critique, visant à mettre en relation les processus physiques, biologiques et chimiques impliqués dans le cycle de l'azote se produisant dans les sols. Les zones humides ont été choisies comme écosystème modèle, car elles représentent des écosystèmes naturels où la dénitrification est fréquemment un processus actif.

Les principaux régulateurs de la dénitrification ont été intégrés dans un cadre de modélisation, qui permet de simuler le fonctionnement des zones humides naturelles, d'anticiper leur évolution et d'identifier les processus fondamentaux impliqués dans leur fonctionnement. Le maintien de la qualité de l'eau dans les écosystèmes aquatiques est directement lié aux zones humides. Le fonctionnement efficace des zones humides se traduit immédiatement par un faible transfert de nutriments vers les écosystèmes aquatiques environnants, évitant ainsi les phénomènes d'eutrophisation. En outre, elles constituent un habitat et un refuge pour la biodiversité et jouent un rôle important dans le cycle hydrologique, en régulant le stockage des crues et en rechargeant les nappes phréatiques.

Pendant des millénaires, l'homme a bénéficié des biens et services naturels de ces écosystèmes, vivant en étroite relation avec leur dynamique hydrologique, comme un élément essentiel à leur développement. Au cours de l'histoire, les intérêts et les "besoins" des sociétés ont changé et, avec eux, la valeur que les sociétés humaines accordent aux zones humides. Le développement économique actuel a entraîné une perte importante de zones humides. Ces dernières étant considérées comme une opportunité en tant que terres arables. Ce changement a fait que les gens sont apparemment devenus moins directement dépendants de l'approvisionnement et des fonctions des zones humides. Nous nous trouvons maintenant dans un scénario où le détachement général des humains de leur environnement naturel a causé une vaste dégradation environnementale et une lourde perte de biodiversité (Alongi et al., 2004; Ayoub, 1999; Bennett et al., 2015).

Dans ce contexte, la présente recherche doctorale a été développée en recherchant des arguments scientifiques, des preuves quantitatives et des outils qui contribuent à relier la biodiversité, les services écosystémiques et le bien-être humain. La contribution de cette thèse porte spécifiquement sur la dynamique de la dénitrification à l'échelle globale dans différentes

typologies d'écosystèmes naturels de zones humides. Cet objectif a été abordé par trois moyens différents: (i) la revue de la littérature, (ii) le travail de terrain, et (iii) la modélisation.

Tout d'abord, une revue exhaustive de la littérature (**chapitre II**) a été utile pour identifier le développement et l'élargissement de la recherche concernant le cycle global de l'azote et la reconnaissance récente de l'importance des zones humides dans la régulation de l'azote réactif terrestre. Dans ce chapitre, une analyse quantitative et qualitative de la littérature sur la dénitrification des zones humides a fourni des informations sur les lacunes actuelles et les tendances de la recherche la plus solide de ces cinquante dernières années. Cette revue a donné une base solide de l'état de l'art de la recherche sur ce sujet, un renforcement que les zones humides sont reconnues comme pertinentes à l'échelle globale, pourtant les estimations globales de la dénitrification ne donnent aucune information précise de la contribution des zones humides naturelles. La conclusion de cette recherche a été la proposition d'une voie conceptuelle qui introduit une dimension spatio-temporelle, pour combler le vide lié aux incertitudes concernant la dynamique des zones humides et le transfert d'azote réactif. Ce concept consiste en une méthodologie basée sur un modèle qui permet d'estimer les moments et les points chauds de la dénitrification dans les zones humides naturelles à l'échelle mondiale en utilisant les observations satellitaires de la Terre.

Pour transformer ce modèle conceptuel en un modèle solide basé sur les processus, une campagne de terrain (**chapitre III**) a été menée, afin de disposer de données de terrain permettant de valider le modèle. Il était prévu d'enregistrer les émissions de  $N_2O$  in situ avec l'inhibition de l'acétylène dans une expérience de protocole en chambre. Pourtant, cette hypothèse n'a pas abouti. L'enregistrement de la dénitrification in situ dans les zones humides naturelles reste une tâche difficile avec les méthodes actuelles disponibles, une campagne plus longue qui permet le suivi à long terme de la zone humide peut aider à attraper les pics de dénitrification, ou s'assurer que les émissions de  $N_2O$  sont suffisamment faibles et donc qu'aucun enregistrement ne soit trouvé. Le protocole de la chambre, dans les champs agricoles, rapporte des résultats réussis, car la dynamique de l'azote est bien connue, que des engrais à base d'azote sont ajoutés et que l'azote réactif est disponible. Outre l'absence d'émissions enregistrées sur le terrain, la campagne a été très utile. Une grande diversité d'écosystèmes de zones humides a été observée et les échantillons de sol collectés ont ensuite été analysés dans des conditions contrôlées en laboratoire. Ces expériences ont fourni des informations exploitables sur la capacité de dénitrification des sols des zones humides. La littérature, les expérimentations au terrain et en laboratoire ont donné des éléments pour proposer des

changements spécifiques pour évaluer la dénitrification dans les écosystèmes des zones humides par la modélisation d'une manière plus spécifique. La majorité des modèles sont développés pour être utilisés dans les champs agricoles et à l'échelle du bassin. Des recherches antérieures dans notre groupe avaient déjà fait quelques pas en avant. Une équation de dénitrification avait déjà été validée dans les zones riveraines et des données satellites avaient déjà été utilisées à l'échelle du bassin. Cependant, l'application à l'échelle globale manquait encore. Par conséquent, un modèle spécifique aux zones humides a été développé et nommé Soil Denitrification Model (SDM).

Ce modèle a été présenté, validé et testé dans le **chapitre IV**. La validation a été faite en utilisant les données collectées et analysées dans le **chapitre III**. Cette étape était importante, car la principale difficulté était d'estimer la capacité de saturation des sols des zones humides. Cette constante a été adaptée aux écosystèmes des zones humides en utilisant la diversité des sols échantillonnés. Ce chapitre est divisé en deux parties. La partie I concerne la validation numérique du SDM avec des échantillons de sol, et la partie II se concentre sur le développement des algorithmes pour pouvoir exécuter le modèle à l'échelle mondiale, avec un pas de temps quotidien pendant une période de neuf ans. Les principales hypothèses, limites et incertitudes sont présentées dans ce chapitre. Elles sont principalement liées à l'imprécision des taux de dénitrification lors de l'analyse à l'échelle locale. En dehors de ces incertitudes, le modèle pourrait fournir une bonne estimation de la dénitrification à l'échelle globale.

Le **chapitre V** n'a été possible que grâce à l'intégration des principaux résultats des **chapitres II, III et IV**. Chacun de ces chapitres était essentiel pour avoir une base solide pour développer un modèle capable d'évaluer la dénitrification dans les zones humides à l'échelle globale. Ce chapitre a pour but de présenter une synthèse des principales fonctions du modèle pour comprendre le rôle des zones humides à l'échelle globale, de manière spatiale et dynamique. L'analyse annuelle et mensuelle a mis en évidence les principaux moments chauds et les principaux points chauds de la dénitrification. Par la suite, les points chauds ont été identifiés en fonction de leur position dans le paysage et le bassin, ainsi que de l'activité humaine. SDM ne calcule pas le ratio d'émission  $R_{N_2O}$ , au lieu de cela différents ratios de la littérature ont été appliqués et la discussion a été placée à ce point. L'évaluation de la dénitrification dans les sols des zones humides exclusivement, n'avait jamais été proposée auparavant à l'échelle mondiale. Ce modèle représente la première tentative de quantifier leur activité, en espérant être la ligne de base pour les études futures qui visent à réduire les incertitudes de la présente évaluation.

Malgré les incertitudes, il montre que la dénitrification dans les zones humides est une fonction importante qui peut être sous-estimée. Elle souligne que le fonctionnement efficace des zones humides absorbe le  $N_2O$  qui pourrait être émis ou transféré vers les écosystèmes aquatiques environnants, ce qui contribue à maintenir une bonne qualité de l'eau. Ces écosystèmes ont une importante capacité de dénitrification, qui, dans un scénario perturbé, est ou sera à l'origine d'une importante rétroaction des émissions de gaz à effet de serre qui contribuent au changement climatique mondial.

Le SDM dans sa forme actuelle donne des résultats satisfaisants du point de vue de l'identification et de l'évolution dans le temps de la fonctionnalité de la dénitrification dans les zones humides, ainsi que de l'identification des moments et des points chauds.

Un grand nombre des points chauds indiqués sont sous-étudiés en termes de capacité de dénitrification. Ces points chauds devraient être des zones prioritaires pour la communauté scientifique afin de développer des recherches plus approfondies. La précision du SDM dépend des données d'entrée, si une classification plus précise des zones humides et de la capacité de saturation en nitrates des écosystèmes locaux est connue, le modèle pourrait fournir des informations plus précises.

La création d'un module qui calcule les émissions de  $N_2O$  avec des taux différenciés en fonction de l'impact anthropique pourrait fournir une estimation plus précise de  $N_2O$  que l'adoption des ratios génériques  $R_{N_2O}$ . Par la suite, la SDM pourrait être corrélée avec les anomalies climatiques et les scénarios climatiques futurs, fournissant ainsi des informations importantes pour réduire la dégradation des écosystèmes.

En retour, cette étude suggère quelques implications politiques, et conseille d'autres études pour l'évaluation compréhensive du GIEC. Mettre l'accent sur le processus de dénitrification et la distribution spatiale par type d'écosystème. Reconnaître les zones humides comme les principaux acteurs du processus de dénitrification à l'échelle mondiale.

Explorer comment le facteur humain peut contrôler le dépôt d'azote qui, à son tour, améliorera les émissions de  $N_2O$  et réduira le déséquilibre des écosystèmes.

Articuler les co-bénéfices potentiels de la dénitrification des zones humides vers les services écosystémiques des zones humides déjà reconnus (par exemple, la qualité de l'eau et la biodiversité).

Promouvoir la préservation des zones humides naturelles pour le contrôle du  $N_2O$  et le retour du  $N_2$  dans l'atmosphère.

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# Appendices

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## APPENDIX CHAPTER II

## Results

Table A2.1. General concepts keywords, no time filter, and last ten years (2009-2019)

Keywords	Most cited article ALL YEARS	Total	LAST 10 YEARS	Total
Nitrogen + Cycling	(Vitousek et al., 1997)	3120	(Tilman et al., 2011)	1637
	(Galloway et al., 2004)	2318	(Xiang et al., 2011)	1077
	(Valko et al., 2005)	2306	(Zhang et al., 2015)	1065
	(Galloway et al., 2008)	2250	(Guo et al., 2010)	1056
	(Gorham, 1991)	2126	(Jeong et al., 2011)	1001
Denitrification	(Galloway et al., 2004)	2 318	(Ettwig et al., 2010)	663
	(Zumft, 1997)	2104	(Butterbach-Bahl et al., 2013)	545
	(Vitousek and Howarth, 1991)	2004	(Jenkyns, 2010)	478
	(Cambardella et al., 1994)	1507	(Paerl et al., 2011)	395
	(J. N. Galloway et al., 2003)	1334	(Haroon et al., 2013)	343
Wetlands soils	(Carpenter et al., 1998)	2856	(Aufdenkampe et al., 2011)	474
	(Davidson and Janssens, 2006)	2692	(Page et al., 2011)	376
	(Raich and Schlesinger, 1992)	2097	(Koven et al., 2011)	364
	(Baldocchi et al., 2001)	1970	(Koegel-Knabner et al., 2010)	354
	(Whiticar, 1999)	1399	(Clark et al., 2011)	325
Wetland* Modelling	(Baldocchi et al., 2001)	1970	(Kirschke et al., 2013)	647
	(MacKenzie et al., 2002)	1905	(Koven et al., 2011)	365
	(Richter et al., 1996)	1094	(Clark et al., 2011)	325
	(Lehner and Döll, 2004)	827	(Bridgham et al., 2013b)	308
	(Smith, 2003)	811	(Kirwan et al., 2010)	290
Global Nitrogen	(Vitousek et al., 1997a)	4660	(Butchart et al., 2010)	1837
	(Foley et al., 2005)	4532	(Tilman et al., 2011)	1640
	(Sala et al., 2000)	4238	(Bobbink et al., 2010)	1014
	(Wright et al., 2004)	3138	(Hooper et al., 2012)	761
	(Vitousek et al., 1997b)	3120	(Canfield et al., 2010)	670

Table A.2.2 Specific concepts keywords, no time filter, and last ten years (2009-2019)

Keywords	Most cited article	Total citations	Last 10 years	Total citations
Denitrification, Wetlands	(Conrad, 1996)	1 073	(Deegan et al., 2012b)	320
	(Vymazal, 2007)	1062	(Martins et al., 2010)	243
	(Howarth et al., 1996)	1042	(Liu et al., 2010)	192
	(Bohlke and Denver, 1995)	415	(Pardo et al., 2011)	181
	(Vymazal, 2005)	407	(Garcia et al., 2010)	180
	(Schlesinger, 2009)	403	(van Groenigen et al., 2011)	174
	(Reddy et al., 1989b)	360	(Giltrap et al., 2010)	152
	(Hedin et al., 1998)	349	(Collins et al., 2010)	132
	(Deegan et al., 2012b)	320	(Bakken et al., 2012)	114
(Craft et al., 2009)	309	(Finlay et al., 2013)	113	
Denitrification Modelling	(Zumft, 1997)	2104	(Butterbach-Bahl et al., 2013)	545
	(Wrage et al., 2001)	947	(Beaulieu et al., 2011)	215
	(Seitzinger et al., 2006)	765	(Sanford et al., 2012)	199
	(Li et al., 1992)	712	(Philippot et al., 2013)	180
	(Tyrrell, 1999)	695	(Jones et al., 2013)	177
	(Mulholland et al., 2008)	654	(Hwang et al., 2011)	165
	(Hellinga et al., 1998)	643	(Bernot et al., 2010)	165
	(Mino et al., 1998)	614	(Saggar et al., 2013)	145
	(Gujer et al., 1999)	552	(Kalvelage et al., 2013)	135
(Butterbach-Bahl et al., 2013)	545	(Mason et al., 2014)	120	
Nitrogen Wetland*	(Carpenter et al., 1998)	2856	(Vymazal, 2011a)	333
	(Davidson and Janssens, 2006)	2692	(Deegan et al., 2012b)	320
	(Lal, 2004)	1241	(Saeed and Sun, 2012)	253
	(Conrad, 1996)	1073	(Vymazal, 2011b)	191
	(Vymazal, 2007)	1062	(Wu et al., 2015b)	184
	(Howarth et al., 1996)	1042	(Pardo et al., 2011)	181
	(LeBauer and Treseder, 2008)	978	(Yuan and Chen, 2010)	172
	(Koerselman and Meuleman, 1996)	977	(Vymazal, 2013)	169
	(Smith, 2003)	811	(Wu et al., 2014)	166
	(Bobbink et al., 1998)	796	(Chen et al., 2013)	162

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Global wetlands	(Davidson and Janssens, 2006)	2692	(Friedl et al., 2010)	1213
	(Dudgeon et al., 2006)	2266	(Kirschke et al., 2013)	644
	(Raich and Schlesinger, 1992)	2097	(Aufdenkampe et al., 2011)	474
	(Baldocchi et al., 2001)	1970	(Page et al., 2011)	374
	(Lal, 2004)	1241	(Koven et al., 2011)	364
	(Friedl et al., 2010)	1213	(Bulleri and Chapman, 2010)	363
	(Conrad, 1996)	1073	(Deegan et al., 2012b)	320
	(LeBauer and Treseder, 2008)	978	(Butman and Raymond, 2011)	319
	(Tockner and Stanford, 2002)	829	(Bridgham et al., 2013b)	307
Global Wetlands Modelling	(Lehner and Döll, 2004)	827	(Sallenger et al., 2012)	284
	(Baldocchi et al., 2001)	1970	(Kirschke et al., 2013)	644
	(Lehner and Döll, 2004)	827	(Koven et al., 2011)	364
	(Smith, 2003)	811	(Bridgham et al., 2013b)	307
	(Kirschke et al., 2013)	644	(Sallenger et al., 2012)	284
	(Raich and Schlesinger, 1992)	644	(Pekel et al., 2016)	283
	(Gill and Jackson, 2000)	617	(Yvon-Durocher et al., 2014)	226
	(Fung et al., 1991)	585	(Fan et al., 2013)	225
	(Bousquet et al., 2006)	518	(Mitsch et al., 2013b)	217
Nitrogen-cycle wetland*	(Raich et al., 1991)	503	(Teixeira et al., 2013)	216
	(McGuire et al., 2009)	478	(Melton et al., 2013)	201
	(Liao et al., 2008)	406	(Pardo et al., 2011)	181
	(Schlesinger, 2009)	403	(Laanbroek, 2010)	150
	(Cirimo and McDonnell, 1997)	244	(Zhu et al., 2010)	100
	(Saunders and Kalff, 2001)	232	(Yang et al., 2012)	97
	(Richardson et al., 2009)	228	(Denmead et al., 2010)	84
	(Kadlec and Reddy, 2001)	189	(Wang et al., 2011)	70
	(Pardo et al., 2011)	181	(Sims et al., 2012)	68
Nitrogen-cycle wetland*	(Hefting et al., 2004)	154	(Aguilera et al., 2010)	68
	(Laanbroek, 2010)	150	(Jordan et al., 2011)	57
	(Hadad et al., 2006)	130	(Ding et al., 2014)	54

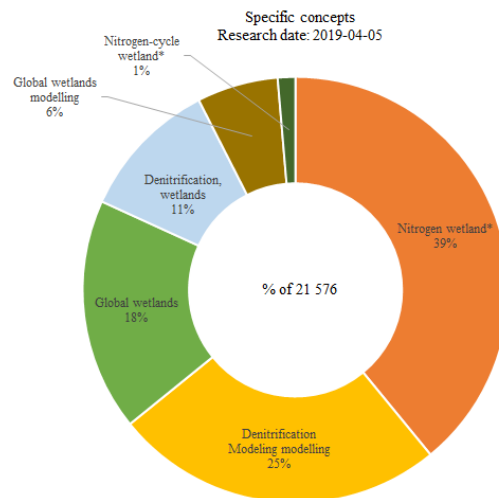
Table A.2.3. General and specific concepts keywords, last five years (2014-2019)

Keywords	Last 5 years	Keywords	Last 5 years
Denitrification	(Hansen et al., 2018) (Strong et al., 2015) (Hu et al., 2015) (Ma et al., 2016) (Craine et al., 2015) (Shu et al., 2015)	Nitrogen cycling	(Zhang et al., 2015) (Pavlova and Thompson, 2016) (Hou et al., 2015) (Liu et al., 2015) (Seh et al., 2016)
Nitrogen-cycle wetland*	(Coban et al., 2015) (Wu et al., 2014) (Shen et al., 2015) (Zhu et al., 2015) (Zhou et al., 2016)	Wetland* Modelling	(Pekel et al., 2016) (Saunio et al., 2016) (Kirwan et al., 2016) (Lovelock et al., 2015) (Schaefer et al., 2016)
Global Wetlands Modelling	(Pekel et al., 2016) (Saunio et al., 2016) (Kirwan et al., 2016) (Schaefer et al., 2016) (Neubauer and Megonigal, 2015)	Wetlands soils	(Kirwan et al., 2016) (Lovelock et al., 2015) (Gao and Wen, 2016) (King et al., 2015) (Neubauer and Megonigal, 2015)
Global Wetlands	(Pekel et al., 2016) (Saunio et al., 2016) (Bennett et al., 2015) (Kirwan et al., 2016) (Schaefer et al., 2016)	Denitrification Modelling	(Hu et al., 2015) (Graham et al., 2016) (Gomez-Velez et al., 2015) (Speth et al., 2016) (Kazakis and Voudouris, 2015)
Nitrogen wetland*	(Wu et al., 2015b) (Kizito et al., 2015) (Herbert et al., 2015) (Shu et al., 2015) (Stanley et al., 2016)	Denitrification Wetlands	(Shu et al., 2015) (Zhi et al., 2015) (Wang et al., 2015) (Wu et al., 2015a) (Zhong et al., 2015)
		Global nitrogen	(Steffen et al., 2015) (Waters et al., 2016) (Diaz et al., 2016) (Zhang and Wang, 2015) (Le Quere et al., 2015)

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**Figure A.2.1.** Percentage of publication per discipline for each general concept: a. Nitrogen + cycling b. Global nitrogen c. denitrification, d. wetlands soils, e. wetland\*modelling.



**Figure A.2.2.** Distribution of number of results by specific keywords found the 05-04-19.

## CURRICULUM VITAE

## APPENDIX CHAPTER IV

Values of denitrification rates from literature in different wetlands ecosystems are reported in table 26, where the present study results are also shown.

**Table 26.** Comparison of denitrification rates from literature and the present study

Land Use	Location	Org Carbon (%)	Mean Denitrification rate	Units	Reference
Riparian soils		2.9	4.32		(Oehler et al., 2009)
Hill slope soils		2.3	2.88		
Uphill Loamy clay wetland	Brittany, France	3	33.6		
Hillslope Loamy clay wetland		5.5	60	mg N kg <sup>-1</sup> d <sup>-1</sup>	(Clément et al., 2003)
Riparian clay wetland		6.1	115.2		
Garonne floodplain undisturbed wetlands	Ocitanie, France		1.92		(Pinay et al., 2000)
Disturbed wetlands	New Jersey (USA)		Mean: 140 Range 20-260	μmoles N m <sup>-2</sup> h <sup>-1</sup>	(Seitzinger, 1994)
Swamp forest		Minesota (USA)		Mean: 220 Range 180-260	μmoles N m <sup>-2</sup> h <sup>-1</sup>
Unenriched sites-Red maple swamps	Rhode island (USA)		Mean: 5 Range: 2-8		(Zak and Grigal, 1991)
Enriched sites-Red maple swamps			Mean: 2.876 Range 0.5-1.6	mg N m <sup>-2</sup> d <sup>-1</sup>	(Hanson et al., 1994)
Mesohaline marsh Forested treatment wetland	Virginia (USA)		Mean: 6.30 Range 0.7-3.9		(Hanson et al., 1994)
Forest soil swamp	Louisiana, USA		1.8-17.6	mmol N m <sup>-2</sup> h <sup>-1</sup>	(Tobias et al., 2001)
Forested wetlands	Beasley Lake watershed Mississippi, USA		100	mg N m <sup>-2</sup> d <sup>-1</sup>	(Boustany et al., 1996)
Rotations rice/soy beans		Bermasoandro Madagascar		157 Range: 82-232	
Trees plantations (eucalyptus and/or legumes and savanna)	Pointe-Noire, Brazzaville		28.32	mg N kg <sup>-1</sup> d <sup>-1</sup>	(Ullah and Faulkner, 2006)
Trees plantations (eucalyptus and/or legumes and savanna)		Congo-		0.037 Range : 0.005-0.115	μg N-N <sub>2</sub> O g <sup>-1</sup> soil
Rainforest	Paracou, French Guiana		0.006 Range : < 0.001-0.006	μg N-N <sub>2</sub> O g <sup>-1</sup> soil	(Barthès et al., 2010)
Mangrove wetland		Kaper Estuary - Laemson Marine National Park, Thailand		0.093 Range : 0.004-0.02071	μg N-N <sub>2</sub> O g <sup>-1</sup> soil
Drying sediment of an Amazon Floodplain lake	Central floodplain, Manaus Brazil		Range: <0.001-0.014	μg N-N <sub>2</sub> O g <sup>-1</sup> soil	(Barthès et al., 2010)
Lowland old-growth tropical	Tapajos National Forest, Brazil		29.5 Range : 13-46	μmoles N m <sup>-2</sup> d <sup>-1</sup>	(Kristensen et al., 1998)
			5.8	μmoles N m <sup>-2</sup> h <sup>-1</sup>	(Koschorreck, 2005)
			6.1-6.9	kg N-N <sub>2</sub> O ha <sup>-1</sup> yr <sup>-1</sup>	(Keller et al., 2005)

## APPENDIX CHAPTER IV

moist forest ecosystem					
Freshwater wetlands		10- 600		mg N m <sup>-2</sup> d <sup>-1</sup>	(Wells et al., 2019)
Constructed wetlands	Model-predicted	3-1020		mg N m <sup>-2</sup> d <sup>-1</sup>	(Martin and Reddy, 1997)
River and stream sediments		18-116		mg N m <sup>-2</sup> d <sup>-1</sup>	(Seitzinger, 1988)
River and Stream sediments		34-57		mg N m <sup>-2</sup> d <sup>-1</sup>	(Seitzinger, 1988)
Coastal and marine sediments		<0.1-359		mg N m <sup>-2</sup> d <sup>-1</sup>	(Seitzinger, 1988)
Swamp peat	Quistochocha floodplain	lake 58 and 65		µg N <sub>2</sub> O-N m <sup>-2</sup> h <sup>-1</sup>	(Pärn et al., 2021)
Freshwater marsh	Central floodplain, Manaus Brazil	1135		mg N m <sup>-2</sup> d <sup>-1</sup>	The present study
Forested wetlands	Central floodplain, Manaus Brazil	20117.5		mg N m <sup>-2</sup> d <sup>-1</sup>	The present study
		Range :12-2209			
		Range :941-3551			

## PARAMETERS

The SDM is associated to a xml file where input data directories, constants and thresholds are defined. The latitude and longitude of the region of interest where the model wants to be run need to be written here. This xml file, facilitates the interaction of the user with the algorithms. Avoids having to modify the code for each case study.

Two xml files were used. One for running the model and then a second to analysed the model outputs.

### PARAMS.XML

```
<?xml version="1.0"?>
<!-- GE_DENIT - Parameter file for GE_DENIT_py code - Coordinates for Asia Central -->
<params>
<gen>
  <smos_SMRZ_dir>../data/SM1SM2/SM1SM2</smos_SMRZ_dir>
  <smos_maxSM_file>../data/SM1SM2/SM2max_hr_test02022021.nc</smos_maxSM_file>
  <ecmwf_dir>../data/AUX_CDFECD/AUX_CDFECD</ecmwf_dir>
  <ease_landcover>../data/AUX_LANDCOVER/ /SM_TEST_AUX_LANDCO_007_001_5.DBL</ease_landcover>
  <soil_prop_dir>../data/SOIL/NetCDF_files</soil_prop_dir>
  <wet_typo_file>../data/landcover/land_cover.nc</wet_typo_file>
  <land_class_file>../data/landcover/kOC_CopyRaster_RasterToNetCD.nc</land_class_file>
  <start_date>01/01/2011</start_date>
  <end_date>01/01/2020</end_date>
  <dt>1.0</dt>
</gen>
<roi>
  <lonmin>50</lonmin>
  <lonmax>150</lonmax>
  <latmin>5</latmin>
  <latmax>50</latmax>
  <res_reduc>1</res_reduc>
</roi>
<selected_RS_variables>
  <selected_SM>SM2</selected_SM>
  <selected_Tsoil_layer>1</selected_Tsoil_layer>
</selected_RS_variables>
```

```

<conf_sat_denit>
  <denit_rate>
    <K_OC_water>0</K_OC_water>
    <K_OC_25_wetlands>0.072</K_OC_25_wetlands>
    <K_OC_irrigated_croplands>0.0</K_OC_irrigated_croplands>
    <K_OC_crop_rainfed>0.0</K_OC_crop_rainfed>
    <K_OC_cropland_mosaic>0.0</K_OC_cropland_mosaic>
    <K_OC_flooded_forest>0.016</K_OC_flooded_forest>
    <K_OC_shrubland>0.0</K_OC_shrubland>
    <K_OC_floodplain>0.062</K_OC_floodplain>
    <K_OC_peatland>0.022</K_OC_peatland>
    <K_OC_brackish>0.076</K_OC_brackish>
    <K_OC_forest>0.0</K_OC_forest>
    <K_OC_grassland>0.0</K_OC_grassland>

    <Th_SM_nit>0.7</Th_SM_nit>
    <Th_SM_denit>0.7</Th_SM_denit>
    <redfr>5</redfr>
    <depth1>0.3</depth1>
    <Temp_opt>25</Temp_opt>
  </denit_rate>
</conf_sat_denit>

<output_options>
  <out_nb_days>5</out_nb_days>
  <save_forc>1</save_forc>
  <save_anc>1</save_anc>
  <extract_TS_pid>1</extract_TS_pid>
  <extract_TS_pid_file>../database/cal_val/L4_ge_denitsample_points.txt</extract_TS_pid_file>
</output_options>
</params>

```

## PARAMS\_ANALYSIS.XML

```

<?xml version="1.0"?>
<!-- GE_DENIT - Parameter file for GE_DENIT_py code - ANALYSIS -->

<params>
<gen>
  <data_dir>../ge_denit_simu/world_SMmax/ROI/out/deni</data_dir>
  <forc_dir>../ge_denit_simu/world_SMmax/ROI/out/forc</forc_dir>
  <data_anc>../ge_denit_simu/world_SMmax/ROI/out/anc/ge_denit_anc.npz</data_anc>
  <data_analysis>../ge_denit_simu/world_SMmax/ROI /Analysis/</data_analysis>
  <ROI_name>Central_Asia</ROI_name>
  <world_watersheds> /data/watersheds/world</world_watersheds>
  <Watershed_name>Yangtze</Watershed_name>
  <watershed_id>96</watershed_id>
  <start_date>01/01/2011</start_date>
  <end_date>01/01/2020</end_date>
  <dt>1.0</dt>

</gen>
<roi>
  <lonmin>50</lonmin>
  <lonmax>150</lonmax>
  <latmin>5</latmin>

```



```

    <latmax>50</latmax>
    <res_reduc>1</res_reduc>
</roi>
<conf_sat_denit>
    <denit_rate>
        <depth1>0.3</depth1>
    </denit_rate>

</conf_sat_denit>

<output_options>
    <out_nb_days>5</out_nb_days>
    <save_forc>1</save_forc>
    <save_anc>1</save_anc>
    <extract_TS_pid>1</extract_TS_pid>

<extract_TS_pid_file>D:/drive1/L4_GE_DENIT/database/cal_val/L4_ge_denitsample_points_Manau.txt</extra
ct_TS_pid_file>
</output_options>
</params>

```

## SCRIPTS

The SDM is composed by modules, that interact to each other and that are needed to run the model dynamically. (I) Ge\_denit\_io, (II) Ge\_denit\_model, (III) Ge\_denit\_plots, (IV) Ge\_denit\_tools, (V) Ge\_denit\_plots.

### 1. GE\_DENIT\_IO

```

## import modules and libraires
from xml.etree import ElementTree
from scipy.io import netcdf
import numpy as np
import scipy.interpolate
import glob
import os

```

```

#####
# functions: Reading main input
#####

```

```

def readXML(xmlFile):
    """ read and parse xml file """
    params={}
    with open(xmlFile, 'rt') as f:
        tree = ElementTree.parse(f)

    for node in tree.iter():

        if not node.text:
            text = "none"
        else:

```

```

    text = node.text
    params[node.tag] = text.split(',')
try:
    params[node.tag]=list(map(int,params[node.tag]) )
except:
    try:
        params[node.tag]=list(map(float,params[node.tag]) )
    except:
        pass
    params.pop('params', None)
    params.pop('\n', None)
return params

def read_ecmwf(filename, soil_layer, llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and Skin temperature from AUX_ECMWF file for a given ROI"""
    nc = netcdf.netcdf_file(filename,'r')
    lon = nc.variables['lon'][[llonmin:llonmax].copy()]
    lat = nc.variables['lat'][[llatmin:llatmax].copy()]
    # lon = nc.variables['lon'][[llonmax:llonmin].copy()]
    # lat = nc.variables['lat'][[llatmax:llatmin].copy()]
    #Tskin = nc.variables['Skin_Temperature'][0,[[llatmin:llatmax,llonmin:llonmax].copy()]
    Tsoil = nc.variables['Soil_Temperature'][0,[[llatmin:llatmax,llonmin:llonmax,soil_layer].copy()]
    #TAir2 = nc.variables['Air_Temperature_2m'][0,[[llatmin:llatmax,llonmin:llonmax].copy()]
    nc.close()
    ## convert to Celcius
    #Tskin=Tskin -273.15
    Tsoil=Tsoil -273.15
    #TAir2=TAir2 -273.15
    return lon, lat, Tsoil

def read_SM1SM2(filename, variable, llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and Soil moisture file for a given ROI"""
    ###Open SMgrid and interpolate
    nc = netcdf.netcdf_file(filename,'r')
    lon = nc.variables['lon'][[llonmin:llonmax].copy()]
    lat = nc.variables['lat'][[llatmin:llatmax].copy()]
    SM = nc.variables[variable][[[llatmin:llatmax,llonmin:llonmax].copy()]
    nc.close()
    return lon, lat,SM
#####
# functions: Finding ROI and fields
#####
def read_SMmax(filename, variable, llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and SM1SM2 from SM1SM2 file for a given ROI"""
    nc = netcdf.netcdf_file(filename,'r')
    if variable=='SM1':
        SMmax = nc.variables['SM1max'][[llatmin:llatmax,llonmin:llonmax].copy()]
    elif variable=='SM2':
        SMmax = nc.variables['SM2max'][[llatmin:llatmax,llonmin:llonmax].copy()]
    else:
        print('SM variable for max not given')

```

```

nc.close()
SMmax=np.flipud(SMmax)
return SMmax

def read_EASE_AUX_LANDCOVER(filename, llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and SM1SM2 from SM1SM2 file for a given ROI """
    nc = netcdf.netcdf_file(filename,'r')
    lon = nc.variables['lon'][[llonmin:llonmax].copy()]
    lat = nc.variables['lat'][[llatmin:llatmax].copy()]
    land_sea = nc.variables['Land_Sea_Mask'][[llatmin:llatmax, llonmin:llonmax].copy()]
    nc.close()
    return lon, lat, land_sea

def get_lon_lat_vectors(filename):
    nc = netcdf.netcdf_file(filename,'r')
    lon = nc.variables['lon'][:].copy()
    lat = nc.variables['lat'][:].copy()
    nc.close()
    return lon , lat

def get_ROI_coord_indexes(lon, lat, lonmin, lonmax, latmin, latmax):
    """get the min and max indexes for the region of interest """
    idx_lonmin = find_nearest_idx(lon, lonmin)
    idx_lonmax = find_nearest_idx(lon, lonmax)
    idx_latmin = find_nearest_idx(lat, latmin)
    idx_latmax = find_nearest_idx(lat, latmax)
    return idx_lonmin, idx_lonmax, idx_latmin, idx_latmax

def find_nearest_idx(array, value):
    """find index """
    array = np.asarray(array)
    idx = (np.abs(array - value)).argmin()
    return idx

def match_index(lon,lat,lon_wise,lat_wise):
    temp_lon=np.empty((len(lon_wise)))
    temp_lat=np.empty((len(lat_wise)))

    for i_lon in range(len(lon_wise)):
        temp_lon[i_lon]=find_nearest_idx(lon, lon_wise[i_lon])

    for i_lat in range(len(lat_wise)):
        temp_lat[i_lat]=find_nearest_idx(lat, lat_wise[i_lat])

    idlat, idlon = np.meshgrid(temp_lat, temp_lon, sparse=False, indexing='ij')
    return idlon,idlat

def read_soilprop(soil_prop_dir,llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and bulk for a given ROI """

```

```

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'BULK.nc'),'r')
lon = nc.variables['lon'][:lonmin:lonmax].copy()
lat = nc.variables['lat'][:latmax:latmin].copy()
Bulk = nc.variables['BULK_1.tif'][:latmax:latmin,lonmin:lonmax].copy()
#Bulk=np.flipud(Bulk)
nc.close()

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'ORGC.nc'),'r')
OrgC = nc.variables['ORGC_1.tif'][:latmax:latmin,lonmin:lonmax].copy()
#OrgC=np.flipud(OrgC)
nc.close()

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'CLPC.nc'),'r')
CLPC = nc.variables['CLPC'][:latmax:latmin,lonmin:lonmax].copy()
# CEC=np.flipud(CEC)
nc.close()

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'CNrt.nc'),'r')
CNrt = nc.variables['CNrt.tif'][:latmax:latmin,lonmin:lonmax].copy()
#CNrt=np.flipud(CNrt)
nc.close()

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'TCEQ.nc'),'r')
TCEQ = nc.variables['TCEQ'][:latmax:latmin,lonmin:lonmax].copy()
nc.close()

nc = netcdf.netcdf_file(os.path.join(soil_prop_dir,'SDTO.nc'),'r')
SDTO = nc.variables['Sand'][:latmax:latmin,lonmin:lonmax].copy()
nc.close()
return lon, lat, Bulk,OrgC,CLPC,CNrt,TCEQ,SDTO

def read_wet_typo(file_wetlands,lonmin, lonmax, latmin, latmax):
    """ Read longitudes, latitudes and landuse for a given ROI"""
    nc = netcdf.netcdf_file(file_wetlands,'r')
    lon = nc.variables['lon'][:lonmin:lonmax].copy()
    lat = nc.variables['lat'][:latmax:latmin].copy()
    wet_typo = nc.variables['land_use'][:latmax:latmin,lonmin:lonmax].copy()
    #lat=np.flipud(lat)
    nc.close()
    return lon,lat,wet_typo

def read_land_class(file_landclass,lonmin, lonmax, latmin, latmax):
    """ Read longitudes, latitudes and landuse for a given ROI"""
    nc = netcdf.netcdf_file(file_landclass,'r')
    lon = nc.variables['lon'][:lonmin:lonmax].copy()
    lat = nc.variables['lat'][:latmax:latmin].copy()
    land_class = nc.variables['land_class'][:latmax:latmin,lonmin:lonmax].copy()
    nc.close()
    return lon,lat,land_class

```

```

def read_EASE_wetlands(filename, llonmin, llonmax, llatmin, llatmax):
    """ Read longitudes, latitudes and SM1SM2
        from SM1SM2 file for a given ROI"""
    nc = netcdf.netcdf_file(filename,'r')
    lon = nc.variables['lon'][:,llonmin:llonmax].copy()
    lat = nc.variables['lat'][:,llatmin:llatmax].copy()
    wetlands = nc.variables['wetlands'][:,llatmin:llatmax,llonmin:llonmax].copy() #to create
    nc.close()
    return lon, lat, wetlands

def find_time(SM_files_all_list,start_d,end_d):
    SM_files_list=[]
    str_date=int(start_d[0][6:10]+start_d[0][3:5]+start_d[0][0:2])
    end_date=int(end_d[0][6:10]+end_d[0][3:5]+end_d[0][0:2])
    for i_file in range(len(SM_files_all_list)):
        print(i_file)
        cur_file=SM_files_all_list[i_file]
        idate=int(cur_file[-48:-40])
        if idate >= str_date and idate <= end_date:
            SM_files_list.append(cur_file)
    return SM_files_list

def find_time_deni(deni_all_list,start_d,end_d):
    deni_files_list=[]
    str_date=int(start_d[0][6:10]+start_d[0][3:5]+start_d[0][0:2])
    end_date=int(end_d[0][6:10]+end_d[0][3:5]+end_d[0][0:2])
    for i_file in range(len(deni_all_list)):
        print(i_file)
        cur_file=deni_all_list[i_file]
        idate=int(cur_file[-19:-11])
        if idate >= str_date and idate <= end_date:
            deni_files_list.append(cur_file)
    return deni_files_list

# if __name__ == "__main__":

```

## 2. GE\_DENIT\_MODEL

```

## import modules and libraires
import numpy as np
import os
import matplotlib.pyplot as plt
import pandas as pd
from scipy.io import netcdf

#####
# functions: Soil model denitrification
#####

def soil_sat (OrgC, CLPC, SDTO):

```

```

""" Compute soil saturation based in texture input:
    OrgC: Organic carbon g/kg
    CLPL: Clay (%)
    SDTO : Sand (%)
    Output: SMSat (%)
"""

#Prepare input with correct units
clay=CLPC/100
sand= SDTO/100
teta33_t= (-0.251*sand)+(0.195*clay)+(0.011*OrgC)+(0.006*sand*OrgC)-
(0.027*clay*OrgC)+(0.452*sand*clay)+0.229
teta_S33_t=0.278*sand+ 0.034*clay + 0.022 * OrgC - 0.018*sand*OrgC-0.027*clay*OrgC-
0.584*sand*clay+0.078
teta_s33_ = teta_S33_t+((0.636*teta_S33_t)-0.107)
teta33= teta33_t+(1.283*teta33_t*teta33_t - 0.374*teta33_t - 0.015)
tetasat= teta33+teta_s33_-(0.097*sand)+ 0.043
SMSat = tetasat/100

return SMSat

def mineralization(OrgC, C_N, bulk, TCEQ, CLPC,SM,SMmax,Temp, Th_SM_mina):
    """ Compute nitrates content ( $\mu\text{g/g}$ ) = ( $\text{mgN/kg}$ ) (eq.2)
    input:
        OrgC: Organic carbon g/kg
        C/N ratio
        Bulk: Bulk denisty
        TCEQ: Carbonate content gC/kg
        CLPL: Clay (%)
        SM: Soil moisture ( $\text{m}^3$  water  $\text{m}^{-3}$  soil)
    """

    WP=SMmax/3
    SME = np.nan_to_num((np.nan_to_num(SM)-WP)/(SMmax-WP))
    k2 = ((1200)/((CLPC+200)*((0.3*TCEQ)+200)))*bulk*(0.2*(Temp-10))
    OrgN= OrgC/C_N
    Nitrates= OrgN * SME * k2
    value=(Nitrates*1000)/365

    NO3_act= np.where(SME > Th_SM_mina,0.0,value)
    NO3 = np.nan_to_num(np.where(NO3_act>0, NO3_act, 0.0))
    return NO3

def denit_rate(K_OC,BULK,ORG_C,NO3_act,K_NO3,redfr,SM,SMmax, Temp, Temp_opt,Th_SM_denit,depth1):
    """ Compute denitrification Rate (eq. 3)
    K_OC: Rate of decomposition of available organic matter (d-1)
    ORG_C: organic carbon (g C/kgSoil)
    Bulk: dry sediment density (kg/ dm3)
    PORO: sediment porosity (no unit))
    NO3_act: nitrate concentration ( $\mu\text{g N/g soil}$ )
    K_NO3: half-saturation constantfor each soil type

```

```

SM: soil moisture (m3/m3)
SMmax: maximum soil moisture (m3/m3)
R_Denit_mol (denitrification rate) (mol_NO3/ dm3 soil /d)
output:
R_Denit (denitrificaiton rate) (µg/g) =(mgN/kg)
"""

#1. compute soil characteristics

PORO=(1-(BULK/2.65))
SOIL =(BULK*(1-PORO)/PORO )

# temperature factor
T_fac= np.nan_to_num(np.exp(-(Temp - Temp_opt)**2)/(Temp* Temp_opt))

#2. compute orgc_decomp (mol/d)(conversion to mol using Carbon molar mass)
DECOM =( K_OC *(ORG_C/12))

#3. compute Nitrate in soil limiting factor (unitless) input in (mgN/kg)

NO3_CONC=np.true_divide(NO3_act,NO3_act+K_NO3, where=((NO3_act+K_NO3)!=0))
FN=np.nan_to_num(NO3_CONC)

#3. compute soil moisture effect (unitless)
WP=(SMmax/3)

SME_1 = np.nan_to_num((np.nan_to_num(SM)-WP)/(SMmax-WP))

SME= np.where (SME_1 < 0,0,SME_1)

#4. agregate components
R_Denit= np.nan_to_num(0.8 * redfr * SOIL * DECOM * FN * SME * T_fac * 0.5)
#5. Apply thresholds

R_Denit_mole = np.nan_to_num(np.where(SME >= Th_SM_denit, R_Denit,0.0))

#6. Conertion from mol/dm3 d-1 to (µg/g)=(mgN/kg) d-1
R_Denit_fin = np.nan_to_num(R_Denit_mole/SOIL * 14 *1000)
return R_Denit_fin

def NO3_budget(NO3_t1,R_Denit,NO3_act,dt):
    """ compute NO3 budget (eq.1) output: nitrates in soil (mgN/kg)d-1 """
    NO3_t2=np.where(NO3_t1 + NO3_act* dt - R_Denit* dt < 0, 0.0, NO3_t1 - R_Denit * dt + NO3_act * dt)
    return NO3_t2

def denit_update(R_Denit, NO3_t1, NO3_act):
    """ adjust the denitrification according to the NO3 budget available output: real dneitrification (mgN/kg)d-1 """
    R_Denit_Update = np.where(NO3_t1 + NO3_act - R_Denit < 0, NO3_t1 + NO3_act, R_Denit)

```

```

return R_Denit_Update
#####
# if __name__ == "__main__":

```

### 3. GE\_DENIT\_PLOTS

```

## import modules and libraires
import numpy as np
import matplotlib.pyplot as plt
from datetime import datetime
from mpl_toolkits.basemap import Basemap

def make_forcplot(filename):
    data=np.load(filename)
    ## plots
    plt.subplot(211)
    plt.imshow(data['Tsoil'], interpolation='none',cmap='jet')
    plt.title('Tsoil')
    plt.colorbar()

    plt.subplot(212)
    plt.imshow(data['SM'], interpolation='none',cmap='jet')
    plt.title('SM')
    plt.gcf().set_size_inches(6, 6)
    plt.colorbar()

    plt.show()

def make_denitplot(filename):
    data=np.load(filename)
    make_map(data['lat'],data['lon'],data['R_NO3'],'R_NO3.png','R_NO3',0.01,data['R_NO3'].max())

def make_ancplot(filename):
    data=np.load(filename)
    for key in data:
        print(key)
    #### soil properties plots
    make_map(data['lat'],data['lon'],data['Bulk'],'bulk.png','Bulk_opt',0.001,0.1)

    plt.subplot(321)
    plt.imshow(data['Bulk'],cmap='gist_ncar')
    plt.title('Bulk')
    plt.colorbar()

    plt.subplot(322)
    plt.imshow(data['OrgC'],cmap='gist_ncar')
    plt.title('OrgC')
    plt.colorbar()

```



```
plt.subplot(323)
plt.imshow(data['TCEQ'],cmap='gist_ncar')
plt.title('TCEQ')
plt.colorbar()
```

```
plt.subplot(324)
plt.imshow(data['CNrt'],cmap='gist_ncar')
plt.title('CNrt')
plt.colorbar()
```

```
plt.subplot(325)
plt.imshow(data['CLPC'],cmap='gist_ncar')
plt.title('CLPC')
plt.colorbar()
```

```
plt.subplot(326)
plt.imshow(data['SMmax'],cmap='gist_ncar')
plt.title('SMmax')
plt.colorbar()
```

```
plt.gcf().set_size_inches(6, 10)
plt.show()
# KOC_plots
plt.subplot(211)
plt.imshow(data['KOC_opt'],cmap='jet')
plt.title('KOC_opt')
plt.colorbar()
```

```
plt.subplot(212)
plt.imshow(data['land_class'],cmap='nipy_spectral')
plt.title('land_class')
plt.gcf().set_size_inches(12, 12)
plt.colorbar()
plt.show()
```

```
def make_ancmap(filename):
    data=np.load(filename)
    for key in data:
        print(key)
    ## soil KOC plots
    make_map(data['lat'],data['lon'],data['KOC_opt'],'test.png','KOC_opt',0.001,0.1)
```

```
def make_map(lat,lon,DATA,outfilename,title,v_min,v_max):
    plt.figure(figsize=(12,12))

    plt.title(title)
    lon=np.squeeze(lon)
    lat=np.squeeze(lat)
    parallels = np.arange(-55.,83.,20.)
    meridians = np.arange(-180.,180.,20.)
```

```
map= Basemap(projection='cyl', llcrnrlon=lon[0],llcrnrlat=lat[-1],urcrnrlon=lon[-1],urcrnrlat=lat[0],
resolution = 'h')
```

```
map.readshapefile('*\* \wetlands','Wetlands',color='white', linewidth=0.1)
```

```
#####for denitrification
cmap=plt.cm.get_cmap('YlOrRd')
cmap.set_under('slategray')
grid_x,grid_y = np.meshgrid(np.squeeze(lon),np.squeeze(lat))
im=map.pcolormesh(grid_x, grid_y, DATA, cmap=cmap, vmin=v_min, vmax=v_max)
## labels = [left,right,top,bottom]
map.drawparallels(parallels,labels=[True,False,False,False], color='k', linewidth=0.05)
map.drawmeridians(meridians,labels=[False,False,False,True], color='k', linewidth=0.05)
map.drawcoastlines(linestyle="solid",color='gray' , linewidth=0.07)
map.drawmapboundary(fill_color='azure')
##### map.readshapefile()
im_ratio = DATA.shape[0]/DATA.shape[1]
plt.colorbar(im,fraction=0.046*im_ratio, pad=0.05)
plt.savefig(outfilename, bbox_inches='tight',dpi=200)
plt.show()
```

```
def create_plot(table,variable_name,path_out, Basin,color):
```

```
for i in range(0,len(data)):
    table['DATES'][i]= datetime.strptime(str(table['Date'][i]),'%Y%m%d')
if table.empty :
    print(Basin,' table is empty')

else:
    table['DATES'] = pd.to_datetime(table['DATES'])

    median_list=table.groupby(table['DATES'].dt.month)[variable_name].median()
    sem_list=table.groupby(table['DATES'].dt.month)[variable_name].sem()

    plt.plot(table['DATES'].dt.month.unique(), median_list,color=color)
    plt.fill_between(x=table['DATES'].dt.month.unique(),y1=median_list-sem_list,y2=median_list+sem_list,
alpha=0.3,color=color)

    plt.title("Monthly variation of "+variable_name)
    plt.xlabel("Months")
    plt.ylabel(variable_name+" (kgN.$ha^{-1}$)")
    plt.savefig(path_out+variable_name+'_Monthly_variation_'+str(table['DATES'].dt.year[0])+'_'+str(table['DATES']
).dt.year[len(table['DATES'])-1])+'_'+Basin+'.png',dpi=300)
    plt.show()

if __name__ == "__main__":
```

#### 4. GE\_DENIT\_TOOLS

```
## import modules and libraires
```

```

import os
import glob
from datetime import datetime
import numpy as np
from scipy.io import netcdf
import scipy
import time

import ge_denit_io

```

```

def resample_soil(Bulk,OrgC,CLPC,CNrt,TCEQ,dx):

```

```

    Bulk_int=Bulk[:,dx,::dx]
    OrgC_int=OrgC[:,dx,::dx]
    CLPC_int=CLPC[:,dx,::dx]
    CNrt_int=CNrt[:,dx,::dx]
    TCEQ_int=TCEQ[:,dx,::dx]

```

```

    Bulk_int=np.where(Bulk_int<0.0,np.nan,Bulk_int)
    OrgC_int=np.where(OrgC_int<0.0,np.nan,OrgC_int)
    CLPC_int =np.where(CLPC_int<0.0,np.nan,CLPC_int)
    CNrt_int=np.where(CNrt_int<0.0,np.nan,CNrt_int)
    TCEQ_int=np.where(TCEQ_int<0.0,np.nan,TCEQ_int)

```

```

    return Bulk_int,OrgC_int,CLPC_int,CNrt_int,TCEQ_int

```

```

def generate_KOC(land_class,params):

```

```

    land_class_int = land_class[:,params['res_reduc']][0,::params['res_reduc']][0]
    KOC_opt_int = np.zeros(np.shape(land_class_int))+params['K_OC_grassland'][0]

```

```

    KOC_opt_int=np.where(land_class_int==12 ,params['K_OC_25_wetlands'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==11 ,params['K_OC_irrigated_croplands'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==14 ,params['K_OC_crop_rainfed'][0],KOC_opt_int)

```

```

    KOC_opt_int=np.where(land_class_int==20 ,params['K_OC_cropland_mosaic'][0],KOC_opt_int)

```

```

    KOC_opt_int=np.where(land_class_int==5 ,params['K_OC_flooded_forest'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==160,params['K_OC_flooded_forest'][0],KOC_opt_int)

```

```

    KOC_opt_int=np.where(land_class_int==30 ,params['K_OC_shrubland'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==110,params['K_OC_shrubland'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==150,params['K_OC_shrubland'][0],KOC_opt_int)

```

```

    KOC_opt_int=np.where(land_class_int==4 ,params['K_OC_floodplain'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==9 ,params['K_OC_floodplain'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==10 ,params['K_OC_floodplain'][0],KOC_opt_int)
    KOC_opt_int=np.where(land_class_int==180,params['K_OC_floodplain'][0],KOC_opt_int)

```

```

    KOC_opt_int=np.where(land_class_int==8 ,params['K_OC_peatland'][0],KOC_opt_int)

```

```

KOC_opt_int=np.where(land_class_int==6 ,params['K_OC_brackish'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==7 ,params['K_OC_brackish'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==170,params['K_OC_brackish'][0],KOC_opt_int)

KOC_opt_int=np.where(land_class_int==40 ,params['K_OC_forest'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==50 ,params['K_OC_forest'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==60 ,params['K_OC_forest'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==70 ,params['K_OC_forest'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==90 ,params['K_OC_forest'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==100,params['K_OC_forest'][0],KOC_opt_int)

KOC_opt_int=np.where(land_class_int==120,params['K_OC_grassland'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==130,params['K_OC_grassland'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==140,params['K_OC_grassland'][0],KOC_opt_int)

KOC_opt_int=np.where(land_class_int==1 ,params['K_OC_water'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==2 ,params['K_OC_water'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==3 ,params['K_OC_water'][0],KOC_opt_int)
KOC_opt_int=np.where(land_class_int==210,params['K_OC_water'][0],KOC_opt_int)

# KOC_opt_int=np.where(land_class_int==-46,0.0,KOC_opt_int) #remapping of land cover on 32bit float

return KOC_opt_int,land_class_int

##### resample all the other databases (SM, TEMP, LANDUSE,FERTILIZERS)

def log_info_message(info_message,message):
    message="[info]" + str(datetime.now())+' '+message
    info_message.append(message)
    print(message)
    return info_message

def remap(values,index_list,shape):
    mapx= np.empty(shape) #, dtype='float32')
    # mapx[index_list[0],index_list[1]]=values.astype(np.float32)
    n=0
    #bg=values.astype(np.float32)
    for i in range(np.size(index_list[0])):
        mapx[index_list[0][i]][index_list[1][i]]=values[n]
        n=n+1

    return mapx

def SMmax(smos_dir):
    SM_files_list=sorted(glob.glob(smos_dir+'/*/*.nc'))
    SM1max=np.zeros((584,1388))
    SM2max=np.zeros((584,1388))

```

```

nc = netcdf.netcdf_file(SM_files_list[0], 'r')
lon = nc.variables['lon'][:].copy()
lat = nc.variables['lat'][:].copy()
nc.close()

for i_file in range(len(SM_files_list)):
    print(SM_files_list[i_file])
    nc = netcdf.netcdf_file(SM_files_list[i_file], 'r')
    # SM1 = nc.variables['SM1'][:,:].copy()
    SM2 = nc.variables['SM2'][:,:].copy()
    nc.close()
    # SM1max= np.maximum(SM1max,SM1)
    SM2max= np.maximum(SM2max,SM2)
    # SM1max=np.flipud(SM1max)
    SM2max=np.flipud(SM2max)
    df=xr.DataArray(SM2max,dims= dict(lon=(lon),lat=(lat)),
attrs=dict(description="SM2MAX_lr.",units="m3/M3"))

    df.to_netcdf('T:/GMOD/Students-CDD/PhD/Columba_MARTINEZ/columba/data/SM1SM2/SM2max_lr.nc')
    return lon,lat,SM1max,SM2max

def SMmax_hr(data_dir):
    # get list of files:
    # SM_files_list=sorted(glob.glob(os.path.join(data_dir,'SM1SM2/SM1SM2/*/*201201*T*.nc')))

    SM_files_list=sorted(glob.glob(os.path.join(data_dir,'SM1SM2/SM1SM2/*/*201[1,2,3,4,5,6,7,8,9]*T*.nc')))
    #SM_files_list=sorted(glob.glob(smos_dir+'/*/**.nc'))

    #1 read one file to get lat, lon of the EASE2 grid 25km SMOS
    nc = netcdf.netcdf_file(SM_files_list[0], 'r')
    lon_lr = nc.variables['lon'][:].copy()
    lat_lr = nc.variables['lat'][:].copy()
    nc.close()

    #2 get the land sea mask for EASE2
    nc =
netcdf.netcdf_file(os.path.join(data_dir,'AUX_LANDCOVER/ .././SM_TEST_AUX_LANDCO_20050101T000000_2
0500101T000000_007_001_5.DBL'), 'r')
    # nc = netcdf.netcdf_file('T:/GMOD/Students-
CDD/PhD/Columba_MARTINEZ/columba/data/AUX_LANDCOVER/SM_TEST_AUX_LANDCO_20050101T000000_
20500101T000000_007_001_5/SM_TEST_AUX_LANDCO_20050101T000000_20500101T000000_007_001_5.D
BL', 'r')
    ease_land_sea = nc.variables['Land_Sea_Mask'][:,:].copy()
    nc.close()

    #4 read lat, lon of the high resolution grid SMOS
    nc = netcdf.netcdf_file(os.path.join(data_dir,'SOIL/NetCDF_files/BULK.nc'),'r')
    lon_hr = nc.variables['lon'][:].copy()

```

```

lat_hr = nc.variables['lat'][:].copy()
nc.close()

#5 initialize the global map SMmax
SM2max_world=np.zeros((np.size(lat_hr,0),np.size(lon_hr,0)))

# define regions

world_coord_cut_name=["zone1","Zone2","Zone3","zone4","zone5"]
world_coord_cut_lon_min=[-170,-20, 39, 69,99]
world_coord_cut_lon_max=[-32, 40, 70, 100,179]
world_coord_cut_lat_min=[-60, -45,-45,-45,-45]
world_coord_cut_lat_max=[75, 75 , 75, 75,75]

# 6. run over regions
for i_wise in range(len(world_coord_cut_name)):

    #6.1 determine world continent limit coordonates
    lonmin=world_coord_cut_lon_min[i_wise]
    lonmax=world_coord_cut_lon_max[i_wise]
    latmin=world_coord_cut_lat_min[i_wise]
    latmax=world_coord_cut_lat_max[i_wise]
    print("Reading",world_coord_cut_name[i_wise],"coordinates ")
    #6.2 extract the selected grid

    [idx_lonmin, idx_lonmax, idx_latmin, idx_latmax]=ge_denit_io.get_ROI_coord_indexes(lon_hr, lat_hr,
lonmin, lonmax, latmin, latmax)
    lon_wise_hr = lon_hr[idx_lonmin:idx_lonmax]
    lat_wise_hr = lat_hr[idx_latmax:idx_latmin]

    [idx_lonmin_lr, idx_lonmax_lr, idx_latmin_lr, idx_latmax_lr]=ge_denit_io.get_ROI_coord_indexes(lon_lr,
lat_lr, lonmin-0.5, lonmax+0.5, latmin-0.5, latmax+0.5)
    lon_wise_lr = lon_lr[idx_lonmin_lr:idx_lonmax_lr]
    lat_wise_lr = lat_lr[idx_latmin_lr:idx_latmax_lr]

    # 6.3 generate meshgrid
    [lon_wise_hr_mesh,lat_wise_hr_mesh]=np.meshgrid(lon_wise_hr,lat_wise_hr)
    [lon_wise_lr_mesh,lat_wise_lr_mesh]=np.meshgrid(lon_wise_lr,lat_wise_lr)

    SM2max=np.zeros((np.size(lat_wise_hr,0),np.size(lon_wise_hr,0)))

    #3 mesh grid the lat lon EaSE25km
    for i_file in range(len(SM_files_list)):
        print("proc file:",SM_files_list[i_file])
        nc = netcdf.netcdf_file(SM_files_list[i_file],'r')
        SM2 = nc.variables['SM2'][idx_latmin_lr:idx_latmax_lr,idx_lonmin_lr:idx_lonmax_lr].copy()
        nc.close()

    t = time.time()

```

```

SM2_hr=scipy.interpolate.griddata((lat_wise_lr_mesh.flatten()),lon_wise_lr_mesh.flatten()),SM2.flatten(),(lat_
wise_hr_mesh,lon_wise_hr_mesh),method='linear')
    elapsed = time.time() - t
    print(elapsed)
    SM2max= np.maximum(SM2max,SM2_hr)
    SM2max_world[idx_latmax:idx_latmin,idx_lonmin:idx_lonmax]=SM2max

return lon_hr,lat_hr,SM2max_world

```

```

def sub2ind(array_shape, rows, cols):
    ind = rows*array_shape[1] + cols
    ind[ind < 0] = -1
    ind[ind >= array_shape[0]*array_shape[1]] = -1
    return ind

```

```

def ind2sub(array_shape, ind):
    ind[ind < 0] = -1
    ind[ind >= array_shape[0]*array_shape[1]] = -1
    rows = (ind.astype('int') / array_shape[1])
    cols = ind % array_shape[1]
    return (rows, cols)

```

```

def extract_somme_wetl_type(target_array,array_selection,type_wetl):
    temp=array_selection
    temp[temp!=type_wetl]=0
    temp[temp==type_wetl]=1
    # np.unique(temp)

    target_array_select=target_array*temp

    sum_target_array_select=target_array_select.sum()

    return sum_target_array_select

```

```

def cut_mask(target_array,params):
    rasterD = rasterio.open(params['mask'][0])
    # bsn_msk=params['Watershed_name'][0]
    bsn_msk = rasterD.read(1)
    ## Cut the region interest in the mask
    [LON_wise, LAT_wise] = ge_denit_io.get_lon_lat_vectors('../data/SOIL/NetCDF_files/BULK.nc')
    [idx_lonmin_wise, idx_lonmax_wise, idx_latmin_wise, idx_latmax_wise]=
ge_denit_io.get_ROI_coord_indexes(LON_wise, LAT_wise, params['lonmin'][0],
params['lonmax'][0],params['latmin'][0], params['latmax'][0])

    bsn_msk_select=bsn_msk[idx_latmax_wise:idx_latmin_wise,idx_lonmin_wise:idx_lonmax_wise]
    bsn_msk_select = bsn_msk_select.astype("float")
    bsn_msk_select[bsn_msk_select==255]=np.NaN

```

```
target_array_new=target_array*bsn_msk_select
```

```
return target_array_new
```

## 5. GE\_DENIT\_MAIN

```
## GE_DENIT
## import modules and libraires
import os
import glob
import time
import numpy as np
import scipy.interpolate
import shutil
import matplotlib.pyplot as plt

#####
import ge_denit_io
import ge_denit_model
import ge_denit_tools

info_message=[]
warning_message_ecmwf=list()
##### 0. Initialize simulation #####
message("0. Initialize simulation")
info_message=ge_denit_tools.log_info_message(info_message,message)

##### 0.1 generate folders #####
message("0.1 generate folders ")
info_message=ge_denit_tools.log_info_message(info_message,message)

#clean dirs
cwd=os.getcwd()
cwd

runs_path=os.path.join("../I4_ge_denit_runs","ROI")
param_path=os.path.join(runs_path,"inp","ROI.xml")
outpath =os.path.join(runs_path,'out')
logpath =os.path.join(runs_path,'log')
ease_lat_lon_path=os.path.join(runs_path,"inp","inp_EASE25v2_lon_lat.nc") # add to params

shutil.rmtree(outpath, ignore_errors=True)
shutil.rmtree(logpath, ignore_errors=True)

try:
    os.makedirs(outpath)
    os.makedirs(os.path.join(outpath,'deni'))
    os.makedirs(os.path.join(outpath,'forc'))
    os.makedirs(os.path.join(outpath,'anc'))
    os.makedirs(logpath)
except:
    print('[warning] unable to make outdirs: check if they already exist')

##### 0.2 read params file #####
message("0.2 read params file ")
info_message=ge_denit_tools.log_info_message(info_message,message)
params = ge_denit_io.readXML(param_path)
```



## APPENDIX CHAPTER IV

```
print('Start /end of processing:',params['start_date'][0],'->',params['end_date'][0])
print("ROI: region of
interest:",params['lonmin'][0],params['lonmax'][0],params['latmin'][0],params['latmax'][0])

##### 1. Read Static Inputs #####
message=("1. Read Static Inputs")
info_message=ge_denit_tools.log_info_message(info_message,message)

##### 1.1 Read soil data for ROI #####
message=("1.1 Read soil data for ROI")
info_message=ge_denit_tools.log_info_message(info_message,message)
[LON_wise, LAT_wise] = ge_denit_io.get_lon_lat_vectors(os.path.join(params['soil_prop_dir'][0],'BULK.nc'))
[idx_lonmin_wise, idx_lonmax_wise, idx_latmin_wise, idx_latmax_wise]=
ge_denit_io.get_ROI_coord_indexes(LON_wise, LAT_wise, params['lonmin'][0],
params['lonmax'][0],params['latmin'][0], params['latmax'][0])
[lon_wise, lat_wise, Bulk,OrgC,CLPC,CNrt,TCEQ,SDTO] =
ge_denit_io.read_soilprop(params['soil_prop_dir'][0],idx_lonmin_wise, idx_lonmax_wise, idx_latmin_wise,
idx_latmax_wise)

##### 1.2 landcover classes assing kOC
message=("1.2 Read landcover class for ROI")
info_message=ge_denit_tools.log_info_message(info_message,message)
[lon_wise, lat_wise, land_class] = ge_denit_io.read_land_class(params['land_class_file'][0],idx_lonmin_wise,
idx_lonmax_wise, idx_latmin_wise, idx_latmax_wise)

##### 2. generate grid #####
message=("2. generate grid")
info_message=ge_denit_tools.log_info_message(info_message,message)

##### 2.1 generate new grid for ROI #####
message=("2.1 generate new grid for ROI")
info_message=ge_denit_tools.log_info_message(info_message,message)
if (params['res_reduc'][0]) != 1:
    lon_grid=lon_wise[:,params['res_reduc'][0]]
    lat_grid=lat_wise[:,params['res_reduc'][0]]
else:
    lon_grid=lon_wise
    lat_grid=lat_wise
[lon_grid_mesh,lat_grid_mesh]=np.meshgrid(lon_grid,lat_grid)

##### 2.2 apply new grid to soil data #####
message=("2.2 apply new grid to soil data")
info_message=ge_denit_tools.log_info_message(info_message,message)

[Bulk_int,OrgC_int,CLPC_int,CNrt_int,TCEQ_int]=ge_denit_tools.resample_soil(Bulk,OrgC,CLPC,CNrt,TCEQ,para
ms['res_reduc'][0])
del Bulk,OrgC,CLPC,CNrt,TCEQ,lon_wise,lat_wise

##### 2.3 generate new grid for KOC #####
message=("2.3 generate new grid for KOC")
info_message=ge_denit_tools.log_info_message(info_message,message)

[KOC_opt_int,land_class_int]=ge_denit_tools.generate_KOC(land_class,params)
mask=np.where(KOC_opt_int == 0.0)

##### 2.4 generate ease index and masks #####
```

## APPENDIX CHAPTER IV

```

message=("2.4 generate ease index and masks ")
info_message=ge_denit_tools.log_info_message(info_message,message)

[lon, lat] = ge_denit_io.get_lon_lat_vectors(ease_lat_lon_path)
[idx_lonmin, idx_lonmax, idx_latmin, idx_latmax]= ge_denit_io.get_ROI_coord_indexes(lon, lat,
params['lonmin'][0], params['lonmax'][0],params['latmin'][0], params['latmax'][0])
[lon, lat,ease_land_sea]= ge_denit_io.read_EASE_AUX_LANDCOVER(params['ease_landcover'][0], idx_lonmin,
idx_lonmax, idx_latmin, idx_latmax)
[lon_ease_mesh,lat_ease_mesh]=np.meshgrid(lon,lat)
lat_ease_mesh_masked=lat_ease_mesh[np.where(ease_land_sea>0)]
lon_ease_mesh_masked=lon_ease_mesh[np.where(ease_land_sea>0)]

##### Mask for SMOS_max, Temperature and Landcover
message=("2.3.1 SMOS_max MASK, Temperature and landcover")

SMmax_test=np.load('T:/GMOD/Students-
CDD/PhD/Columba_MARTINEZ/columba/data/SM2hrmax_final.npy')

SM2max_hr=SMmax_test[idx_latmax_wise:idx_latmin_wise,idx_lonmin_wise:idx_lonmax_wise]

##### Mask for Temperature

Tsoil= ge_denit_io.read_ecmwf(params['ecmwf_dir'][0]+os.sep+'2010'+
os.sep+'SM_RE04_AUX_CDFECD_20100113T000000_20100113T235959_300_001_7.DBL',params['selected_Ts
oil_layer'][0],idx_lonmin, idx_lonmax, idx_latmin, idx_latmax)
Tsoil_int=scipy.interpolate.griddata((lat_ease_mesh_masked.flatten(),lon_ease_mesh_masked.flatten()),SM2m
ax_hr[np.where(ease_land_sea>0)].flatten() , (lat_grid_mesh,lon_grid_mesh),method='linear')
Tsoil_int[mask]=np.nan

##### Mask for Landcover
if params['save_anc'][0]==1:
    message=("2.5 saving anc file before loop")
    info_message=ge_denit_tools.log_info_message(info_message,message)
    out_filename = 'ge_denit_anc'
    np.savez(os.path.join(outpath,'anc',out_filename),
lon=np.float16(lon_grid),lat=np.float16(lat_grid),KOC_opt=np.float16(KOC_opt_int),land_class=np.float16(land
_class_int),Bulk=np.float16(Bulk_int),OrgC=np.float16(OrgC_int),CLPC=np.float16(CLPC_int),CNrt=np.float16(C
Nrt_int),TCEQ=np.float16(TCEQ_int),SMmax=np.float16(SM2max_hr))

##### 3. main loop #####
message=("3.0 main loop")
info_message=ge_denit_tools.log_info_message(info_message,message)

SM_files_all_list=sorted(glob.glob(params['smos_SMRZ_dir'][0]+os.sep+'*'+os.sep+'*.nc'))
## Extract files list based on simulation params
SM_files_list=ge_denit_io.find_time(SM_files_all_list,params['start_date'],params['end_date'])

Tstart=time.time()

## initialiez Nitrate stock
NO3_t1=np.zeros(np.shape(Bulk_int))
NO3_t2=np.zeros(np.shape(Bulk_int))
R_NO3_tot=np.zeros(np.shape(Bulk_int))

```

```

NO3_act_tot=np.zeros(np.shape(Bulk_int))
NO3_budget=np.zeros(np.shape(Bulk_int))

#i_file= is the time that will be analyzed as first
i_file=0

for i_file in range(len(SM_files_list)): #len(SM_files_list)):

    if i_file == 0:
        # first file ==> get initial time
        time1=0.0
        NO3_budget
    if i_file == 10: # give estimates for the run
        T10=time.time()
        message=('Expected time to process all files: ' + str((T10-Tstart)*len(SM_files_list)/10.0/60.0)+ ' min')
        info_message=ge_denit_tools.log_info_message(info_message,message)

##### 3.1.read files and interpolate
##### 3.1.a- read, interp and apply mask to SM product
smos_SMRZ_filepath = SM_files_list [i_file]
path_split=smos_SMRZ_filepath.split(os.sep)
message='processing file :'+ str(i_file+1) + '/' + str(len(SM_files_list)) + ' '+ path_split[-1]
info_message=ge_denit_tools.log_info_message(info_message,message)

# get time info
time2=time1+1
print(time2)

[lon, lat, SM] = ge_denit_io.read_SM1SM2(smos_SMRZ_filepath,params['selected_SM'][0],idx_lonmin,
idx_lonmax, idx_latmin, idx_latmax)

SM_int=scipy.interpolate.griddata((lat_ease_mesh_masked.flatten(),lon_ease_mesh_masked.flatten()),SM[np.
where(ease_land_sea>0)].flatten() , (lat_grid_mesh,lon_grid_mesh),method='linear')
SM_int[mask]=np.nan

##### 3.1.b- read, interp and apply mask to ECMWF product
try:
    name_ecmwf_temp='*'+path_split[-1][19:34]+'*.DBL'
    smos_ecmwf_filepath=glob.glob(os.path.join(params['ecmwf_dir'][0],path_split[-2],name_ecmwf_temp))
    [lon, lat, Tsoil] =
ge_denit_io.read_ecmwf(smos_ecmwf_filepath[0],params['selected_Tsoil_layer'][0],idx_lonmin, idx_lonmax,
idx_latmin, idx_latmax)
#interp temp

Tsoil_int=scipy.interpolate.griddata((lat_ease_mesh_masked.flatten(),lon_ease_mesh_masked.flatten()),Tsoil[
np.where(ease_land_sea>0)].flatten() , (lat_grid_mesh,lon_grid_mesh),method='linear')
Tsoil_int[mask]=np.nan
except:
    message='[Warning] ECMWF file not available for : ' + SM_files_list[i_file]
    info_message=ge_denit_tools.log_info_message(info_message,message)
    warning_message_ecmwf.append(SM_files_list[i_file])

##### 3.2. run physical model modules on masked pixels only
##### budget is: NO3_t2 = NO3_t1 - R_NO3 * Dt + R_N_nit * Dt - R_N_assim * DT + R_DNRA * DT +
R_N_input * DT

```

```

#####3.2.1- compute Denitrification Rate R_NO3
# K_OC = ge_denit_model.decom_organic_matter(KOC_opt_int[mask],params['Temp_opt']][0]
,TCEQ_int[mask])
NO3_act = ge_denit_model.mineralization(OrgC_int,CNrt_int,Bulk_int,TCEQ_int,
CLPC_int,SM_int,SM2max_hr,Tsoil_int,params['Th_SM_nit']][0])

KNO3=605

##### 3.2.2 - compute Nitrification
# R_NO3 =
ge_denit_model.denit_rate(KOC_opt_int[mask],Bulk_int[mask],OrgC_int[mask],NO3_act,KNO3,params['redfr']
[0],SM_int[mask],SMmax_int[mask],Tsoil_int[mask],params['Temp_opt']][0],params['Th_SM_denit']][0])
♪
if i_file == 0:
# first file ==> get initial time
NO3_budget = NO3_act

R_NO3 =
ge_denit_model.denit_rate(KOC_opt_int,Bulk_int,OrgC_int,NO3_budget,KNO3,params['redfr']][0],SM_int,SM2
max_hr,Tsoil_int,params['Temp_opt']][0],params['Th_SM_denit']][0], params['depth1']][0])
print(R_NO3.max())
# Calculate denitrification total over the time period
NO3_act_tot=np.nan_to_num(NO3_act_tot+NO3_act)
R_NO3_tot= np.nan_to_num(R_NO3_tot+R_NO3)

##### 3.3 save outputs

# ##### ### 3.3.1 remap outputs
# NO3_act_int = ge_denit_tools.remap(NO3_act,mask,np.shape(Bulk_int))
NO3_act[mask]=np.nan
NO3_act_int = NO3_act
# K_OC_int = ge_denit_tools.remap(K_OC,mask,np.shape(Bulk_int))
#R_NO3_int = ge_denit_tools.remap(R_NO3,mask,np.shape(Bulk_int))
R_NO3[mask]=np.nan
R_NO3_int = R_NO3
# N_sur_int = ge_denit_tools.remap(N_sur,mask,np.shape(Bulk_int))
# NO3_budget = ge_denit_tools.remap(NO3_t2,mask,np.shape(Bulk_int))
NO3_budget = NO3_t2

# if i_file % 2 == 0:

##### ### 3.3.2 save outputs
out_filename = 'ge_denit_out_' + path_split[-1][19:34]
#np.savez(os.path.join(outpath,'deni',out_filename), lon=lon_grid,lat=lat_grid,
NO3_act=NO3_act_int,R_NO3=R_NO3_int,NO3_t2=NO3_budget)
np.savez_compressed(os.path.join(outpath,'deni',out_filename),
lon=np.float16(lon_grid),lat=np.float16(lat_grid),
NO3_act=np.float16(NO3_act),R_NO3=np.float16(R_NO3),R_NO3_tot=np.float16(R_NO3_tot))

if params['save_forc']][0]==1:

out_filename = 'ge_denit_forc_' + path_split[-1][19:34]
np.savez_compressed(os.path.join(outpath,'forc',out_filename),
lon=np.float16(lon_grid),lat=np.float16(lat_grid),Tsoil=np.float16(Tsoil_int),SM=np.float16(SM_int))

```

```
##### end of main loop
message=('End of main loop')
info_message=ge_denit_tools.log_info_message(info_message,message)

### 4. save log files

message=('4. Save log files')
info_message=ge_denit_tools.log_info_message(info_message,message)

log_filename = ('ge_denit_log')
np.save(os.path.join(logpath,'ge_denit_log'),info_message)
np.save(os.path.join(logpath,'ge_denit_warning_ecmwf'),warning_message_ecmwf)

#####
### End of simulation
message=('##### End of simulation ##### \n check: \n' + logpath + '\n ' +
outpath ) info_message=ge_denit_tools.log_info_message(info_message,message)
```

## 6. GE\_DENIT\_ANALYSIS

```
## import modules and libraires
#####
# TO UPDATE
#####
import ge_denit_io
import ge_denit_plots
import ge_denit_tools
import ge_denit_io

import os
import glob
import time
import numpy as np
import scipy.interpolate
import shutil
import rasterio
import matplotlib.pyplot as plt
from datetime import datetime, date, time, timedelta
import pandas as pd

#####
runs_path=r"*/*/*/Analysis"
param_path=os.path.join(runs_path,"inp","param_analysis.xml")
ease_lat_lon_path=os.path.join(runs_path,"inp","inp_EASE25v2_lon_lat.nc")

##### 0.1 read params file #####
message=("0.2 read params file ")

params = ge_denit_io.readXML(param_path)
```

```

data_dir= params['data_dir'][0]
data_anc= params['data_anc'][0]
forc_dir= params['forc_dir'][0]
print('Start /end of processing:',params['start_date'][0], '-->',params['end_date'][0])
outpath= os.path.join(runs_path,'out')
shutil.rmtree(outpath, ignore_errors=True)
try:
    os.makedirs(outpath)
except:
    print('[warning] unable to make outdirs: check if they already exist')

##### 0.2 load data #####

deni_all_list=sorted(glob.glob(data_dir+os.sep+'/*.npz'))
forc_all_list=sorted(glob.glob(forc_dir+os.sep+'/*.npz'))
data=np.load(deni_all_list[0], mmap_mode='r')
print(data.files)
forc=np.load(forc_all_list[0], mmap_mode='r')
print(forc.files)
Tsoil=forc["Tsoil"]
SM=forc["SM"]
dnit=data["R_NO3"]
deni_files_list=ge_deni_io.find_time_deni(deni_all_list,params['start_date'][0],params['end_date'][0])
print ('0.2 load data R_NO3')

##### 0.3 data initialaton #####

init=np.load(deni_all_list[0], mmap_mode='r')
Deni_max=np.zeros(np.shape(init["R_NO3"]))
deni_sum=np.zeros(np.shape(init["R_NO3"]))
sum_month=np.zeros(np.shape(init["R_NO3"]))
Deni_mean=np.zeros(np.shape(init["R_NO3"]))
print ('0.3 initialization')

##### 0.4 input parameters for conversion #####

anc=glob.glob(data_anc)
anc=np.load(anc[0])
Bulk_int=anc["Bulk"]
depth=params['depth1'][0]

##### maximum by day by pixel

for i_file in range(len(deni_files_list)):
    print(deni_files_list[i_file][-19:-11])
    data=np.load(deni_files_list[i_file], mmap_mode='r')
    dataD=np.nan_to_num(data["R_NO3"])
    Deni_max= np.maximum(Deni_max,dataD)

### #out percentile 90 and 10%
Deni_max99 = np.where(Deni_max>np.percentile(Deni_max[Deni_max!=0], 99),0.001,Deni_max)

```

## APPENDIX CHAPTER IV

```

ge_denit_plots.make_map(data['lat'],data['lon'],Deni_max99,'deni_max','deni_max',0.0,np.percentile(Deni_max[Deni_max!=0], 99))

####transforme to kg/ha
RDenit_kg= Deni_max* Bulk_int* depth*10
#### plot
ge_denit_plots.make_map(data['lat'],data['lon'],Rdenit_mask,'deni_max','deni_max',0.001,
np.nan_to_num(Rdenit_mask).max())
#### save
np.save(data_dir+'max',RDenit_kg,allow_pickle=True)

##### interannual mean in kg/ha
i_file=1
for i_file in range (len(deni_all_list)):
    data=np.load(deni_all_list[i_file], mmap_mode='r')
    deni_sum=np.nan_to_num(data["R_NO3"])+deni_sum

#### Total denitrification in mg_g in the whole period
RDenit_mg_g=np.nan_to_num(deni_sum)
##### Total denitrificaiton in kg_ha in the whole period
Denit_kg_ha_tot=(RDenit_mg_g*Bulk_int* depth*10)
##### Average denitrification in kg_ha_yr
R_Denit_kg_yr=Denit_kg_ha_tot/8 ##years of simulation period (8) if less or more update it!

out_filename='denit_interannual'
np.savez(os.path.join(runs_path,out_filename),R_denit_year=np.float16(R_Denit_kg_yr),
Denit_tot=np.float16(Denit_kg_ha_tot))

##### total denitrification by area (kg/ha)
R_Denit_total=RDenit_kg_yr_tot.sum().sum() #in the total period
R_denit_year=R_Denit_kg_yr.sum().sum() #Interannaul mean

#####plot mean annual denitrification by kg/ha
qa_sum=np.quantile(R_Denit_kg_yr,0.999)

ge_denit_plots.make_map(data['lat'],data['lon'],R_Denit_kg_yr,'deni_interannual_mean','Interannual mean
denitrification (kgN ha-1 year-1 )',0.001,qa_sum)
ge_denit_plots.make_map(data['lat'],data['lon'],Denit_kg_av,'deni_interannual_daily_average','Interannual
daily denitrification (kgN-NO3 ha-1 day-1)',0.0001,qa_av)

##### year sum and annual mean in kg/ha

year=0
list_year=('2012','2013','2014','2015','2016','2017','2018', '2019')

i_file=1
for year in range(len(list_year)):
    print(list_year[year])
    count_day=0
    for i_file in range (len(deni_all_list)):

```

```

if deni_all_list[i_file][-19:-15]==list_year[year]:
    count_day=count_day+1
    data=np.load(deni_all_list[i_file], mmap_mode='r')
    deni_sum=np.nan_to_num(data["R_NO3"])+deni_sum

###transforme to kg/ha

RDenit_kg= deni_sum * Bulk_int*depth*10
np.savez(os.path.join(outpath,list_year[year]+'_analysis'), denit_annual_sum=np.float16(RDenit_kg))
deni_sum=np.zeros(np.shape(init["R_NO3"]))

#####plot mean annual denit
path_year=r"*/*/Analysis"
path = params['data_analysis'][0]

for infile in glob.glob(path_year + "/out\\20" + "*" + ".npz"):
    annuel = np.load(infile)
    denit_sum_yr=annuel['denit_annual_sum']

    denit_sum = np.nan_to_num(denit_sum_yr)
    print(denit_sum.max())
    qa_sum=np.quantile(denit_sum,0.999)
    print(qa_sum)
    title_sum = 'annual denitrification ' + str(infile[96:100]) + ' (N\u2082-N+N\u2082O-N) kgN.ha$^{1}$.$$.yr$^{1}$'
    filename=params['ROI_name'][0]+ '_annual_denitrification_' + str(infile[96:100])
    ge_denit_plots.make_map(data['lat'],data['lon'],denit_sum_yr,filename,title_sum,0.0001,700)

##### sum of the same pixel in period of one month and the max is the highest value of the sum.
month=0
list_month=['01','02', '03', '04','05','06','07','08','09','10','11','12']
list_month_name=['Jan','Feb', 'Mar', 'Apr','May','Jun','Jul','Aug','Sep','Oct','Nov','Dec']
Deni_max=np.zeros(np.shape(init["R_NO3"]))

i_file=1
count_day=0
for month in range(len(list_month)):
    print("month=",month+1)
    for i_file in range(len(deni_all_list)):
        # print(deni_files_list[i_file][-19:-11])
        if deni_all_list[i_file][-15:-13]==list_month[month]:
            count_day=count_day+1
            # print(month," and ",i_file)
            data=np.load(deni_all_list[i_file], mmap_mode='r')
            sum_month=np.nan_to_num(data["R_NO3"])+sum_month
            Deni_max= np.maximum(Deni_max,np.nan_to_num(data["R_NO3"]))
    print(sum_month.max())
    print("Day in month",list_month_name[month]," = ",count_day)

#transforme to kg/ha

```



## APPENDIX CHAPTER IV

```

sum_month_kg= sum_month* Bulk_int* depth*10
Deni_max_kg= Deni_max* Bulk_int* depth*10

np.savez(os.path.join(outpath,list_month_name[month]+'_analysis'), Denit_tot=np.float16(sum_month_kg),
Denit_sum=np.float16(sum_month_kg/len(list_year)), Denit_mean=np.float16(sum_month_kg/count_day),
Denit_max=np.float16(Deni_max_kg))
sum_month=np.zeros(np.shape(init["R_NO3"]))
Deni_max=np.zeros(np.shape(init["R_NO3"]))
count_day=0
#end of loop

#####plots for month #####
path_1 = r"*\*\Analysis\out_month"
for infile in glob.glob(path_1 + "/*_analysis.npz"):
    monthly = np.load(infile)
    denit_sum=monthly['Denit_sum']
    print (str(infile[111:114])) ##### upload for showing month
    title_sum = 'monthly denitrification ' + str(infile[111:114] + ' (N\u2082-N+N\u2082O-N) kgN.ha$^{1}$'
1}$\cdot$month$^{1}$') ##### upload for showing month
    filename=params['ROI_name'][0] + '_monthly_denitrification_' + str(infile[111:114]) ##### upload for showing
month
    ge_denit_plots.make_map(data['lat'],data['lon'],denit_sum,filename,title_sum,min,max)#####upload min max

#####
##### ROI ANNUAL OR MONTHLY CUMULE
#####
yearly_path= runs_path + '\out_year'
# monthly_path= runs_path + '\out_month'

ROI=[]

for infile in glob.glob(yearly_path + "/*.npz"):

    data=np.load(infile)
    year = str(infile[101:105]) m
    denit= (data['denit_annual_sum'])
    denit_sum=np.nan_to_num(denit.sum().sum())
    ROI.append([year, denit_sum])
    print (year)
    print(denit_sum)

ROI = pd.DataFrame(ROI, columns = ['Date', 'Denitrification'])
ROI.to_csv(runs_path+'annual_denit_'+params['ROI_name'][0]+''.csv')

#####
##### ROI DAILY
#####

```

```

ROI=[]
for infile in deni_all_list:
    data=np.load(infile)

    fecha = int(infile[-19:-11])

    denit= np.nan_to_num(data['R_NO3'])
    # denit= (data['R_NO3'])
    nitri= np.nan_to_num(data['NO3_act'])
    # nitri= (data['NO3_act'])
    # budget= np.nan_to_num(data['NO3_t2'])

    ##### transformation to kg in ha
    denit_sum=(data['R_NO3']*Bulk_int*depth *10)
    denit_sum=np.nan_to_num(denit_sum.sum().sum())
    print ('denit_sum=',denit_sum)
    bulk=np.nan_to_num(Bulk_int)
    denit=np.nan_to_num(denit*bulk)
    mxim=denit.max().max()
    print ('max=', denit.max().max())

    nitri=np.nan_to_num(nitri*bulk)
    print ('max=', nitri.max().max())

    denit=np.nan_to_num(denit.sum().sum())
    print (denit)
    nitri=np.nan_to_num(nitri.sum().sum())

    denit= denit * depth *10
    print ('denit_sum=' , denit)
    nitri= nitri * depth * 10
    print ('nitri_sum=', nitri)

    ROI.append([fecha, denit, nitri,mxim, denit_sum])
    print (fecha)

ROI = pd.DataFrame(ROI, columns = ['Date', 'Denitrification', 'Nitrification', 'maximum', 'denit_sum'])

ROI.to_csv(runs_path+'/daily_denit_'+params['ROI_name'][0]+'+'.csv')

DATES = []

for l in range(0, len(ROI)):
    date_file = np.array(ROI['Date'], dtype = 'str')
    year = int(date_file[l][0:4])
    month = int(date_file[l][4:6])
    day = int(date_file[l][6:8])

    DATES.append((datetime(year,month,day)).date())

```

```
ROI['Time'] = DATES

fig, ax = plt.subplots(figsize=(27,10), sharex = True)

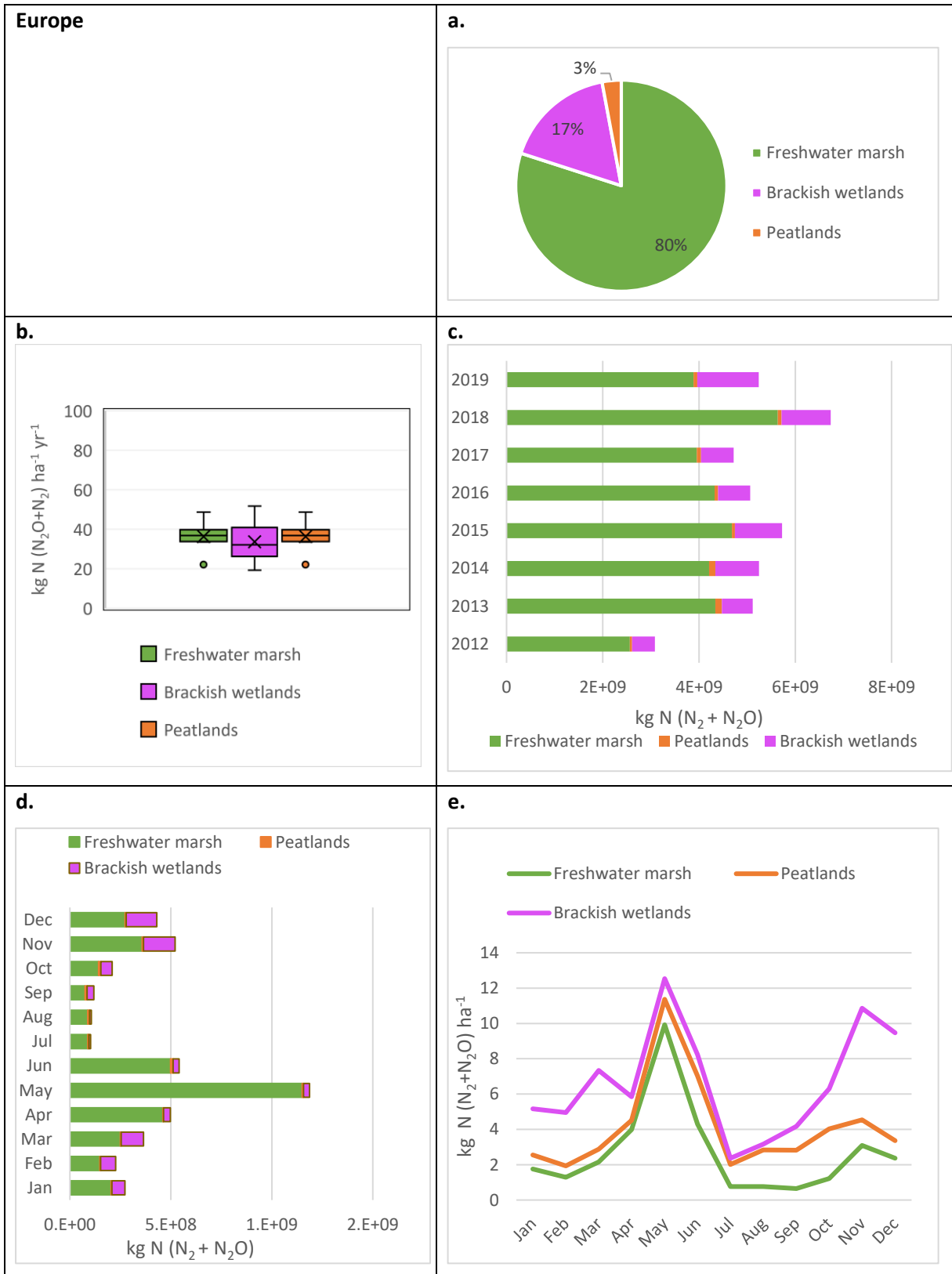
p0 = plt.plot(ROI['Time'], ROI['Denitrification'], color = 'black', linewidth = 1.5, label = "Denitrification")

ax.legend((p0[0]), 'Denitrification in kgN', fontsize = 'x-large', bbox_to_anchor = (0.23,1))
ax.set_xlabel('Date', fontsize = 'xx-large')
ax.set_title("Total Denitrification (kgN) over South America between 2012 - 2019")
ax.set_ylabel('Denitrification kgN')
plt.savefig(runs_path + '/daily_denit'+ params['ROI_name']+'.png', bbox_inches= 'tight')

plt.show()
```

# APPENDIX CHAPTER V

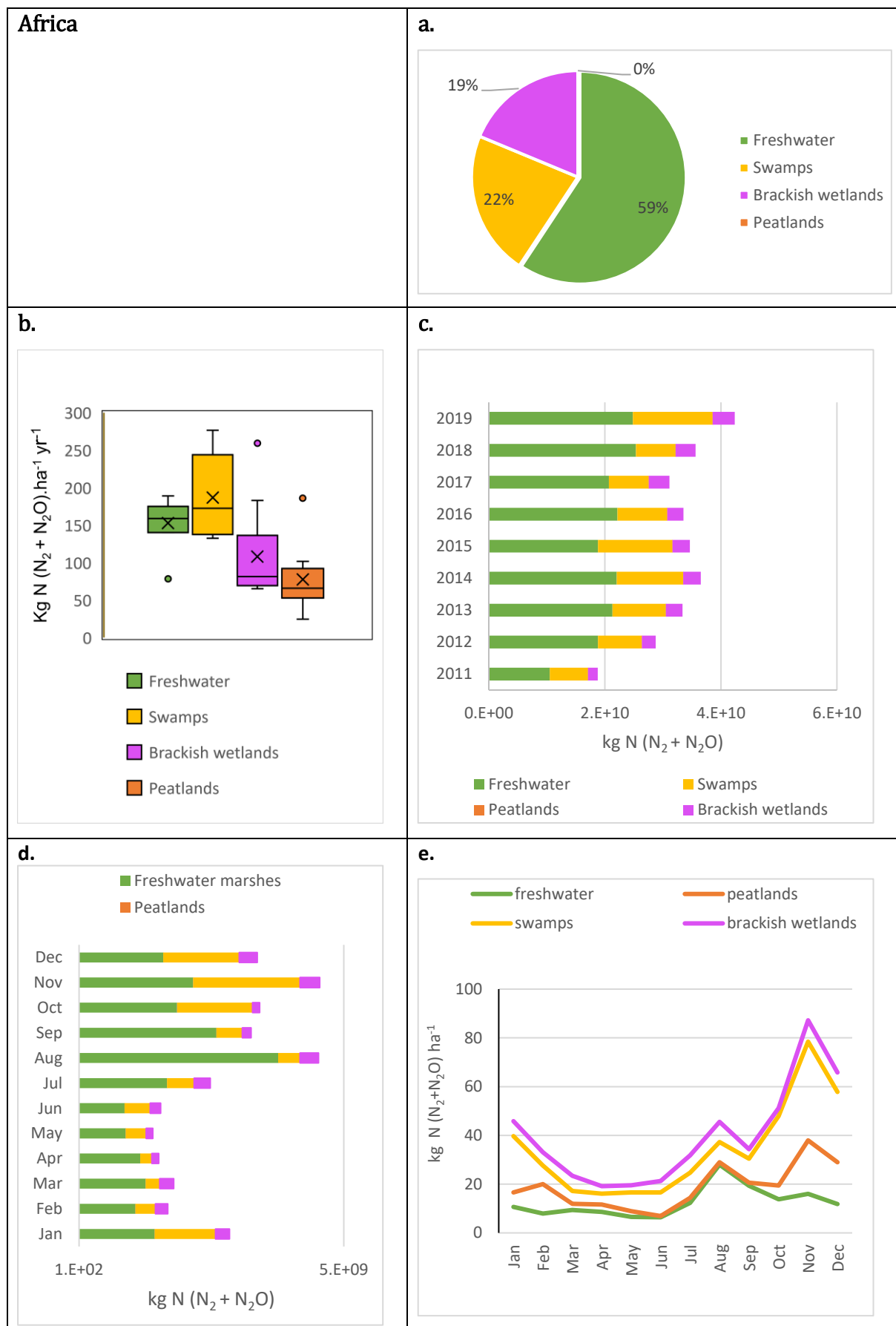
Regional analysis of the SDM at montly and yearly basis.



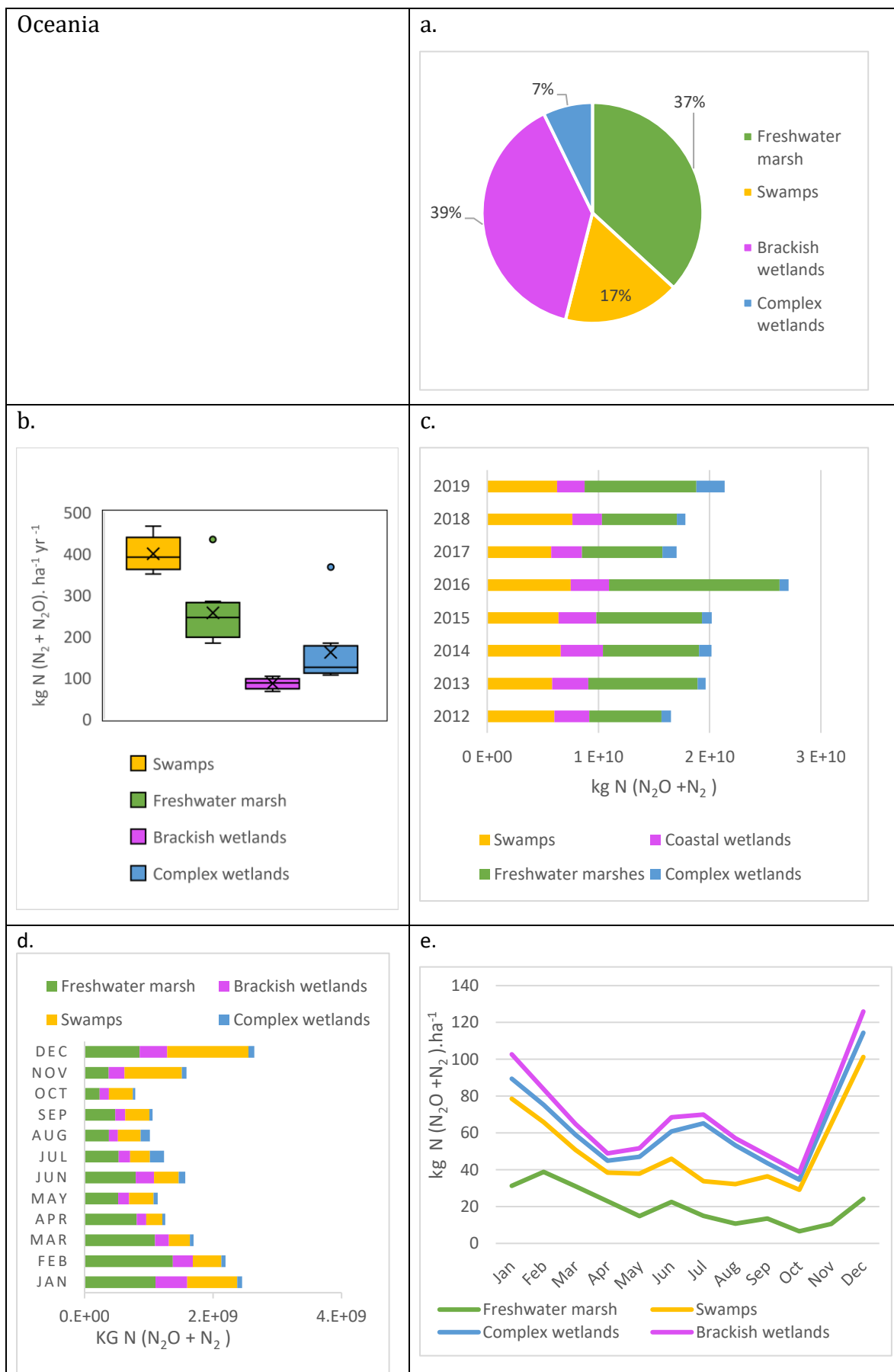
**Figure 49.** Analysis by wetland typologies in European region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.



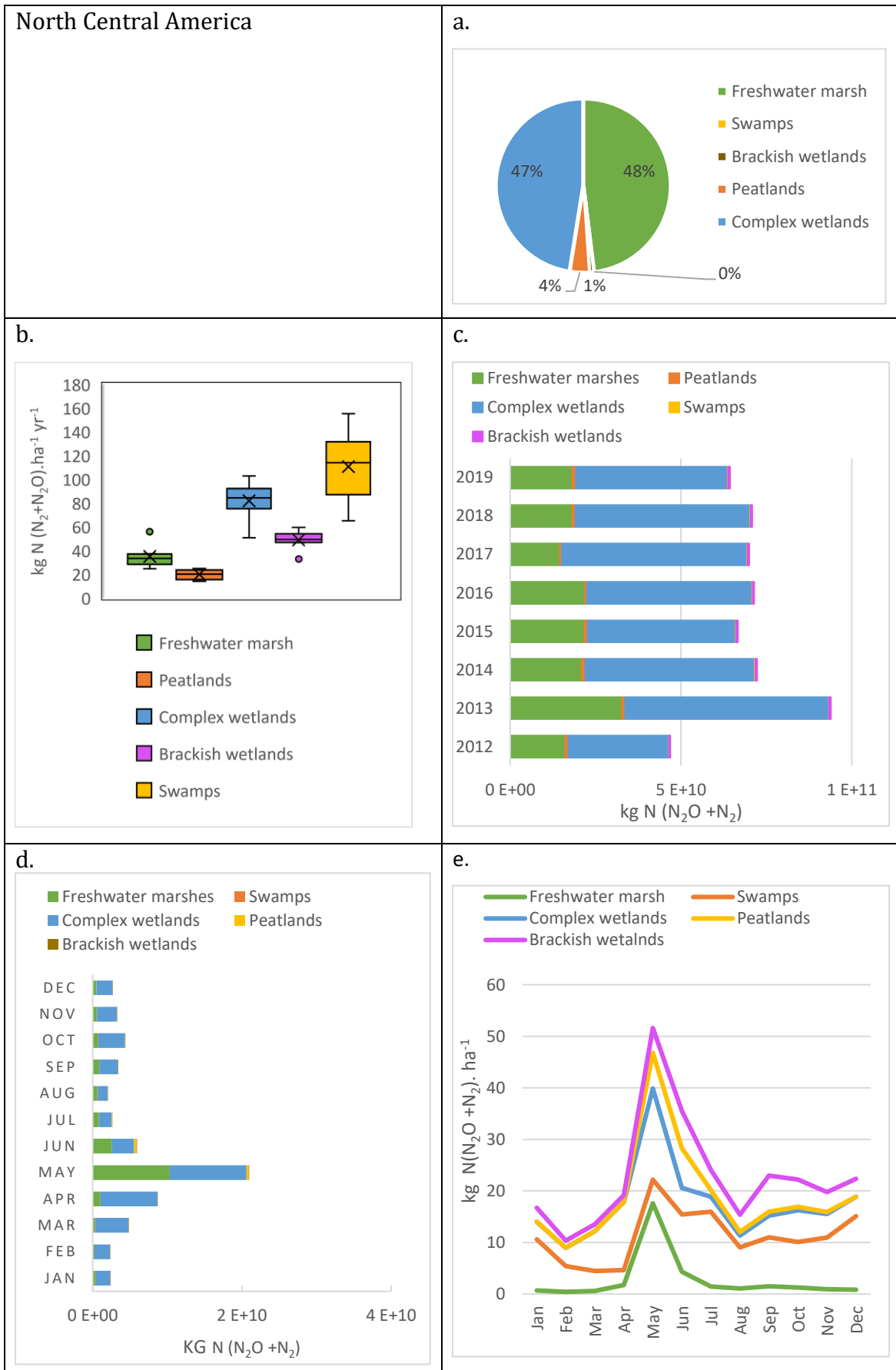
**Figure 50.** Analysis by wetland typologies in South America region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.



**Figure 51.** Analysis by wetland typologies in African region **a.** Wetlands distridution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.

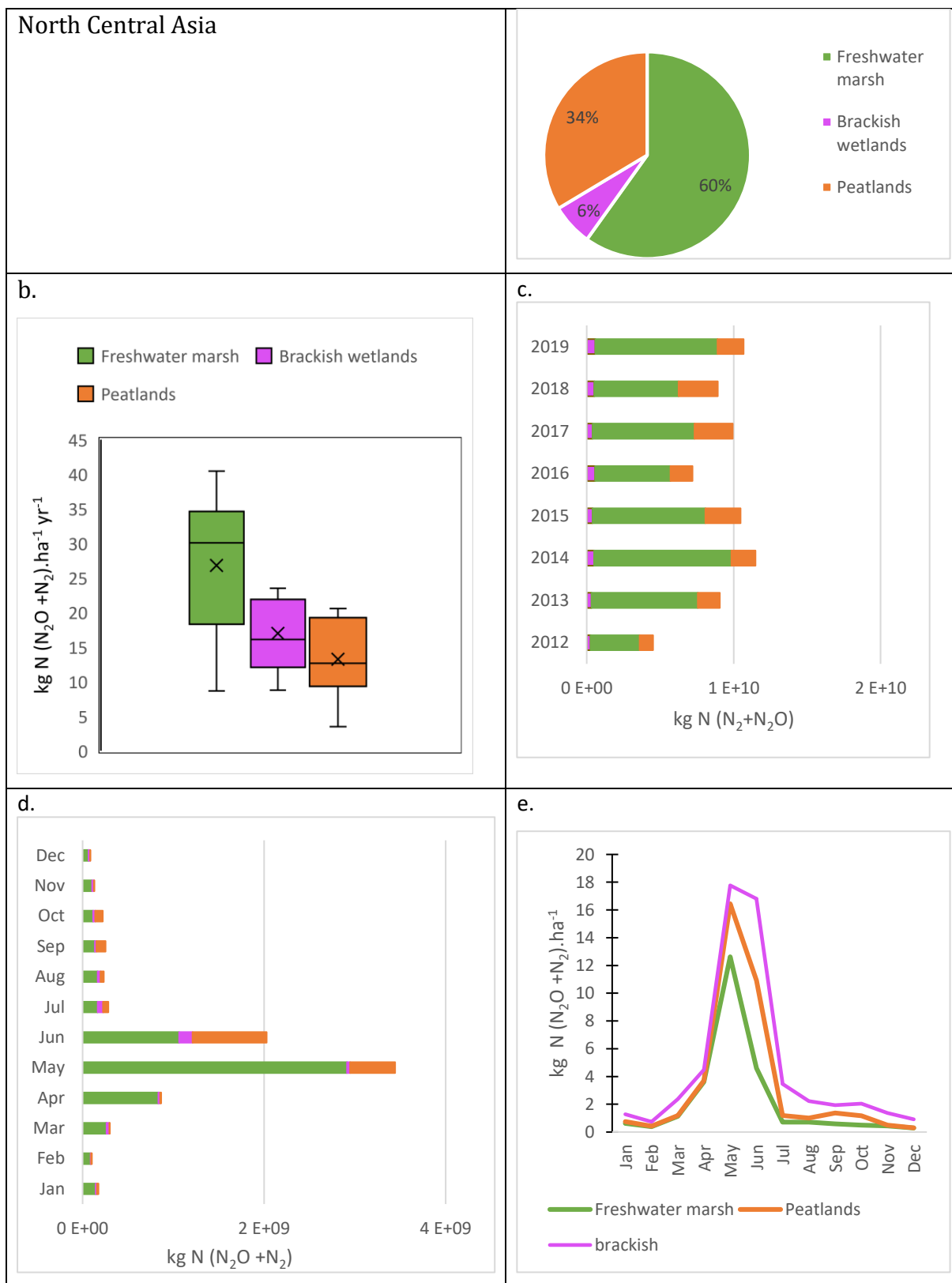


**Figure 52.** Analysis by wetland typologies in Oceania region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.

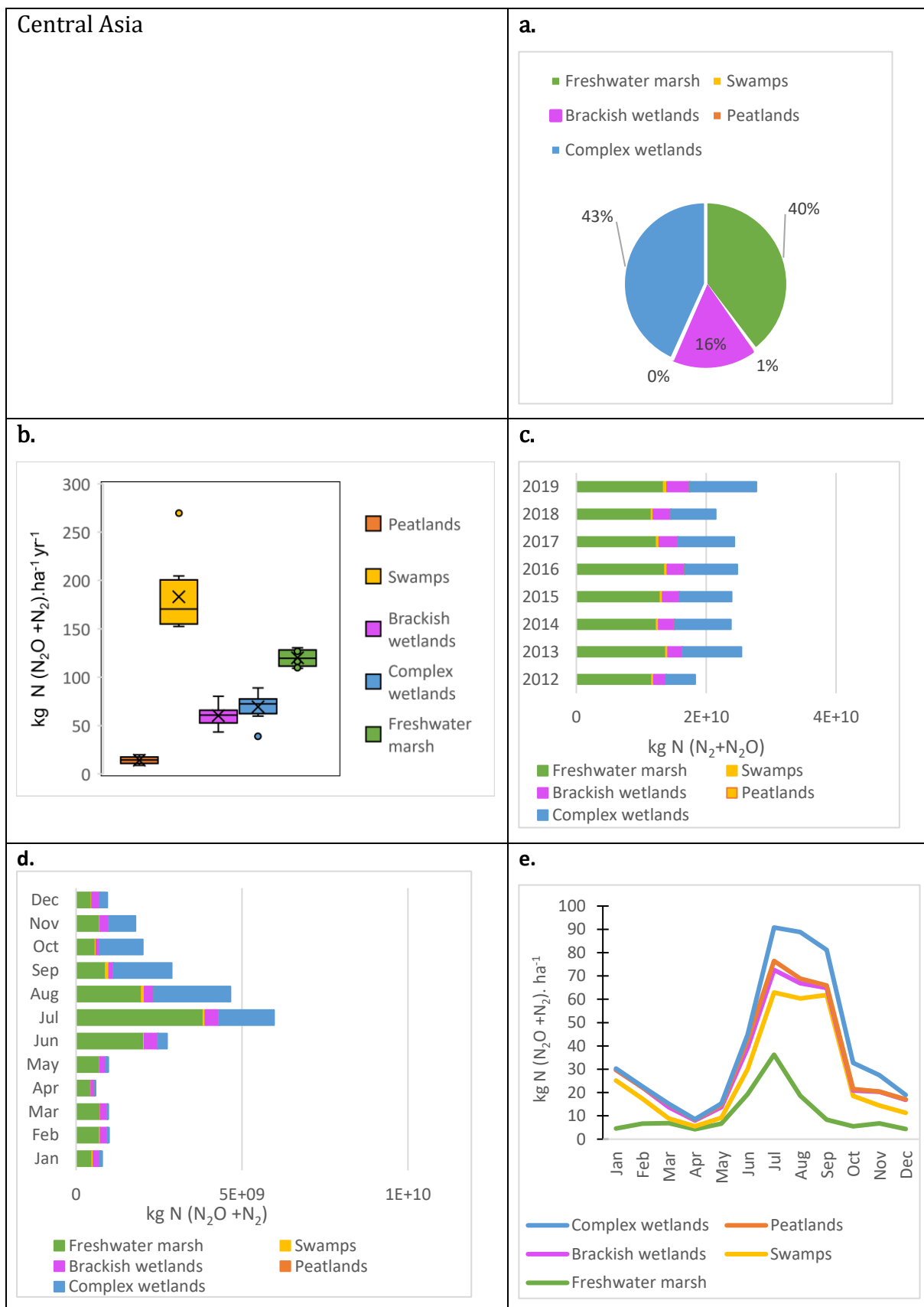


**Figure 53.** Analysis by wetland typologies in North Central America region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.





**Figure 54.** Analysis by wetland typologies in North Central Asia region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.



**Figure 55.** Analysis by wetland typologies in Central South Asia region **a.** Wetlands distribution, **b.** variance of wetland efficiency by year, **c.** total yearly contribution, **d.** Contribution by month, **e.** efficiency by month.

# COLUMBA MARTÍNEZ-ESPINOSA

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## OBJECTIF

Promouvoir des connaissances scientifiques capables d'améliorer les politiques de conservation de la biodiversité et la gestion efficace des ressources naturelles. Poursuivre la compréhension de la dynamique écologique des zones humides à l'échelle locale et mondiale.

## INTÉRÊTS DE RECHERCHE

Dynamique des écosystèmes, développement durable, Interaction homme-nature, zones humides, Modélisation des cycles biogéochimiques, télédétection, données satellitaires, modélisation à l'échelle mondiale, changement climatique.

## FORMATION ACADÉMIQUE

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**LABORATOIRE D'ÉCOLOGIE FONCTIONNELLE ET D'ENVIRONNEMENT** Toulouse, FR  
*Doctorat en Ecologie Fonctionnelle* Sept 2017 – Oct 2021  
Encadrants: Dr. José Miguel Sánchez-Pérez et Sabine Sauvage

**UNIVERSITÉ LIBRE DE BRUXELLES – VRIJE UNIVERSITEIT BRUSSEL** Bruxelles, BE  
*M.Sc. en Biodiversité et écosystèmes tropicaux* Sept 2015 - Jul 2017  
Première classe avec la plus grande distinction (17.3/20)  
Encadrants: Prof. Dr. Farid Dahdouh-Guebas (ULB,BE); Dr. Jean Huges (UFA,NL); Dr. Behara Satyanarayana (UMT, MY); et Stefano Cannicci (UHK, HK)

**UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO (UNAM)** Mexico, MX  
*B.Sc. Biologie* Aug 2010 - May 2015  
Deuxième classe avec mention, division supérieure (8,8/10)  
Encadrant: Dr. Marcelo Rojas Oropeza

## EXPÉRIENCES SCIENTIFIQUES

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- 2021 New York: Séjour de recherche à l'Initiative des sciences de l'environnement avec le professeur Charles J. Vörösmarty, Ph.D. 2019 [Advanced Science Research Center, GC/CUNY ]
- 2020 Manaus: HyBAM Campagne de terrain dans les plaines inondables de l'Amazonie [HyBAM:Hydrology of the Amazon basin]
- 2019 New York: Séjour de recherche à l'Initiative des sciences de l'environnement avec le professeur Charles J. Vörösmarty, Ph.D. 2019 [Advanced Science Research Center, GC/CUNY ]
- 2018 Toulouse: Bourse de recherche - Programme des leaders de la politique d'innovation [Founded by:Campus France, Harvard, MIT, CONACYT, MUFRAMEX]
- 2016 Nepal: International Sustainable School 2016 [Hands-On Institute ]
- 2015 Mexico: Research Assistant Universidad Nacional Autónoma de México, [Funded by: NAPECA 730.01313.037, UNAM40152-3342-1-XII-14]. Responsable: Prof.Dr. Nathalie Cabirol
- 2014 Italy: Internship- Department of Life Sciences and Biotechnology, Università degli Studi di FerraraProject: "Ecosystem services of the Mesola Forest" Responsable: Prof. Anna Elisa Fanno
- 2013 Egypt: Research Assistant - Desert Development Center, American University of Cairo Project:"Water Scarcity Program".[Responsable: Dr. Tina Jaskolski]

## FORMATIONS COMPLÉMENTAIRES

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Formation pratiques théâtrales pour la didactique  
 Formation en ligne Apprendre à coder avec Python  
 2020

UPS- 2021  
 ULB-MOOC

Systèmes d'Information Géographique et l'initiation à la télédétection spatiale ENSAT 2017  
 Diplôme de plongée scientifique avancée FMAS  
 2012

## COMPÉTENCES

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### LANGUAGES

Spanish (Langue maternelle)  
 French (Avancée B2)

English (Avancée C1 - IELTS, 2014)  
 Italian (Avancée C2, CILS, 2011)

### OUTILS

#### MS Office

Word, Excel, Powerpoint  
 Latex

#### Langage de programmation

R, Python,

#### Analyse spatiale et modélisation

ArcGIS, Python

### SCIENTIFIQUES

#### Évaluation des écosystèmes

- Planification des campagnes de terrain
- Analyse des échantillons (sols et eau)
- Protocole expérimental

#### Modélisation environnementale

- Analyse des big data
- Gestion des données satellitaires
- Construction d'algorithmes

### PERSONNELLES

- Discours public
- Gestion du stress
- Travail d'équipe
- Apprentissage rapide

## LEADERSHIP ET DISTINCTIONS

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Bourse Bourse de doctorat CONACYT, Mexique Sept 2017 - Août 2021

Mention Meilleur poster étudiant EuroScience Open Forum ESOF Jul 2018

Mention Best Student presentation IUCN-SSC Mangrove Symposium Sep 2017

Bourse Master's Thesis Grant ULB-VUB, Belgique Aug2016

Bourse Bachelor's Thesis Grant UNAM, Mexique Feb 2014

- Apr 2019 - Création - Président de l'association des étudiants des zones humides de l'Occitane
- Apr 2019 - Present Membre actif de Society of Wetlands Scientist (SWS)
- Jan 2021 - Present Membre actif de Biodiversity Action Europe

## PUBLICATIONS

### 1 Publications

**Martínez-Espinosa, C.,** Sauvage, S., Al Bitar, A., Green A. P., Vörösmarty, J.C., Sánchez-Pérez J. M., **Denitrification in wetlands: a review towards a quantification at global scale** *Sciences of the Total Environment*. CiteScore: 8.6—Impact Factor: 6.551 [DOI:10.1016/j.scitotenv.2020.142398]

**Martínez-Espinosa, C.,** Wolfs, P., Velde, K.V., Satyanarayana, B., Dahdouh-Guebas, F. and Hüge, J., 2020. **Call for a collaborative management at Matang Mangrove Forest Reserve, Malaysia: An assessment from local stakeholders' view point.** in *Forest Ecology and Management*, 458, p.117741. CiteScore:5.6—Impact Factor:3.17 [DOI:10.1016/j.foreco.2019.117741]

Otero, V., Van De Kerchove, R., Satyanarayana, B., Martínez-Espinosa, C., Fisol, M.A.B., Ibrahim, M.R.B., Sulong, I., Mohd-Lokman, H., Lucas, R. and Dahdouh-Guebas, F., 2018. **Managing mangrove forests from the sky: Forest inventory using field data and Unmanned Aerial Vehicle (UAV) imagery in the Matang Mangrove Forest Reserve, Peninsular Malaysia.** in *Forest Ecology and Management*, 411, pp.35-45. CiteScore:5.6—Impact Factor:3.17 [DOI:10.1016/j.foreco.2017.12.049]

Otero V, Martínez-Espinosa C, Dahdouh-Guebas F, Van De Kerchove R, Satyanarayana B, Lucas R., 2017 **Variations in mangrove regeneration rates under different management plans: An analysis of Landsat time-series in the Matang Mangrove Forest Reserve, Peninsular Malaysia** 9th International Workshop on the Analysis of Multitemporal Remote Sensing Images (MultiTemp) 2017 Jun 27 (pp. 1-3). IEEE. [DOI:10.1109/Multi-Temp.2017.8035238]

### 2 International conferences

- Toulouse: HyBAm Scientific Meeting, 2019, presentation of "Natural denitrification in alluvial floodplains of the Amazon, Congo and Orinoco rivers: a modelling approach" [8th HYBAM Scientific Meeting]
- Aarhus: Wetpol international symposium, 2019, presentation of "Nitrogen outgassing (N<sub>2</sub>, N<sub>2</sub>O) by denitrification in wetlands ecosystems worldwide: a modeling approach" [8th International Symposium on Wetland Pollutant Dynamics and Control]
- Toulouse: EuroScience Open Forum ESOF-2018, poster: "Role of wetlands in the regulation of nitrate flows on surface water to N emissions at global scale." [EuroScience Open Forum 2018]
- Bruxelles: European Conference of Tropical Ecology, 2017, presentation of "Crab community structure as ecological indicator of Matang mangrove forest in Malaysia" and poster of "Flying drones over mangroves: monitoring of the Matang Mangrove Forest Reserve in peninsular Malaysia." [European Conference of Tropical Ecology]
- Bremen: Annual Mangrove Symposium of the IUCN-SCC Mangrove Specialist Group, 2017, presentation of "Local stakeholder perception as a key component to improve mangrove management in Matang, Malaysia" [IUCN-SCC Mangrove Symposium 2017]
- Bruges: VLIZ Marine Science Day, 2017, presentation of "Crab community structure as ecological indicator of Matang mangrove forest in Malaysia" [VLIZ Marine Science Day 2017]
- Edinburgh: World water congress XV, 2015, presented "Local actions on water management, for sustainable development in two study cases: Mexico and Egypt" [World Water Congress XV]

# ABSTRACT

The biosphere is undergoing an environmental crisis caused by our energy-intensive economic model. Understanding the regulation and exchange processes of global ecosystems is the key challenge to improve our resilience and reduce our impact on the Earth. The aim of this thesis is to assess the dynamic role of wetland ecosystems in the global nitrogen cycle. The Soil Denitrification Model (SDM) was developed using soil moisture and temperature satellite Earth Observations. The model was validated at local scale with laboratory measurements, then upscale global scale. Identification of hot moments and hot spots in natural wetlands. Southeast Asia and Oceania was identified as the main hot spot. The hot moments varied by region and by typology. May was the hot moment for freshwater marshes and complex wetlands. While brackish wetlands are active all year long and flooded forest, have their peak in December and January. Quantitative estimation of denitrification was estimated at  $169.32 \pm 18.31 \text{ TgN (N}_2\text{O-N + N}_2\text{-N).yr}^{-1}$  and evolution of denitrification in the last 8 year was analysed and linked to global climate anomalies.

## Key words

Wetlands, Denitrification, Global modeling, Earth Observations, Remote Sensing

# RÉSUMÉ

La biosphère subit une crise environnementale causée par notre modèle économique énergivore. Comprendre les processus de régulation et d'échange des écosystèmes globaux est le défi majeur pour améliorer notre résilience et réduire notre impact sur la Terre. L'objectif de cette thèse est d'évaluer le rôle dynamique des écosystèmes des zones humides dans le cycle global de l'azote. Le modèle de dénitrification du sol (SDM) a été développé en utilisant les observations satellitaires de l'humidité et de la température du sol. Le modèle a été validé à l'échelle locale avec des mesures de laboratoire, puis à l'échelle globale. Identification des moments et des points chauds dans les zones humides naturelles. L'Asie du Sud-Est et l'Océanie ont été identifiées comme le principal point chaud. Les moments chauds varient selon la région et la typologie. Le mois de mai a été le moment chaud pour les marais d'eau douce et les zones humides complexes. Alors que les zones humides saumâtres sont actives toute l'année et les forêts inondées, ont leur pic en décembre et janvier. L'estimation quantitative de la dénitrification a été évaluée à  $169.32 \pm 18.31 \text{ Tg N (N}_2\text{O-N + N}_2\text{-N).an}^{-1}$  et l'évolution de la dénitrification au cours des 8 dernières années a été analysée et mise en relation avec les anomalies du climat mondial.

## Mots clés

Zones humides, Denitrification, Modélisation global, Télédétection