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Review

Denitrification in wetlands: A review towards a quantification at global scale



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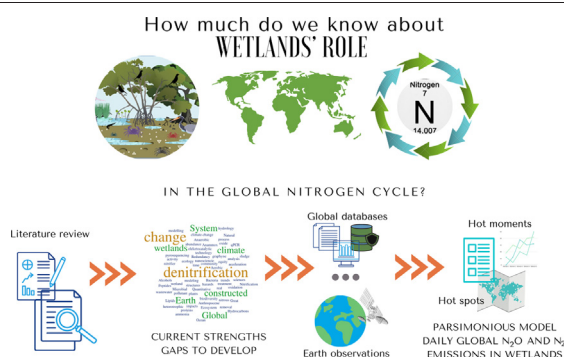
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HIGHLIGHTS

- A review of the last 5 decades of research concerning denitrification is presented.
- Wetlands represent potential denitrification hot spots worldwide.
- Earth Observations are promising tools for improving denitrification modelling.
- Identification of relevant Earth observation data for global denitrification studies.
- Parsimonious model development for daily global N₂O and N₂ emissions in wetlands.

GRAPHICAL ABSTRACT



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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 N₂ and N₂O 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.

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1. 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., 2008) 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 food consumption depends on it (Erisman et al., 2008). 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

Tg $N\ yr^{-1}$ in 1860 to 6.9 Tg $N\ yr^{-1}$ in 2006 (Ciais et al., 2014; Davidson and Kanter, 2014; Tian et al., 2018). Agricultural sector is responsible of ~60% N_2O emissions, cropping is linked to intense irrigation, yet this emissions can be compensated with the crop yield (Denmead et al., 2010). Nevertheless, the main source of greenhouse gases is coming from the industry (Troost et al., 2016), the production of mineral N fertilizer is one of those energy and greenhouse gas intensive process (Lal, 2004).

To counteract the negative impacts of Nr, 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 Nr 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 Nr 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 reproduce 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, 2011). 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 what allows the process to happen regularly (Czuba et al., 2018; Howarth et al., 1996; McDonald et al., 2011; Saunders and Kalf, 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% 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 Nr to the atmosphere (Burgin and Hamilton, 2007).

Nitrogen cycle is summarized in Fig. 1, 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 Nr 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.

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 divide 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^2 , or about 5 to 8% 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., 2017; 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 Nr to N_2 to the atmosphere (Bridgman et al., 2013; 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).

2. Bibliometric analysis

2.1. Research popularity

A comprehensive literature review was done based on the methodology in (Pickering and Byrne, 2014; Torracio, 2005). For details on the used criteria and methodology the reader can refer to Appendix (A.1).

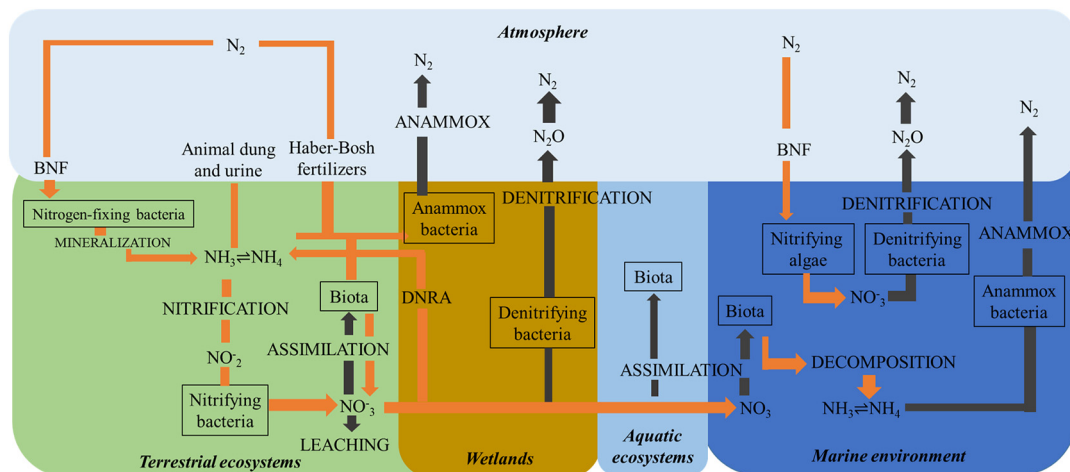


Fig. 1. Simplified diagram of the biogeochemical nitrogen cycle. Lithosphere is divided in terrestrial, wetlands and aquatic ecosystems and hydrosphere as a marine environment. In orange, the fluxes into the biosphere and in black the outputs.

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 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 (Fig. 2). 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 Fig. 2.

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 to 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 citation prove the popularity that Earth Observation data has gained in the last decade.

Nitrogen cycling scored the greatest number of results (44352), followed by Denitrification (26699) 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 <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 A.2 (Fig. A.2.1 and A.2.2).

2.2. Keywords variety

The top-articles keywords of all research exercises were extracted, and word clouds were generated for each time span filter (Fig. 3a-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 increment on studies to develop technology to optimize constructed wetlands.

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.

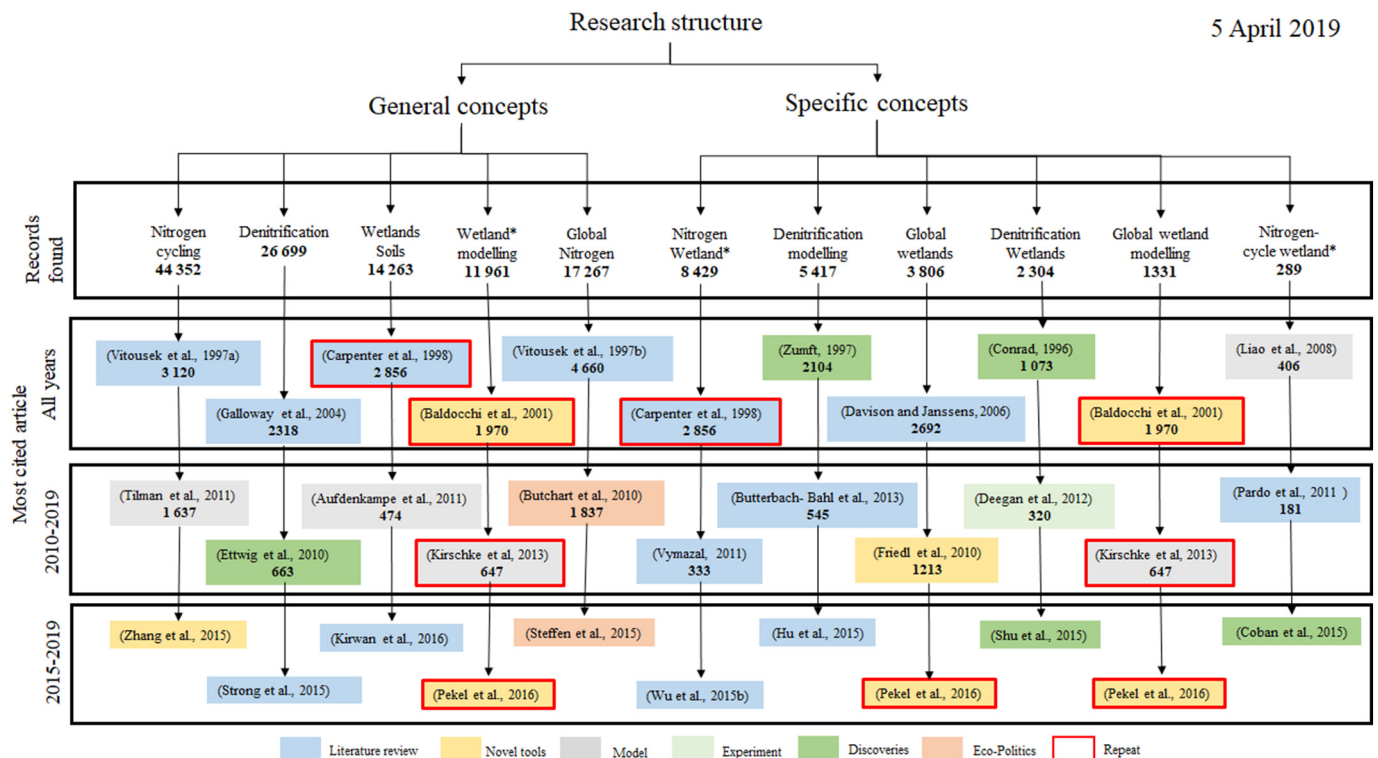


Fig. 2. Diagram showing the top cited articles of each search exercise, on the top, the total of records found per each research exercise. First level is the most cited of all years since 1974 until the day of the research (5/04/19), second level is when a date filter (2010–2019) was applied. In third 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

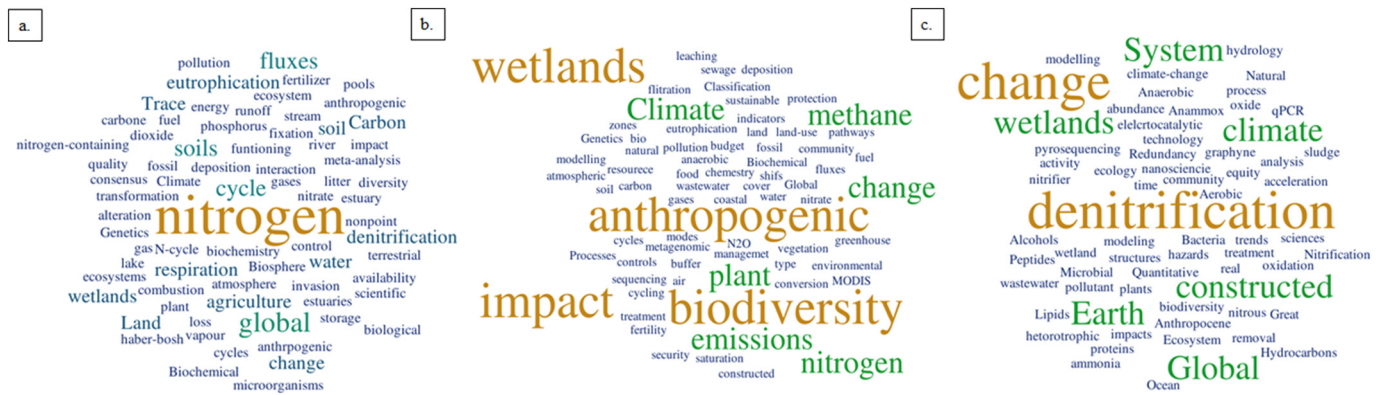


Fig. 3. Word clouds created with the keywords of the top articles in each research exercise. **a.** no filter, **b.** 2010–2019, **c.** 2015–2019. The biggest word represents the most frequent, and the size gets smaller with lower frequencies. The colors represent the number of repetitions the keyword was found. Dark blue (one time), light blue (2–3 times), green (4 times), yellow (five or more times). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Nitrogen centred vision is shown from the most popular research papers resulted from this analysis (Fig. 3a). 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 nitrogen cycle with temperature (Davidson and Janssens, 2006); (iv) consequences of production methods promoting plants invasion (Liao et al., 2008) as well as pollution sources (Carpenter et al., 1998).

Further on, the common output of research (Fig. 3b) 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, 2011). N_2O (Butterbach-Bahl et al., 2013; Pardo et al., 2011) and CH_4 (Ettwig et al., 2010; Kirschke et al., 2013) emissions occurrence and its consequences is accounted for climate change. Global observations from satellite (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 (Fig. 3c), 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.

2.3. Nitrogen cycle

2.3.1. 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., 1997a, 1997b). These articles account for the general human impact on the global nitrogen cycle recognised 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., 1997b), 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 Haber-Bosh process was already more than all natural terrestrial sources combined (80 Tg/year in 1990) and expected to increase to 135 Tg/year 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_2 emissions were a direct impact of the industrial revolution. It was already depicted at that time that the ascending emission rate of CO_2 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 mention about other type of greenhouse gases like N_2O . As mentioned in Vitousek et al. (1997b) 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_x) from fossil fuels by 2020 will be $\approx 46 \text{ TgN yr}^{-1}$ (Galloway et al., 1994) and by 2004 the emissions were already 41 TgN yr^{-1} (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., 2012).

Vitousek et al., 1997a, recognised wetlands and riparian areas as significantly important nitrogen traps, and they appeal 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 (Tilman et al., 2011; Zhang et al., 2015), 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 of only ~0.2 billion ha, greenhouse gas emissions of ~1 Gt y⁻¹, and global N use of ~225 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 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-Bosch 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).

2.4. Denitrification

2.4.1. 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., 2012). 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 resulted also relevant and appeared in

the top five of some of the other research exercises (Appendix A2 –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 Tg Nyr⁻¹ in 1860 to ~156 Tg Nyr⁻¹ in the early 1990's. Projecting that by 2050 anthropogenic reactive nitrogen (Nr) creation will be ~270 Tg Nyr⁻¹. 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 improving. 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 N₂ 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 N₂O 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 N₂. 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 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 NO₃⁻ to surface or groundwater, helping to understand the hotspots of denitrification at watershed scale. These results could be extrapolating to another similar landscape configuration Cambardella et al. (1994).

Moreover, Conrad (1996), established the soil microorganism as controllers of atmospheric trace gases (H_2 , CO, CH_4 , OCS, N_2O , and 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 microorganism, 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 N_2O to N_2 , with novel technology (isotope tracing, and metagenomics) have increased our understanding and measurement precision of N_2O and N_2 emissions. However, our knowledge is mainly based on studies in controlled laboratory conditions, and there is still a lot to know about N_2O and 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 N_2O emissions based on 23 studies revealed no clear dose-response effect for N deposition and N_2O emissions (Liu and Greaver, 2009). Nonetheless, a significant increase of N_2O 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 N_2O emissions was estimated at $0.0087 \pm 0.0025 \text{ kg N}_2\text{O-N ha}^{-1} \text{yr}^{-1}$ per 1 kg N $\text{ha}^{-1} \text{yr}^{-1}$, and tropical forest emitted more N_2O under N enrichment (on average + 739%) (Liu and Greaver, 2009). Emission rates of NO and N_2O 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 denitrifiers to N_2 , nonetheless, wetland soils are especially important sources of atmospheric CH_4 (Bridgman et al., 2013). Surprisingly, Conrad (1996) reported that submerged rice fields seem to sink N_2O (occasionally) (Minami and Fukushima, 1984). Even though wetlands 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., 2012) 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 Fig. 4, where the upscaling of processes is explained. The main driver is determined at genetic level (10^{-8} m), a lot of progress has been done identifying the genes that codify the enzymes that carry out anaerobic respiration, using NO_3^- as 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). Microcosms 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 scale 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 of composed by different gases, this composition changes according to the biosphere activity. In the past it had changed from anoxic to oxic, and in the present 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).

2.5. Wetlands

2.5.1. 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, 2011; Wu et al., 2015), 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

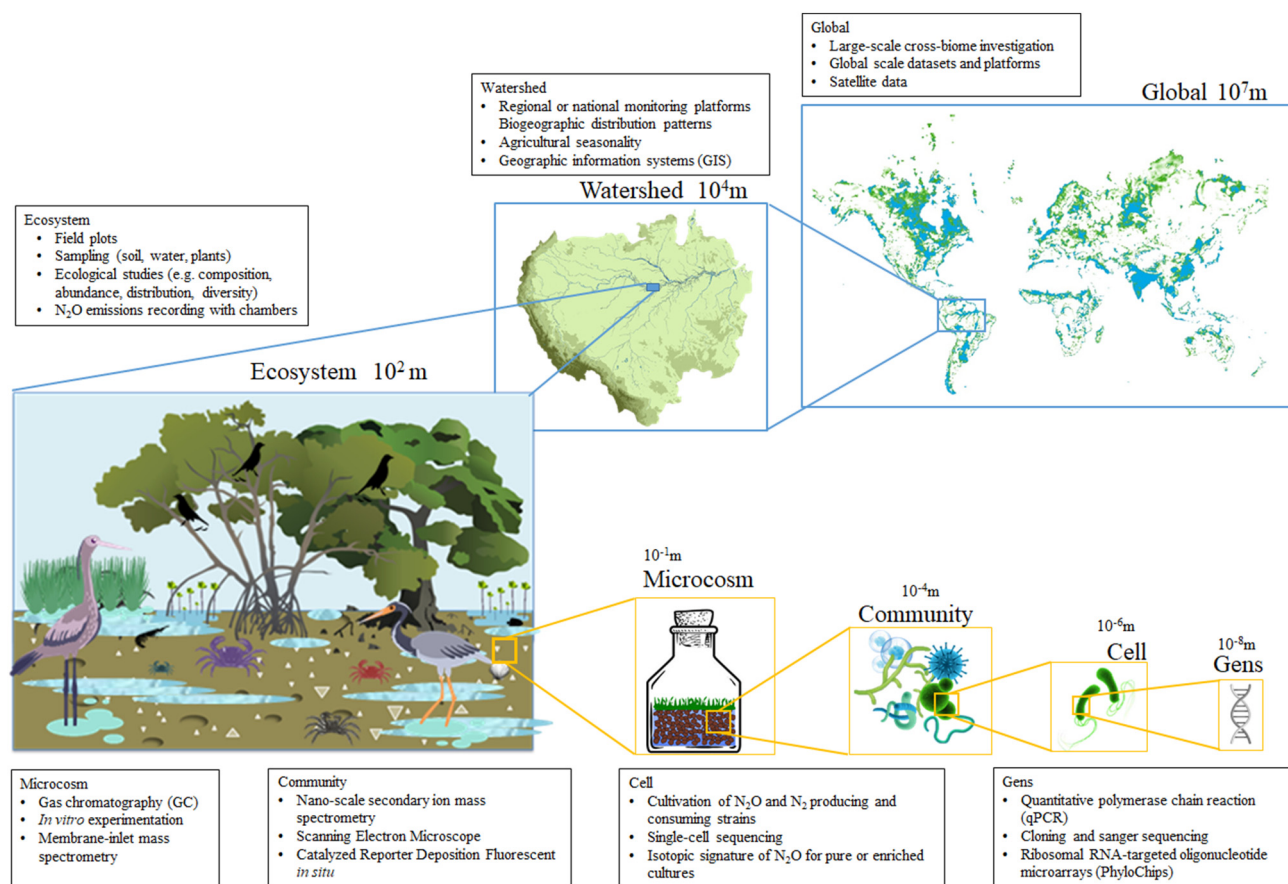


Fig. 4. Methodological framework of the different dimensional range of processes involved in wetlands soil denitrification.

(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).

2.5.2. 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 (Bridgman 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., 2013).

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 CO₂ exchange at ecosystem level (Baldocchi et al., 2001) nothing similar has been achieved for nitrogen. Soil carbon reservoirs in peatlands, wetlands and permafrost 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 CO₂) although methane (CH₄) efflux and hydrologic leaching of dissolved and particulate carbon compounds can also be important (Davidson and Janssens, 2006; Mitsch et al., 2013; 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 Q₁₀ of decomposition equal two. Hence, theoretical and experimental evidence showed that the Q₁₀ = 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 (N₂ and N₂O emissions) has not yet been understood, quantified and modelled at the level achieved regarding carbon cycling (CH₄ 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.

2.5.3. 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, 2011), 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; Tournebise et al., 2017; Vymazal and Březinová, 2015). Regarding nitrogen significant improvements have been achieved (Coban et al., 2015; Vymazal, 2011). 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., 2015). 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.

3. 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 Organization 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 (A.3 - Table A.3.1) and static (A.3 - Table A.3.2) observations. Section 3.2 explains their adequacy or limitations for the evaluation of the denitrification at global scale.

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_2 , N_2 and N_2O) 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 Fig. 5 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.

3.1. Earth observations data in support of denitrification studies

3.1.1. 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° 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-

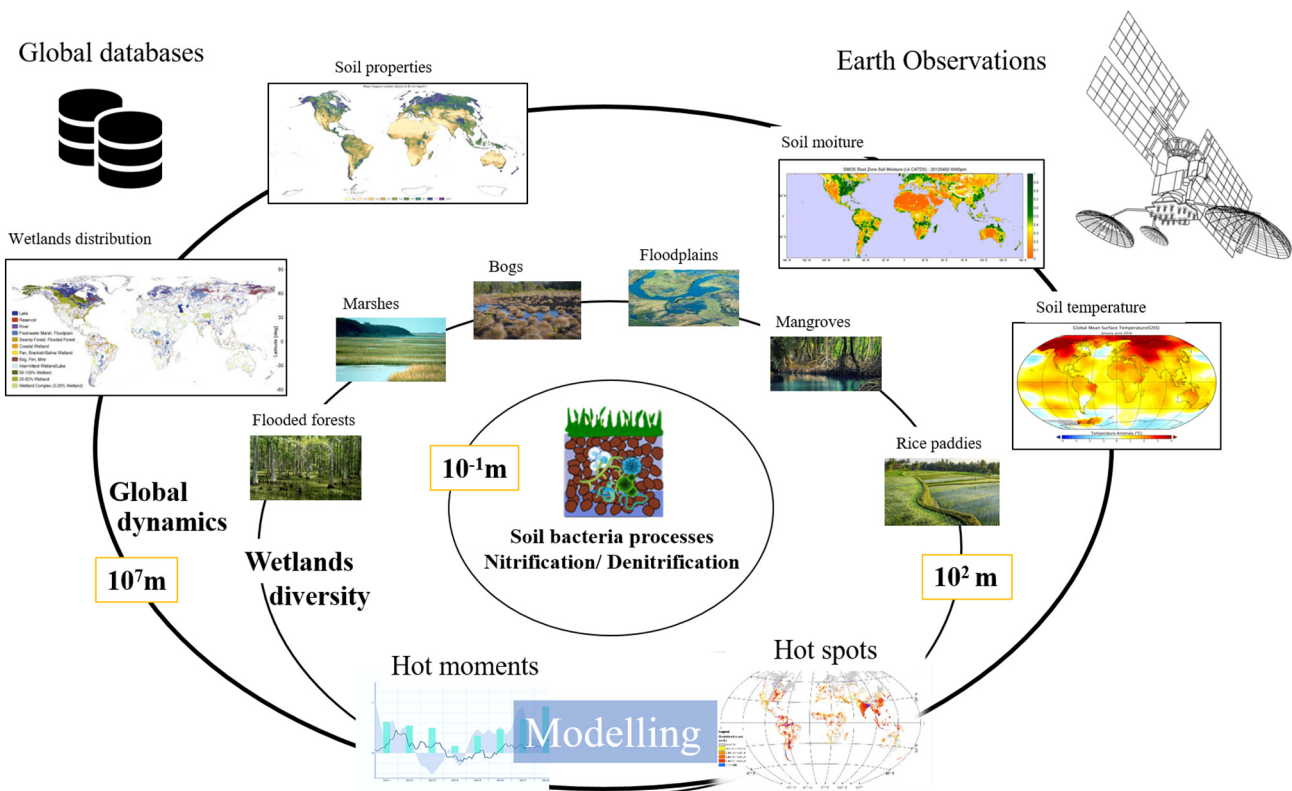


Fig. 5. Illustration of the proposed multi-scale conceptual model. Each ring represents different spatial scale (i.e. soil, wetlands and Earth) where parameters and information regarding dynamics of denitrification process in wetlands soils worldwide is occurring.

derived Global Surface Water (GSW) dataset (Pekel et al., 2016) has raised considerable attention for the description of wetlands from a high resolution (30 m) 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/SSMI 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 (>25 km). 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.

3.1.2. 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 (SSMI, 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.

3.1.3. 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 150 m 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 500 m to 1 km spatial resolution. The meteorological satellites (e.g. METEOSAT, GEOS & GMS) due to their geostationary orbits provide LST at a very high temporal (15 min) and low spatial (<3 km) 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.

3.1.4. 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). Observation 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).

3.1.5. Soil characteristics

It has been proven that the rates of N₂O 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., 2005), delivered now as the Digital Soil Map of the World (DSMW). Recognizing 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.

3.2. Limitations of Earth Observations

3.2.1. 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.

3.2.2. 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 A.3.1). 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 decakilometric 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).

4. 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 Nr 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 Nr to N_2 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 Nr 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 of 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 ecosystems conservation and a 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.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.142398>.

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