

Impacts of Anthropogenic Perturbations on Reactive Nitrogen Dynamics in Mangrove Ecosystem: Climate Change Perspective

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Received March 4, 2019; revised and accepted June 6, 2019

Abstract: This review paper deals with the most pressing problems of increasing anthropogenically induced reactive nitrogen (Nr) and investigates how they severely altered the global nitrogen cycle and its enhanced effect on climate change. Global scale assessment reveals that Nr loading increases dramatically from pre-industrial (111 Tg/year) to the contemporary era (223 Tg/year) and shows shifting of Nr loading from primary fixation based (89%) in the pre-industrial state to heterogeneous mix in modern times. Globally, natural ecosystems like wetlands, estuaries and mangrove are acting as net sink of reactive nitrogen and can mitigate the negative consequences of excess Nr loading on climate change. Pristine mangrove act as a sink of Nr while impacted/eutrophied mangrove may act as a source of it. Nr removal efficiency varies with latitude, wetland class, and Nr loading. Fresh water and natural wetlands have more efficiency in removing Nr than tidal and constructed wetlands as salinity negatively affects anammox reaction. Comparing the warming effects of Nr (N_2O emission, tropospheric ozone formation and phytotoxic effects) with the cooling effects (carbon sequestration, altered methane lifetime and aerosol formation) reveals the net cooling of -16 (-47 to $+15$) mWm^{-2} and -240 (-500 to $+200$) mWm^{-2} for European and global Nr release respectively. Radiative forcing on global scale reveals that positive and negative forcing to some extent balance each other with net cooling effect but growing anthropogenic Nr is rapidly decreasing the part that is cooling, and increasing the part that is warming.

Keywords: Reactive nitrogen; Anthropogenic; Watershed; Mangroves; Climate change.

Introduction

Nitrogen (N), in the environment, mostly exists in its inert form as N_2 , but in this state, it is completely unusable by most of the organisms. In order to be biologically functional, this unreactive nitrogen must be converted into various other reactive forms, together called “Reactive Nitrogen”. Hence any form of nitrogen compound which is photochemically, biologically, and radiatively active in the biosphere and atmosphere of Earth can be referred to as Reactive Nitrogen (Nr).

Nitrogen is of utmost importance for food security and survival of both animals and mankind as they are an important component of proteins, amino acids, and nucleic acids. Since the last few decades, the nitrogen input to the aquatic and terrestrial environment increases several times. This dramatic increase in Nr is mainly contributed by enhanced anthropogenic activities like increase in the manufacture of fertilizer and fossil fuel combustion, extensive cultivation activities of nitrogen-fixing crops and animal husbandry intensification, etc. Limited natural nitrogen fixation maintains the health of

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the ecosystem as the molecules of reactive nitrogen are conserved efficiently and can be re-used in the natural environments, therefore does not allow the nitrogen to accumulate in the environment (Ayers et al., 1994). After the industrial revolution, these natural sources of reactive nitrogen were not sufficient to support the increasing food demands of the growing population. Therefore manufacture of anthropogenically induced reactive nitrogen was introduced by Fritz Haber and Carl Bosh known as Haber Bosh process which increasingly added Nr, thus costing the environment. Therefore, this review paper deals with the increase in reactive nitrogen due to anthropogenic perturbation from pre to post-industrial era, the alteration in Nr cycle and its biogeochemistry as it passes through various ecosystems (riverine, estuarine, wetlands and mangrove etc.) and their enhanced effect on climate change.

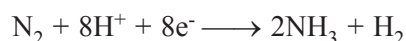
Sources of Reactive Nitrogen

Nitrogen Fixation

It is the process of conversion of highly inert atmospheric N to ammonia (NH_3). There are mainly two mechanisms for natural N fixation – Biological Nitrogen fixation (BNF) and Non-Biological Nitrogen fixation, i.e., by Lightening.

Biological Nitrogen Fixation

It occurs in the presence of nitrogenase enzyme in the diazotrophs which are sensitive to oxygen. The reaction of BNF is as follows:



Non-biological N Fixation or Lightening

Lightening converts atmospheric nitrogen into nitrogen oxides (NO_x). This NO_x reacts with moisture in the air to form a nitrous oxide or nitric acid which ultimately leaches to the soil where it gets converted to nitrate and finally gets used by plants.

Crop Residues and Animal Manure

India constitutes the major percentage of world's population of poultry (34.1%) which is followed by cattle (24.7%), goats (17.1%) and buffalo (13.4%) (Rao et al., 2017). The organic waste generated by these animals supply Nr to crops. These organic sources contributed approximately 5 million tons of available annual nutrients (NPK) in 2011 and are estimated to contribute about 7.75 million tons by 2025 which is further estimated to increase to 10.25 million tons by 2030 (IISS 2015).

Atmospheric Deposition

It occurs in the form of dry and wet deposition and in the form of Nr gases that interact with soil, water and vegetation. There is not only a significant change in total atmospheric emission of N over the past few hundred years due to increase in total nitrogen fluxes on global scale (Galloway et al. 1995) but it also changes the nature of the source due to the evolution of agriculture and industry on the global level (Paerl et al., 2002 and Galloway et al., 2004).

Fertilizers

Fertilizer is the major anthropogenic source of Nr, which is being created and used in the agricultural field at an alarming rate to meet increasing food demands of the growing population. Application of N fertilizer shows continuous increasing trends from 1960-61 to 2015-16 (Figure 1) and its projected demand and supply is shown for 2016-17 to 2030-31 (Figure 2) where it is further estimated to increase in future (Tewatia and Chanda, 2017). After China, India is the second major consumer of fertilizer. During 1960s NP/NPK fertilizer was used extensively which later changed to nitro-phosphate in 1965, further DAP came into existence in 1967. Nowadays, DAP has become the most accepted carrier of N- and P-. The production of reactive nitrogen increased five times (i.e., 2.16- 10.94 Mt) during the period of 1980-81 to 2000-01. During this time, India comes out to be the second largest producer of reactive nitrogen after China. Further increase in Nr production could be seen during one decade of 2000-01 to 2010-11 where Nr production is found to increase by 1.24 Mt. Yet again after a long time gap, an increment of 1 Mt could be seen during 2015-16 which might be due to some changes in the existing policy.

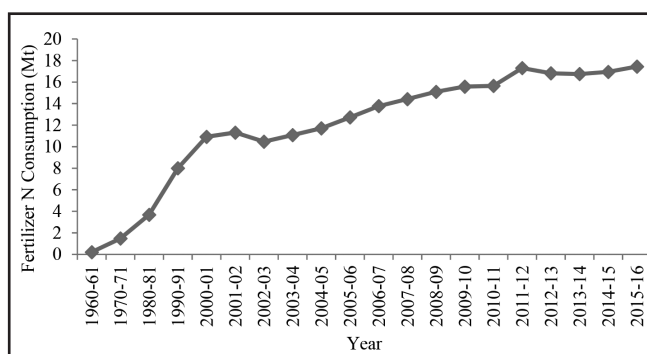


Figure 1: Indian trend of Fertilizer-N consumption during 1960-61 to 2015-16.

(Source: Tewatia and Chanda, 2017)

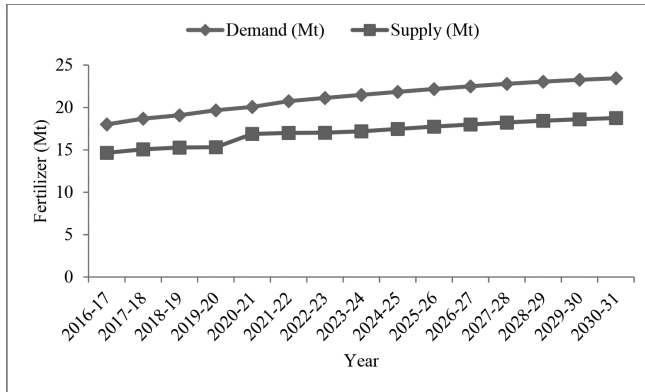


Figure 2: Projected demand and supply of fertilizer N from 2016-17 to 2030-31.

(Source: Tewatia and Chanda, 2017)

Impacts of Reactive Nitrogen on Natural Ecosystem

Acidification

With the rapid decline of sulfur emissions in the mid-1980s, reactive nitrogen has become the main constituent of acidification in the aquatic ecosystem in many regions of Europe and North America. It causes the alteration in the species composition at the base of the food chain and favours macrophytes and phytoplankton, which has the capacity to tolerate acids.

Eutrophication

High nutrient enrichment originating from sewage discharge, use of nitrogenous and phosphate fertilizer (NPK) and agricultural runoff cause eutrophication of coastal, wetland and mangrove ecosystem, e.g. Sundarban Mangroves (both India and Bangladesh) (Manna et al., 2010), Pichavaram mangroves (Alongi et al., 2005; Prasad and Ramanathan, 2008), Tapi estuary (Ram et al., 2014); Zuary estuary (Mochemadkar et al., 2013) and seasonal algal bloom in Coringa waters (Nayak and Bahuguna, 2001; Justic et al., 2003).

Effect on Plant and Microbial Biomass

If present in higher concentration, Nr can directly damage the foliar structure, especially in lower plants. A chronically elevated level may cause broader changes in soil and vegetation of ecosystem. Some nitrogen species, like NH_3 , NO_x , and NH_4 are especially known for its phytotoxic characteristics (Van et al., 2003). Reactive nitrogen in higher amount favour graminoids but do not favour bryophytes, forbs, lichens, etc. Its presence, over time, can cause changes in the species composition, decline in diversity and distinct species of oligotrophic, mesotrophic and circumneutral habitat are surpassed by more nitrophilic and acid resistant plant.

Ozone Exposure

The production of ozone at ground level enhanced the formation of hydroxyl radical ($\cdot\text{OH}$), which is considered to be a major sink for atmospheric methane (Toet et al., 2011), thereby reducing forest productivity and affects carbon sequestration.

Global Nr Scenarios from Pre and Post Industrial Era

Global scale analysis reveals that from 1860 to the early 1990s, reactive nitrogen creation through various processes increased from pre-industrial to contemporary times, as shown in Table 1. During the period 1960-2014, world population rose from 3 to 7 billion increasing N consumption from 11.8 to 113 million tons and production of cereal from 877 to 2801 million tons. Green et al. (2004) suggested that total nitrogen fluxes from river basins have increased to double from the pre-industrial era (21 Tg N/year) to the contemporary period (40 Tg N/year) with many industrialized areas showing an increase up to five fold. Fluxes of dissolved inorganic nitrogen from river basins have enhanced approximately six times, i.e., from 2.4 Tg N/year to 14.5 Tg N/year from the pre-industrial era to contemporary era respectively.

Table 1: Reactive nitrogen creation and distribution (Tg N yr⁻¹) at the global level from 1860 to 1990s to 2050

Sources of Nr		1860	1990	2050
Nr creation	Natural	246	233	224
	Anthropogenic	15	156	267
Atmospheric emission	$\text{NO}_x + \text{NH}_3 + \text{N}_2\text{O}$	45.6	119.4	218.9
Atmospheric deposition	$\text{NO}_y + \text{NH}_x$	31.6	103	195
Riverine fluxes	Nr input to rivers	69.8	118.1	149.8
	Nr export to inland systems	7.9	11.3	11.7
	Nr export to coastal areas	27	47.8	63.2

Source: Galloway et al., 2004

Regional Reactive Nitrogen Budget

The creation of reactive nitrogen, their use and distribution are regionally dependent due to anthropogenic activities which make regional basis

analysis equally important to completely understand the degree of change and its ultimate consequences. Figure 3 shows a global continental specific approximation of mobilization of reactive nitrogen (N_{mob}) load on a continental landmass, comparing pre-industrial and contemporary situations. N_{mob} loading during the pre-industrial era is 111 Tg/year and that during the contemporary era is 223 Tg/year. Thus there is a shifting in the total Nr load to the landscape from primary fixation based system (89%) in the pre-industrial state to heterogenous mix in modern times. The increase of Nr in contemporary times is owing to its extra supply due to the introduction of additional sources from anthropogenic managed crop related fixation (15%), livestock (24%) and atmospheric deposition as a result of fossil fuel combustion (15%) (Green et al., 2004). Further Purvaja et al. (2008) reveals that Nr creations by anthropogenic activities are more than natural sources by approximately 74% in Asia, 61% in North America and 59% in Europe while Natural Nr creation (BNF) dominates in Africa (79%), Oceania (79%) and Latin America (72%). The regional differences in Nr creation and distribution illustrate that some of the countries are producing Nr in excess amount (like Asia, North and South America, and Europe), others producing Nr during food production are N deficient (Australia and Oceania) (UNEP, 2003).

Importance of Asia

Asia is the largest contributor of Nr to the world. The fluxes of Nr from Asia to the coastal zone are 16.7 Tg N yr⁻¹ and inland waters are 5.1 Tg N yr⁻¹ is supposed to be largest in the world (Boyer et al., 2006). Zheng et al. (2002) suggested that approximately 66% of total DIN Asian riverine discharge occurs in China and India; and if we suppose to remove Asia's contribution of anthropogenic Nr, then its enrichment rate would be reduced by 18%. According to Caraco and Cole (1999),

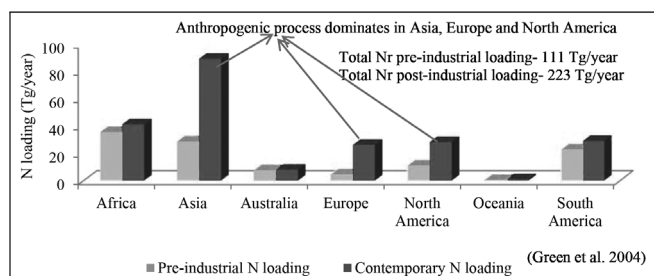


Figure 3: Global continental-specific estimates of mobilizable N loading contrasting pre-industrial and contemporary conditions.

Nr out of watershed of Ganges, Yangtze, Huanghe and Mekong get exported in the form of nitrates at the rate of 601, 495, 276 and 144 kg Nyr⁻¹ km² respectively (Figure 4). According to Sen Gupta et al. (1989), Mahim Bay, Mumbai, alone receives nearly 2,236 Mg of nitrogen every year through different sources. Such a large amount of Nr discharge to coastal waters may cause phytoplankton bloom, which is found to occur near rapidly developing agricultural areas in South Asia (Beman et al., 2005).

Anthropogenic Contribution of Reactive Nitrogen in Indian Ecosystems

From the Indian mainland, around 400% enhancement in the consumption rate of N fertilizers in agricultural areas has been reported between the period of 1981-82 and 2012-14 (Ramesh et al., 2017). The anthropogenic N added to the agro-ecosystem undergoes through the process of nitrification and denitrification, resulting in the emission of N₂O (Smil, 1999). The sectoral shares indicate that maximum contribution of total N₂O emissions came from the use of synthetic N fertilizer (63%) and from crop field burning (12%) which is further followed by indirect emissions, industrial processes, coal combustion, livestock, oil product combustion and natural BNF which indicates that N₂O emission from various sources shows constant growth in all years as shown in Figure 5.

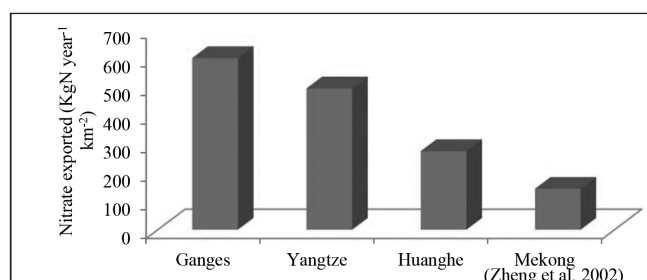


Figure 4: Nitrate exported from the different watersheds of Asian rivers.

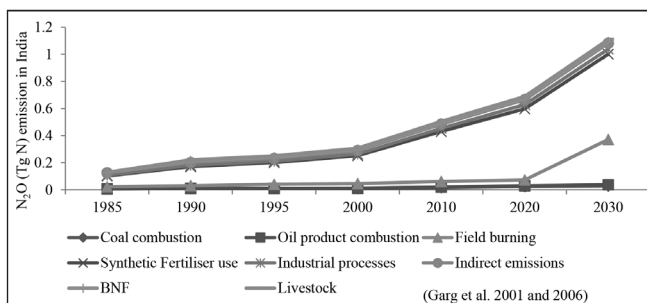


Figure 5: N₂O emission from various source categories in India.

Reactive Nitrogen in the Coastal and Wetland Ecosystem

Enhancement in the consumption rate of fertilizers in agriculture leads to the speedy rise in the bioavailable N load to the coastal and estuarine waters in a significant amount (Souza et al., 2010; Nixon, 1995). 75% of this biologically active N is known to be removed by the process of denitrification before it reaches the open ocean (Howarth et al., 1996). Wetlands are considered to remove around 17% of the anthropogenic Nr inputs worldwide. Major wetlands classes in the U.S. are known to remove 20-21% of anthropogenic Nr (Jordan et al., 2011). Mangroves and salt marsh also have high denitrification rates and nitrogen burial capacity (Kaplan et al., 1979; Seitzinger, 1988). Many studies have justified that mangrove ecosystem acts as a net sink for N and P (Nedwell et al., 2002). Shenzhen mangrove, China is reported to remove waste water nitrogen (Yang et al., 2008). Devol and Christensen (1993) suggested that both mangrove and estuarine sediment are supposed to be Nr sink and do not allow it to make its way to the ocean and sea water. In India, a recent study of Coringa mangroves and Godavari estuary reveals that they act as a sink of nitrogen and captures 24.79% and 58.9% of nitrate, respectively (Rao et al., 2018). Similarly, 14-32% of nitrate removal has been observed in Mandovi-Zuari (De Sousa et al., 1981) and Mahanadi (Sen Gupta and Upadhyay, 1987). 14-16% nitrate removal in adjoining coastal waters in Godavari estuary has been suggested by Padmavathi and Satyanarayana (1999). Box model approach determines that Sundarban mangrove acts as a sink of atmospheric (NO_x , N_2 , and NH_3) and dissolved inorganic nitrogen (Ray et al., 2014). This sink potential may be due to uptake by primary producers including mangrove trees, grazing within the system, recycling through mineralization and sedimentation. Mangroves sediments provide favourable conditions for the bacterial activities for the removal of anthropogenically derived reactive nitrogen (Dong et al., 2009). Goa mangroves are reported to remove 99% of the nitrate by dissimilatory nitrate reduction to ammonium (DNRA) in mangrove sediments (Fernandes et al., 2012). They also observed that the process of DNRA was almost twice greater in the pristine mangroves than in anthropogenically affected mangroves. Thus it can be concluded that the pristine mangroves or sites receiving low extraneous nutrients input, efficiently conserves and re-circulates N through DNRA than anthropogenically impacted mangroves.

In mangroves where there are high N inputs due to anthropogenic interferences, the excess N removal process plays an important role in moderating the N level by eliminating them in various forms; one of them is N_2O form, which poses a threat being one of the potent Greenhouse Gases (GHGs). Therefore some mangroves act as a source of N_2O , which is the only form of reactive nitrogen that clearly has global implications by its effect on climate change. The production of N_2O increases with external inorganic N soil input in an exponential manner (Corredor et al., 1999). Thus minimizing the anthropogenic N inputs into the estuarine system would help to reduce the flux of radiative gas to the atmosphere. The contribution of marine ecosystems is estimated to be 14% of the world N_2O emission (Seller and Conrad, 1987) while estuaries and coastal regions account for approximately 60% of the total oceanic N_2O flux (Bange et al., 1996). The study of N_2O flux by mangrove has been done on the east coast, but the study of the west coast is scarce. The range of air-water N_2O flux for East coast is 1.1-11.4 mmol N/ m^2/s with the mean value for 5.36 mmol N/ m^2/year . The sediment-air N_2O flux was estimated to be an average of 5.8×10^3 g N_2O year⁻¹ (Selvam, 2003). Among all mangroves studied so far, N_2O emission is highest in Bhitarkanika, which is almost 100 times more than its emission by Pichavaram mangroves (Table 2).

Table 2: The rate of N_2O emission in various Indian mangroves

<i>Mangroves</i>	<i>Range (mg/ m^2/day)</i>	<i>Mean (g N_2O year^{-1})</i>	<i>References</i>
Bhitarkanika	0.22 to 4.99	1.4×10^6	Chauhan et al., 2008
Pichavaram	0.94 to 1.90	5.6×10^4	Senthilkumar et al., 2008
Muthupet	0.43 to 0.81	0.63 mg/ m^2/day	Krithika et al., 2008

Fernandes et al. (2012) revealed that the mangrove areas which are vulnerable to increase nutrient levels produce almost three times more benthic nitrous oxide than natural production rates. Majority of the mangroves are situated near the end of the city or town where the effect of rapid urbanization and industrialization are maximum, thereby receiving high urban effluent, sewage, agricultural and industrial as well as aquaculture waste (Krithika et al., 2008). These effluents consist of high amount of nitrogenous waste, which further

enhances the N_2O emission. Thus various mangroves act as a source of N_2O , but the release of nitrous oxide in mangrove is affected by several environmental factors, e.g., pH, DO, water retention time, seasonal changes (Inamori et al., 2007), soil condition (oxic/anoxic) (Schulthess et al., 1995), availability of NO_3^- , NO_2^- , and NH_4^+ (Firestone and Davidson, 1989), temperature and supply of organic carbon (van Raaphorst et al., 1992), C/N ratio (Park et al., 2000) etc. These environmental conditions are different in different mangroves, and thus some mangroves act as a source of N_2O emission while others may act as a sink of it. For example, Australian mangroves act as sink of N_2O for 5 out of 6 mangroves (Maher et al., 2016) as they were N deficient ecosystem resulting in N_2O uptake from atmosphere by these waters while the mangrove which acts as N_2O source had the lowest salinity and found to be super-saturated with N_2O suggesting freshwater as the probable source of N_2O super-saturation. Hence anthropogenically induced eutrophication in the coastal waters may change mangroves from sink to source of Nr in the atmosphere, thus causing positive feedback to climate change. Some exception to this may also exist, like Adyar estuary which despite being highly polluted by anthropogenic activities shows low N_2O emission (and high CH_4 values and low dissolved O_2 , NO_3^- and NO_2^-). The reason might be the utilization of N_2O as an electron acceptor during high denitrification process. Thus denitrification process, in this estuary, acts as a strong N_2O sink. In mangrove ecosystems, the process of nitrification, denitrification, and ammonium oxidation (anammox) is important in the context of the nitrogen cycle in marine environment (Dalsgaard et al., 2003; Nakajima et al., 2008). Among this process, anammox accounts for up to 67% of N removal (Thamdrup and Dalsgaard, 2002) and denitrification accounts for 55% of total N loss (Chiu, 2004). Therefore N removal capacity of mangrove ecosystem supersedes the N_2O emission capacity indicating that overall, this ecosystem acts as Nr sink. This is supported by mangrove N mass balance study by Alongi et al. (2018) where he suggests that nitrogen burial capacity of mangrove constitutes about 25% of total nitrogen input while nitrogen fixation constitutes about <5% of total N input and loss of N via denitrification and N_2O emission is about <10%, suggesting that burial is an important mechanism of N conservation.

Apart from the mangroves, the salt marsh is also known to have high Nr removal capacity (Brin et al., 2010). New England salt marsh are reported to remove reactive nitrogen continuously and efficiently

with increasing Nr loading despite salt marsh receiving decades of Nr enrichment. According to Valiela et al. (1973) fertilized salt marsh store 80-94% of Nr added. They give an estimation of the amount of anthropogenically or land-derived Nr which is most probably captured by wetland areas in each estuary and thus denotes the magnitude of N which would have made their way to sea/ocean if wetlands were absent (Figure 6a and b). This explains the importance of salt marsh and mangrove wetlands in managing the N budget and protecting the natural ecosystems like sea grasses and ocean.

A significant portion of Indian coastal waters has been covered with sea grasses, and many other communities like macrophytes are widely known for their high potential for carbon (C) storage and sequestration (Singh et al., 2015) and are susceptible for light intensity and nitrogen concentration. Seagrasses are slow growing and have higher potential for nutrients and C storage than fast-growing plants and are also extremely susceptible to low light and high N availability (Zimmerman et al., 1987; Dennison and Alberte, 1982). The increase in anthropogenically derived N load lowers the light supply indirectly due to increase in macroalgae (Hauxwell et al., 1998), epiphytes (Borum, 1985) and biomass phytoplankton (Tomasky et al., 1999), all of which otherwise would have reached seagrasses. Particularly in Cape Cod, it has been found that anthropogenically derived N to estuaries, and coastal ecosystems in excess value of $20\text{-}30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$

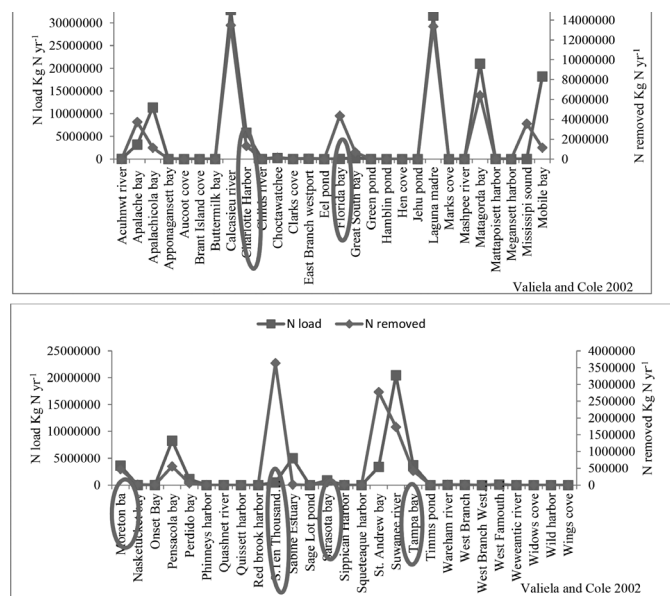


Figure 6a and b: N load and N removed by different wetlands annually across the globe; circled ones are mangrove wetlands; rest are salt marshes.

were enough to reduce the production of seagrass and meadows (Hauxwell, 2001; Hauxwell et al., 1998). 20-100 kg N ha⁻¹ yr⁻¹ is found to be the crucial range especially for seagrass meadows and cause 50-100% decrement in the production of seagrass habitat. Data collected from various literature showed that if there are the large region of fringing wetlands between lands and seagrasses, then the production of seagrasses habitat per unit area get enhanced, and its losses get decreased (Valiela and Cole, 2002). This is because fringing wetlands are at such a position to receive land derived Nr first in a magnitude which can damage the seagrass down-estuary. This Nr can be stored and trapped here through the process of denitrification and burial and thus shields N sensitive seagrass habitats.

Removal Efficiency of Reactive Nitrogen by Wetland Ecosystems

The amount of Nr load removal within the wetland ecosystem is termed as Efficiency. It's a ratio between Nr removal mass per area and Nr input in the same area. It is calculated in percentage. Latitude is a substitute for annual average temperature. The latitude is associated with both the Nr uptake by wetland plants and rates of microbial processes (denitrification) that removes Nr. At higher latitude, the plants have shorter growing season while summer temperature matches with those of tropical areas. Efficiency is affected by latitude and wetland class, as shown in Tables 3 and 4.

Latitude

Table 3: The mean reactive nitrogen removal capacity of wetlands decreases with increase in latitude

<i>Latitudes</i>	<i>Nr removal efficiency</i>
50° or more	25%
Mid-latitude	47%
30° or less	59%
Overall mean efficiency	46.7% (range: 0.25 to 99.6%)

Jordan et al., 2011

Wetland Class

Increase in salinity negatively affects the anammox reaction more than denitrification process (Koop-Jacobsen and Giblin, 2009), so removal of Nr is more efficient in freshwater wetlands than estuarine wetlands. The efficiency of non-tidal wetlands is more (48.6%) than tidal wetlands (38.5%). The efficiency of the natural wetland is more (48.2%) than constructed wetlands (45.7%) as their plant communities are

well established. This nitrogen removal capacity may reduce N₂O emissions, which indirectly reduces GHG's emissions from N fertilizer use.

Table 4: Nr removal efficiency for different wetland class

<i>Types of wetlands</i>	<i>Nr removal efficiency</i>
Non-tidal wetland	48.6%
Tidal wetland	38.5%
Natural wetlands	48.2%
Constructed wetlands	45.7%
Estuarine emergent	32.9%
Palustrine forested (swamp and riparian forest)	62.7%
Palustrine emergent (constructed wetlands)	45.7%

Jordan et al. 2011

Nr Loading

Strong relationship can be established between Nr loading and removal could be due to a rise in Nr loads and nitrate availability, which ultimately increases the denitrification processes.

Considering that approximately 50% of the native wetlands and mangroves have been diminished over the past few centuries (Spiers, 2001), if the decrease in the wetlands continued like this, it would be a loss of great Nr removal potential. Hence the preservation of existing wetlands and their restoration on a large scale and Nr source diversion from waterways to various wetlands could cause a great relief.

Effect of Anthropogenically Induced Nr on Climate Change

Indian agricultural soils are estimated to emit 70% N₂O-N through the application of N fertilizer in 2010 which is projected to increase by about 50% in 2020 and by 60% upto 2030 due to increase in use of N fertilizer. Though N₂O contributes around 5-6% of the GHGs (Houghton et al., 1995), its residence time of about 114 years is responsible to make its global warming potential about 298 times more than that of CO₂ over 100 year time frame (Forster et al., 2007). Compilation of total sources of N₂O (both anthropogenic and natural sources) reveals that it is slightly more (17.1 TgN/yr) than the known identified sinks (16.4 TgN/yr) (Table 5). If this rate of increase in anthropogenic sources continues in future, it will supersede the sink capacity.

Table 5: Global nitrous oxide budget in the atmosphere (all units in TgN/yr (10^{12} g/yr))

<i>Natural sources</i>	<i>Annual fluxes</i>	<i>References</i>
Soil	3.4	Zhuang et al., 2012
Ocean Surface	6.2	Bianchi et al., 2012
Anthropogenic Sources		
Agricultural Soil	2.8	Bouwman et al., 2002
Cattle and Feed lots	2.8	Davidson, 2009
Biomass burning	0.9	Kaiser et al., 2012
Industry and Transportation	0.8	Davidson, 2009
Human Sewage	0.2	Mosier et al., 1998
Total Sources	17.1	
Sinks		
Stratospheric destruction	12.3	Prather et al., 1995
Soil destruction	0.1	Syakila and Kroeze, 2011
Atmospheric increase	4.0	IPCC, 2007
Total Identified Sink	16.4	

Apart from NO_2 , NO_x emission ($\text{NO}_x = \text{NO} + \text{NO}_2$) are supposed to be accelerated over few years where the diesel powered vehicle are considered to constitute about 84% of total NO_x emission (Sharma et al. 2008). NO_x , in turn, produces O_3 at ground level, a greenhouse gas and reduces plant productivity, thus reducing CO_2 uptake efficiency by the plants from the atmosphere and increasing atmospheric carbon dioxide.

Further application of urea fertilizer contributes nearly 90% of the NH_3 emission. Though agriculture are the largest contributor of nitrogen emissions, recently nitrous and nitrogen oxides emissions from non-agricultural sources like sewage, biomass burning in power, industry and transport sector are also leading the trend. So the current geological era is the period where human activities are dominating the climate and environment and costing the natural ecosystem.

One of the most controversial role of Nr in climate change is it increased plant capacity of carbon sequestration. According to Zaehle et al. (2011), carbon storage due to nitrogen accumulation had decreased the contemporary radiative forcing of carbon dioxide by $96 \pm 14 \text{ mWm}^{-2}$. However nitrous oxide emissions offset these effects by increasing the radiative forcing by $125 \pm 20 \text{ mWm}^{-2}$ (Galloway et al., 2008). The increase in N_2O emission amounts to further NO_x and leads to

the formation of more ozone (O_3) which reduces the atmospheric CH_4 lifetime, affecting its consumption and production in soils (De Vries et al., 2011). Further formation of tropospheric O_3 together with NH_3 enhances the sulfur dioxide (SO_2) oxidation to sulfate aerosol. Emissions of NH_3 and NO_x also contribute to the formation of the nitrate and ammonium aerosols. These aerosols, in turn, affect the vegetation cover by affecting the albedo of land surface and an increasing amount of chlorophyll in vegetation (Hollinger et al., 2010). According to the estimates of recent European Nitrogen Assessment (ENA), the net effect of Nr on climate is cooling as a result of aerosol effects and atmospheric deposition of Nr in forest which tends to offset the warming effects of excess Nr emission and its contribution in tropospheric ozone formation (Butterbach-Bahl et al., 2011). The results of various Nr interactions imply net global cooling of 16 (-47 to +15) mWm^{-2} and -240 (-500 to +200) mWm^{-2} for European and global Nr release (Erisman et al., 2011) respectively. Quantification of Nr effect on climate shows various positive and negative influences on GHG balance and radiative forcing (Table 6). This radiative forcing balance each other, thus showing net cooling effect of 0.24 W/m^2 . The uncertainty is very large in individual process, thus it is safe to say that the effect of cooling and warming is nearly balanced, with slight inclination towards cooling side. These cooling effects are for short-term and are considered to affect more societal cost than climate-related benefits. So we can conclude that in current scenarios, both warming and cooling effect of Nr to some extent balance each other (Pinder et al., 2012). But the constant increase in the application of N containing fertilizer on a global scale will certainly enhance the emission of agricultural nitrous oxide in the near future, thereby shifting the climatic balance towards warming.

Effect of Indian agriculture indicates that on GTP_{20} (Global Temperature Potential) basis, the overall effect of Nr were 8.28 and 53.43 Tg CO_{2e} in 1961 and 2010 respectively. The results on the basis of GTP_{100} were 11.52 in 1961 and 74.37 Tg CO_{2e} in 2010 (Pathak and Bhatia 2017) while the difference between warming caused by nitrous oxide alone and overall warming on GTP_{100} basis was less when compared to GTP_{20} year basis which reflects cooling effect of short lived aerosols. Over a 100 year scale, aerosol effects are negligible. Thus it can be concluded from above data that anthropogenic activities are rapidly decreasing the part that is cooling, and we are either increasing or keeping constant the part that is warming.

Table 6: Estimate of N influence on radiative forcing on global scale

<i>Process</i>	<i>Forcing (W/m^2)</i>	<i>References</i>
N ₂ O emission	0.16	Parry et al., 2007
NO _x emission atmosphere	-0.09	Shindell et al., 2009
NH ₃ emission atmosphere	-0.29	Shindell et al., 2009
N and C in terrestrial and ocean system	-0.2	(Terrestrial system) Zaehle et al., 2010; Arneth et al., 2010
	-0.2	(Oceans) Duce et al., 2008
	0.25	(Mineralization) Arneth et al., 2010
O ₃ phytotoxicity	0.13	Arneth et al., 2010
Total	-0.24	

Conclusions

Nr has increased dramatically from pre-industrialization to post industrialization era due to increase in anthropogenic activities to meet food demands of the rapidly growing population.

On the global scale, the Nr contribution by Asia is found to be largest where China is the largest contributor to Nr, followed by India. Maximum anthropogenic Nr contributor is found to be synthetic fertilizer followed by field burning, indirect emission, industrial processes, coal combustion, livestock, oil product combustion, and natural BNF. Mangroves act as both sink of Nr and source of N₂O but this sink/source potential of mangrove depends on various environmental parameters. Overall, mangroves sink capacity is found to supersede the source capacity. Further pristine mangroves store Nr while impacted/anthropogenically disturbed mangroves act as a source of it. Therefore damaging effects caused due to land-derived N loads may be narrowed down by fringes of mangroves, and coastal wetlands interpose between land and seagrass meadows/oceans as they act as a sink of Nr. Nr removal efficiency varies with latitude, wetland class, and Nr loading. Fresh water and natural wetlands are supposed to remove more Nr than tidal wetlands and constructed wetlands, respectively. Comparing the warming effects of Nr (N₂O emission, tropospheric ozone formation and phytotoxic effects) with the cooling effects (carbon sequestration, altered methane lifetime and aerosol formation) reveals the net cooling of atmosphere. Growing anthropogenic Nr is rapidly decreasing the part that is cooling, and increasing the part that is warming, thus may shift the climate from net cooling to net warming.

Acknowledgement

The authors would like to thank the financial aid

provided by the Council of Scientific and Industrial Research, Govt. of India for providing the necessary Ph.D. fellowship.

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