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# Rethinking the Nitrogen Cycle in the Era of Energy and Food Security

**Reema Tiwari and Umesh Kulshrestha***
School of Environmental Sciences, Jawaharlal Nehru University, New Delhi – 110 067
✉ umeshkulshrestha@gmail.com

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**Abstract:** Being a fundamental component of global food and energy security, nitrogen cycle has undergone massive transformation in their structure and functions at various scales. This is reflected in their altered transport, conversion and exchange processes providing increased N losses and transfers between different environmental compartments. Investigation of their additional fluxes has shown ecosystem malfunctioning and environmental consequences with continual climate change accelerating the rates of reactive nitrogen (Nr) formation through a chain of chemical reactions and multi transport processes. However, inequities in their global distribution have resulted in food production in some regions of the world being nitrogen-deficient. The present article, therefore, intends to trace such disturbances in N cycle as well as the changing dynamics of its coupling-decoupling with other elemental cycle for delineating their consequent impacts on C:N:P balance of the ecosystem. This requires a comprehensive assessment of their global atmospheric fluxes for which changes in N cycle driven by atmospheric chemistry and climate have been discussed under different emission scenarios. Considering the nature and importance of nitrogen-carbon-climate interactions, a review of their feedback mechanism across major N conversion and exchange processes has also been provided for highlighting major environmental impacts on N cycle.

**Keywords:** Air pollution; Reactive nitrogen; Ammonia; Agriculture activities; Vehicular emissions.

## Introduction

Sustenance of mankind through centuries has always been intrigued with the shifting dynamics of global nutrient cycling. By providing leakages to the material flow and manipulation in the ecological services, their imbalances have often been linked with the changing stoichiometry of nutrient's availability. Such alterations have been consistent with the changing patterns in the land uses characterized by the increasing fertilization and nutrient transfer across the ecosystem boundaries (Downing et al., 1999). This is clearly reflected from the nutrient losses to the atmosphere and aquatic ecosystem occurring through anthropogenic modification of their natural inputs over the past two decades. Lack of synchrony in their use and release are, therefore, becoming detrimental to the nutrient buffering functionality usually expressed by the altered rates, pathways and cycling efficiencies of key elements i.e. nitrogen, carbon, phosphorus and sulphur (Lavelle et al., 2005). Though carbon cycle may be getting more press from the global increases in temperature and atmospheric $CO_2$ concentrations, it is the global nitrogen (N) cycling that has undergone alteration more than any other biogeochemical cycle (Suddick et al., 2012). Considering the ever increasing rates of anthropogenic input of nitrogen with its multi transport processes providing losses to environment, there is a need for understanding the dynamics as well as the major driving forces for their possible alterations in N cycle.

*Corresponding Author

Being the most abundant element of the Earth's atmosphere, nitrogen in its molecular form ($N_2$) remains unusable by the majority of biota. But owing to its increasing demand in food and energy sectors across the globe, there has been a ten-fold rise in the transformation rates of inert $N_2$ into biologically active, photo chemically reactive and radiatively active N compound also known as the reactive nitrogen (Nr) compounds (Galloway et al., 2004; Phoenix et al., 2006). This has greatly enabled the role of N as a nutrient for all the biota but with a cascade of environmental problems ranging from global acidification to eutrophication of terrestrial and aquatic ecosystems (Gruber et al., 2008). World's focus of the nitrogen cycle has, thereby, undergone dramatic shifts towards minimizing their environmental losses from the large N inputs occurring through global food production system (van Groenigen et al., 2015). A thorough investigation of Nr creation rates, their movement through different environmental reservoirs and the resulting trends have resulted in a need of an integrated approach dealing with the anthropogenic nitrogen problem and their management strategies. However, our scope of understanding the N cycle remains complicated due to its coupling dynamics with other biogeochemical cycles creating pushes to our climate system towards uncharted territory (McGuire et al., 2001; Denman et al., 2007). The central question now lies in the sensitivity of nitrogen availability to climate variability and changes. The present article intends to address all these issues pertaining to the N cycle dynamics in the context of its changing interaction with the climate system and human actions.

## Changing Trends in the Global Nr Budget

By placing the current alterations into historical context, significant changes have been observed in N cycle over the last two centuries from the doubling of their turn-over rates (Gruber et al., 2008). Formation of additional Nr through food production and mobilization of sequestered Nr from the energy demands has increased the N availability by ten folds. This has resulted in 120% rise in the Nr creation rates in correspondence with 78% increase in the global population since pre-industrial times (Galloway et al., 2004). Such an exceedance has been characterized by its higher N inputs in comparison to their hydrological outputs at all scales (Boyer et al., 2002; Groffman, 2008). Thus, any alterations occurring in the amount of reactive nitrogen could be directly attributed to the processes of biological nitrogen fixation, denitrification, fertilization, atmospheric deposition and their complex interplay (Figure 1).

Growing significance of atmospheric deposition in the N cycle imbalances is clearly reflected from the rising contribution of the anthropogenic inputs to the atmospheric Nr (Fowler et al., 2013; Paulot et al., 2013; Kulshrestha et al., 2014). Prior to its extensive human modifications, the state of N cycle had the annual atmospheric flux of 90-140 TgN $yr^{-1}$ which was more or less balanced by its reverse denitrification flux. But with the steadily increasing food and energy production on absolute and per capita basis, an additional deposition flux of 210 TgN $yr^{-1}$ has been created from chemical fertilizers (80 TgN $yr^{-1}$), N fixing crops (40 TgN $yr^{-1}$),

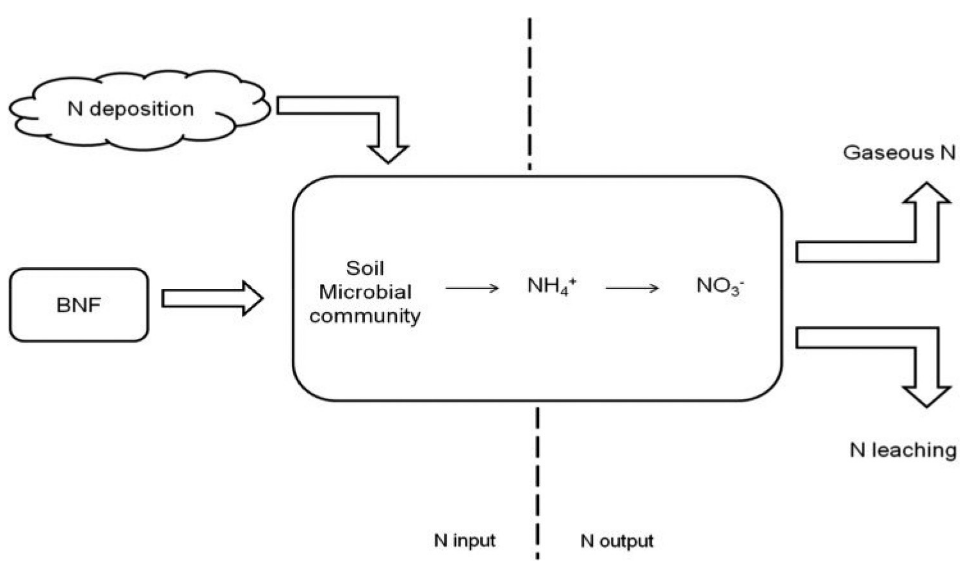


**Figure 1: Leaky nitrostat model of terrestrial nitrogen cycle.**

biomass burning (40 TgN $yr^{-1}$), fossil fuel combustion (20 TgN $yr^{-1}$), land clearing (20 TgN $yr^{-1}$) and wetland drainage (10 TgN $yr^{-1}$) (Lavelle et al., 2005). This has led to the deposition fluxes accounting for 60-80% of its total annual N emissions occurring as NOx (35 Tg), $NH_3$ (60 Tg) and $N_2O$ (13 Tg) of which only ~2.5% of $N_2O$ has been accountable for their tropospheric accumulation (Galloway et al., 2004; Zhang et al., 2012; Fowler et al., 2013; Jia et al., 2014).

However, the missing links in the N balances has largely been highlighted by the unmeasured N inputs occurring in agricultural systems and aggrading forest as biological nitrogen fixation (BNF). Of the total 170 TgN $yr^{-1}$ added to the global agro ecosystem in early 1990's, 120 TgN $yr^{-1}$ has led to new Nr addition through fertilizer and cultivation induced BNF with the remaining 50 TgN $yr^{-1}$ adding only the existing Nr via atmospheric deposition, animal manure and crop residues (Galloway et al., 2004). Anthropogenic or cultivation induced N fixation (C-BNF) is represented by its excess background rates in the natural communities that the legume crops have replaced. Together with industrial N fixation through Haber-Bosch process, they have sustained the agricultural demands by providing 20% rise in the cereal production and 26% rise in the meat production rates. Increasing soybean and meat production over the past decade have shown a rise in the C-BNF estimates from 31.5 TgN in 1995 to 40 TgN in 2005 (Galloway et al., 2008). But owing to the substantial uncertainty associated in their level of estimation, it still remains a critical area with more precise data requirement.

Recent sampling methods have shown mean rates of BNF in a typical primary tropical forest (1.2 kgN $ha^{-1}$ $yr^{-1}$) to be much lower than the previously modelled data range (11.7-31.9 kgN $ha^{-1}$ $yr^{-1}$) of which 20-50% alone has been attributable to symbiotic BNF (Sullivan et al., 2004; van Groenigen et al., 2015). This has fundamentally altered our assessment of N cycle by substantiating a much larger contribution of atmospheric N deposition in tropical forests from wild fires, livestock and fossil fuel combustions than previously assumed. $N_2$ fixation rates in boreal forest (1-29 kgN $ha^{-1}$ $yr^{-1}$), on the other hand, has been ten times higher than the current atmospheric N deposition rates, thereby, suggesting a significant contribution of BNF to the N budgets of peatlands (Gundale et al., 2012; Larmola et al., 2014). Though such temporal and spatial variability of BNF has been constrained by their large uncertainties, even less is known of their future trajectories in view of global change.

Thus, the last fifty years have become a witness to the annual production of anthropogenic reactive nitrogen surpassing the total N fixed through natural processes (Figure 2). Dominance of agricultural activities and growing prevalence of biofuels has added to the rapidly changing dimensions of Nr creation rates having enormous increase from 15 Tg in 1860 to 156 Tg in 1995 further reaching upto 187 Tg in 2005 (Galloway et al., 2008). This has increased the total denitrification rates by 56% from the terrestrial ecosystem resulting in a less than 20% of fertilizer N actually reaching for human consumption. Much of the remaining 80% of the fertilizer N has either been lost into air as $NH_3$ and NOx or into the rivers and groundwater as $NO_3^-$ (Lavelle et al., 2005; Braun, 2007). However, a poor understanding of its ultimate fate especially how much is getting denitrified back to $N_2$ has limited our ability for determining the Nr accumulation rate in environmental system.

## Changing Nr Distribution Pattern

Increasing production of reactive nitrogen has been characterized by the spatial heterogeneity of its creation and distribution rates based on the level of regional development and geographic location. Regions with high energy and food production, primarily the industrialized nations, have excess Nr accumulating in its air, water and soil, moving between each compartment and causing subsequent environmental and socio economic problems. Regions with low soil fertility and scarce crop nutrients such as the Sub Saharan regions, on the other hand, are grappling with a different set of challenges associated with the deficiency of Nr. Agriculture in such areas is unable to meet the basic food requirement to sustain neither its population nor its economic development. This has led to the developing nations facing challenges from the combination of both excess as well as deficient Nr (Braun, 2007).

Uneven distribution of Nr across the globe is clearly reflected from the regional estimates showing differences in the Nr creation and distribution rates (Figure 3). Asia dominates in the Nr creation from food production with twice the rate of its fertilizer N production and cultivation- induced BNF in comparison to Europe and N. America respectively. Though N. America leads the way for Nr creation by energy production, the overall Nr production in Asia alone has been in close approximation with Europe and N. America combined (Galloway et al., 2004). Of the total 187 Tg Nr created in 2004, about 45 Tg has been traded internationally

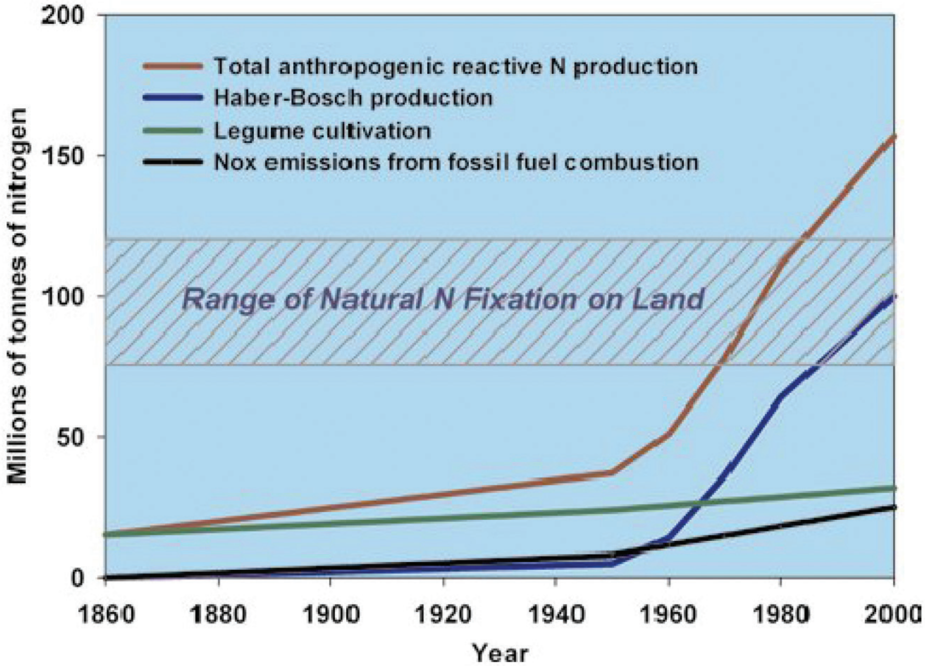


**Figure 2: Anthropogenic fixation of N in comparison with the natural biological fixation of N in a terrestrial ecosystem (UNEP, 2007).**

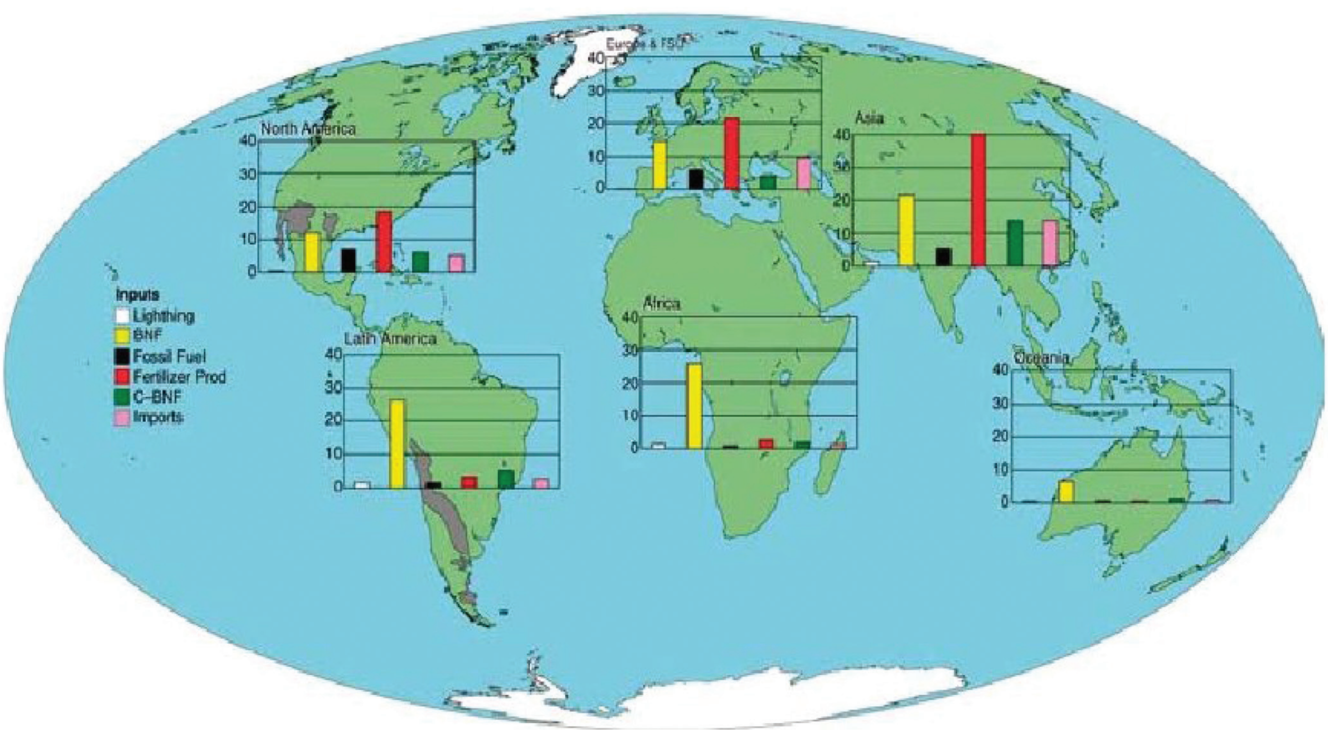


**Figure 3: Regional estimates of Nr distribution pattern (UNEP, 2007).**

as N commodities. This has led to Nr being injected into ecosystems in highly concentrated doses but with a possibility of a greater control over Nr releases unlike the aquatic and atmospheric transport. Thus, with human activities doubling the transfer of atmospheric N to biologically available pools on terrestrial ecosystem, there has been a growing significance of atmosphere in the changing Nr distribution patterns on a global basis

(Vitousek et al., 1997; Galloway et al., 2008; Dentener et al., 2014; Aas et al., 2014).

Given the short atmospheric lifetime of $NO_y$ ($NO_x$, $HNO_3$, $NO_3^-$) and $NH_x$ ($NH_3$, $NH_4^+$), the changing dynamics of the Nr spatio-temporal distribution pattern are becoming the clear indicators of their altered emissions and subsequent interactions with the atmospheric transport and removal dynamics. Their global estimates (Table 1) have shown $NH_3$ emissions to be 25% higher than $NO_x$ emissions and oceanic emissions of $NH_3$ contributing a higher fraction (13.7%) than the oceanic $NO_x$ emissions (5.8%). This has resulted in $NH_3$ accounting for the highest proportion in the global N emissions (55.7%) with dominant contribution from Asia alone (39.4%). Emission changes in total N ($NO_x$ + $NH_3$) from their three year average values (2000-2002 to 2005-2007) have shown a rising trend over Africa (+56%) and Asia (+15%), unlike a declining trend over Europe (–2.7%) and North America (–4%). Keeping in sync with these emission changes, a similar trend has also been observed in their deposition pattern over Africa (+19%), Asia (+13.6%), Europe (–2.7%) and North America (–4.3%) for the three year average. The % ratio of $NH_x/NO_y$ in deposition showed a dominance of $NH_x$ over $NO_y$ by more than 60% at major agricultural regions (Central North America; regions of South America, east-central Africa, China, Pakistan and India) as well as over the oceans of Southern hemisphere. $NO_y$, on the other hand, were the dominant contributor (Nreduced < 40%) in the $NO_x$-dominated emission areas as well as over the oceans of Northern Hemisphere. Such a pattern clearly depicts the consistency existing between deposition and emission trends with additional influence of long range transport (Vet et al., 2014).

The present-day atmospheric mixing ratio of $NO_y$ on five types of pre-existing aerosol types have shown mineral dust contributing highest fraction to the nitrate mass (58%) with the remaining fractions showing their association with sulphate (23%), carbonaceous aerosols (2%) and sea salt particulates (17%). Mass fraction of gaseous ammonia, on the other hand, has been predicted mostly with pure sulphate (79%) with the remaining fraction showing coatings on carbonaceous aerosols (17%), dust (1%) and sea salt particulates (3%) (Xu et al., 2012). This has consequently affected their deposition rates which over the metropolitican Mid Atlantic Coastal Bay of U.S. has shown a higher deposition fluxes of particulate $NO_3^-$ (11 μmol $m^{-2}$ $day^{-1}$) than the $NH_4^+$ particulate fluxes (2.8 μmol $m^{-2}$ $day^{-1}$) despite the dominance of particulate $NH_4^+$ levels (69.6 nmol N $m^{-3}$) over the $NO_3^-$ particulate levels (33.1 nmol N $m^{-3}$) (Russell et al., 2003). Significance of the size shift of the $NO_3^-$ particulates towards the larger particles over the marine boundary layer has been well represented by the works of Matsumuto et al. (2009),

**Table 1: Area integrated 2001 global estimates of $NO_X$, $NH_3$ emissions and $NO_y$, $NH_x$ depositions (TgN)**

| *Region* | *$NO_x$ emissions (TgN)* | *$NO_y$ deposition (TgN)* | *$NH_3$ emissions (TgN)* | *$NH_x$ deposition (TgN)* |
|---|---|---|---|---|
| *Continents* | | | | |
| Asia | 12.5 | 11 | 23.1 | 20.2 |
| Africa | 7.8 | 6.2 | 7.4 | 6.4 |
| Europe | 7 | 5.6 | 5.9 | 5.2 |
| North America | 8.7 | 6.8 | 5.3 | 4.8 |
| South America | 5.1 | 3.5 | 6.0 | 5.4 |
| Oceania | 2.8 | 2 | 2.8 | 2.5 |
| *Oceans* | | | | |
| North Atlantic | 5.7 | 7.8 | 3.5 | 5 |
| South Atlantic | 0.6 | 1.6 | 1.6 | 2.2 |
| North Pacific | 4 | 6.9 | 5.1 | 7.4 |
| South Pacific | 0.8 | 2 | 2.7 | 3.2 |
| North Indian | 1.3 | 1.9 | 2.2 | 3.7 |
| South Indian | 1.0 | 2.1 | 2.3 | 2.8 |
| Arctic | 0 | 0.3 | 0 | 0.2 |
| Southern | 0 | 0.1 | 0.1 | 0.1 |

where the size segregated measurement of the major ions showed the dominance of $NO_3^-$ in the coarse mode fraction (0.05-0.58 µg $m^{-3}$) subsequently resulting in a high deposition flux of $NO_3^-$ (20.1-228.5 µg N $m^{-2}$ $day^{-1}$) in comparison to $NH_4^+$ (10.1-47.7 µg N $m^{-2}$ $day^{-1}$) over the Sea of Japan. An increase in the dry deposition flux of total nitrate (120 µmol $m^{-3}$ $day^{-1}$) along the west coast of Ireland wind has been observed to be caused by the efficient scavenging of $HNO_3$ (g) by the sea salt resulting in its rapid deposition during the south westerly flow of the North Sea (Spokes et al., 2000). The total nitrate, therefore, tends to undergo a tremendous rapid phase change (>85%) from the predominant gaseous $HNO_3$ over the continent to the particulate $NO_3^-$ over the oceans (Lefer et al., 1999). On the other hand, virtually no scavenging of $NH_4^+$ has been observed over the ocean owing to the high pH value of the sub-micron sea salt aerosol. This has subsequently resulted in the $NH_3$ dominating the total flux of $NH_4^+$ over the coastal areas as reported by the findings of Kenee et al. (2002).

Unlike the European and North American regions, the atmospheric condition of India is reported to be alkaline in nature. This has been attributed to the crustal sources contributing significantly to the dust mass loading rich in carbonates and bi-carbonates of Ca and Mg (Khemani et al., 1985, 1989; Naik et al*.*, 1988; Mahadevan et al*.*, 1989; Kulshrestha et al., 1990; Saxena et al., 1991; Kumar et al., 1993). Abundance of soil resuspended dust in the Indian atmosphere has already been well established for its role in combating the acidification of the environment through $SO_2$ scavenging (Kulshrestha et al., 2003a; 2003b; Kulshrestha and Sharma, 2015). Atmospheric dust also affects relative abundance of $NH_3$ and $NH_4$ (Singh and Kulshrestha, 2012). Deposition of coarse mode reactive nitrogen species has been reported through dustfall in Indian region (Tiwari et al., 2016). A high uptake coefficient of nitrates by mineral dust irrespective of the relative humidity level has, therefore, resulted in $NO_y$ being removed faster near the dust source regions rather than being subjected to the long range atmospheric transport as given in the equation (1).

$$HNO_3\,(g) + CaCO_3\,(s) \longrightarrow Ca(NO_3)_2\,(s) + H_2O\,(l) + CO_2\,(g) \quad (1)$$

Temperature and relative humidity dependent transitions in the gaseous and particulate phases of ammonia, on the other hand, have resulted in more of $NH_3$ being dry deposited close to their emission sources unlike the downwind atmospheric transport of fine mode $NH_4^+$ particulates as given below (Singh and Kulshrestha, 2014)

$$NH_3\,(g) + HNO_3\,(g) \longrightarrow NH_4NO_3\,(s) \quad (2)$$

This has eventually resulted in high deposition fluxes of reactive nitrogen being observed over the arid western regions of India with a 2-3 order of its higher wet deposition fluxes than the corresponding dry deposition fluxes (Table 2). Significance of $Ca^{2+}$ and $SO_4^{2-}$ in the Nr scavenging by mineral dust has been evident from the summer time dustfall fluxes over Delhi-NCR (Tiwari et al., 2016). The abundance of gaseous Nr species over the urban-rural land use pattern, on the other hand, showed high concentration of $NH_3$ (51.57 ± 22.8 µg/$m^3$) over the rural site and high concentrations of $NO_x$ over the urban land use pattern (24.4 ± 13.5 µg/$m^3$) depending on the emission sources of the different land use pattern (Singh and Kulshrestha, 2014).

Current deposition rates have resulted in 11% of the world's natural vegetation exceeding their critical load threshold of 1 kg $m^2$ $yr^{-1}$. This is clearly reflected from its growing extent affecting most of the Eastern Europe (80%), western Europe (30%), South Asia (60%), Japan (50%), east Asia (40%), south-east Asia (30%) and United States (20%). Thus, the future deposition fluxes driven primarily by emission changes is only expected to increase the global nitrogen loads in excess of their critical thresholds by 17% under current air quality emission scenario or by 25% under the contrasting

**Table 2: Wet and dry deposition fluxes of Nr over arid western regions of India**

| *Location* | *Dry deposition flux $NO_3^-$ (mg/m²/d)* | *Dry deposition flux $NH_4^+$ (mg/m²/d)* | *Wet deposition flux $NO_3^-$ (mg/m²/yr)* | *Wet deposition flux $NH_4^+$(mg/m²/yr)* | *Ref.* |
|---|---|---|---|---|---|
| Ahmedabad | 0.28 | 0.03 | 138 | 319 | Rastogi and Sarin, 2006 |
| Delhi | 0.66 | - | 64 | 283 | Parashar et al., 2001 |
| Agra | 1.63 | 0.44 | 584 | 584 | Satsangi et al., 1998 |
| Hisar | 2.6 ± 1.3 | 0.43 ± 0.28 | - | - | Rengaranjan et al., 2007 |
| Mt Abu | 0.07 ± 0.09 | 0.05 ± 0.03 | - | - | Kumar and Sarin, 2010 |

pessimistic IPPC A2 emission scenario (Dentener et al., 2006). Though the critical load calculation for the oceans remains constrained with uncertainties, increasing atmospheric inputs of Nr have been speculated to increase marine biological productivity by 3% and their resulting $N_2O$ emissions by ~1.6 TgN $yr^{-1}$ (Galloway et al., 2008).

## Interaction Dynamics of Nitrogen with Other Elemental Cycle

As a direct consequence of the organism's constitutional need at molecular level, an inextricable linkage amongst different biogeochemical cycling has been provided by the broad proportionalities existing in the nutrient content of an ecosystem. This has resulted in nitrogen coupling with different elemental cycle at their specific elemental stoichiometries whose value and flexibility has been detrimental to the relative speed of cycles being coupled (Lavelle et al., 2005). The natural components of the carbon and nitrogen cycle have shown a tighter coupling than the anthropogenic components owing to their close linkage with the microbial mineralization. Dynamics of phosphorus, on the other hand, may not be closely associated with carbon and nitrogen cycles due to their prime derivation from the mechanical rock weathering (Smeck 1985; Gruber et al., 2008).

Considering the limiting role of nitrogen in the global primary productivity, alterations in C/N ratios of the autotrophs has provided rapid and large changes to the productivity of Earth's biosphere without the need for affecting the biologically available N amounts (Figure 4). This has resulted in a tight coupling of productivity to the biologically available N with direct implication on the atmospheric $CO_2$ and climate. By regulating the responses of terrestrial C cycle to increasing $CO_2$ and climate changes, N availability have shown strong constrain on the $CO_2$ fertilization effect on plants productivity under increasing $CO_2$ levels. This has led to N dynamics providing an overall negative climate-C feedback through increased N mineralization and its subsequent sequestration in the plant biomass under climate warming (Thornton et al., 2007). Lack of coupled N dynamics, on the other hand, has shown a positive climate-C feedbacks from the global warming induced reduction in the terrestrial carbon storage (Sokolov et al., 2008). This has consequently resulted in N saturated ecosystems observing a sharp decline in C/N ratios leading to ~20% decrease in the tree leave of a temperate forest and ~12% decrease in sagebush-crested soil (Chen and Stark, 2000). Thus, a close coupling of C and N cycles has been significant in the alteration of terrestrial C cycling by providing indirect feedbacks from the perturbation in N cycle.

In response to environmental changes, the balance of major nutrients (C:N:P) has greatly been altered with organism either trying to eliminate excess nutrients or developing strategies for the better capture of the limiting nutrients. Increasing dry land aridity from the continuous N deposits has eventually increased the phosphorous availability primarily from the rock weathering leading to a decoupled C, N and P cycle (Delgado-Baquerizo, 2013). Similarly a higher remineralization efficiency for P than N has produced shifts in N/P ratios from the increasing anthropogenic inputs in large water bodies. This has resulted in either the development of new phytoplankton community aligned to the new N/P ratios or modification of C:N:P composition of the existing phytoplankton itself with their consequent effect on the nutritional values for the primary consumers (Lavelle et al., 2005). However, variability and flexibility of the C/N ratios in the autotrophic phytoplanktons have been remarkably less than the terrestrial plants which also tend to be larger than the marine phytoplankton.

## Changing Nr-Climate Interactions

With the exception of $N_2O$, the effect of $NO_y$ and $NH_x$ on climate and its feedback mechanism has largely remained ignored by the virtue of their short lifetimes in atmosphere. But considering their relevance in the anthropogenic changes of N cycle and the biosphere-atmosphere exchange of Nr compounds, the significance of these short lived species to the Earth's radiative budget cannot be completely excluded (Erisman et al., 2011). Increased scattering efficiency of aerosols through direct (–0.12 $W/m^2$) as well as indirect anthropogenic forcing (–0.09 $W/m^2$) of particulate nitrate and ammonium has been evident in their global chemistry transport model with most of the indirect forcing being provided by the condensation of gaseous nitric acid (–0.08 $W/m^2$) at the top of the atmosphere (Xu et al., 2012). A thermodynamic equilibrium treatment of nitrate aerosols, on the other hand, has given a significantly lower forcing (–0.07 $W/m^2$) from their overestimated coarse mode fraction (Jacobson et al., 2001; Feng and Penner, 2007). However, a complete neglect of its heterogeneous chemistry on dust and sea salt particulates has given a comparatively higher estimates of nitrate aerosol forcing (–0.3 $W/m^2$) especially over the high emission regions of Eastern

Asia, Europe and N. America (Adams et al., 2001). This has resulted in the global burden of nitrate and ammonium contributing 13% of the total anthropogenic forcing but with a two-fold rise from their pre-industrial to present day scenario as shown in Figure 5.

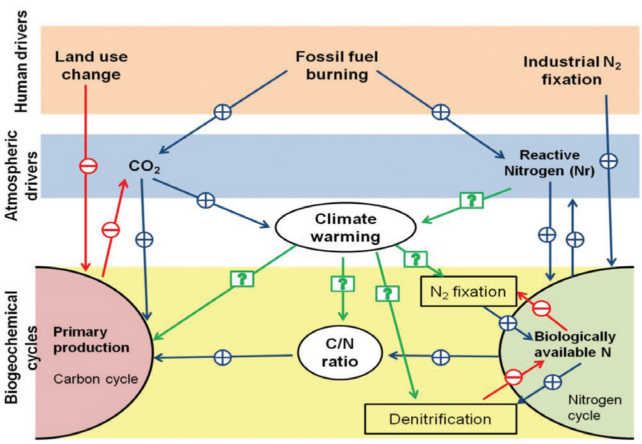


**Figure 4: Nitrogen-carbon cycle interactions. ("+" indicates increase, "–" indicates decrease and "?" indicates an unknown impact factor)**

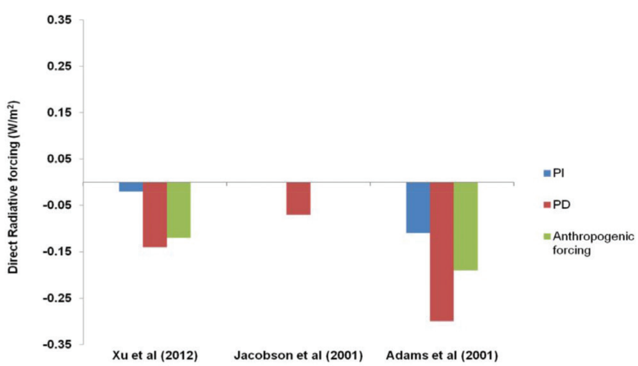


**Figure 5: Comparison of direct radiative forcing of nitrate and ammonium (W/m$^2$) under different simulation conditions. (PI: Pre-industrial; PD: present day)**

A series of sensitivity studies under different climate and emission scenarios by Bauer et al. (2007) and Koch et al. (2007) have simulated a 6% rise in the global mean burden of nitrate aerosols under present-day climatic conditions. Inclusion of $SO_2$ emission scenarios of year 2000 have additionally shown an overall 8% rise in the nitrate aerosol mass loading by favouring the reactions of ammonia with nitric acid instead of sulphates. Exclusion of the mineral dust reactions, on the other hand, have shown a 10% rise in the nitric acid precursor gas with simulations reaching up to 60% rates over India alone. However, a higher sulphate concentration resulting in a 30% decline in free ammonia is likely to reduce the nitrate aerosol production over the tropics. Therefore, an overall change in the radiative forcing (RF) of nitrates is likely to show strongest negative values over India, China and exceptionally over North Pacific Ocean where the dominance of Asian pollution plumes becomes attributable to its negative forcing (Metzger et al., 2002; Liao et al., 2004; Bauer et al., 2007).

Influence of N cycle under elevated $CO_2$ levels has shown an increased N mineralization rates in the future climate change scenario of the ARPEGE climate models (Salmon-Monviola et al., 2013). These effects are derivable not only from a single climate change variable but a number of factors exerting a complex control on the nitrogen cycling in changing environment. This has been evidently shown in the dramatic nitrate decline occurring in the northeastern forest of United States which could only be explained by a combination of climate change and long lasting effects of early forest cutting creating 50-60% of N exports over the past 46 years (Bernal et al., 2012). Additionally, $CO_2$ enrichment conditions have also been instrumental in modifying N allocations under different watering regimes with recent reports suggesting well watered conditions providing decreased plant N leaf content (Xu et al., 2007). Together these effects may result in a reduced N turnover with climate change with consequent weakening in the regulatory responses of plant's growth and productivity to elevated $CO_2$ (Scholze et al., 2006; Penuelas et al., 2013; Oris et al., 2013).

## Conclusions

Growing significance of N as a nutrient for all biota have resulted in a need of further understanding and measuring the complexity of biological, chemical and physical factors regulating the N cycling processes under an ever increasing rate of N anthropogenic inputs and its resulting losses to the environment. Missing links in the N balance has largely been explained by the highly uncertain biological nitrogen fixation (BNF) with values 10 times larger in peatlands than the tropical forests. With emerging evidences indicating towards a more substantial contribution of atmospheric deposition to the tropical forests, there is a need for warranting a careful attention to the global changes in temperature, moisture and N depositions affecting their N cycle dynamics. However, only a few studies have been attempted in scaling up the local estimates of BNF and denitrification of terrestrial ecosystem with the uncertainty of their N budget being as tentative as that of the oceans. In addition, significant alterations in the features and stoichiometries of N cycling has been provided by the land use changes as evidently shown in their shifting N:P ratios. This has created the problem of global inequities in Nr with their distribution pattern being primarily controlled by atmospheric transport and deposition processes.

Though wet deposition of Nr is considered to be the major removal process (amounting to >80% of its scavenging in many regions), the arid and semiarid regions of the world with less than 40 cm $a^{-1}$ precipitation depths and greater than 2 kg N $ha^{-1}$ $a^{-1}$ Nr emissions have shown dominance of dry deposition over parts of eastern U.S., western Europe, northern India, Bangladesh and eastern China. Such a pattern has been evident from the closely tied peaks of nitrate aerosols and dust at the major dust regimes of the world which has resulted in 38% of the gaseous $NO_y$ removal through particulate nitrate formation. Preferential association of ammonia with sulphate aerosols, on the other hand, has resulted in 85% removal of particulate $NH_4^+$ through wet deposition and 57% removal of gaseous $NH_3$ occurring through dry deposition. Together, they have been responsible for a net negative radiative forcing where an increasing nitrate burden under the current and extreme IPCC A2 future emission scenario is likely to show the decreased radiative forcing of sulphate aerosols by allowing a larger formation of ammonium nitrate under ammonia excess condition.

**Future Challenges**

Response of the global nitrogen cycling has been sensitive to the large swings in the Earth's changing climate especially over the arid and semi-arid regions of the world driven by water deficit. This has been evident from the closely linked carbon and nitrogen cycle which has shown an increased mineralization of N providing an overall negative climate-carbon feedback under elevated temperature and $CO_2$ conditions. Thus, a world with both high $CO_2$ and N levels would eventually result in greater carbon storage by soil microorganism by changing the stoichiometry balance and availability of N. This would profoundly affect the bioprocesses at regional and global scales through N reallocation between above ground and below ground parts of the plants under high $CO_2$ and future climate change scenario. However, unclear mechanism of global climate changes controlling the N availability and turnover rates still pose a huge challenge while assessing N cycle with climate models. A close association of anthropogenic NOx emissions with other climate change factors such as $O_3$ formation, nitrate aerosol formation and decline in $CH_4$ levels warrants a further investigation that are known for their complementary feedback to the global warming.

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