

An Overview of Atmospheric Reactive Nitrogen Research: South Asian Perspective

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Abstract

The unprecedented increase in reactive nitrogen (Nr) is causing several environmental problems such as eutrophication, ozone depletion and climate change etc. Excessive Nr creation is also responsible for poor plant and human health, soil acidification, groundwater contamination etc. Inhabiting ~ one-fourth population of the world and sharing only 4.9% land of the total global landmass, the South Asian region consumes 60% of the total global fertilizer nutrient. India is the largest consumer of synthetically produced fertilizer in the South Asia. According to estimates, India consumes ~ 17 million tonnes Nr/yr, making South Asia and India a hot spot for the deposition of N species. In India, the fertilizer N consumption is increased 314 folds from 1950-51 to 2013-14. In 1951-52, fertilizer N consumption was 0.44 kg/ha while it was 86.2 kg/ha in 2013-14. Since, rains are limited to few months, most of the time the weather is hot and dry. Hence, the dry deposition is the key mechanism of atmospheric pollutant removal in the region. Wet deposition predominantly occurs during monsoon period. The wet deposition of $\text{NH}_3\text{-N}$ observed to be the highest in the Indo-Gangetic plains. The annual $\text{NO}_3\text{-N}$ deposition at urban, suburban, rural and industrial site found to be 4.48, 2.10, 4.06 and 3.92 kg/ha respectively, and the annual deposition of $\text{NH}_4\text{-N}$ at the urban, suburban, rural and industrial site found to be 2.38, 2.10, 2.38 and 5.05 kg/ha respectively. The average total wet deposition of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in India is estimated to be 6.01 kg/ha which is equivalent to 1.97 Tg N/yr. The average total dry deposition of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ through dust fall found to be 0.37 kg/ha and 0.84 kg/ha respectively. The average total dry deposition of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in the form of aerosols found to be 0.28 and 1.65 kg/ha while through gaseous dry deposition it was 4.72 kg/ha and 0.28 kg/ha for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ respectively. This study highlights the need of integrated nitrogen monitoring and assessment in South Asia.



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Introduction

In spite of frequent and significant alterations in the past, the earth's environment has been amazingly constant for the past ten thousand years.^{1,2} This period is known as Holocene. In the Holocene epoch, nature driven the environmental change by virtue of that regular temperature, biogeochemical flow, and fresh water availability, all confined within a comparatively narrow range, which allowed human development. But ever since the industrial revolution, the activities of the Anthropocene era significantly affected the global environment.^{3,4,5} The addition of nitrogen, phosphorus and carbon accelerated by the anthropogenic activities, are now so massive that they have the potential to significantly perturb global cycles of these biogeochemically important elements.^{6,7} It is important to mention that the earliest Earth's nitrogen cycle was controlled by the sluggish geological processes and the atmospheric reactions, but by 2700 million years ago in the archaean eon, the microbial activities were evolved which shaped the modern nitrogen cycle with strong natural controls and feedback.⁸

In the present era, the anthropogenic activities are constantly transforming the global nitrogen cycle at an unprecedented speed. This transformation is attributed to the proliferating demand of nitrogen for intensive agriculture, industrial activities, burning of fossil fuels and ubiquitous inefficiencies in its use. The large emission of anthropogenic nitrogen makes its way to the air, water and land resulting in the environmental degradation and human health problems.⁹ Diatomic nitrogen (N_2) is an inert gas which comprises 78% of the atmosphere. Only certain bacteria and cyanobacteria, those are able to synthesise nitrogenase enzyme, can break the triple bond – a strong bond which holds both atoms of molecular nitrogen together. In spite of having the ability to produce nitrogenase enzyme, these nitrogen fixers are not able to readily fix the atmospheric nitrogen. The constraints behind this inefficiency are the high energy cost of running nitrogenase and the massive requirement of other elements to produce this enzyme. This is why that productivity of many ecosystems and plant and algal biomass limited by nitrogen.^{10,11}

Agricultural Productivity and Nitrogen Cycle

During early periods of agricultural practices, human returned human and animal waste to the field thus adding nitrogen (and phosphorus) and enhanced crop production. In the beginning of 20th century, Fritz Harber and Carl Bosch developed an industrial process to synthesize reactive nitrogen (Nr) from atmospheric N_2 . This process soon became a mean to synthesize nitrogen rich fertilizers. At the same time, the industrial processes and adoption of the internal combustion engine led to the ubiquitous emissions of oxidized nitrogen (NO_x) to the atmosphere.¹² Very soon promotion of food production through intensive agricultural practices using synthetic fertilizers became a source of environmental deterioration. It is surprising to note that since the 1970s, the increase in world population is 78% while the creation of reactive nitrogen has enhanced by 120% and every year it is continued to increase. Anthropogenic activities, primarily manufacturing of fertilizer for intensive agriculture and farming of leguminous crops transform ~ 120 million tonnes of atmospheric N_2 per year into Nr which is very huge quantity. Much of this newly produced Nr makes its way to the environment, accumulating in land system, polluting waterways and coastal zones and adding a number of gases to the atmosphere.¹³

Sources of Reactive Nitrogen

Natural Sources

Biological Nitrogen Fixation (BNF) in Marine Ecosystems

BNF is the microbial mediated group of reactions which transform diatomic Nitrogen (N_2) into ammonia (NH_3). BNF act as input process by which Nr enters into the ocean and land environment. With a suggested range of 60 - 200 TgN / yr,¹⁴ BNF in global marine ecosystems has been calculated as 125 TgN / yr.¹⁵ In addition to this, other estimates show its rate as 140 TgN / yr¹⁶ and 145 TgN / yr.¹⁷ In the same flow Voss *et al.*,¹⁸ suggested this value of 140 (± 50) TgN / yr for global marine BNF.

Biological Nitrogen Fixation (BNF) in Terrestrial Ecosystems

BNF is considered as a primary, non-anthropogenic input of fixed nitrogen, making it an important

reference in the quantification of the magnitude of anthropogenic inputs to global nitrogen cycle.¹⁹ Since its identification in late 19th century, BNF has been considered as a topic of ecological interest.¹⁷ In a review, Vitousek *et al.*,²⁰ estimated that the pre-industrial terrestrial BNF was 58 (the range of 40-100) TgN / yr. However the range of uncertainty is broad and there is scope of more work on BNF estimates.²⁰

Lightning

Lightning represents a crucial source of Nr species (NO_x) in the troposphere.²¹⁻²² Levy *et al.*,²³ bracketed the global annual NO_x emission in the range of 2 - 6 TgN/yr, with most the probable range between 3-5 TgN / yr, with more latest value of closer to 5 TgN / yr.

Anthropogenic Sources

In spite of being uncertain, human induced nitrogen fixation is well known than natural nitrogen fixation.²⁴ The Anthropogenic creation of reactive nitrogen is mainly attributed to three sources.

The Harber - Bosch Industrial Synthesis

Haber - Bosch synthesis used to reduce N_2 into NH_3 , primarily for the synthesis of nitrogen fertilizers and also as feedstock for some industrial processes.

From the beginning of this century, each year, 120 TgN / yr or NH_3 is produced by the Harber - Bosch process has produced. Eighty per cent of this NH_3 has been utilized in the synthesis of nitrogen fertilizer and reaming 20% is utilized for industrial processes as feedstock.⁹

Cultivated Biological Nitrogen Fixation (CBNF)

In a latest review, Herridge *et al.*,²⁵ have reported Nr creation by CBNF in the range between 50 and 70 TgN / yr. The central value of this range is 60 TgN / yr. These authors have used, combined unpublished and published data reporting the fixation of nitrogen with the data on the yields and areas of cereals and legumes from the FAO database on agricultural production (FAOSTAT).²⁵ It is apparent that the value of CBNF (60 TgN / yr.) is very near to BNF (58 TgN / yr.) in the pre-industrial period.²⁴

Burning of Fossil Fuels

Combustion of fossil fuel is attributed to release nitrogen into the atmosphere from the coal and petroleum which are the long term geological reservoir of fixed nitrogen. Moreover, the high temperature combustion processes fixe a tiny fraction of atmospheric nitrogen. Combustion of fossil fuels within internal combustion engines and

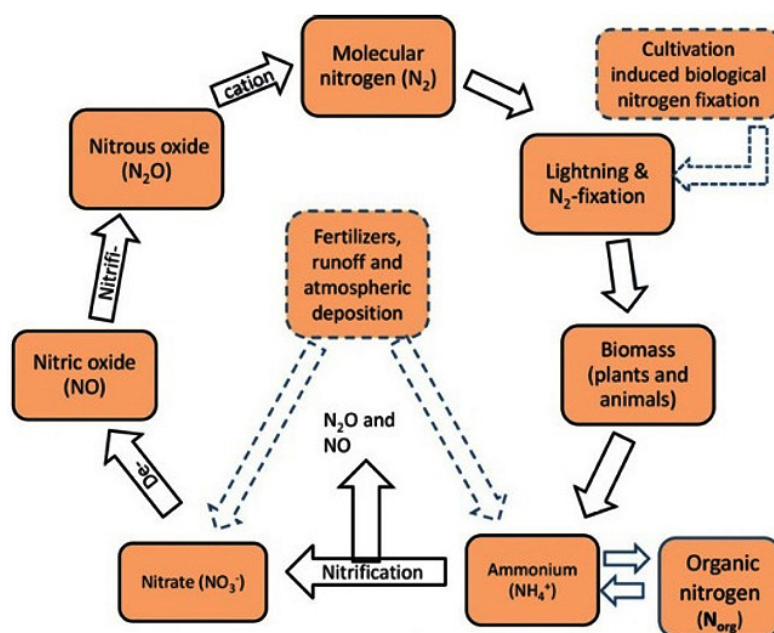


Fig. 1: The nitrogen cycle. The dotted arrow depicts anthropogenic additions to the natural cycle (modified from Battye and co-workers²⁶).

in power plants particularly for electricity generation, are the most prevalent processes attributed to the creation of oxidized nitrogen compounds. The commonly generated compounds are mainly NO and NO₂, which come into existence when atmospheric N₂ is oxidized, albeit nitrogen compounds in the fuel also contribute additionally to the formation of these compounds.²⁷ An estimate from van Vuuren *et al.*,²⁸ suggests that, for the year 2000, global production and emission of NO_x is ~ 40 TgN / yr. Out of this total ~ 40 TgN / yr, 30 TgN / yr is contributed by the combustion of fossil fuels, 5 TgN / yr comes from NO emission of soil, and 5 TgNy/r comes from burning of biomass. It is assumed, although with a large uncertainty, that in spite of continued industrial development, control measures for emission in Africa and Asia, will reduce the emission approximately to a value of 30 TgN / yr, by the mid of 21st century.²⁴

Other Sources

Worldwide biosphere contains 10¹⁹ g of N in fixed form that is considerably less than the 10²¹g of fixed nitrogen in total sedimentary rocks.¹⁷ This nitrogen is present in sedimentary rocks and particularly emanates when organic matter buried in freshwater and marine sediments. During this burial N is incorporated within sedimentary strata in the form of ammonium in silicate minerals or in the form of

organic nitrogen.²⁹ Moreover, biologically available nitrogen in the form of nitrate also found in arid regions in subsoil zones. It has been accumulating there throughout the Holocene epoch of the quaternary period.³⁰

Limitations and the typical example of nutrient cycling postulated that terrestrial ecosystems gain new nitrogen only from the atmosphere, but Morford *et al.*,³¹ have shown that a tiny flux of Nr is also released from the sedimentary rocks rich in nitrogen (not shown in figure 2). This source of ecologically available nitrogen has been overlooked since a long time.

Impacts of Nr

Unprecedentedly increasing demand for more food and energy production massively leading to increase in fertilizer use and fossil fuel combustion that are ultimately leading to intensified loss of Nr to the environment. The adverse impacts of these nitrogen additions are ubiquitous and manifolds, for example, degrading water (increasing nitrate concentration) and air quality (smog, ground level ozone, particulate matters), biodiversity loss, climate change, fresh water eutrophication, stratospheric ozone depletion, and creation of dead zones in costal ecosystems.^{25,32} The impacts of Nr under different categories have been discussed below.

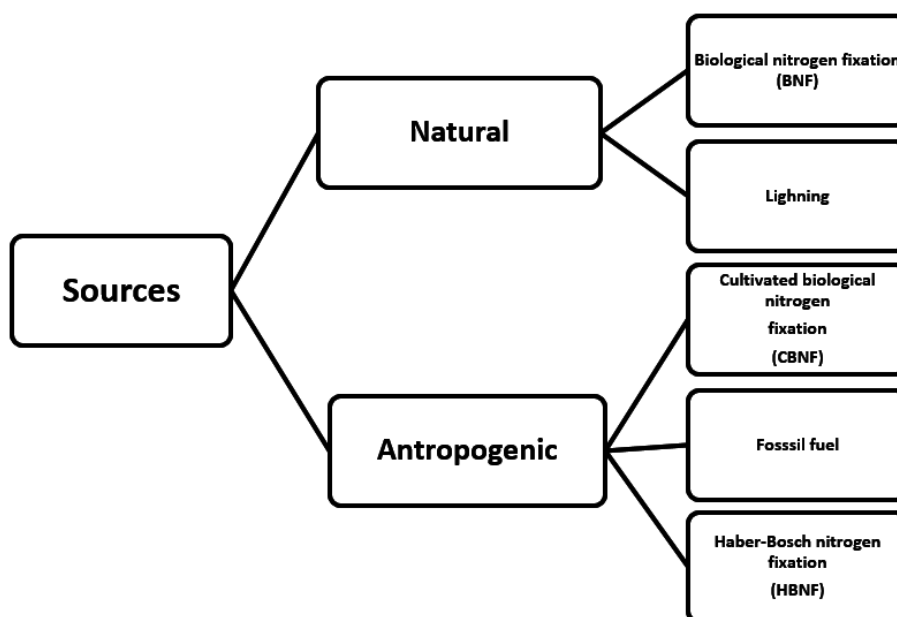


Fig. 2: Sources of reactive nitrogen.

Impacts on the Atmosphere

Unlike atmospheric CO₂ which has increased ~40% above its pre-industrial level,³⁴ the amount of nitrogen in the environment has been increased more than 100%. This increase is mainly attributed to anthropogenic activities.⁹ Only ¼ fraction of anthropogenically produced nitrogen by fossil fuel burning and industrial nitrogen fixation, per year makes its way to inert N₂ gas,⁶ while most of the

remaining ¾ fraction remain as reactive nitrogen and continues to recycle and accumulated through the environment for years or decades⁹ consequently many trace gases including N₂O, NO and NH₃ liberated to the atmosphere.³⁵ Nitrous oxide (N₂O) is a very potent greenhouse gas.³⁶ Emission of N₂O directly affects global warming and its warming effects are long term since its residence time in the atmosphere is >100 years.³⁷ N₂O enters in the

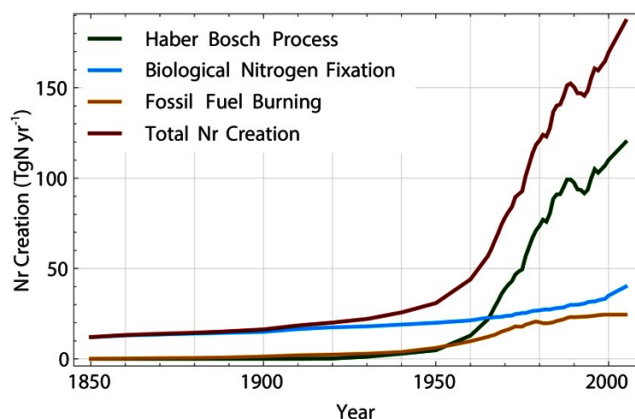


Fig. 3: Anthropogenic reactive nitrogen (Nr) creation rates (in TgN/yr) from fossil fuel burning (orange line), cultivation-induced biological nitrogen fixation (blue line), Haber–Bosch process (green line) and total creation (red line).^{32,9} The data are only reported since 1850, as no published estimate is available since 1750.³⁸

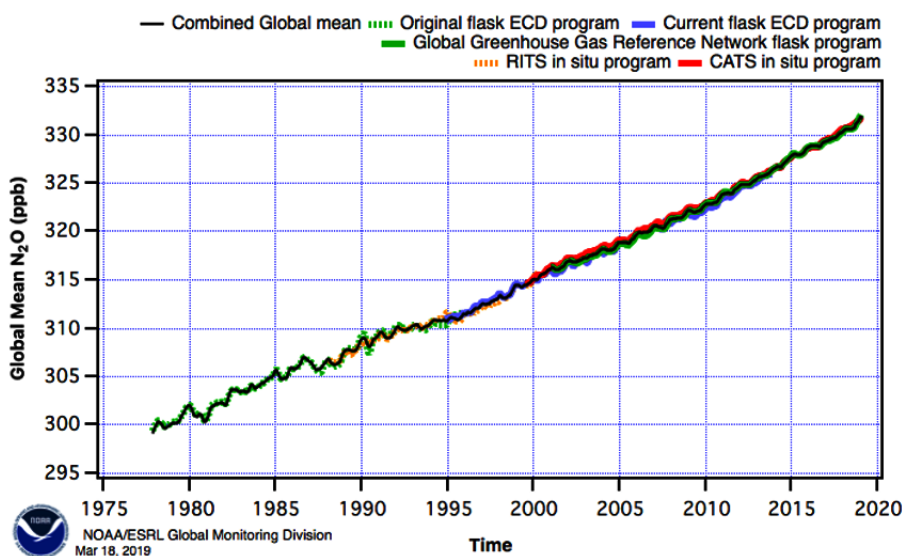


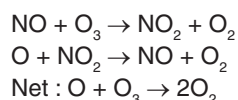
Fig. 4: The atmospheric increase of nitrous oxide.³⁹

troposphere primarily by soil microbial activities such as nitrification and denitrification. In the troposphere, N_2O is unreactive while in the stratosphere, it is destroyed by reaction with excited oxygen atoms or by photolysis, where it can catalyse the process of the stratospheric ozone destruction. During the time interval from 1750 to 2011, N_2O emission has increased by 20%, from 271 ppb to 324.2 ppb. Over the last three decades, atmospheric concentrations of N_2O are increased at a rate of 0.73 ± 0.03 ppb/yr and its emissions by anthropogenic activities increased steadily over the last two decades and were 6.9 Tg/yr. The main emission sources of N_2O are nitrification and denitrification reaction (see figure1) of N_r in the ocean and the soil environment.^{40,38}

Change in the concentration of NO and NH_3 needs to be evaluated at local, regional and sub-continental scales because the reason behind this fact is that both these gases are more reactive than N_2O in the atmosphere. In fact, NO plays very crucial role in many atmospheric reactions. It affects the concentration of OH radical- the main oxidizing agent- in the atmosphere.⁴¹ In addition to this, NO plays a key role in the photochemical formation of tropospheric ozone (O_3), the most important gaseous pollutant that adversely affects the plant productivity and human health.^{41,42} When there are high concentrations of NO, the oxidation of methane, non-methane hydrocarbons and carbon monoxide, leads to net production of ozone,^{43,44} but during

the time of low concentrations of NO, oxidation of these compounds acts as sink for ozone. Finally, the oxidation of NO leads to the formation of HNO_3 , which is the principal component of acid rain. NO is emitted from a number of sources including microbial activities in fertilized soil but combustion is the largest source of NO emission.⁴⁵

Study conducted by Crutzen⁴⁶ and Johnston⁴⁷ revealed that the nitrogen oxides ($NO_x = NO + NO_2$) catalytically destroy ozone via



The surface emission of N_2O is the primary source of stratospheric NO_x .⁴⁸ The N_2O is emitted in the troposphere where it is very stable and is transported to the stratosphere where it releases the active chemicals that destroy stratospheric ozone through nitrogen oxide-catalysed processes.⁴⁹

In the atmosphere, ammonia acts as primary acid neutralizer and influences the pH of rain water, cloud and aerosols. Akin to NO, after being emitted from its sources, ammonia is transported into the atmosphere and makes its way to ecosystems via dry deposition, gas absorption or in solution form. There are many studies which have demonstrated the volatilization of NH_3 from nitrogenous fertilizers.^{50,51} Almost 70% of all global ammonia emissions come

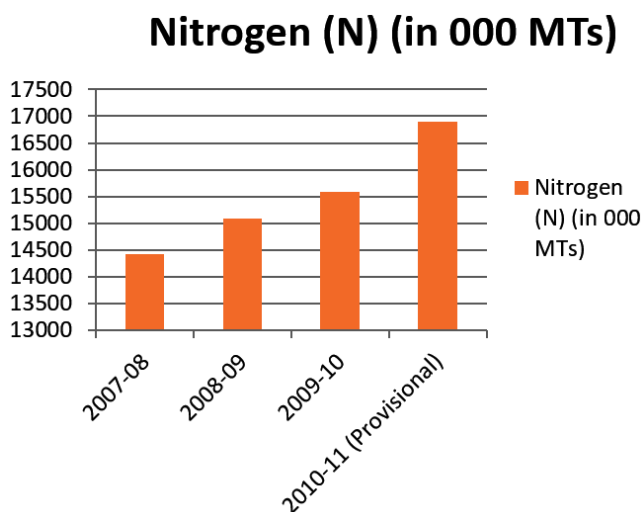


Fig. 5: All India consumption of fertilizer nutrient (nitrogen) from 2007-08 to 2010-11

from anthropogenic sources.⁵² An accelerated deposition of nitrogen on land and in the ocean is concomitant to the accelerated emissions of nitrogen to the atmosphere.⁵³

Impacts on Human Health

It is obvious that a sustained and active biosphere requires addition of nitrogen into biologically important molecules.⁵⁴ For example, the synthesis of protein and nucleic acid requires nitrogen.⁵⁵ Presumably, 40% of the world's dietary protein currently comes from syntactic fertilizers⁵⁶ and in the absence of nitrogenous fertilizer - synthesized by the Haber-Bosch process- current food production would not be sufficient to sustain the unprecedentedly increasing world population.²⁵ Although, products obtained from intensive agricultural practices in many developed countries, lead to unhealthy diets yet elsewhere depleted soil nutrient reserve, coupled with lack of synthetic fertilizers ultimately leads to widespread malnutrition.⁵⁷ After entering to the environment, Nr affects, terrestrial, atmospheric and aquatic realms, and can affect human health and welfare in different ways.⁵⁸ Creation of reactive nitrogen by humans can influence health in both negative and positive ways, but health benefits presumably saturates when the creation of reactive nitrogen increase, while negative impacts prevail and

diversify. The increasing reactive nitrogen, negatively affects human health both directly (e.g. air and water pollution) and indirectly (e.g. ecological feedback to disease).

The anthropogenic increase of reactive nitrogen in the environment leads to some direct and clear health consequence for human. The term "direct" means health consequences due to the consumption of Nr particulates and other compounds e.g. nitrate in drinking water. Both in the developed as well as in the developing regions, ground water nitrate contamination are attributed to the fertilizer use. WHO has set a maximum standard concentration of 10 ppm nitrate-N in the safe drinking water.^{59,60} Several potential health consequences are attributed to the high nitrate level including cancer, methamoglobinemia or blue baby syndrome- infant are more prone to it- and reproductive system related problems.^{61,62}

Increasing NO_x level due to fossil fuel and biomass burning and the use of fertilizers, leads to production of tropospheric ozone.⁶³ Moreover, NO_x and O_3 exposure can cause severe health effects such as eye irritation, cough, asthma, and induces inflammation of the respiratory tract etc.⁶⁴ NO_2 at high levels may be responsible for almost 2 million deaths

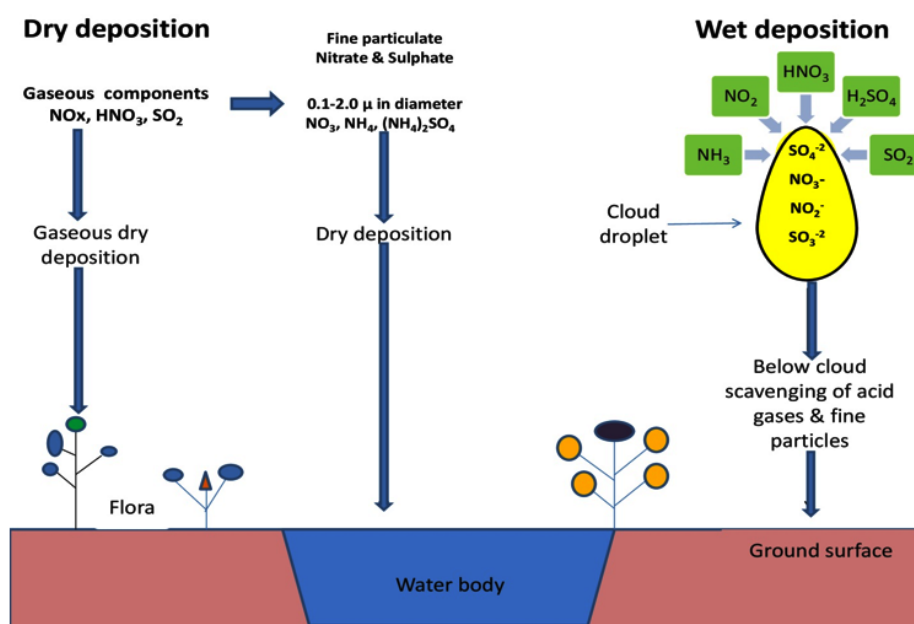


Fig. 6: Mechanism of the dry and wet deposition of acids in the troposphere.

per year due its indoor pollution effect,⁶⁵ A positive correlation between fine particulate air pollution and respiratory disease, cardiovascular disease, overall mortality and asthma has been shown by multiple studies.⁶⁶

Fixed inorganic nitrogen, most commonly nitrate (NO_3^-) and ammonium (NH_4^+) have very critical role in controlling the primary productivity of the biosphere^{67,25} and the anthropogenic augmentation of N to the environment can cause a substantial range of changes in ecology which almost certainly comprises the dynamic of some disease.⁶⁸ There are now some evidences which suggest that the distribution and abundance of many crucial vectors, including the West Nile River and mosquito host of malaria, may be affected by the variation in nitrogen availability. A substantial number of studies have suggested that there is a positive correlation between the larval abundance of malaria *Anopheles sp.* mosquitoes and concentration of inorganic nitrogen in surface water.^{69,70} Positive correlations between the larval abundance of *Anopheles* and indices of algal productivity in Africa and Latin America have also been found^{69,71} but not such all correlation are positive.⁷¹ Eutrophication of marine and costal ecosystem is also a ubiquitous and clear effect of the proliferated nitrogen cycle.⁷² As an ecological change eutrophication may also affect human health since the ubiquitous increase in harmful algal blooms (HABs) has been attributed to nutrient loading caused by human activities.^{73,72} HABs may include toxins synthesized by the *Pfiesteria shumwayii* and *P. piscicida* -the estuarine dinoflagellates- and by various cyanobacteria as well as amnesic, neurological, paralytic and/or diarrhetic shellfish poisoning.⁷³ Moreover, HABs can disrupt the source of nutrition and ecosystem. In such a way they can indirectly affect humans.⁷² Ultimately, outbreaks of cholera have long been associated with algal bloom in coastal areas and the *Vibrio cholera* is associated with a broad range of marine life.^{74,75}

How Nr Affects to the Natural Ecosystem?

Several factors, including the form and the total amount of nitrogen, the duration of exposure, the intrinsic ecosystem properties such as acid neutralizing capacity and fertility and sensitivity of the species, determine the impact of Nr on the species.⁷⁶

Organisms that uptake elements directly from the environment such as sensitive algae, bryophytes or lichens, can face toxicity at high concentrations of Nr (especially reduced N).⁷⁷ Generally, Nr affects living creature through routes such as water or soil acidification, nutrient enrichment, oxygen depletion (in aquatic ecosystems), intensifying the effect of other stressors such as climate change or pathogens, or altering nutrient ratios.

The Eutrophication

The supply of essential nutrients such as N and P to the waters bodies from anthropogenic sources can provoke intensive production of algal biomass. This process is known as eutrophication. When microbes consume this organic matter, oxygen level plummets in water. Moreover, CO_2 is produced when microbes respire, which enhance the acidity of water.⁷⁸⁻⁸⁰ Usually surface sources such as fertilizer run-off, erosion of nutrient-rich sediments or sewage discharge emanate nutrient enrichment of coastal and freshwater ecosystems. Diversity or biomass may proliferate with the increasing nutrient load in an oligotrophic ecosystem.⁸¹ However, when there is an increase in the availability of Nr and phosphorus, phytoplankton those are efficient assimilator of these nutrients progressively favoured over species more limited by other factors (e.g. benthic primary producers, requiring light, or diatoms, requiring silica). It can result in algal and cyanobacteria bloom of low diversity which can lead to release of toxic compounds and surface water hypoxia. Consequently, this can adversely affect organism of high trophic level such as invertebrates and fish.^{82,83} Surface sediments and bottom waters particularly in ecosystems having low rates of water turnover, can be oxygen depleted due to the sedimentation and decomposition of phytoplankton bloom biomass.⁸⁴ This again places the benthic community towards less tolerant species. This change in nutrient cycling, feedbacks to further alteration of ecosystem. Alteration in benthic community alters the cycling of nutrients in the sediment and overlying water.⁸⁵

The Terrestrial Ecosystem

The high concentrations of reactive nitrogen directly lead to foliar damage and especially lower plant species are at high risk. Some reactive nitrogen species are particularly toxic to plants.⁸⁶

In many terrestrial ecosystems, nitrogen act as limiting nutrient for the growth of plants⁸⁷ and reactive nitrogen deposited through atmospheric deposition, potentially attenuates the plant species richness- considered as an important component of biodiversity- which can be defined as “the number of species in a given community”.⁸⁸ Chronic nitrogen enrichment is attributed to gradual increase of nitrogen availability to several types of vegetation. This increased availability of Nr leads to competitive exclusion –that is two or more species cannot coexist on a single resource, which is scarce relative to the demand for this resource- of characteristics species by the plants which are nitrophilic in nature, especially where soil conditions are oligo to mesotrophic.⁶ When plant roots get bountiful amount of reactive nitrogen from nitrogen fertilization, they are less rely on the mycorrhizal fungi for their reactive nitrogen requirement which can led to reduction in organic carbon allocation from plant to mycorrhizal fungi within the soil.⁸⁹ Reactive nitrogen also affects to free living bacteria and nitrogen fixing fungi which can adversely affect important physical process of soil, like nutrient cycling and mineralization of organic matter. Change in microbial processes, microbial community or composition and growth of vegetation are the ways in which fauna present in soil react with nitrogen.^{90,91} When there is any alteration in the microbiota of soil occurs, it causes a concomitant alteration in important physical properties of soil such as organic matter turnover, water infiltration and soil aggregation.^{92,93}

South Asian Scenario

Almost one-fourth population of the world lives in South Asia while it shares only 4.9% land of the total global landmass with 2.98% world's forested land, 15.4% arable land of the world and 4% coastline of the world and comprises countries like Bangladesh, Afghanistan, Bhutan, Maldives, Nepal, Pakistan, Sri Lanka and India. Since Asia is agriculture dominated land, over the last three decades, it has witnessed the unprecedented hike in the consumption of nitrogenous chemical fertilizer that resulted in the degradation of environment and impairment of the ecological functioning. In spite of low external nitrogen use efficiency (as low as 30–35%), the South Asian region consumes 60% of the total global fertilizer nutrient. Satellite pictures for global ammonia column (mg m^{-2}) taken by IASI (Infrared

atmospheric sounding interferometer) emanate that Indo-Gengetic Plains (IGP) and it surrounding regions manifested by a massive atmospheric column of ammonia.⁹⁴

Moreover, as a one of the largest consumer of synthetically produced nitrogenous fertilizer, India consumes ~ 17 million tonnes N/yr (figure 5). In India, the fate of the bountiful amount of anthropogenically released nitrogen to the environment is not completely known.⁹⁵

It is worthy to notice that in 2015-2016 India consumed 15.5% of global fertilizer nitrogen production. Between 1970 and 2010 consumption of fertilizer nitrogen has witnessed a hike of 11 times and concomitantly Nr lost to the environment raised by ~4% and fertilizer nitrogen consumption by crops raised by 3 times for the same time duration. In addition to this CBNF is also an input pathway for nitrogen in the biosphere. Global CBNF has been estimate from 50-70 Tg/Nyr. Out of this 5.20 TgN / yr to 5.76 TgN / yr is contributed by India alone out of this 43% is contributed by legumes and 32% by grains.

Mineral Dust and its Interaction with HNO_3

Mineral dust affects atmospheric process both directly and indirectly. Moreover, soil particulates, blown by wind also significantly affect nutrient cycle or biogeochemical cycles. Soil receiving this deposition may become enriched with nutrients those otherwise were not present in these soils. Unlike temperate, tropical atmosphere has been attributed with high loading of mineral dust.^{96,97} The transport of nutrients through mineral dust can affect the primary production of terrestrial systems.⁹⁸⁻¹⁰⁰ Those regions where atmospheric dust is in abundance, almost all of the atmospheric nitrate is in the form of nitrate on dust. In addition to this, in both northern and southern hemisphere, more than 40 % concentration of nitrate is associate with mineral dust. Since calcium shows high buffering capacity for nitric acid, the presence of calcium in mineral dust consolidate the fact that major components of total atmospheric nitrate is in the form of dust-associated nitrate. Transportation of nitric acid in the form of gas- phase is improbable to the longer distances but, adsorbing on the surface of mineral dust from source locations, nitric acid may reach in remote locations those initially do not have

significant concentrations of HNO_3 . When associated with large particle of mineral dust, HNO_3 removed from atmosphere more faster in comparison of its dry deposition.¹⁰¹

In the troposphere, involving liquid phase (rain water, fog and cloud), gas phase and possibly certain suspended particles, there are many chemical pathways by which oxides of nitrogen and sulphur and organic compounds converted into acids. Reaction kinetics and rate at which oxidizing species generate in the troposphere, critically affect the rate of acid generation.¹⁰² Figure 6 is depicting the mechanisms of wet and dry deposition in the troposphere.

Particle of mineral dust collected from the various part of the world shows association with nitrate as a result of heterogeneous reaction and maximum peak intensity of nitrate ion found to be higher during the late afternoon, a time when the peak of gas-phase nitric acid was also highest.¹⁰³ Several studies emanate the relation between nitrate and calcium ions. One such study is conducted by Pakkanen¹⁰⁴ in southern Finland, which suggest that ambient nitric acid is neutralized by CaCO_3 present in the dust particles. Study conducted by Hanke *et al.*,¹⁰⁵ buttress the fact that particles of mineral dust efficiently uptake the gas phase HNO_3 . This type of uptake may be significant for tropical countries like India.

Application of Fertilizer Nitrogen and Dry and Wet Deposition NH_3 and NO_3 per Hectare in India

Since 1950-51, fertilizer-N consumption in India has increased exponentially which is attributed to the intensive agricultural practices performed to feed the rapidly increasing population. A 314 fold increase in fertilizer N has been observed during a period of 64 years. It has increased from a value of only 0.055 Mt in 1950-51 to 16.75 Mt in 2013-14. Moreover, in 1951-52 per hectare fertilizer N consumption was 0.44 kg ha^{-1} while it was 86.2 kg ha^{-1} in 2013-14. Currently, after China and United States, India rank third for fertilizer N consumption in the world. In India, agricultural consumption of total nitrogen has increased 3.58 in 1961 to 23.17 Tg in 2010.¹⁰⁶

Deposition of Atmospheric Reactive Nitrogen

Once emitted in atmosphere, in atmosphere gas-phase Nr species begin to transform and transport in the atmosphere and deposited away from the source region. These Nr species removed from the atmosphere through dry and wet deposition mechanisms. Weather dry or wet deposition will prevail; it depends on the climatological condition. In temperate regions, precipitation is the main mechanism for the scavenging of atmospheric pollutants, including Nr species throughout the year. But in the regions where dry conditions persist for a long period of time (having no or less precipitation), dry deposition is the key mechanism responsible for the removal of atmospheric pollutants. The last mechanism dominates in India, since in India, ~90% precipitation takes place only during the monsoon period that extends from June to September month. In the rest months of the year dry deposition is the dominating mechanism responsible for the removal of atmospheric pollutants. Since the tropical regions are dominated by ubiquitous solar radiation and atmospheric water vapour content, consequently there is a high rate of gas-phase to the particle-phase transformation of Nr species. Moreover, the fate of Nr species is determined by atmospheric acidity, particulate loading, land use dynamics, and photochemistry of the atmosphere.¹⁰⁷ Mineral and soil dust suspended in the atmosphere, act as the primary scavenger for acidic nitrogenous species by heterogeneous chemical reactions.¹⁰⁸⁻¹¹⁰

Wet Deposition Flux of Nr Over Indian Subcontinent

Atmospheric deposition of Nitrate and ammonium aerosols can lead to eutrophication and acid deposition in the receiving environment. Moreover, gaseous Nr species like NO_2 and NH_3 can adversely affect ecosystem functioning. Kulshrestha *et al.*,¹¹¹ reported NH_4^+ and NO_3^- depositional flux at four sites of different land-use pattern like industrial, urban, sub-urban and rural. In this study the highest NO_3^- -N depositional flux found on urban and highest NH_4^+ -N depositional flux found to be on industrial site. The annual deposition of NO_3^- -N at urban, suburban, rural and industrial site found to be 4.48, 2.10, 4.06 and 3.92 kg ha^{-1} respectively. On the other hand, the annual deposition of NH_4^+ -N at the urban, suburban,

rural and industrial site found to be 2.38, 2.10, 2.38 and 5.05 kg ha⁻¹ respectively.¹¹¹ A multimodal evaluation of nitrogen deposition on regional and global scales has been reported by Dentener *et al.*,¹¹² The wet flux of total average NO₃-N and NH₄-N are estimated to be 6.01 kg ha⁻¹ nitrogen deposition. For India, this value is equivalent to the wet deposition of 1.97 Tg N/yr. This depositional flux is far less than the amount nitrogenous fertilizer applied in agricultural practices.¹¹³

Dry Deposition Flux of Nr Over the Indian Sub-continent

The processes "Dry deposition" act as a crucial agent in the removal of Nr from the atmosphere.¹¹⁴ In India, together with wet deposition, dry deposition of particles and gases is also equally significant and atmospheric dust play a key role in the dry deposition of Nr species. Depending upon the particle chemistry and atmospheric conditions, dust provides a crucial sink for gaseous HNO₃, and NO₂. Moreover, dust fall of NO₃⁻ and NH₄⁺ emanates crucial information regarding how gases and coarse particles interact. Study conducted by Tiwari *et al.*,¹¹⁵ on six sites of Delhi NCR showed that the dust fall flux ranged from 1.24 mg/m²/day at Chuchchakwas village to 16.45 mg/m²/day at SMA industrial state while dust fall NH₄⁺ flux ranges from 0 mg/m²/day at Chuchchakwas village to 16.33 mg/m²/day at SMA industrial state, clearly showing that the industrial state site has the highest amount of dry deposition of NH₄⁺ in dust fall flux while lowest at Chuchchakwas village. These results indicate that as a significant contributor of different Nr species, the dust fall plays a crucial role in the dry deposition of these species.

The dry deposition velocities of NH₄⁺ and NO₃⁻ on natural surface (Cassia leaf) found to be 1.60 cm s⁻¹ and 1.09 cm s⁻¹ respectively.¹¹⁶ These relatively high deposition velocities of NH₄⁺ and NO₃⁻ clearly indicate that the dry deposition of nitrogenous particles is a significant mechanism to remove these species from the atmosphere. In India the average total deposition of NH₄-N and NO₃-N through dust fall found to be 0.37 kg ha⁻¹ and 0.84 kg ha⁻¹ respectively. Deposition of NH₄-N and NO₃-N in the form of aerosols found to be 0.28 and 1.65 kg ha⁻¹ while through gaseous dry deposition it found to 4.72 kg ha⁻¹ and 0.28 kg ha⁻¹ for NH₄-N and NO₃-N respectively.¹¹⁷

According to the estimates given by Kulshrestha,¹¹⁷ India emits 6.24 TgN, as major Nr but the average total Nr deposition (NH₄-N and NO₃-N) is found to be 3.61 TgN / yr indicating a gap which is probably because all the nitrogenous species not included in the deposition calculation. The average total dry and wet deposition of (NH₄-N and NO₃-N) found to be 1.64 and 1.97 TgN / yr respectively, indicating that both dry and wet deposition processes are of equal importance.

Long Range Trans-Boundary Movement of Pollutants

As with the different regions of the world, long range transport and trans - boundary movement of air pollutants have threats to South Asian ecosystems too. As a function of seasons, air masses from different regions like the Middle East, the Indian Ocean, Africa, and Europe and so on, reach to south Asia. As revealed by trajectory analysis associated with wet deposition events, the air masses having their origin from the Middle East and Europe transfer the high amount of acidic pollutants in the Himalayan region.¹¹⁸ Similarly, long distance transport of pollutants over Hudegadde in north Karnataka is an indicator of threat to the sensitive ecosystem of Western Ghats.¹¹⁹ Hence, the policy makers should focus on this issue of long range transport and trans-boundary pollution coming from far Europe, Middle East as well as from nearby countries.

Conclusion

1. Anthropogenic acceleration in the atmospheric nitrogen fixation is significantly perturbing the normal flow of the global nitrogen cycle at an unprecedented speed due to the increasing demand of fixed nitrogen in agriculture and industrial sectors, combustion of fossil fuel and cultivated biological nitrogen fixation.
2. India is the largest tropical country of the South Asian region consuming ~ 17 million tonnes N/yr which makes it a significant hot spot of the sources and transformations of Nr species. However, the region has high dust loading than temperate regions and heterogeneous chemistry of dust particles affecting the abundance of Nr species in the atmosphere. Moreover, there is the high rate of gas phase to particle phase conversion in tropical regions due to the presence of much

- solar radiation and ubiquitous water vapour content.
3. Most of the studies have been carried out on short term basis, hence, there are several gaps and queries about budgets. Hence, the South Asian region needs very robust emission and deposition budgets for various reactive nitrogen species for which a systematic network is required. Based on relatively long term monitoring, an integrated assessment can be attempted which can be the basis for the recommendations of new policies.
 4. In this region, the dry deposition is the key mechanism responsible for the removal of Nr species from the atmosphere. This is because the wet deposition in India prevails mostly during the monsoon period which extends July to September. During the rest
- eight months of the year there is no or very little precipitation. The annual depositions of NO₃-N found to be higher at the urban site while annual depositions of NH₄-N found to be the higher at the industrial site out of for sites of different land use pattern.
5. Deposition of Nr species is also affected by the long range transport and trans-boundary movement of pollutants. An increased deposition of Nr species has been reported at Himalayans due to air masses coming from western regions.

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