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Fertilizer nitrogen and global warming – A review

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ABSTRACT

Global warming is a burning issue today and agriculture especially the fertilizer nitrogen contributes to it significantly. It is also true that fertilizer nitrogen has been and will continue to be the key plant nutrient for increased cereal production in the world. It is estimated that by 2050 about 225–250 Tg N (Teragram or million metric tonnes) may be applied to agricultural crops as against 116 Tg N applied in 2016. In 2010, an estimated 100 Tg N was surplus from agricultural fields and released as nitrate (NO_3) to ground and surface inland and marine waters and as ammonia (NH_3) and nitrous oxide (N_2O) to the atmosphere; the latter contributing to global warming. The NO_2 so emitted has 298 times Global Warming Potential (GWP) as compared to CO_2 and contributes significantly to global warming. The only way to reduce N_2O emission from N fertilizer is to increase NUE in agriculture. Average nitrogen use efficiency (NUE) in cereal production at resent in the world is ~40%. This can be achieved by introducing enhanced efficiency of N fertilizers, better agronomic management of N and by developing of more efficient N using crop plants. Research strategies are necessary in all the three areas and also there is an urgent need for determining eco-friendly dose of N for each crop.

Key words: Carbon footprints, Fertilizer, Global warming, Nitrogen, Nitrous oxide

Global warming is a burning issue today. From the Indian viewpoint, it is important at two fronts: i) India has a big coastline and a large number of people depend upon it for livelihood, ii) Parts of India already suffer from drought each or alternate year (Awasthi 2018, Sharma 2018). Both of these fronts are related to global warming. Furthermore, if not prevented one-third of the glaciers in Hindu Kush Mountains may vanish by the end of 21st century, making not only India but a vast part of Asia go dry (Bhattacharya 2019).

In 2013, Intergovernmental Panel on Climate Change (IPCC) in its Fifth Assessment Report observed that global warming is mainly due to anthropogenic activities, especially since the mid-20th century (IPCC 2013). A recent analysis by Hausfather (2017) also supports this view. A study in USA found that out of total greenhouse emission (GHE) of 6511 Tg (million metric tonnes) of CO_2 equivalent, the contribution of different sectors of human activity was as follows: transportation 28%, electricity 28%, industry 28%, commercial and residential sector 11% and agriculture 9% (USEPA 2018). The contribution of agriculture could be greater in Asian and African countries, which have a primarily agriculture based economy. The major cause is the increase in the emission of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and chlorofluorocarbons (CFCs), which are known as greenhouse gases (GHG) (Montzka *et al.* 2011, Ravishankaran *et al.* 2009, NASA 2018). As per IPCC (2007) the relative Global Warming Potential (GWP) of some GHGs for a 100-year time zone is as follows: carbon dioxide (CO_2) 1 (taken as standard), methane (CH_4) 25, nitrous oxide (N_2O) 298, chlorofluorocarbon-12($CCl_{12}F_2$) 10900, hydroflurocarbon-23(CHF_3) 14800, sulfur hexafluoride (SF_6) 22800 and nitrogen trifluoride (NF_3) 17200. Their atmospheric life time (years) is as follows: carbon dioxide 100, methane 012, nitrous oxide 114, chlorofluorocarbon-12 100, hydroflurocarbon-23270, sulfur hexafluoride 3200 and nitrogen trifluoride 740.

The global N cycle is more severely altered by human activity than the global carbon (C) cycle, and reactive N dynamics affect all aspects of climate change considerations, including mitigation, adaptation, and impacts (Suddick *et al.* 2013). Climate model projections indicate that during the 21st century, the global surface temperature is likely to rise further by 0.3–1.7°C to 2.6–4.8°C depending on the rate of greenhouse gas emissions (IPCC 2013). Atmospheric CO_2 concentration has increased from 280 ppm (parts per million) in the pre-industrial era of 1750s to 400 ppm in 2015, however, a major increase was observed in 20th century, which is the highest for the past 800 millennia (USEPA 2017). Global warming is increasing at fairly fast rate in the 21st Century, since all but one of the 16 hottest years in NASA's 134-year record have occurred since 2000 CE (MacMillan 2016). Methane level has also increased

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two and a half times during the last 800 millennia; the concentration of methane in the atmosphere has risen sharply by about 25 Tg/year since 2006 (NASA 2018). This increase is ascribed to agriculture and fossil fuel use. Again over the past 800 millennia, concentrations of N_2O in the atmosphere rarely exceeded 280 ppb (parts per billion), but the levels have risen since the 1920s, reaching a new high of 328 ppb in 2015. This increase is considered primarily due to agriculture.

Fertilizer nitrogen – the key input in food production

Cereals (wheat, maize, rice) are the staple food in developing countries and meet more than 50% of their energy needs in these countries. In the mid-twentieth century, world cereal production of these three cereals was only 446.8 Tg (million metric tonnes) and it increased 4.5 times in the next 50 years to 2068 Tg during the triennium 2005–2007 and is further estimated to increase to 3009 Tg in 2050 (Alexandratos and Bruinsma 2012). This is necessary to meet the food demand of the human population, which was ~3 billion in 1960's, and more than doubled to 6.6 billion during the triennium 2005–2007 and is estimated to reach 9.7 billion by 2050 (UN 2015). To meet the food demands of the increasing human population, per hectare cereal yields need to be increased by about 130% from 3.32 Mg/ha in 2005–2007 to 4.30 Mg/ha in 2050. Since arable land increase is likely to be minimal, fertilizer N has to play a key role and its consumption is likely to increase to 225–250 Tg by 2050 (Tilman *et al.* 2011) from the 2016 estimated consumption of 116 Tg (FAO 2012). Synder (2010) observed that 40% of the population on Earth owes its existence to increased food production made possible by fertilizer nitrogen (N). No wonder, China and India having ~36% of the world's population consumed 46% (China 31%, India 15%) of the global use of 110 Tg N in 2013 (Table 1) (Lu and Hanqin Tian 2017).

Chinese farmers' use on an average of ~300 kilograms of nitrogen per hectare per year, which is more than four times the global average. This is achieved by high subsidy to the fertilizer industry (Li *et al.* 2013) on one hand and increasing support price for corn on the other hand, which could be roughly double the corn price in USA (USDA 2016). But unprecedented levels of nitrogen could pose risks to earth's environment (Battye *et al.* 2017). Fagodia *et al.* (2017) have observed that the net Global Temperature Change Potential (GTCP) due to nitrogen in 1961 and 2010 was 369.44 and 1088.15 CO_2 equivalent, respectively, on a 20 year span basis; the values were 429.17 and 1264.06 on a 100 year basis.

Table 1 N and P fertilizer consumption in some countries in 2013

Country	N (% of world consumption)	P (% of world consumption)
China	31	27
India	15	13
USA	11	10
Brazil	03	11
Pakistan	03	
Canada		02
Others	37	37

Total world consumption was ~ 110 Tg N/y and ~ 17 Tg P/y
Source: Lu and Hanqin Tian (2017).

In addition to needs for food production, additional fertilizer N will also be needed for biofuel production, the demand for which is increasing. Biofuel blending mandates of the International Energy Agency are now in place in around 60 countries, and in the New Policies Scenario, demand for biofuels in transport is projected to triple over the outlook period, exceeding 4 million barrels of oil equivalent per day (mboe/day) by 2040. That would be up from the present 1.5 mboe/day and 70 percent of it would be ethanol (Schill 2015). Corn grain makes a good biofuel feedstock due to its starch content and its comparatively easy conversion to ethanol. As regards the United States, corn production in 2009 was 13.2 billion bushels (~335,000 metric tonnes) from 86.5 million acres (~34.6 million ha) and using a corn-to-ethanol conversion of 2.8 gallons of ethanol from a bushel of corn, total United States corn production could result in approximately 37 billion gallons of ethanol, which could provide approximately 26% of 137 billion gallon-per-year gasoline consumption in USA (Hay 2015). Efficient use of fertilizer N is thus the need of the day to reduce its global warming effects.

Nitrogen use efficiency (NUE) of fertilizer nitrogen by cereals

NUE or recovery efficiency of nitrogen [100 × (kg N/ha taken up by fertilized crop – kg N/ha taken up in control plot ÷ kg N/ha applied)] from research trials throughout the world was reported to be 63% in maize (corn), 54% in wheat, and 44% in rice, while the values for on-farm trials were 37% in maize and only 31% in rice (Doberman 2005). However, when N application rates were higher as in China (181–219 kg N/ha), NUE even in research trials was 35.7% for wheat, 30.5% for maize, and only 24.8% for rice. Based on these data the average NUE value of 40% was suggested by for cereals for the world as a whole by Prasad and Hobbs (2016). Recently Zhang *et al.* (2015) reported an overall (all crops) average NUE of 25% in China, 30% in India, 52% in Europe, 68% in USA and Canada and 42% for the world as a whole. According to Zhang *et al.* (2015), 100 Tg N that is 57.5% of the 174 Tg N applied in 2010 (column A in Table 2) to crops in agriculture was surplus and contributed to global warming and nitrate enrichment of waters. China and India accounted for a 55% of N surplus as against a consumption of ~46% of the total global N consumption indicating poor N management.

Production of N_2O from fertilizer nitrogen in agricultural fields

Bulk of the N not taken up by crops is lost by ammonia

Table 2 Global surplus N scenario (A) in 2010 and projected scenario (B) in 2050

Country/ Region	2010 Nitrogen scenario (A) and projected scenario for 2050 (B)							
	Input (Tg N/y)		Harvested (Tg N/y)		NUE		Surplus (Tg N/y)	
	A	B	A	B	A	B	A	B
China	51	27	13	16	25	60	38	11
India	25	19	08	11	30	60	17	08
US and Canada	21	25	14	09	68	75	07	06
Europe	14	13	07	10	52	75	07	03
Sub-Saharan Africa	4	13	5	9	72	70	2	4
World-Total	174	160	74	107	42	67	100	52

Input includes fertilizer N, manure N and Biological N; Data not available for the rest of the world. Source: Zhang *et al.* (2015).

volatilization, leaching and denitrification. Denitrification leading to evolution of N_2O is the main cause for global warming as far as the fertilizer N is concerned, although some of the ammonia volatilized gets oxidized and contributes to N_2O production. Among N fertilizers, urea has now emerged as the major solid N fertilizer in the world; in India it makes up about 80% of fertilizer N applied to agricultural fields. Once urea is applied to soil it undergoes hydrolysis and produces ammonia and carbon dioxide. Some of the ammonia formed can be lost by ammonia volatilization, while the rest is oxidized to nitrite (NO_2) by autotrophic bacteria *Nitrosomonas* and then further oxidized to nitrate (NO_3) by autotrophic bacteria *Nitrobacter* (Prasad and Hobbs 2016). Nitrates so formed can leach down the profile and can increase nitrate concentration of underground waters, sometimes beyond the safe limit of 10 mg NO_3^- N/L approved by USEPA (US Environmental Protection Agency). In India, Bharadwaj *et al.* (2012) reported that 28% of shallow well waters in Ludhiana district contained 11–25 mg NO_3^- N/L.

Under anaerobic conditions nitrates are reduced to nitrous oxide (N_2O) by bacteria, fungi and even archaea; the process is known as denitrification. There are over 60 genera of bacteria including *Thiobacillus, Thiomicrospora, Begiagota, Rhodobacter, Bacillus, Achromobacter, Chromobacterium* involved in denitrification (Tiedje *et al.* 1988). There are also about 60 genera of fungi, with 90% among the Acsomycota (*Alternaria, Aspergillus, Botrytis, Fusarium, Penicillium, Trichoderma etc*) involved in denitrification (Mothapo *et al.* 2015). The archaea *Halobacterium denitrificans* (Tomlinson *et al.* 1986) are also involved in denitrification.

In addition to the amount of nitrate and carbon (source of energy) present in soil a number of abiotic factors are known to control denitrification including: water saturation and oxygen concentration (Bateman and Baggs 2005), pH (Van den Heuvel *et al.* 2011), and temperature (Wolf and Brumme 2002). As regards water saturation and oxygen concentration, Chen *et al.* (2015) found that maximum denitrification occurred at 55–90% WFPS (water-filled pore space). However, in an incubation study in Argentina, involving WFPS values of 40, 80, 100, and 120% (the last one achieved with a 2 cm surface water layer), the greatest N_2O emission occurred at 80% WFPS treatment where conditions were not reductive enough to allow the complete reduction to N_2. The N_2O/ ($N_2O + N_2$) ratio was the lowest (0–0.051) under 120% WFPS and increased with decreasing soil moisture content (Ciarlo *et al.* 2007). Similarly, Awale and Chatterjee (2015) reported from an incubation study that when urea was applied at 252 kg N/ha, N_2O production was 0.56 kg N/ha at 30% water holding capacity moisture (WHC), 3.92 kg N/ha at 60% WHC and 16.0 kg N/ha at 90% WHC. In a Chinese incubation study N_2O emission from a paddy soil at 100% WHC (water-holding capacity) was higher than that at 40, 65, 80, 120, and 160% WHC, indicating that 100% WHC was the optimum soil moisture content for N_2O emission (Lan Ma *et al.* 2017). Nitrogen losses are the most under fluctuating moisture conditions as obtained in irrigated rice culture or under semi-aerobic rice cultivation (Prasad 2011). As regards pH, Herold *et al.* (2012) reported that as pH increased from 4.5 to 7.5, the contribution of fungi in denitrification decreased; this would be expected because, bacteria thrive better under neutral and alkaline conditions.

Loss of N due to denitrification is fairly high in lowland rice field, where anaerobic conditions prevail for most time. In a study in rice–wheat cropping system, N loss due to denitrification was found to be 10–15 kg N/ha in rice and 5–10 kg N/ha in wheat (Pathak *et al.* 2006). However, in a Chinese study in rice-wheat cropping system, N_2O loss was 2.04–2.29 kg N/ha in rice and 2.27–4.71 kg N/ha in wheat (Zhang *et al.* 2011). In Malaysia, large amounts of fertilizer N are applied to oil palm plantations and Kusin *et al.* (2015) reported an average production of 19.11–22.17 kg N_2O/ha. Thus, N_2O losses from agricultural fields vary considerably depending upon soil, crop and moisture conditions.

Estimates of N_2O production in the world

According to IPCC (2007) about 17.8 Tg N_2O is produced annually globally, of which 38.2% is of anthropogenic origin (agriculture 25.3%, sewage 1.2%, biomass burning 3.9%, fossil fuel 3.9% and atmospheric 3.9%), and 61.8% is natural in origin (soil under natural vegetation 37.1%, oceans 21.6%, oxidation of NH_3 3.1% etc.). Out of the total anthropogenic contribution ~two-thirds is estimated from agriculture. Country-wise break up shows that China contributes the highest (18.6%) towards nitrous oxide emissions in the world (Table 3); this would be expected, because it has the highest per ha N application rates in the world. As a contrast USA, India and European Union contribute less than 50% of that by China. In India, the release of N as NO_x has increased over years and it is estimated that it represents about 10–15% of GHW (Pathak and Bhatia 2017). Griffis *et al.* (2017) also observed that N_2O production is likely to be higher in warmer and wetter regions.

Table 3 Nitrous oxide emission in some countries and regions (million metric tonnes of CO_2 equivalents)

Country/Region	N_2O emission	% of world	% by agriculture
China	587.2	18.6	74.7
India	239.7	7.6	73.8
European Union	265.9	8.4	60.6
USA	288.9	9.1	57.6
Rest of the world	1579.6	56.2	–
World Total	3153.7	100	70.0

Source: World Bank Group (2017).

Reducing N_2O emission in the world

The first step in reducing N_2O emission in the world is to reduce global N surplus by reducing the rates of N applied to agricultural crops without affecting or rather increasing production. This can be done by increasing NUE. Most of the agronomic research, so far, has been on determining economic optimum dose, but Prasad *et al.* (2016) have stressed the need for determining eco-friendly optimum dose of fertilizer N for each crop in different regions. In a study in China, Yield_{opt}, Economic_{opt} and Ecological_{opt} levels of N for maize were found to be 289, 237 and 171 kg/ha (Wang *et al.* 2014). The Ecological_{opt} resulted in a reduction of N loss by 47%, with a yield loss of only 0.31%. Zhang *et al.* (2015) have projected that the desired global food production is possible with reduced total N consumption to 160 Tg N/year by increasing NUE in India and China to 60%, in US and Canada to 75% and in Sub-Saharan Africa to 70% (Column B Table 2). By doing so the global surplus N can be almost halved from 100 Tg N/year in 2010 to 52 Tg N/year in 2050; N surplus from India would be only 8 Tg N/year.

Ways to increase nitrogen use efficiency (NUE)

NUE can be increased in several ways. The possible agronomic mediation techniques include, deep placement, split applcation and foliar application (Prasad and Shivay 2015, 2016; Pathak *et al.* 2016). From the product viewpoint a number of Enhanced Efficiency Fertilizers (EEFs), such as, sulphur coated urea (SCU), polymer coated ureas (PCU), Isobutylidene diurea (IBDU), neem coaed urea (NCU) etc have been developed (Prasad 2005, Trenkel 2010, Prasad and Hobbs 2016, Ruark *et al.* 2016). In addition to nitrification inhibitors, such as, Nitrapyrin, DCD (Prasad and Power 1995) and urease inhibitors, such as PPD and NBPT (Kiss and Simihian 2002, Ding *et al.* 2011) are available in the market and have shown positive effects in increasing NUE. So far only Government of India has taken a positive step in this direction and decided that all urea manufactured or imported in India will be marked as neem coated urea (NCU) (Kumar 2015). Neem coating of urea is 100% subsidized by the Government of India. It is hoped that such steps are taken by other national governments in the interest of the evironment. Enhanced Efficiency Fertilizers should not be evaluated only on the basis of economic returns but also on the basis of fertilizer N saved and associated environmental gains.

Of course, it would be greatly helpful, if more N-efficient crop varieties become avialable. A requirement for crops that require decreased N fertilizer levels has been recognized in the call for a 'Second Green Revolution' and research in the field of nitrogen use efficiency (NUE) has continued to grow (McAllister *et al.* 2012). This has prompted a search to identify genes that improve the NUE of crop plants, with candidate NUE genes existing in pathways relating to N uptake, assimilation, amino acid biosynthesis, C/N storage and metabolism, signalling and regulation of N metabolism and translocation, remobilization and senescence. Han *et al.* (2015) have also suggested developing crop plants with enhanced NUE, using more classical genetic approaches based on utilizing existing allelic variation for NUE traits, such as, mapping quantitative trait loci (QTLs), and selecting candidate genes for NUE improvement. They have also highlighted the importance of different factors that lead to changes in the NUE components of nitrogen uptake efficiency (NUpE) and nitrogen utilization efficiency (NUtE).

Carbon footprint values of some chemical fertilizers

In recent years some attempts have been made to workout Carbon Foot Print (CFP) (carbon dioxide equivalent) values of different fertilizers. According to Brentrop *et al.* (2016) these values (kg CO_2 per kg nutrient) for some of the fertilizers are: Ammonium nitrate (33.5–0–0) 9.14, Calcium ammonium nitrate (27–0–0) 8.88, Ammonium sulphate (21–0–0) 10.95, Urea (46–0–0) 11.19, Urea ammonium nitrate (30–0–0) 10.43, Diammonium phosphate or DAP (18–46–0) 11.27, NPK (15–15–15) 10.7, Triple superphosphate (0–48–0) 0.56, Muriate of potash (0–0–60) 0.25. Of the various fertilizers diammonium phosphate (DAP) has the highest value of 11.27 followed by urea at 11.19. These are the two most important fertilizers in India; urea meeting 80% of the N needs and DAP meeting two-thirds of the P needs of the country. The lowest value 8.88 kg CO_2 equivalent per kg N was for calcium ammonium nitrate. Some thought has to be given to this in future plans of the country although an easy solution to this is not possible. Phosphate and potassium fertilizers have 0.25–0.56 kg CO_2 equivalent per kg nutrient, mostly at the manufacturing point.

Conclusion

Nitrogen use in the world agriculture is unavoidable due to increased demands for food, feed, fire and biofuel, but it contributes significantly towards global warming. The only way is to increase NUE by the use of enhanced efficiency fertilizers, agronomic management and by developing N efficient plant types. Robust research strategies are necessary in all the three areas and also there is an urgent need for determining eco-friendly dose of N for each crop.

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