

NITROGEN MANAGEMENT IN CALCAREOUS SOILS: PROBLEMS AND SOLUTIONS

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Nitrogen (N) is the most widely applied plant nutrient and is a key constituent of animal manures. Improvement in crop yields and high economic returns have been made possible through supplementation of crops with organic and inorganic fertilizers. The movement of N in the environment has been extensively studied and documented. The fate of N ranges from nitrification, denitrification, nitrous oxide formation, leaching of nitrate, and volatilization of ammonia. Even with this knowledge the variation in N movement within the soil, air and water varies greatly with changed edaphic factors. For instance the fate of N fertilizer under calcareous soil systems still has not been investigated widely. We reviewed the sporadic information available on N fate and management in calcareous soils especially in Pakistan. We discussed the sources and fate of N in calcareous soils of Pakistan and also the currently adopted and newly developed method to reduce the N losses.

Keywords: Nitrogen, volatilization, nitrification, leaching, nitrification inhibitors.

INTRODUCTION

Understanding and regulating nitrogen (N) dynamics is extremely important for the future of the country as it is related to not only food but also for energy. A desire to stimulate agricultural growth requires higher inputs of energy for fertilizers manufacturing and other requirements of agriculture. Pakistan being energy deficient have to put unnecessary pressure on the precious raw materials, gas and also increase the import of oil which is not desirable for economic reasons. It is therefore, necessary to find ways and means to reduce the use of fertilizer and other energy intensive inputs. Advances have been made in finding alternate way of improving nutrient availability N, which is most non-judiciously applied input in our agricultural system. Nitrogen plays an important role in plant growth (Shah *et al.*, 2003) as it is a constituent of the building blocks of almost all plant structures such as proteins, enzymes and chlorophyll (Haque *et al.*, 2001). Optimum concentration of N increases leaf area, photosynthetic processes, leaf area duration and net assimilation rate as well (Ahmad *et al.*, 2009; Munir *et al.*, 2007) which ultimately contributes towards higher grain yield (Cheema *et al.*, 2001; Tsialtas & Maslaris, 2008; Rafiq *et al.*, 2010). Furthermore, N has a unique position as a nutrient because it stimulates root growth and crop development along with uptake of the other plant nutrients (Hofman and Cleemput, 2004). Plants

usually respond quickly to N fertilizers, except legumes which fix N₂ from the atmosphere (Smil, 2001).

The decomposition of plant material in the soil forms organic matter. This organic matter contains about 175 pounds of nitrogen per ton (Subbarao *et al.*, 2006). Nitrogen (N) is added in the soil through rainfall, chemical fertilizers, organic fertilizers, decomposition of native soil organic matter and through nitrogen fixation. It is removed from the soil through crop harvest, leaching, erosion, denitrification and volatilization. Dry plant matter contains 1 to 6% N, while soil contains 0.02 to 0.04% (Mahmood, 1994; Tisdale *et al.*, 1985).

Sustainable agricultural production is the demand of recent period, mainly in developing countries, where there is no control on effect of N fertilization on soil and environment. Most of the N fertilizer in Pakistan is added in the form of urea and it is subject to numerous losses. Nitrogen is the most limiting nutrient element in crop production. Nevertheless, considerable agricultural yield has increased with the introduction of chemical fertilizers. According to FAO (2011), about 42 million tons of N fertilizers are being used annually on global scale for the production of three major crops: wheat, rice and maize. We have done a comprehensive review of the current literature available on N application and potential pathways of N movement in calcareous soils of Pakistan. Furthermore, the manuscript is a review of the technologies available to reduce N losses under our agriculture system.

Nitrogen Cycle and Dynamics in Calcareous Soils:

The nitrogen (N) cycle represents one of the most important nutrient cycle found in the terrestrial ecosystem. Generally the upper 15 cm of soil layer contains 0.1% to 0.6% N depending upon the soil types (Cameron *et al.*, 2013). Nitrogen used by living organism, stored in organic forms such as proteins, amino acids and nucleic acids. This stored N is mineralized in the soil and converted into different inorganic forms such as ammonium (NH_4^+) and nitrate (NO_3^-) which is directly utilized by the plants. Through the processes of nitrification and denitrification, N gets access to the atmosphere, such continuous flow of N from organic to inorganic form, stored in organism and turn back to the environment is called the N cycle.

Nitrogen mineralization and immobilization are the most important processes in N cycle and simultaneously occur in the soil. Organic material when added to the soil converts into inorganic forms (NH_4^+) via mineralization and is easily available to the plants. This process is carried out by various microorganisms like bacteria and fungi (Mckinley *et al.*, 1985). When N concentration is low in soil, it gets immobilized from inorganic to organic forms which ultimately become unavailable to the plants (Myrold and Bottomley, 2008). Mineralized N is vulnerable to numerous losses viz. NH_3 volatilization, nitrate leaching and denitrification. Nitrogen (N) balance equation describes the quantity of N mineralize based on the N cycle (Di and Cameron, 2002).

$$N = N_b + N_f + N_p + N_u + N_m - N_{pl} - N_g - N_i - N_l - N_e$$

Whereas b is the biological fixation, f is fertilizer, p is precipitation, u is urine and dung which is return to the soil, m is mineralization, pl is the plant uptake N, g is gaseous loss of N, i is immobilization, l is leaching (NO_3^-) and e is loss of N through erosion and surface runoff. Jansson and Persson (1982) divided the universal N cycle into three interdependent partial cycles having one or more common pathways. They are the elemental subcycle, which connects biological life to N_2 of the atmosphere (e.g., biological N_2 -fixation and denitrification), the autotrophic subcycle, which includes plant assimilation of mineral N, and the heterotrophic subcycle. Turnover of N through mineralization and immobilization was considered to constitute the basic process of the heterotrophic subcycle. Immobilization leads to incorporation of N into microbial tissue (biomass, or active fraction), following which some of the N is incorporated into stable humus through a process called humification.

Nitrogen Fertilizer Requirement:

Globally people have been facing food crisis in recent decades and as per recent estimates (Tilman *et al.*, 2011), there is need to increase food production by 100 to 110% in 2050 in order to cope with this crisis. Global starvation is increasing progressively and 925 million people estimated to be hungry (FAO, 2011). Asia has the largest share of 575

million followed by Africa standing at 329 million (FAO, 2011). In Pakistan, 25% of the people live below poverty line and in 2008 UN estimated that 77 million people were hungry and 45 million malnourished. Pakistan Nation Nutrition Survey also reported that 50% of the women and children are malnourished (NNS, 2011).

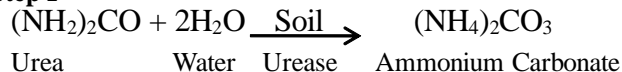
Crop production must be increased in pace with population increase to meet the food requirements. This increase in crop production needs a satisfactory stock of plant accessible N to sustain crop yields (Mosier *et al.*, 2004). Most of the agricultural soils of Pakistan are deficient in N (Shah *et al.*, 2003) and the farmers are using nitrogenous fertilizers, mainly urea, to eliminate its deficiency as crops respond strongly to nitrogenous fertilizers (Ehsanullah *et al.*, 2012; Ali and Noorka, 2013).

Globally, demand of N fertilizer is being increased at the rate of 1.7% annually, while the total N demand in 2015 was estimated at 105.3 million tons. Annual increase in N fertilizer demand is 7.6 million tonnes and asia shares 68% of it. The annual fertilizer demand in Pakistan is about 8.2 million tons in which share of urea is approximately 5.7 million tons. About 3.34 million tons of urea is lost every year due to volatilization, denitrification and leaching causing economic loss of 40.5 billion US \$ and serious environmental issues (Economic survey, 2012-213). Global N fertilization is approximately 151 Tg year⁻¹ (Galloway *et al.*, 2008) and price of urea-N per kilogram is reaching 0.45 US\$ (Tilman *et al.*, 2001). Urea is an important nitrogen fertilizer material being used globally mainly because of its cost effectiveness, desirable handling and storage features.

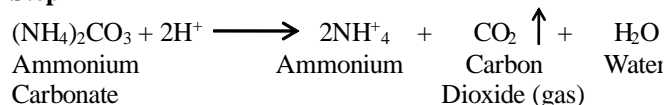
Nitrogen Losses and their Impact on Environment:

Ammonia volatilization and its impact on environment: Gaseous loss of N in the form of ammonia (NH_3) gas to the atmosphere is called ammonia volatilization. Ammonia volatilization is a complex process in which many physical, chemical and biological processes are involved. It is produced in agricultural systems by surface application of N fertilizers, plant residues, and mineralization of organic matter, animal urine and feces (Tisdale *et al.*, 1985). High pH of the soil determines the relative concentration of NH_4^+ and NH_3 , which increase with the application of urea fertilizer in soil. Hydrolysis of urea forms ammonium carbonate, as a result of this ammonia gas is produced and escaped into the atmosphere. Cameron *et al.* (2013) describes the urea hydrolysis and NH_3 volatilization in an equation as under:

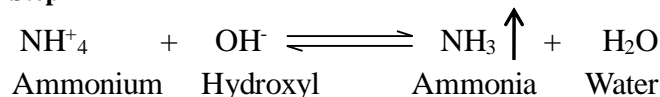
Step I



Step II



Step III



Globally 50% of the NH₃ volatilized is mainly through agriculture (Sommer *et al.*, 2004). For example, greatest risk of NH₃ volatilization from urea fertilizer is about 0 to 65% of the applied N which mostly depends upon the soil types and climatic conditions (Bishop and Manning, 2010; Lara Cabezas *et al.*, 1997; Khan *et al.*, 2013). Various studies indicate that ammonia volatilization losses vary from 11 to 60% depending on the methods through which N is applied. N when applied on the surface causes the heaviest loss when pH of the floodwater is high (9.0-9.5), followed by poor incorporation of N during land preparation (Mikkelsen and De Datta, 1979; Fillery *et al.*, 1986).

The major source of NH₃ volatilization is agricultural ecosystem in which 85% of the NH₃ in gaseous forms escaped into the atmosphere. Global use of N fertilizers from 1960 to onward has increased seven fold due to high requirements of crops (Galloway *et al.*, 2003). The excessive application of N fertilizers, and surface application of manure N leads to approximately 60% of NH₃ being volatilized. In Pakistani soils NH₃ is prone to atmospheric losses due to high soil pH and hot climatic conditions. Hussain and Naqvi, (1998) estimated ammonia volatilization in Pakistani soils was 22 to 53% while in comparison, Zhang *et al.* (1992) measured 32% of N loss as ammonia volatilization in northern China.

Factors affecting Ammonia Volatilization:

Many studies have shown that ammonia volatilization is facilitated by many soil and environmental factors, such as soil pH, temperature, soil cation exchange capacity, soil moisture, rainfall and irrigation, fertilizer use and application methods and ammonium concentration.

Soil pH: Urea, containing 46% N is an important nitrogen fertilizer material used globally but due to its hydrolysis, it increases soil pH and leads to tremendous loss of ammonia through volatilization (Hamid *et al.*, 1998). Similarly, additions of N fertilizers in alkaline soils of Pakistan are more prone to NH₃ volatilization (Khan *et al.*, 2013). The soil's pH also has a strong effect on the amount of volatilization. Specifically, highly alkaline soils (pH~8.2 or higher) have proven to increase urea hydrolysis. Christianson *et al.*, 1993 observed that urea undergoes complete hydrolysis within two days of application on such soils. On the other hand, in acidic soils (pH 5.2) the urea took twice as long to hydrolyse. When urea is applied to soil surface during hydrolysis it increases the pH until nitrification process accelerates (Sommer *et al.*, 2004). So, if the relative concentration of NH₃ increases from 0.1 to 1%, 10% and 50% as the pH changes from 6 to 7, 8 and 9 respectively (Freney *et al.*, 1995).

Temperature: High temperature causes rapid hydrolysis of urea forming ammonium ions which are loosely bound to water molecules and are converted to ammonia gas which is next released into environment from water surface (De Datta, 1985; Xing and Zhu, 2000; Hussain & Naqvi, 1998). Calcareous nature of Pakistani soils also increase the relative rate of NH₃ volatilization when N fertilizers are applied (Hamid and Ahmad, 1988; Wang *et al.*, 2004). This is mainly an interactive effect due to high temperature, high soil pH and low water availability (Zhenghu and Honglang, 2000).

Cation exchange capacity: Cation exchange sites in the soil holds the ammonium (NH₄⁺) on the clay particles due to their negative charges (Robertson *et al.*, 1999). This helps to reduce the ammonium concentration of soil solution, a soil has high CEC, there will be minimum chances of NH₃ volatilization and vice versa (Whitehead and Raistrick, 1993).

Soil salinity: With many other factors, high level of soil salinity is also an important factor involved in ammonia volatilization (Gandhi and Paliwal, 1976; McClung and Frankenberger, 1985). Nitrogen proves to be a limiting factor in salt affected soils (Saleem and Ahmad, 1988). Keeping this in mind, slightly higher dose is recommended in the soils affected by a certain level of salinity (Yadav, 1988). Soil salinity and sodicity strongly influences the rate of NH₃ volatilization and according to Hussain and Naqvi (1998) nitrification process is delayed when N fertilizers were applied to the saline soils. Resultantly, 15 times higher NH₃ emissions were measured as compared to the normal soil. Zafar *et al.* (1998) reported that soil moisture content and salinity have a combined effect on ammonia volatilization. In the soil incubation experiments, they concluded that ammonia losses increased sharply as level of soil salinity increases especially under non-flooded conditions whereas a minor increase was observed under flooded conditions. When salinity level was low, higher ammonia losses were observed under flooded conditions as compared to non-flooded conditions.

Sources of N fertilizers: Loss of N through volatilization was estimated highest from ammonium containing fertilizers when applied to the calcareous soils (Turner *et al.*, 2012). Fenn and Miyamoto (1981) evaluated that ammonia volatilization losses were lowest from NH₄-NO₃ and NH₄-Cl as compared to ammonium sulphate. Black *et al.*, (1985) reported that NH₃ volatilization losses are 5-15% higher when urea is applied compared to other N sources. High soil pH and high temperature cause higher rates of NH₃ volatilization because they increase soil concentrations of NH₃ dissolved in soil water and urea is more prone to hydrolysis under these conditions compared to other nitrogenous fertilizers (Kissel, 1988).

Strategies to minimize Ammonia Volatilization:

A number of strategies and mitigation tools have been tested in the past. The loss of N have been minimized through the application of material which reduce volatilization, by improving soil incorporation of urea and modifying time of application. Reducing the rate of N release from urea have also be observed with the addition of acids, salts of K, Ca and Mg, and by the choice of specific urea's grain size distribution (Allaire and Parent 2004).

Application of urea prior to irrigation or rainfall:

Reduction of volatilization of urea by irrigation and rainfall have been studied by various researchers (Bowman *et al.* 1987; Black *et al.*, 1987) who found that 80-93% reduction in volatilization occurs with the application of 10 -16 mm of water after 3 to 8 hours of urea application while only 33% of reduction occur with the delay of 24 hours. These results depend upon urea hydrolysis in soil and a dry soil may prevent hydrolysis under field conditions until ample supply of irrigation or rainfall occur (Rochette *et al.*, 2009). Ammonia volatilization was significantly reduced when water contents were 55% compared to 30%. Dissolution of ammonium containing fertilizers does not occur when water contents are between 0 to 8%. Maximum losses of NH₃ are observed with 8% water content when N was applied as (NH₄)₂SO₄, and 55% water contents show lower ammonia losses as compared to 8% to 30%, while at 0% all of the applied NH₄⁺-N fertilizer is retained in soil (Fenn and Miyamoto, 1981).

Fertilizer placement: Losses of ammonia volatilization are decreased as soon as the fertilizer is incorporated into the soil (Grant, 1996). Banding fertilizer below the soil significantly decrease volatilization of nitrogenous fertilizers, both by decreasing negative environmental effects and making available to plants for their growth and development. Pakistan soils are calcareous in nature and in these conditions 5 and 7.5 cm below soil surface band placement is recommended to reduce N losses (Sommer *et al.*, 2004). Almost 86-95% reduction in volatilization occurs by placing the urea below 3-5 cm below the surface under moist soil conditions (Connell *et al.*, 1979; Prasertsak *et al.*, 2002).

Additions of acid and chemicals: Volatilization of ammonia is favored in calcareous soils such as in Pakistan. Soil acidification may reduce volatilization of ammonia with the help of amendments such as application of sulfur (Potter *et al.* 2001). Lower soil pH is desired in many production systems to increase the availability of nutrients and at farm level different sulfur containing compounds are used such as ammonium-sulfate or elemental sulfur to achieve this purpose to some extent. Ammonium sulfate reduces volatilization by lowering pH and delaying the urease activity (Kausar *et al.*, 1976).

The N losses can also be reduced using zeolites as additives in the fertilizers to control the retention and release of NH₄⁺

because it can improve the nitrogen use efficiency (Ming and Mumpton, 1989; McGilloway *et al.*, 2003; Gruener *et al.*, 2003; Rehakova *et al.*, 2004). Zeolite minerals are crystalline solids structures made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and/or small molecules may reside (Ming and Mumpton, 1989). These naturally occurring minerals have three main properties, which are of great interest for agricultural purposes: high cation exchange capacity, high water holding capacity in the free channels, and high adsorption capacity. The main action of zeolite in ammonium conservation is a decrease in N concentration in soil solution through cation exchange. Zeolite minerals not only retain huge quantity of ammonium ion but also interfere with the process of nitrification (Bartz and Jones, 1983; Ferguson and Pepper, 1987). The increased efficiency of N utilization when urea is used together with zeolite was demonstrated by Crespo (1989), Bouzo *et al.* (1994), and He *et al.* (2002) in which they concluded the effect of zeolite minerals in a way that it increases in N use efficiency, improves the N uptake and dry matter yield and also reduces the N losses mainly through ammonia volatilization.

Acidity and buffering can be increased around the granule of urea by the addition of various chemicals. The addition of urea co-applied with potash (KCl) reduces volatilization of ammonia by 30% to 50% under laboratory conditions (Rappaport and Axley, 1984; Gameh *et al.* 1990). Urea ammonium nitrates in liquid form which contain 35% of urea reduce 48% of volatilization under field conditions (Grant *et al.*, 1996). Depending upon the soil type and conditions phosphoric acid is known to reduce ammonia volatilization by 30 to 70% (Stumpe *et al.*, 1984), however to achieve these results required level of phosphoric acid is crucial in the product like DAP or MAP. Fifty percent reduction of ammonia volatilization is shown when urea nitric phosphate (23N:12P) was applied compared to urea alone (Christianson, 1989). Urea nitric phosphate provides a balanced and ample supply of N t and P as nitric acid has additional N compared to phosphoric acid fertilizers. Hamid and Ahmad (1989) reported that KH₂PO₄, NH₄H₂PO₄, Ca(H₂PO₄) and H₃PO₄ application suppress the nitrogen losses. Phosphate salts act as carrier and reduce or delayed the activity of urease enzyme and in response volatilization losses are reduced.

Urease inhibitors: Hydrolysis of urea by urease enzyme causes volatilization of ammonia. Urease inhibitors are known to slow or inhibit the urea hydrolysis by decreasing the urease enzyme activity, thus helping to slow the process of volatilization which allows N to retain in soil for longer period of time or used by plants (McCarty *et al.*, 1989; Schwab and Murdock, 2005).

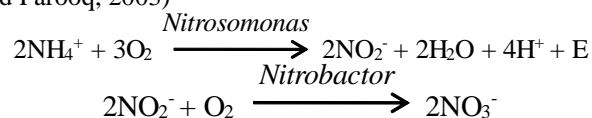
Urease inhibitors such as N-(n-butyl) thiophosphoric triamide (NBPT) or phenyl phosphoro diamidate (PPD) are known to have their effect in reduction of ammonia

volatilization similar to that of placing urea below the soil surface. These chemicals reduce or retard the hydrolysis of urea until irrigation or rain wash the urea into soil. The efficiency of these inhibitors varies depending upon their properties. PPD reduce volatilization of urea by 0 to 91% when applied 0.5 to 1% to that of urea (Watson, 1990), while NBPT cause 54 to 95% reduction in volatilization when applied at 0.28% to added urea (Watson *et al.* 1994). Similar results were also achieved by Carmona *et al.*, 1990 in which they observed that after 8 days, at ambient laboratory temperatures, NH₃ loss from urea was 37.7%. whereas losses from the 0.005 and 0.05% nBTPT products were 13.6 and 1.8%, respectively.

Coated urea: Losses of urea through dissolution-cum volatilization can be minimized with the help some coating substances, however, the rainfall period must be considered as it significantly affects volatilization. The polymer coated material can reduce volatilization of urea ranging from 9 to 40% to that of uncoated urea when applied at 96 to 400 kg N ha⁻¹ (Torello *et al.*, 1983; Blaise and Prasad, 1995; Knight *et al.*, 2007; Rochette *et al.*, 2009). It is evident from these results that the coating of urea is an effective practice to reduce ammonia volatilization. Furthermore, the coated urea at 120 kg N ha⁻¹ can be drilled with seed without disturbing germination of plant seedlings while uncoated urea can only be drilled with seed below 30 kg N ha⁻¹ (McKenzie *et al.*, 2007). Side dressing of urea increases volatilization of urea on soil surface while in case of using polymer coated urea, there is no need of applying side dressing. Incorporation of polymer coated urea in arable crops helps in the release of urea over the whole growing season (Bishop *et al.*, 2008; McKenzie *et al.*, 2007). An increase in dry matter conversion efficiency and reduction in ammonia volatilization can be achieved through surface application of polymer coated urea for both turf and pastures (Torello *et al.*, 1983; Bishop *et al.*, 2008). According to Douglas and Bremner (1971) more than 100 compounds such as dihydric phenols and quinones are important organic inhibitors, these coated materials are used to reduce losses such as sulfur-coated urea (SCU), lac-coated urea (LCU) and neem-cake blended urea (NBU). Slow and control release of nutrients from these fertilizers is a way to reduce volatilization losses.

Nitrification: Nitrification is the bacterial oxidation of ammonium (NH₄⁺) to nitrate (NO₃⁻) through Nitrobacteria. First ammonium is converted into nitrite (NO₂⁻) by *Nitrosomonas* and then nitrate (NO₃⁻) by *Nitrobactor* (Leininger *et al.*, 2006). This oxidation reactions carried out by ammonia mono-oxygenase (AMO) enzyme related with bacteria (Ferguson *et al.*, 2007; Di *et al.*, 2009 a,b). Furthermore, several other fungal species have been identified which oxidize the NH₄⁺ including *Aspergillus falvus* and *Neurospora crassa*. Nitrification is a biological process, carried out by microorganisms *Nitrosamines* sp.

The complete process is given below in equations (Azam and Farooq, 2003)



Nitrification is considered undesirable due to the NO₃⁻ leaching, as it causes various diseases and greenhouse gases emissions. According to a Giles, (2005) 70% of the applied N fertilizer is lost via nitrification and other N transformations. The NH₄⁺ adsorbed on the clay particles is not vulnerable to losses. However, the concentration of NH₄⁺ in soil is generally low i.e. 1 mg Kg⁻¹, due to its immediate conversion to nitrate (NO₃⁻) (Subbarao *et al.*, 2006). Rate of nitrification depends upon the soil properties such as temperature, pH, organic matter, moisture, aeration and availability of NH₄⁺ present in soil.

Does nitrification cause low nitrogen use efficiency?:

Nitrogen (N) constitutes 1 to 6% of total dry matter of plants and is a constituent of many fundamental cell components such as nucleic acids, amino acids, enzymes, and photosynthetic pigments (Bungard *et al.*, 1999). High nitrogen supply favors the conversion of carbohydrates into proteins, which in turn promotes the formation of protoplasm (Arnon, 1972) and ultimately improves crop growth and yield parameters (Bakhsh *et al.*, 1999). Due to bulkiness and inadequate supply of organic sources of N, inorganic fertilizers are in routine use (Clark, 1990). Adequate application of nitrogenous fertilizers and new technologies for water management and other agronomic practices has made it possible to introduce high yielding cultivars to increase crop yields (Clark, 1990). Application of right source, rate, time and method of application of nitrogen fertilizer is thus considered a key to obtain bumper crop yields. Thus, nitrification is not a straight blessing for agriculture production since crop plants use 50 % or even less nitrogen of the applied fertilizer and remaining is lost through volatilization, leaching and denitrification from soil-plant system (Azam and Farooq, 2003).

The quick transformation of NH₄⁺ to NO₃⁻ in the soil reduces the efficiency of applied N fertilizer. Almost 90% of the applied N fertilizers are in the form of NH₄⁺ which is nitrified within four weeks (Sahrawat, 1980 a,b). Thus nitrification is responsible from conversion of highly immobile NH₄⁺ to highly mobile NO₃⁻ which is susceptible to leaching beyond the root zone. Furthermore, this NO₃⁻ also provides the opportunity for the emission of N₂O, NO gases which pollute the environment (Amberger, 1993). These N losses reduce the efficiency of fertilizers and have many environmental implications. To minimize N losses, there is need to improve NUE for sustainable agricultural production to feed the population. Many scientists are trying to minimize these losses though many strategies including soil management practices and or by using different types of

growth enhancer or techniques to improve the efficacy of the nitrogenous fertilizers. Farmers are always concerned about getting the biggest bang for their cash, when it comes to fertilizer, especially today as fertilizer N prices hover near 46 rupees per pound. Nitrogen use efficiency (NUE) for wheat and maize production seldom exceeds 40%, and the worldwide average is at 33% (Raun and Johnson, 1999). This means that for every 1 pound of N applied, 67% of that pound is lost via denitrification, volatilization, plant N loss, and/or leaching. A 20% increase in nitrogen use efficiency worldwide for cereal production would be worth more than 10 billion dollars (Raun and Zhang, 2006).

Factors affecting Nitrification:

Soil air: Nitrification occurs in well aerated soils because it is an aerobic process. Ideal rate of nitrification accomplished when soil air (O₂) reaches about 20% which is equal to O₂ in the atmosphere (Tisdale *et al.*, 1985). On the other hand, nitrifiers requirements of CO₂ are highly depend on atmospheric CO₂ level as they are autotrophs. Nitrification stimulated by the CO₂ level of 1-5% in the incubation vessels (Azam *et al.*, 2004; Keeney *et al.*, 1985). Moreover, they concluded that CO₂ level in incubation vessels severely suppress the nitrification when CO₂ concentration is below the atmospheric concentration.

Soil moisture: The generally more rapid mineralization of organic N occurs in flooded soils as compared with non-flooded soils (Patrick and Wyatt 1964, Borthakur and Mazumdar 1968). The rate of nitrification is maximum adjacent to field capacity from which soil matrix potential takes place at -10 kPa (Haynes *et al.*, 1986). Moisture contents are very crucial to nitrification. It also occurs even at the permanent wilting point of -1500 kPa (Monaghan and Barraclough, 1992). Work by Robinson (1957) on a red loam soil has shown that active nitrification of natural soil N stops at a soil moisture level just below the permanent wilting percentage. Justice and Smith (1962) reported complete inhibition of nitrification at 415 and 115 bars tension but with low moisture tensions of 10, 7, and 1 bar nitrification increased, respectively. Reichman *et al.* (1966) reported that ammonification and nitrification of soil N were almost proportional to soil water content at suctions between 0.2 and 10 bars with a measurable nitrification occurring at the bars tension. Nitrification may not occur at all either when soil moisture is very low or when it approaches saturation.

Alternate soil wetting and drying: Alternate flooding and drying has a distinct stimulating effect on N mineralization. According to Harada (1959) it was observed at the beginning of the 20th century that drying and liming of paddy soils had a remarkable influence on rice production. Shioiri *et al.* (1941) found that native organic N is mineralized much more rapidly in paddy soil kept flooded after air-drying than in the same soil kept continuous flooded. Conversely, it has been shown that total accumulation of N is higher under

conditions of continuous submergence than where dry fallowing between rice crops is practiced (IRRI, 1974).

Soil pH: Optimum pH for nitrification is in the range of 6.7 to 8.5 (Kyveryga *et al.*, 2004). In acidic soils nitrification can occur on pH of about as low as 3.8 (Tisdale *et al.*, 1985), while it is rapid above pH 6 (Vitousek *et al.*, 1982). Groeneweg *et al.*, (1994) found that maximum ammonia oxidation rate occur at 6.7 to 7 pH, however the the general trend is that as the pH decreases, the rate of nitrification decreases. Shammass, (1986) measured the oxidation rates and concluded that optimum pH for nitrobacter is 8.3 to 9.3 and that for nitrosomonas is 8.5 to 8.8.

Temperature: Most biological reactions are influenced by temperature. The optimum range of temperature for nitrification is 25 to 35°C (Haynes *et al.*, 1986 and Frederick, 1956). It is very slow or negligible below 4.4°C (Subbarao *et al.*, 2006). Choudhury and Cornfield (1978) working with two Bangladesh soils concluded that increasing amount of mineral N as NO₃⁻ at temperatures of 20, 30 and 40°C with the peak accumulation of NO₃⁻ occurred at 40°C in one soil (pH 7.6) while in the other soil (pH 5.2) the peak NO₃⁻ accumulation occurred at 30°C. Therefore, the optimum temperature for nitrification ranges between 30 and 40°C.

Organic matter and C:N ratio: The C: N ratio significantly influences the microbial population and tremendous effect on nitrification, as well. High C:N ratio of organic matter leads to the immobilization of NH₄⁺-N which ultimately suppress the nitrification process (Sahrawat, 1996). Globally, most cultivable soils have a C:N ratio of about 10, where rate of nitrification proceeds at a normal rate while immobilization of NH₄⁺ is limited (Vitousek *et al.*, 2002; Tisdale *et al.*, 1985). The narrower the C:N ratio of the applied material, the rate of nitrification will be more.

Nitrogen losses associated with Nitrification and Environmental Implications:

Two major pathways of N loss through nitrification are nitrate leaching under heavy irrigation or ground water contamination of NO₃⁻ by dumping organic wastes. The other major loss followed by leaching is denitrification in which gaseous losses of N (N₂O, NO and N₂) are vulnerable and pollutes the safe environment seriously.

Nitrate leaching: Nitrate (NO₃⁻) leaching is a global problem causing many threats to the agricultural ecosystem and the environment. All N fertilizer when applied to the soil immediately converts to highly mobile form of NO₃⁻ which leached away from the root zone or soil profile (Lehmann and Schroth, 2003). This phenomenon is highly pronounced under heavy irrigation or excessive rainfall and especially on light textured soils. In some studies leaching losses were measured in clay type of soils (Mahmood *et al.*, 2005). There is a greater potential for NO₃⁻ leaching as it moves through the soil with diffusion and mass flow of water (Hermann *et al.*, 2005).

Nitrate is highly mobile anion in soil and it is not adsorbed at cation exchange sites, thus leached down or denitrified in environment. Considerable amount of N fertilizers are lost every year in world and according to 15N-balance studies in Pakistan 33% of N is lost under wheat (Mahmood *et al.*, 1998) and 42% of applied N is lost under cotton crop (Mahmood *et al.*, 2000). Over all total losses of N fertilizer are 30% annually which are responsible for the loss of 69.4 billion rupees annually (Ali *et al.*, 2012). Almost 60% of the applied N lost from the coarse textured soils as NO_3^- leaching (Gaines and Gaines, 1994).

Ground water contamination: Nitrate (NO_3^-) leaching losses from soil into the water bodies are not only the loss of soil fertility but have a tremendous effect on environment and human health (Goulding *et al.*, 2008). Drinking of water and consumption of vegetables contaminated with NO_3^- causing intestinal disease and it is associated with stomach cancer, as well (Andrews *et al.*, 2007). Animal manures and commercial fertilizers have excess of nitrogen which cause many events of nitrate contamination in intensive agriculture especially in greenhouse vegetable production (Zhang *et al.*, 1996; Li *et al.*, 2002; Song *et al.*, 2009). With the increase of agricultural activity, underground drinking water become polluted with NO_3^- causing a disease in infants called methemoglobinemia (blue baby syndrome). The permissible limits of nitrate and nitrite in drinking water are 10 mg L^{-1} and 1 mg L^{-1} respectively (Shuval and Greuner, 1972). It is estimated that 50% or more of the European population lives in areas where 5.6 mg L^{-1} NO_3^- concentration was found while 20% of the people's lives in those areas where 11.3 mg L^{-1} NO_3^- have been found which exceeds the permissible limits set by WHO (Grizzetti *et al.*, 2011; WHO, 1984). The concentration of NO_3^- in different fruits and vegetables increasing day by day but in Pakistan, nitrate concentration in some varieties of rice have exceeded the permissible limits of WHO (Salah-uh-Din *et al.*, 1996).

Eutrophication: Eutrophication is the over enrichment of nutrients (NO_3^-) in water bodies as a result of runoff N and P losses from agricultural land into the nearby water bodies (Wilfried, 2002). Human activities plays a significant role in this process. Eutrophication not only decreases the aesthetic value of lake and rivers but it seriously affects the aquatic life by decreasing the dissolved oxygen (Selman, 2007). These algal blooms decrease the penetration of light causing negative effects on phytoplankton and it also decrease the access of predator to catch their prey due to turbidity (Lehtiniemi *et al.*, 2005).

Factors affecting Nitrate Leaching:

Ground water contamination due to NO_3^- leaching is limited in Pakistan regarding effect of irrigation and N fertilizers. Researchers have found that there was no water pollution hazard with 7.5 cm application of irrigation (Ibrahim and Nisar, 1996; Aslam *et al.*, 1998). In irrigated areas of Pakistan, NO_3^- is mostly below 8 mg L^{-1} which is far below

the standards set by Environmental Protection Agency (EPA) (Latif *et al.*, 1999) however some researchers reported that nitrate leaching does occur in few areas of Pakistan. High concentration of $\text{NO}_3\text{-N}$ was found in water sources of Karachi (Mahmood *et al.*, 1997). Tasneem (1999) noted 1-171 mg/l of $\text{NO}_3\text{-N}$ in Kasur area of Punjab. Ground water of Rawalpindi was contaminated with 111 mg/l of $\text{NO}_3\text{-N}$ (Tahir *et al.*, 1999). Iqbal *et al.*, (2012) demonstrated that increasing irrigation depth and N fertilizer rates cause high nitrate leaching losses making low fertilizer use efficiency. Furthermore, flood and furrow irrigation methods which are most commonly practiced in Pakistan, cause heavy nitrate leaching losses under coarse textured soils (Siyal *et al.*, 2012).

Irrigation: The irrigation applied in summer has no pronounced effect on leaching because nutrient ($\text{NO}_3\text{-N}$) uptake by crops increases with the application of water except over irrigation or flooding (Mahmood *et al.*, 2011). The optimum level of irrigation and fertilizers reduced the N leaching up to 48% of the applied N fertilizers (Hahne *et al.*, 1977). High infiltration rate leads the nitrate out of e root zone (Khan *et al.*, 2013) causing more N fertilizer losses.

Fertilizers: The nitrogen use efficiency is generally low due to poor recovery of applied fertilizers (Goulding *et al.*, 2008). However, the excessive rate of N fertilizers may cause leaching of nutrients away from the root zone in winter (Jenkinson, 2001). The application rate of N applied has a direct effect on N leaching losses. When applied N fertilizers increase the rate at which crop needs N for their optimum yield, then there will be more chances of leaching from the soil (Goulding *et al.*, 2008). R. H. Thorn (1986) found that the amounts of nitrate leached beneath grassland receiving up to 210 kg of fertilizer nitrogen ha^{-1} were small but that above 210 kg ha^{-1} the amounts leached were very variable. Placement of fertilizer also plays an important role in nutrient uptake by plants and leaching of nutrients below the root zone. In Pakistan, nitrogen fertilizers are available in granular form, are usually broadcast manually onto the sides and bottom of the furrow, which cause leaching of nitrate below the root zone at larger rate. To minimize these losses improvement in method of fertilization is necessary and it is observed that that side placement of fertilizers in furrow system near the ridge top or on top of the furrow at the center of the ridge maximize the retention of nitrogen fertilizer within the root zone (Siyal *et al.*, 2012).

Soil physical properties: The soil physical properties are important with respect to nitrate leaching because they determine the movement of water in soil profile (Azam *et al.*, 2002). Heavy textured soils (abundant clay) are less prone to N leaching losses as compared to in light textured soils (sandy soils) because of low water permeability. However, clayey soils are susceptible to denitrification instead of leaching losses (Khan *et al.*, 2013).

Denitrification: In Pakistani soils ammonium fertilizers are quickly nitrified because of warm climate then NO_3^- forms vulnerable to denitrification following reduced conditions or flooding. Denitrification is usually based on the aerobic heterotrophic bacteria that have ability to reduce NO_3^- in limited supply of oxygen (Mahmood *et al.*, 2000; Mahmood *et al.*, 2005) such as *Pseudomonas aeruginosa*, *Bacillus nitrosus*, *Escherichia coli*, and *aspergillus flavus* can reduce NO_3^- to gaseous forms such as N_2O , NO and elemental nitrogen (N_2) into the atmosphere, under poor soil aeration (Di *et al.*, 2002; Subbarao *et al.*, 2006). Denitrification occurs when microbes convert ammonium to nitrate and use the nitrate as a terminal electron acceptor under saturated soil conditions. The complete process of denitrification is illustrated as under:

$$\text{2NO}_3^- \xrightarrow{\text{Nitrate reductase}} \text{2NO}_2^- \xrightarrow{\text{Nitrite reductase}} \text{2NO} \xrightarrow{\text{Nitric oxide reductase}} \text{N}_2\text{O} \xrightarrow{\text{Nitrous oxide reductase}} \text{N}_2 \uparrow$$

Global warming has emerged as a serious concern due to increase in the concentration of greenhouses gases (GHG) in which of N_2O is more potent than CO_2 and others. These gases trap the ultraviolet rays coming from the sun and trap into the atmosphere after bounce back, as result which increase the earth's temperature. The current estimate is that N_2O emission will be double from present 12.8 Tg N y^{-1} to 25.7 Tg N y^{-1} by 2025 (Kroeze, 1994). Doubling of this N_2O in the air, would decrease 10% of ozone (O_3) layer and increase the infrared radiations by 20% reaching on the surface of land (Crutzen and Ehhalt, 1977). Nitrous oxide (N_2O), concentration in the air traps the ultraviolet radiations on the earth surface and limits the escape of N_2O back into the atmosphere, as a results of this an increase of earth's temperature called as global warming. Globally 0.6 °C increase of temperature has been stated during last decades (IPCC, 2001). So nitrous oxide (N_2O) is a potent greenhouse gas, this can be estimating that, global warming potential of N_2O is 310 times greater than that of carbon dioxide (CO_2), and about 14 times more than that of methane (CH_4) (IPCC, 2001).

Agriculture is the dominant source of emission of N_2O ; about 70% emission is through anthropogenic sources (Smith *et al.*, 1997). By 2100, total N_2O emissions from production of chemical fertilizers are estimated to be 4.2 Tg N y^{-1} , which is nearby four times that of present levels of emissions (Kroeze, 1994; Mosier *et al.*, 2004). Nitric oxide (NO) is not a greenhouse gas (GHG) but it has an important role in atmosphere chemistry. Nitric oxide in the atmosphere reacts with ozone (O_3) to form NO_2 , and this way it destroys the layer of ozone. Furthermore, nitric oxide (NO) can be changed into nitric acid (HNO_3), which in turn received as acid rain, paying to the acidification of ecologies (Smith *et al.*, 1997). Life on earth mostly depends upon the range of temperature control by GHG, deviation from that temperature cause disturbance of all ecologies. Globally, N_2O emission has reached about 17.8 Tg of N y^{-1} , being

which 38% from anthropogenic sources. Moreover 2.8 Tg of N y^{-1} released as N_2O which is 15.4% of the total emissions (Denman *et al.*, 2007). These N losses directly or indirectly have tremendous impact on environment as well as reduce soil fertility and plant yield.

Factors affecting Denitrification:

Soil pH: Soil pH is an important factor affecting microbial processes which are the causal agent of dissimilatory nitrate reduction. Whereas soil pH has an influence on the ratio of N_2O and N_2 produced during denitrification. The N_2O emission increases with the increase of soil pH and maximum denitrification was observed in the pH range of 7-8 (Focht and Verstraete, 1977), as most of the agricultural soils of Pakistan are calcareous ($\text{pH} \geq 7.5$) (Mahmood *et al.*, 2000), hence denitrification rate would be high in these soils. Weier and Gilliam (1986) found the strong negative relationship between release of N_2O and pH which showed that N_2O was completely stopped at pH 8.5. This was admitted from later results that at low pH production of N_2O to N_2 inhibited more than that reduction of NO_3^- to N_2O (Burford and Bremer, 1975).

Type of fertilizer: Commonly used fertilizer to supplement N requirement in Pakistan is urea. But the major problem associated with the urea fertilizer is the low N use efficiency (30-40%) due to N loss as denitrification or nitrification due to hot climate (Hamid and Ahmad, 1988). Large amount of NO_3^- susceptible to N_2O emissions in the absence of sufficient supply of oxygen, which is crucial for denitrifying bacteria. Generally, 65% of the applied N converts into NO_3^- -N within eleven days only after urea application where more chances of nitrate reduction and emissions of N_2O into the atmosphere (Prasertsak *et al.*, 2001).

Carbon supply: The organic matter availability is essential for denitrifying bacteria as energy source to keep the denitrification. However denitrification rate strongly correlate with the supply of soil carbon which be in available forms for the denitrifying bacteria (Weier *et al.*, 1998). The addition of organic waste in soil and land management practices increases the availability of organic carbon (Di and Cameron, 2003). Then these organic carbon additions not only increase the microbial growth and respiration but also provide the plentiful organic carbon needed by the denitrifying microorganisms (Taghizadeh-Toosi *et al.*, 2011).

Soil moisture and aeration: Soil moisture contents and aeration correlates to each other, change in moisture level adversely affect the soil air and denitrification rate. It is potentially increased when soil moisture contents reach above the field capacity (Müller and Sherlock, 2004; Saggar *et al.*, 2009). However, denitrification losses are more pronounced in winter or early spring when soil moisture level is high. Heavy irrigation and rainfall also play vital role to denitrification (Di and Cameron, 2003; Phillips *et al.*, 2007). It is also reported that high O_2 concentration favors

the N₂O release while at low level of oxygen, N₂ gas is produced in higher amount. In Pakistan, flooded rice enhances the denitrification rate after nitrification when urea is applied to obtain higher crop yield (Saleem *et al.*, 1986). Rice fields in Pakistan are occasionally submerged, therefore practical significance of denitrification is important under these conditions.

Temperature: The activity and diversity of various denitrifying bacterial population has been found to associate with soil environment. The denitrification rate increase with the temperature (Dobbie and Smith, 2001) while, it is significantly high in non-irrigated dry land as compared to irrigated soils (Hamid and Ahmad, 1988). Stanford *et al.*, 1975 established that within a limited temperature range of 15°C to 35°C, there is a twofold increase in denitrification rate for every 10°C increase in temperature. Between 10 and 5 C it decreases abruptly and at 0 C, it exerts great challenge to denitrifying populations, affecting N₂O breakdown more than the reduction of other N-Oxides of denitrification process (Holtan-Hartwig *et al.*, 2002).

Advantage of NH₄⁺ over NO₃⁻:

Urea application in the soil leads to production of NO₃⁻ through nitrification after urea hydrolysis (Khan *et al.*, 2004). Ammonium (NH₄⁺) is cationic in nature, it is strongly held by the negative charged clay particles and due to the functional group of soil organic matter (SOM) (Sahrawat, 1989; Amberger, 1993). This binding of NH₄⁺ cation on soil particles reduces the N-leaching losses (Amberger, 1993). Whereas, negatively charged NO₃⁻ due to repulsive force on soil clay particles prone to leaching out of the root zone (Khan *et al.*, 2013). The uptake of NH₄⁺ by plants has positive effect (within protein metabolism) on production of growth hormone such as gibberellin, cytokinin and polyamines (Pasda *et al.*, 2001). Another important advantage of NH₄⁺ is an enhanced uptake of phosphorus (P) and micronutrients by plants. During uptake of NH₄⁺, plant roots emit proton (H⁺) in the rhizosphere for equilibrium of charge within plant body. Hence, with the decrease of rhizosphere pH, P uptake increases (Aziz *et al.*, 2011). By the energy point of view, plants prefer ammonium (NH₄⁺) for uptake and assimilation. Plants spend 20 moles of adenosine triphosphate (ATP) for assimilation of nitrate (NO₃⁻), while 5 moles of ATP in terms of NH₄⁺ uptake by plants (Salsac *et al.*, 1987). Hence ammonium forming fertilizers are preferred source of N.

Strategies to Minimize Denitrification Losses (NO₃⁻, N₂O, NO, N₂):

Inefficient use of nitrogen fertilizer not only causes considerable monetary economic loss to producers due to denitrification, but also leads to sever environmental pollution due to nitrate leaching and nitrous oxide emission (Freney *et al.*, 1995; Azam *et al.*, 2002; Reeves *et al.*, 2002). Fields under alternate flooding and drying, show significant amount of nitrogen loss due to nitrification followed by

denitrification as a result of oxidation and reduction (Burford & Bremner, 1975). Due to these conditions, N use efficiency for crop production is decreasing with time. For upland grain crops, it hardly exceeds 50% (Roy & Chandra, 1979) and for irrigated flooded and lowland rice, it varies between 30-45% (Mikkelsen & DeDatta 1979; Zia & Waving, 1987). In view of the high cost of nitrogen fertilizers, it is important to improve the N utilization efficiency for crop production with the objective to reduce cost of production.

Use of Nitrification inhibitors: The principal forms which contribute to N losses in a soil is through leaching and denitrification but NO₃⁻ is most important in terms of N₂O emission which is a potent green house gas. The economic and environmental cost of N fertilizers as NO₃⁻ can be reduced by using nitrification inhibitors. These are the compounds (synthetic or natural material) that delay the bacteriological oxidation of ammonium (NH₄⁺) to nitrate (NO₃⁻) for the shorter period of time (Herrman *et al.*, 2005).

Many synthetic natural nitrification inhibitors (NIs) have been introduced which block the path of enzyme, particularly ammonia monooxygenase (AMO), which is the responsible for oxidation of ammonium to nitrate. Ammonia monooxygenase (AMO) can be inhibited by the compounds having thiono-S and bind to the Cu in their active sites, while some inactive the AMO by their heterocyclic ring of N (McCarty *et al.*, 1989). There are two types of nitrification inhibitors: Chemical nitrification inhibitors and natural nitrification inhibitors (NIs). There are three major synthetic NIs are being used are Dicyandiamide (DCD), Nitrapyrin and 3, 4-Dimethyl pyrazol phosphate (DMPP) (Subbarao *et al.*, 2006). These chemical NIs have some drawbacks such as more expensive, cause phytotoxicity, not efficient and some have harmful effects on soil micro-flora (Adair and Schwartz, 2008). So, it is necessary to select those NIs which are less persistent, cheap and should environment friendly (McCarty *et al.*, 1989). Therefore, it is the need of hour to explore natural material for NIs, which are easily available, cheap and have no harmful effects on plant growth and environment. Some plant produces terpenes, triterpenes, tetranorterpenoids, phenolic, polyphenols and flavonoids are the compounds inhibit the process of nitrification by blocking the activity of AMO enzyme (Subbarao *et al.*, 2006). There are many plant products or byproducts which are being used as NIs including neem (*Azadirachta indica*), Karanj (*Pongamia glabra*) (Majumdar, 2002), vegetable tannins, waste products of tea, mint oil (Patra *et al.*, 2006), Japanese mint and Mustard (*Brassica juncea* L.) (Kiran and Patra, 2003) having strong antibacterial activities and are being used in agriculture to increase the NUE (Kumar *et al.*, 2007). Some of the natural products such as neem have ability to inhibit urease activity, as well (Patra *et al.*, 2006). Animal manure and application of commercial fertilizers are often assumed to add more N than it is drawn from the

agriculture system by the crops. The quantity of N applied to the soil is the N taken up by the crops plus the N which is lost from the agriculture system by any mean (Stanford, 1973; Bock & Hergert, 1991). Nitrogen use efficiency and NO_3^- leaching can be minimized by using slow releasing N fertilizers. Moreover, agronomic as well as environmental benefits can also be achieved by using these materials. (Zerulla *et al.*, 2001, Shaviv and Mikkelsen 1993). **Appropriate N application rate:** The most important and widely accepted reason for N leaching is its extensive and inappropriate use. After the harvest of the crop, much amount of N remains in the soil which did not take up by the plants and eventually leached down. There are many dissertations which observed that N leaching increased by the extensive use of N sources (Zvomuya *et al.*, 2003, Guo *et al.*, 2006). Therefore it is a dire need that N should be applied in the right proportion which crop requires. Soil and plant analysis are the best tool for N monitoring but unfortunately most of the recommendation of N for crops are on the higher side which causes its loss from the system.

Appropriate time of N application: Timing of N application should be in harmony with crop demand. It is necessary to take account the application of N with the growth stages of crops. Accumulative N demand for many crops generally follows an S-shaped curve, in which slow uptake rate during establishment and very high utilization in the vegetative and reproductive phases. This is why split dose of N is generally recommended in many crops which help in better utilization of N and cause great reduction in N losses. (Liu Zhaohui *et al.*, 2012). It was observed that yield of potato increases and NO_3^- leaching decreases when N is applied in a split dose system. (Kelling and Hero, 1994; Errebhi *et al.*, 1998; Waddell *et al.*, 2000).

Introducing cover crops: A catch crop is a cover crop grown to take up available N in the soil and thereby reduce N losses in a cropping system. Introduction of the cover crops to manage the nitrate leaching is also well-established technique. The main objective behind this technique is to trap the residual N in the soil after the harvesting of the main crop. This technique is becoming very much popular (Delgado, 1998; Logsdon *et al.*, 2002) as it has an extra benefit of protecting soil from salinization. The choice of crop cover depends upon many factors such as in which area it will be applied and what type of cropping pattern is being followed there. Type of soil, climate and amount of fallow time are also important (Tonitto *et al.*, 2006).

Crop rotation: Crop rotation is the practice of growing a series of dissimilar/different types of crops in the same area in sequenced seasons to increase soil fertility and crop yield. Planting of different crops or varieties on the field where continuous corn was planted showed better result for the use of residual N (Ju *et al.*, 2007). There is a negative relationship between nitrate leaching and root length so according to rotation of potato with barley, wheat or any

cover crop proved as a good choice for reducing nitrate leaching (Delgado, 1998 and Delgado *et al.*, 2007).

Conclusion: Even though extensive research has been conducted on N dynamics and management worldwide, still a lot of gaps are present in information regarding fate of N fertilizers in soil and its impact on crop growth and environment in Pakistan's agricultural systems. Most of the work found was conducted under controlled conditions in pot and lab trials that lack field validation. According to the published data available, nitrogen use efficiency (NUE) for major crops including wheat, maize and rice seldom exceeds 40%. In Pakistan, about 22 to 53% NH_3 is predisposed to atmosphere due to high soil pH and hot climatic conditions. Studies have also shown that soil moisture content and salinity have a combined effect on increasing NH_3 volatilization. The second major source of N losses in Pakistan's agro-climatic conditions is de-nitrification. The ammonium fertilizers are quickly nitrified because of warm climate and NO_3^- is vulnerable to denitrification following reduced conditions or flooding.

Nitrogen losses through volatilization may be reduced by up to 80% by adopting a few management practices such as application of irrigation after 8 hours of urea application, placing the urea below 3-5 cm below the surface under moist soil conditions and urea co-applied with potash. Use of urease inhibitors such as N-(n-butyl) thiophosphoric triamide (NBPT) or phenyl phosphoro diamidate (PPD) and polymer coating of N fertilizers have shown significant reduction in volatilization. However, information is lacking on their effects under various cropping systems in Pakistan. More recently the use of cheap natural plant products or byproducts including neem (*Azadirachta indica*), Karanj (*Pongamia glabra*), vegetable tannins, waste products of tea, mint oil, Japanese mint and Mustard (*Brassica juncea* L.) are being used as nitrification inhibitors and to increase the NUE (Personnel Communication). However, no extensive research has been conducted on use of these natural substances in the field which is direly needed. Research is still lacking in understanding and quantification of N budgets in different cropping zones and scientist should conduct research on this aspect as well as test new and cheap means to reduce the losses of N in calcareous soils of Pakistan.

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