nitrogen, soils and environment

Agricultural productivity has been greatly increased by the use of N fertilisers, however, the accompanying risk of damaging the environment cannot be ignored, as *Louis A. Schipper*, Associate Professor, and Graham P. Sparling, Research Fellow, Department of Earth and Ocean Sciences, The University of Waikato, Hamilton explain:

Forms of nitrogen

Nitrogen (N) is one of the essential macro-elements. Along with carbon (C), oxygen (O), phosphorus (P), sulphur (S), and a range of minor elements, nitrogen atoms are bonded to carbon and form the basis of life. Nitrogen occurs in the largest trees to the smallest microbes. It is also one of the most abundant elements on Earth. However, nearly all (about 99%) of the N on Earth exists in the atmosphere as an almost inert colourless, odourless gas. The Earth's atmosphere is 78% N (by volume). This gaseous N (dinitrogen gas, N_2) in the atmosphere is usually not reactive. The great chemist Lavoisier found it was so inert that he named it azote, meaning without life. Gaseous N_2 is ultimately the source of a wide range of other inorganic and organic N compounds, but the gas needs to be 'fixed' by specialist microorganisms, or converted by chemical reactions before it can enter the life cycle.

In contrast to the huge amount of largely unreactive N_2 in the atmosphere, other forms of N are present in smaller quantities but are much more reactive. Examples of the reactive forms of N are inorganic compounds such as ammonia gas, ammonium salts, oxides of nitrogen, nitrates and nitrites, and organic molecules such as amines and amides, and complex proteins and humic compounds (Table 1).

Nitrogen in the environment

Before human intervention, reactive N accumulated in the environment through naturally-occurring biological N fixation, and conversion during electrical storms in the atmosphere. If the latter seems surprising, remember that, globally, there are 3-8 million electrical storms each day.

Lightning storms create NO_x gasses and nitrates which ultimately find their way into terrestrial and aquatic environments. Biological N fixation by a restricted range of microorganisms results in the formation of organic N compounds, which can be decomposed to ammonium and subsequently nitrate, by another biological process – nitrification. However, reactive N compounds do not accumulate indefinitely in the environment because another important microbial process – denitrification – converts nitrate back into N_2 gas completing the N cycle (Figure 1).

Biological N fixation occurs when specialist groups of microbes convert atmospheric N_2 to organic forms of N (typically $R-NH_2$). For example, Rhizobium bacteria form a symbiotic association in the root nodules of legume plants. The plant supplies the Rhizobia with carbohydrate in exchange for the soluble N compounds "fixed" by the bacteria from atmospheric N_2. Within New Zealand, fixation by *Rhizobia* associated with clover is the dominant biological fixation process. However, in other parts of the world, particularly tropical rice-growing areas, large amounts are fixed by the fern *Azolla* which grows in rice paddies, and forms a mutual association with the Cyanobacterium *Anabaena* which grows in cavities within the fern leaf, and fixes nitrogen. Some Actinomycetes (now termed Actinobacter) can also fix nitrogen gas, and form nodules on the roots of Alder trees, again supplying N to the tree in exchange for carbohydrates derived from photosynthesis.

In contrast to the small specialist groups of microbes that fix N_2, virtually all soil microorganisms are able to decompose organic forms of N to inorganic NH_4^+, a process known as mineralisation, or ammonification. Any released NH_4^+ is available to plants and microbes for growth. Depending on the C:N ratio of the organic source, the NH_4^+ can be immediately taken up by plants and microbes (immobilised) or released in the soil. Generally organic substrates with a C:

Table 1: Some common forms of nitrogen	
Unreactive inorganic forms of nitrogen	**Symbol**
Gaseous dinitrogen in the atmosphere (often inaccurately called "nitrogen")	N_2
Reactive inorganic forms of nitrogen	
Ammonia (gas) and ammonium ion	NH_3, NH_4^+
Nitric oxide, nitrous oxide, nitrogen dioxide, (NO_x gasses)	NO, N_2O, NO_2
Nitrite and nitrate	NO_2^-, NO_3^-
Reactive organic forms of nitrogen	
The organic forms of nitrogen are a very diverse group of nitrogen-containing organic molecules including simple amino acids through to large complex proteins and nucleic acids in living organisms, and humic compounds in soil and water	Numerous, typically $R-NH_2$

Table 2: Global increase in reactive N ($Tg\ N\ y^{-1}$) between 1860 and 2000 (adapted from Galloway et al., 2003).

Mechanism	Year	
	1860	**2000**
Biological fixation	15	33
Fossil fuel combustion	<1	25
Haber Bosch	0	100
Total	15	158

Box 1: Fertilisers versus urine patches

In pastoral systems improved legumes and nitrogen fertilisers have boosted productivity. These systems can also leak N into the environment, but most of this comes from concentrated N in urine patches deposited by the grazing animals. It is not the original extra nitrogen that causes the problem, it is the fact that extra nitrogen grows more grass, which allows more cows, which deposit more urine. The urine patch N can be equivalent to 1000kgN/ha, is far in excess of the amount the pasture plants can take up and is an important source of NH_3, NH_4^+, NO_3^-, NO_x and N_2O.
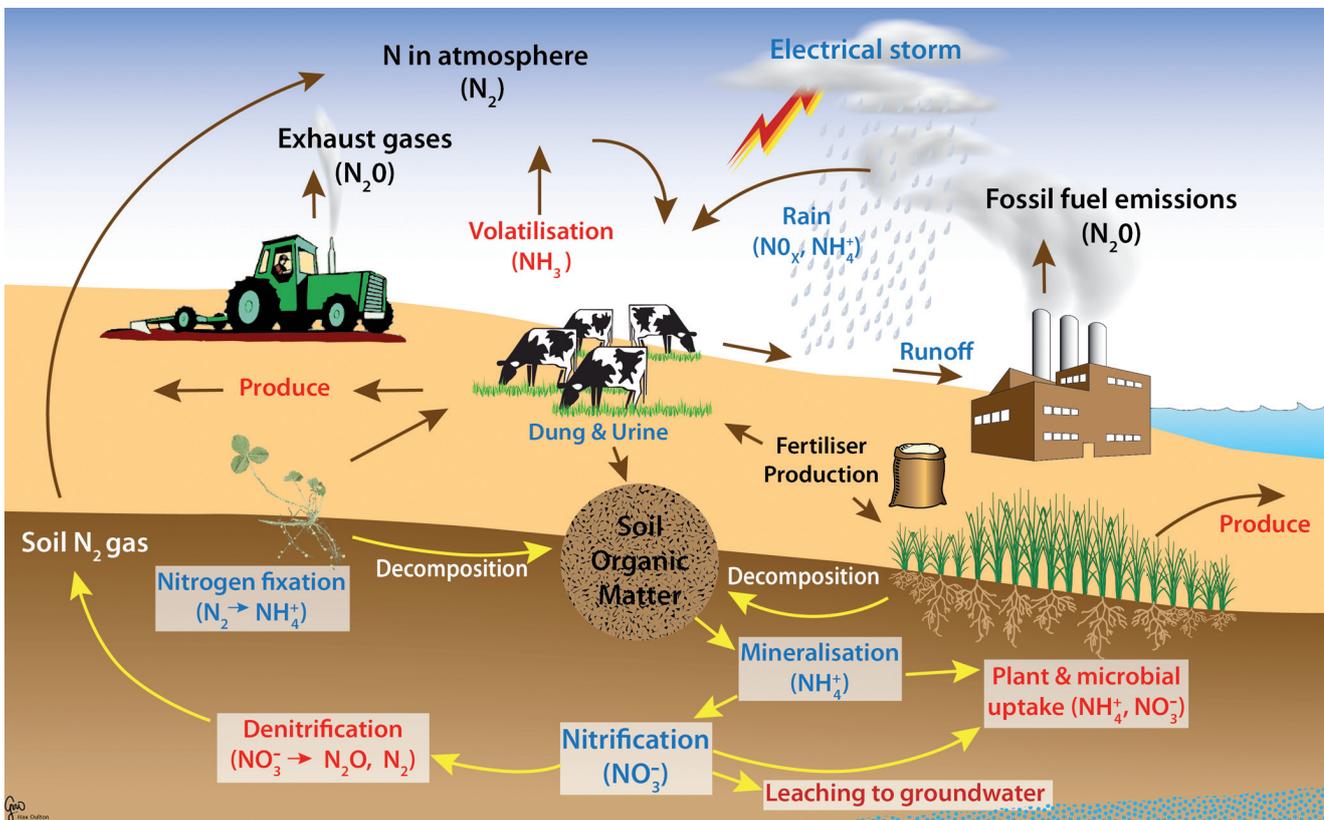
Figure 1: Schema showing the principle components of the terrestrial nitrogen cycle.

N ratio of less than 20 will mineralise N, while those with a C:N ratio of more than 25 will immobilise N. Most agricultural soils tend towards organic matter C:N ratios of 10–12, while forest and native bush soils tend to have C:N ratios more than 15–20. Ammonium is a positive cation that adsorbs onto soil clays and organic matter which are negatively charged. Consequently, ammonium tends to be retained in the topsoil and together with nitrate is the form of N taken up by pasture and forest plants. Some ammonia and ammonium reaches soil directly by being washed out of the atmosphere and from volcanic vents.

In the natural environment, most nitrate is formed from the oxidation of ammonium. Again, this is a microbial process but can only be achieved by a relatively small and specialist group of bacteria – the nitrifiers. The first stage – the oxidation of ammonia to nitrite – is achieved by bacteria such as *Nitrosomonas* species. Other bacterial species such as *Nitrobacter* are responsible for the oxidation of nitrite to nitrate. It is important that nitrite does not accumulate in soil as it is toxic to plants and other microbes. The bacteria responsible for nitrification are generally slow growing, not tolerant of acid conditions and require well-aerated soil. Consequently, nitrification can be slow in acid or waterlogged soils, although some soils do show nitrification at low pH, possibly by tolerant groups of autotrophic bacteria or by nitrification occurring at microsites in the soil. Once formed, nitrate being a negatively-charged ion, is not strongly bound to soil, and can consequently be rapidly washed out of the soil through leaching during heavy rain (Figure 1).

Denitrification is the process whereby the N cycle is completed and the various forms of reactive N are returned to N_2 gas. The process is undertaken by bacteria and is restricted to conditions where there is a supply of NO_3^-, low oxygen levels and an energy source, usually organic matter. A wide range of microbes is able to denitrify NO_3^-. If the reactions do not go to completion, then some N_2O is also formed. The formation of N_2O is of concern as N_2O is a potent greenhouse gas and over a 100 year timespan is estimated to have some 300 times more warming potential than CO_2 (IPCC 1995). Some N_2O can also be formed during the nitrification process. New Zealand is unusual in being a developed nation where about half of the national greenhouse gas (GHG) emissions are produced from soil and animals in the rural sector rather than from urban industry and vehicles, and that 17% of total GHG emissions in New Zealand are attributable to nitrous oxide (N_2O) (Ministry for the Environment, 2005).

In the last century, large amounts of reactive N have been generated by humans through industrial and agricultural development that have supported increased food production needed for a growing population (Table 2). Some reactive N is from by-products that occur during the combustion of fossil fuels generating NO_x gasses such as exhaust gasses from combustion engines; others are specific industrial processes such as the Haber-Bosch process that converts atmospheric N_2 and hydrogen (usually from fossil fuel) into NH_3, some 85% of which is used to make N fertilisers. Improved land management practices and plant breeding have also increased the growth of plants such as clover to enhance nitrogen-fixation.

Consequences of excess reactive N in the environment

There is no doubt that mankind has benefited enormously from the use of nitrogen fertilisers and the cultivation of N-fixing plants. It has been estimated that about half the world's current population is now dependent on the use of these nitrogen inputs. The ability to grow more crops on the same area of land has allowed the continued expansion of the human population. However, these benefits are somewhat offset by harmful effects of too much reactive nitrogen. Plants are rather inefficient at using N fertiliser and typically, only around 50% of the applied fertiliser is taken up. The rest is lost from the soil/plant system through leaching, run-off, erosion and gaseous emissions. Urine

Box 2: Nutrient budgets

Nutrient budgeting is a method of calculating nutrient inputs and outputs for a farm, with the intention of efficient use of resources. Only the adequate amount of N needed is added to maximise economic returns, and to compensate for the N lost in harvested products (like milk) and to the environment. New Zealand farmers are encouraged to use the computer program "Overseer Nutrient Budgets Modeltm". Based on long-term averages, the program calculates nutrient movement on a whole farm basis according to particular inputs supplied by the user. Also estimated are the potential leaching losses and greenhouse gas emissions. Overseertm is available free of charge and can be downloaded from: **http://www.agresearch.co.nz/overseerweb**.

Table 3: Estimates (Gg y^{-1}) of the inputs of N to the New Zealand environment in 1850 and 2000 (from Parfitt et al. 2008).

	Year	
Inputs	**1860**	**2000**
Pasture legumes	51	461
Other biological fixation	20	30
Atmospheric deposition[1]	63	175
Fertilisers	0	309
Imports[2]	0.04	38
Total	133	1023

[1] Mainly ammonia deposition; [2] e.g. food and animal feedstuffs.

patches deposited by grazing animals on pastures are another potent source of excess N (see Box 1).

Excess reactive N can leave the site of application and then there are a number of adverse downstream effects. N can leach from the soil into groundwater and surface waters. Too high a nitrate concentration in groundwater reduces drinking water quality, and excess nitrogen in surface waters acts as a fertiliser causing nuisance growth of algae, and eutrophication of streams, rivers, lakes and the sea. Reactive N is responsible (together with S) for acidification and loss of biodiversity in lakes and streams in many regions of the world.

N is returned to atmosphere by denitrification as N_2 and/or N_2O or volatilized as NH_3. Increases in reactive N in the atmosphere lead to production of troposphere ozone and aerosols that induce serious respiratory illness, cancer, and cardiac disease in humans. Despite much of the reactive N eventually being converted back to N_2 gas completing the N cycle, damage has been done along the way, and both terrestrial and aquatic ecosystems are becoming enriched in N.

A nitrogen balance for NZ

The Nanjing Declaration on Nitrogen Management calls upon national governments to optimise N management in their countries. One way to identify national inputs and outputs of N is to prepare a national N balance and to identify changes over time. The N inputs to the New Zealand environment have increased substantially since around 1860 following substantial forest clearances and the introduction of European agriculture for pastoral farming, with biological fixation by pasture legumes and N fertilisers showing particularly large increases (Table 3).

Box 3: Nitrification inhibitors

Nitrification inhibitors are chemicals applied to soils to slow the bacterial conversion of ammonium to nitrate. Ammonium, from N fertilisers, organic matter, dung and urine, is a positively charged ion and much less readily leached from soil than nitrate. By slowing the conversion of ammonium to the more readily leached nitrate, more N can be retained in the soils and N uptake by plants may be improved. Keeping the N concentrations low also reduces gaseous losses as N_2O. The inhibitors such as DCD (dicyandiamide) can persist for some weeks in soil, particularly under cold dry conditions.

Table 4: Estimates (Gg/y) of the outputs (losses) of N to the New Zealand environment in 1850 and 2000 (from Parfitt et al. 2008).

	Year	
Outputs	**1860**	**2000**
Produce (exports)	1	165
Leaching	72	304
Denitrification	27	153
Effluent discharge	1	35
NH_3 volatilisation	1	241
Erosion	153	190
Trees and fires	11	17
Total	266	1105

The large increase in inputs has been matched by correspondingly large increases in outputs. Once exports of produce leave our shore, or are discharged to the sea they no longer contribute to the NZ nitrogen balance (but there can be some redeposition to land from atmospheric discharges).

In both years examined, inputs and losses for NZ were almost in balance, but note that in 2000 much of that balance was accounted for by leaching, volatilisation and denitrification on the losses side. These are all processes that increase the movement of reactive N through our terrestrial and aquatic environments with an associated increased risk of environmental damage.

While there is no doubt that agricultural productivity and the export of produce has been greatly increased by the use of N fertilisers, the accompanying risk of damaging the environment cannot be ignored. Some countries have considered introducing an N tax (Finland, Sweden) to discourage overuse of N, and most developed countries including NZ regulate against discharges of effluents that are too high in N. A range of techniques to moderate N inputs includes use of computer models (e.g. Overseer™) to optimise N application on farms (see Box 2). Other land management practices are also encouraged, such as fertiliser application only to suitable crops and soils, restoration or protection of wetlands adjacent to waterways, regulation to restrict intensive land use on vulnerable soils and areas, and possible control of some soil processes using nitrification inhibitors (see Box 3). Parfitt et al. (2008) suggest that rather than NZ aiming for greater agricultural intensification, implying greater use of fertilisers and more production, an alternative strategy would be to switch to a greater proportion of high value crops where bulk production is not the main objective.

For further information contact:
schipper@waikato.ac.nz

3. Low – N feed supplements

The use of low protein feeds such as maize silage to supplement high protein pastures has been suggested as a means to reduce relative use of N litre^{-1} of milk while increasing production ha^{-1}. Efficient N fertiliser use can be achieved by matching N fertiliser application to maize plant requirements. Further efficiencies can be gained when maize is used as a dietary supplement as this results in lower urine Nr deposition back on to pastures (Luo et al., 2008).

Efficient removal:

1. Denitrification walls

Denitrification walls have been used to intercept shallow ground water and can greatly reduce NO_3 entering surface waters. Denitrification walls are constructed by digging a trench that will intercept an area of high NO_3 runoff. The walls are composed of a carbon substrate, such as sawdust, mixed with soil that will allow runoff water to pass through the wall. The organic matter reduces oxygen concentration by stimulating aerobic respiration and also supplies an energy source for anaerobic microorganisms capable of reducing the NO_3 to N_2 gas (or intermediate NO_x gases), and can thereby remove most NO_3 from the groundwater passing through the wall (Schipper et al., 2005). A key part of the design is to achieve an infiltration rate that allows enough residence time for denitrification, but does not reduce flow to such an extent that by-pass flow occurs around or beneath the wall.

2. Wetlands

Wetlands, whether natural or constructed, have the potential to intercept and remove significant amounts of Nr before runoff waters enter larger surface water bodies. So long as runoff travels through anaerobic zones where there is decaying plant material, rather than flowing over these areas, much of the NO_3 entering these systems may be completely reduced back to N_2 gas.

3. Standoff pads

Luo et al. (2008) calculated a 10% reduction in total farm N_2O emissions could be achieved when cows grazing pastures on poorly drained soils spent 18 hours day^{-1}, for 3 months of the year (winter period when cows were not lactating) on a standoff pad, compared with pastures that were continuously stocked. This reduced the amount of urine entering the soil at a time of the year when denitrification leading to N_2O emissions was highest. They also stated that reductions may be significantly increased if denitrification inhibitors were used on the standoff pad to reduce NO_3 from pad effluent, and also by timing of effluent disposal to pasture to avoid times of high denitrification potential (during saturated soil conditions).

Conclusion

As part of the global imperative to reduce GHG emissions and environmental degradation, New Zealand must address

---

Looking to natural systems for solutions

In low nutrient forest systems it has been shown that virtually no NO_3 is leached due to very efficient use of N by forest species. This is accomplished through plants having mycorrhizal associations, whereby the mycorrhiza can directly access organic forms of N (in plant litter), thus bypassing the soil mineralisation processes that can lead to N leaching losses. These processes are not well understood, but there is growing interest in how mycorrihizal associations with grassland species may be used to reduce nitrate leaching from pastoral systems (Leake et al., 2004).

issues about excess Nr in its agro ecosystems. While Nr is critical, whether naturally or anthropogenically fixed, to continued food production for a hungry world, we must learn to use it more efficiently. This may ultimately reduce costs of fertilisation, but, more importantly, reduce losses from agriculture that can result in a cascade of environmental damage.

While significant work is currently underway to understand soil nitrogen cycles and fluxes, new information (such as accurate spatial data) and new methods need to be combined to develop effective strategies to manage Nr fluxes between the soil, other environmental compartments, and the atmosphere.

For further information contact:
FraserS@landcareresearch.co.nz

References

de Klein, C.A.M., Sherlock, R.R., Cameron, K.C., & van der Weerden, T.J. (2001). Nitrous oxide emissions from agricultural soils in New Zealand - a review of current knowledge and directions for future research. *Journal of The Royal Society of New Zealand*, 31, 543-574.

Galloway, J.N. (1998). The global nitrogen cycle: Changes and consequences. *Environmental Pollution*, 102, 15-24.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger. S.P., Howarth. R.W., Cowling. E.B., & Cosby. B.J. (2003). The nitrogen cascade. *Bioscience*, 53, 341-356.

Leake, J., Johnson, D., Donnelly, D., Muckle, G., Boddy, L., & Read, D. (2004). Networks of power and influence: The role of mycorrhizal mycelium in controlling plant communities and agroecosystem functioning. *Canadian Journal of Botany*, 82, 1016-1045.

Ledgard, S.F., Menneer, J.C., Dexter, M.M., Kear, M.J., Lindsey, S., Peters, J.S. ,Pacheco, D. (2008). A novel concept to reduce nitrogen losses from grazed pastures by administering soil nitrogen process inhibitors to ruminant animals: A study with sheep. *Agriculture, Ecosystems and Environment*, 125, 148-158.

Luo, J., Ledgard, S.F., de Klein, C.A.M., Lindsey, S.B., & Kear, M. (2008). Effects of dairy farming intensification on nitrous oxide emissions. *Plant Soil*, 309, 227-237.

MacLeod, C.J., & Moller, H. (2006). Intensification and diversification of New Zealand agriculture since 1960: An evaluation of current indicators of land use change. *Agriculture, Ecosystems and Environment*, 115, 201-218.

Menneer, J.C., Sprosena, M.S., & Ledgard, S.F. (2010). Effect of timing and formulation of dicyandiamide (DCD) application on nitrate leaching and pasture production in a Bay of Plenty pastoral soil. *New Zealand Journal of Agricultural Research*, 51, 377-385.

Schipper, L.A., Barkle. G.F., & Vojvodic-Vukovic, M. (2005). Maximum rates of nitrate removal in a denitrification wall. *Journal of Environmental Quality*, 34, 1270-1276.

References

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., & Cosby, B.J. (2003). The Nitrogen Cascade. *BioScience,* 53, 341-356.

Intergovernmental Panel on Climate Change. (1995). The Science of Climate Change: Summary for Policymakers and Technical Summary of the Working Group I Report, page 22. Global warming Potentials http://unfccc.int/ghg_data/items/3825.php

Nanjing Declaration on Nitrogen Management. Third International Nitrogen Conference, Nanjing, People's Replublic of China, 12–16 October 2004. http://www.initrogen.org/fileadmin/user_upload/nanjing/nanjing_declaration-041016.pdf

MFE. (2005). New Zealand's greenhouse gas inventory 1990–2003. Ministry for the Environment, Wellington, New Zealand.

Parfitt, R.L., Baisden, W.T., Schipper, L.A., & Mackay, A.D. (2008). Nitrogen inputs and outputs for New Zealand at national and regional scales: past present and future scenarios. *Journal of the Royal Society of New Zealand*, 38(2), 71-87.