

Project number: 5605
Funding source: DAFM

Date: Sept 2012
Project dates: Oct 2006 - Dec 2011

Quantifying subsurface denitrification across contrasting agri-environmental settings



Installing groundwater investigation wells.

Key external stakeholders:

All farmers
Department of Agriculture, Food & Marine
Environmental Protection Agency

Practical implications for stakeholders:

The fate of nitrate leaching from agricultural soils is not well known internationally and subsoil/groundwater denitrification could potentially reduce nitrate transport to sensitive receiving waters. Our project has shown that subsurface denitrification is an important sink for nitrate and nitrous oxide during transport in subsoil and groundwater.

- Main points
 - **Farmers:** This research demonstrates that that nitrate leached from the root zone can be reduced substantially through denitrification and this supports allowing higher nitrate leaching on soils with higher denitrification potential.
 - **Policymakers:** There is considerable potential for nitrate leaching reduction through denitrification on lower permeability soil/aquifers. Indirect N₂O emission factors were potentially considerably higher than the IPCC default value.
 - **Scientific:** This research quantifies nitrate reduction, indirect nitrous oxide, methane and CO₂ emissions from groundwater for the first time in Ireland and provides valuable international data in a much ignored process.

Main results:

- Subsoil denitrification rates are low and predominantly releases environmentally benign di-nitrogen.
- Groundwater denitrification resulted in nitrate leaching reductions on lower permeability sites was 57% compared to 6% on high permeability sites with di-nitrogen the main end product.
- Groundwater denitrification was negatively associated with groundwater oxygen and redox potential.
- Groundwater can be an important source of indirect greenhouse gas emissions with emission factor (EF_{5g}) ranged 0.0029-0.0041.

Opportunity / Benefit:

- Identification of areas with high and low groundwater denitrification potential could provide an important N management tool in agricultural systems for decreasing nitrate delivery to rivers and indirect N₂O emissions to atmosphere.
- Indirect GHG emissions from groundwater are an important part of farm and national inventories.

Collaborating Institutions:

Trinity College Dublin, NUI Galway

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Mr Paul Johnston and Dr Catherine Coxon (TCD)
International Steering Group

1. Project background:

Internationally, subsurface denitrification has received only limited attention, due to methodological limitations that have more recently been overcome. Denitrification may prove to be the key process in determining nitrate occurrence in receiving waters. The indirect emission of nitrous oxide via subsurface denitrification has large uncertainties and little data is available nationally or internationally. These indirect emissions can account for up to 70% of direct emissions from soil and further data is needed for global greenhouse gas budgeting. Understanding the microbial denitrification process within subsoil/groundwater will lead to a better understanding of the fate of nitrate delivery to groundwater and may also lead to management procedures for reducing both nitrous oxide emissions and nitrate leaching.

2. Questions addressed by the project:

This research addressed the following questions:

- Is subsurface denitrification an important process for reducing nitrate transport to ground and surface waters?
- Do agricultural practices and soil type/hydrogeology influence the denitrification rate?
- Is subsurface denitrification a sink or source of indirect greenhouse gas emissions?

3. The experimental studies:

An integrated multidisciplinary team assessed the fate and transport of nitrate at a range of depths beneath the rooting zone. The research approach used the most up to date, state of the art methodologies, for the quantification of denitrification in subsoil, groundwaters and the microbial community responsible for denitrification. Within the subsoil zone, the rates of denitrification and the partitioning between N_2 and N_2O were assessed ex-situ. Groundwater denitrification was quantified by the measurement of actual denitrification products (N_2 and N_2O) in a range of agricultural/hydrogeological situations and potential groundwater denitrification quantified using the "push-pull" method. The project used novel, direct methods to study the rates and distributions of denitrifying bacteria in soils and aquifer samples. This project established Irelands only Membrane Inlet Mass Spectroscopy unit for the quantification of argon and di-nitrogen gases. The project established protocols for the extraction and analysis of dissolved nitrous oxide, carbon dioxide and methane concentrations in water by gas chromatography. In addition the project quantified, for the first time, the microbial community in soil and groundwater response to N inputs.

4. Main results:

Soil carbon concentration strongly positively influenced denitrification rate. Soil denitrification rates reduced significantly with soil depth and were 25, 12 and 3% in the soil A, B and C horizons (Jahangir et al 2012a). Addition of carbon to soil increased denitrification rates in the A and B horizons by 100% and by 600% in the C horizon. Although the rate of denitrification is lower in the subsoil, due to carbon availability, the ratio of $N_2:N_2O$ is much higher. Thus subsoil denitrification is a sink for the emission of N_2O and nitrate. The coupling of low rates of denitrification with long residence times in subsoil is likely to consume considerable quantities of nitrate. Denitrification will be considerably reduced in free draining aerobic soils with rapid flow paths to groundwater.

Landuse and hydrogeological settings are both important variables in determining groundwater nitrate occurrence. Mean groundwater nitrate concentrations were high on the two free draining sites. Groundwater nitrate concentrations were correlated with physiochemical parameters such as DO, redox potential and saturated hydraulic conductivity. Sites with low groundwater DO and redox potentials had low nitrates and vice versa (Jahangir et al. 2012b). The chemical data suggest that denitrification could be responsible for the low groundwater nitrate concentrations observed at two sites.

Our results indicated that groundwater N_2O can leach to the water table with recharge. The push-pull experiments, using in situ ^{15}N tracer, showed that N_2O was also produced in the groundwater and identified in-situ ammonia generation from dissimilatory nitrate reduction to ammonium (DNRA). The fate of

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groundwater N_2O requires further research to quantify the actual emissions to the atmosphere during groundwater transport.

Groundwater denitrification ($\text{N}_2 + \text{N}_2\text{O}$) was a significant pathway of groundwater nitrate depletion resulting in 45, 70, 7 and 3% losses of $\text{NO}_3\text{-N}$ (Figure 1). The main end product of denitrification (N_2) was significantly higher in the less well drained sites than the well drained sites. Across the sites, the mean indirect N_2O emission factors were considerably higher (0.0048-0.0259) than the IPCC default value of 0.0025 (EF5g). The results also identified groundwater can be an important source of CO_2 and CH_4 emissions to the atmosphere. Denitrification functional genes, nitrous oxide reductase 'nosZ' and nitrite reductase 'nir', were observed across all soil types and groundwaters. The abundance of nirK and nirS gene varied across the six sites tested, whereas the nosZ gene concentration remained relatively constant, suggesting that bacterial populations with nosZ gene are less opportunistic. N_2 and N_2O emissions were found to be significantly correlated with gene copy number.

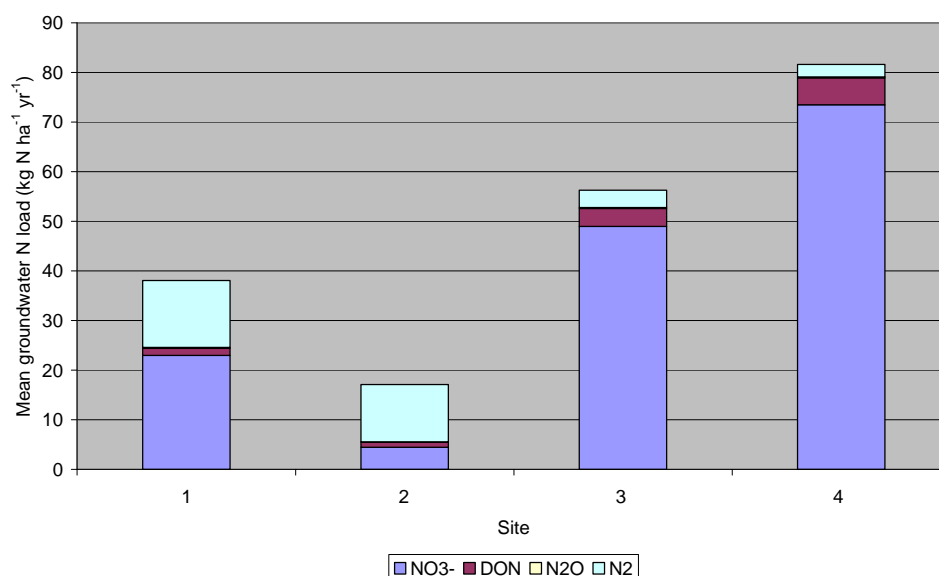


Figure 1 Mean annual nitrogen load in groundwater disaggregated in to nitrate (NO_3^-) dissolved organic N (DON), nitrous oxide (N_2O) and excess di-nitrogen (N_2) across 4 sites. Sites 1&2 had lower permeability soil/aquifers and sites 3&4 had higher permeability soil/aquifers (Jahangir et al. 2012c)

Subsurface denitrification has been found to be an important process that can substantially reduce nitrate leaching but can contribute to indirect greenhouse gas emissions. Further research is needed to refine indirect greenhouse gas emissions and to further evaluate denitrification as groundwater discharges to surface water. Indirect emissions need further consideration in the carbon foot printing of Irish agricultural systems.

5. Opportunity/Benefit:

The primary stakeholders for this research are both farmers and policy makers. Policy makers will be interested in the potential for denitrification to reduce nitrate leaching and achievement of water quality targets particularly in lower permeability settings. In addition indirect greenhouse gas emissions from groundwater is important and the first Irish emission factors have been produced by the project. For farmers there is justification for having higher acceptable nitrate leaching rates on lower permeability soils. This unique national research has led to a capacity for quantifying indirect emissions.

6. Dissemination:

The results of the project have been presented at over 30 national and international conferences. There are four scientific papers under review in international journals and five papers have been published in high impact scientific journals to date (see below). The outputs from the project have been sent to relevant national policy makers.

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Main publications:

Jahangir, M.M.R., Khalil, M.I., Johnston, P., Cardenas, L., Hatch, D., Butler, M. and Richards, K.G. (2012a) Total denitrification potential in subsoils: a mechanism to reduce nitrate leaching to groundwater, *Agriculture Ecosystems and the Environment* 147: 13-23.

Jahangir, M.M.R., Johnston, P., Khalil, M.I. and Richards, K.G. (2012b) Linking hydrogeochemistry to the abundances of nitrate in groundwater at diverse landscape settings, *Journal of Hydrology* 448-449, 212-222.

Jahangir, M.M.R., Johnston, P., Khalil, M.I., Hennessy, D., Humphreys, J. Fenton, O., Richards, K.G. (2012c) Groundwater: A pathway for terrestrial C and N losses and indirect greenhouse gas emissions, *Agriculture, Ecosystems and Environment* 159: 40- 48.

Jahangir, M.M.R., Johnston, P., Khalil, M.I., Grant, J., Sommers, C. and Richards, K.G. (2012d) Evaluation of headspace equilibration methods for quantifying greenhouse gases in groundwater, *Journal of Environmental Management* 111: 208-212.

Jahangir, M.M.R. (2012e) Denitrification in subsoils and groundwater in Ireland, *PhD Thesis*, Trinity College Dublin, Dublin 2.

Khalil, M. I. and Richards, K.G. (2011) Denitrification enzyme activity and potential of subsoils under grazed grasslands assayed by membrane inlet mass spectrometer, *Soil Biology and Biochemistry* 43, 1787-1797.

Popular publications:

Richards, K.G., Khalil, M.I., Fenton, O., Hara, A., Barrett, M., Jahangir, M.M.R., Johnston, P., O'Flaherty, V. (2009) Discovering subsurface denitrification, *Tresearch* 4 (3) 26-27.

7. Compiled by: Dr. Karl Richards