Benign de-nitrification in the subsurface environment

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Periphyton (benthic algae)
Grows on the bed and on solid objects such as logs and stones in rivers

Associated with nutrient enrichment (excess of nutrients, nitrogen and phosphorus)
Sources and contributions to nutrient loadings?

Predicts catchment N loss from Root zone

Source: Environment New Zealand 2007, MfE.
Root zone N losses (catchment average):
$N_{\text{root zone}} = 16.2 \text{ kg per ha per year}$

Nitrogen attenuation factor ($AF_n$)

\[
AF_n = \frac{N_{\text{root zone}} - N_{\text{river}}}{N_{\text{root zone}}}
\]

\[
AF_n = \frac{16.2 - 6.9}{100} = 9.3 / 16.2 = 0.6
\]

Nitrogen assimilative capacity:
Catchment average ~ 60% of root zone losses

River N load (catchment average):
$N_{\text{river}} = 6.9 \text{ kg per ha per year}$

Source: Elwan et al. (2015), Massey University
Sustainable primary production

Nitrogen Attenuation Capacity

Green

> 80 % N reduction

Yellow

50 – 80 % N reduction

Red

< 50 % N reduction

Targeted investment in solutions, e.g.

High Capacity Areas:
Sustainable Land Use
Intensification

Medium Capacity Areas:
Reduce Nitrogen Leaching via
Best Effluent and Nutrient
Management Practices

Low Capacity Areas:
Duration controlled grazing
Sheep/Goat milking
Cut and Carry Systems

Example: The Danish national map of nitrate reduction classes.
(Source: Ernstsen et al., 2008)
A collaborative, co-developed and co-funded research programme

Programme Co-ordination

Dr. Ranvir Singh
Assoc. Prof. Dave Horne
Dr. Uwe Morgenstern
Ms. Abby Matthews
Dr. Jon Roygard
Prof. Mike Hedley

Programme Partners

Massey University
Horizons Regional Council
Landcare Research
Manaaki Whenua
Fertilizer & Lime Research Centre
Dairynz
GNS Science
Developing techniques, methods and models

Objective - Assess and map nutrient flow pathways and their potential attenuation

Four piezometers at depth ranging from 5.8 to 8.7 m below ground level (bgl)

Suction cups (depth, bgl)
- 30 cm
- 60 cm
- 100 cm
- 200 cm
In-field monitoring and observations

Source: Aldrin Rivas, PhD Student, Massey University

1. Massey No. 1, Dairy
2. Pahiatua site, Dairy
3. Woodville site, Sheep & beef
4. Dannevirke site, Dairy

Study sites

1. Massey No. 1, Dairy
2. Pahiatua site, Dairy
3. Woodville site, Sheep & beef
4. Dannevirke site, Dairy

Source: Aldrin Rivas, PhD Student, Massey University
De-nitrification: the key nitrogen attenuation process

Methods:

- Lab incubations and in-field ‘push-pull’ tests
- Isotope tracer techniques
- **Excess N\textsubscript{2}** (being developed by GNS Sciences)
- **Molecular techniques** (being developed by Massey FLRC and Landcare Research)

**Single Well ‘Push-Pull’ Test**

- Adding Acetylene, Bromide and Nitrate
- Test solution injection
- Groundwater extraction and analysis
- Groundwater
De-nitrification: the key nitrogen attenuation process

Groundwater de-nitrification? benign or not-benign?

• Direct measurement of the terminal products of denitrification, \( \text{N}_2\text{O} \) and \( \text{N}_2 \)

• Direct measurement of the de-nitrifiers, \( \text{nir}^S \), \( \text{nir}^K \) and \( \text{nos}^Z \) genes

\[
\text{NO}_3^- \xrightarrow{\text{Nar}} \text{NO}_2^- \xrightarrow{\text{Nir}} \text{NO} \Rightarrow \text{N}_2\text{O} \xrightarrow{\text{Nor}} \text{N}_2
\]

\[
\text{N}_2\text{O} \xrightarrow{\text{Nos}} \text{N}_2
\]
Relationships between nitrogen attenuation and catchment characteristics

Nitrogen attenuation factor \((A_{Fn}) = (N_{\text{rootzone}} - N_{\text{river}}) / N_{\text{rootzone}}\)

Spatial distribution of the nitrogen attenuation factor for 15 sub-catchments in the Tararua Groundwater Management Zone (TGWMZ) (Elwan et al, 2015).
Prediction of nitrogen loads in the Rangitikei River

Model - Variable nitrogen attenuation factor (based on soil and rock types – FSL and QMAP layers)

\[
River N load (ton yr^{-1}) = m \sum_{i=1}^{n} A_i \times N_i \times (1 - AF_{NRT})(1 - AF_{NST})
\]

Comparison of predicted vs. measured average annual soluble inorganic nitrogen (SIN) loads in different sub-catchments of the river

Prediction of nitrogen loads in the Rangitikei River

De-intensify (~9,800 ha) and Intensify (~83,000 ha) landuse (S3)

- Root zone N losses increase by 55%
- River N load decreases by 6%

Concluding Remarks

• Opportunity to spatially align intensive high-value primary production with naturally high contaminant attenuation capacity areas

• Reduce water quality impacts, hence sustain and/or enhance cultural resources, mahinga kai, taonga species.

• Collaborative, co-developed, co-funded research programme

• Developing cost-effective practical techniques, methods and models

• Aligned with the OLW Challenge ‘Sources and Flows’ & ‘Land Suitability’ programmes for wider applications
Thank you – Questions and suggestions please!
De-nitrification is a biogeochemical process, which converts nitrate-nitrogen to gaseous forms of nitrogen; predominantly to dinitrogen in groundwater systems.

This capacity is mainly governed by the physical, chemical and biological characteristics, and importantly by nutrient and oxidisable carbon in flow pathways. It requires:

- Low oxygen environment (influenced by hydrogeological settings);
- Carbon source (dissolved organic carbon); and
- Denitrify bacteria
De-nitrification: the key nitrogen attenuation process

Electrochemical succession of electron-accepting processes and sequential production of final products

De-nitrification: the key nitrogen attenuation process

### Table 1
Threshold Concentrations for Identifying Redox Processes in Regional Aquifer Systems

<table>
<thead>
<tr>
<th>Redox Process</th>
<th>Water Quality Criteria (mg/L)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O₂</td>
<td>NO₃⁻-N</td>
</tr>
<tr>
<td>Oxic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ reduction</td>
<td>≥0.5</td>
<td>—</td>
</tr>
<tr>
<td>Suboxic</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Anoxic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻ reduction</td>
<td>&lt;0.5</td>
<td>≥0.5</td>
</tr>
<tr>
<td>Mn(IV) reduction</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Fe(III)/SO₄²⁻ reduction</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Mixed</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Source: McMahon & Chapelle (2008)*

de-nitrification? benign or not-benign?
Direct measurement of the terminal products of denitrification, $\text{N}_2\text{O}$ and $\text{N}_2$

The Dynamics of Denitrification
Gas Chromatograph (DDGC)

- Automatic sampler
- Peristaltic pump
- 25 sealed vials
- Gas Chromatograph With 3 detectors: ECD, FID and TCD

- Helium Headspace
- 20 g dwt soil
- 125 mL Serum Vial

how “benign” the de-nitrification, i.e. calculate the $\text{N}_2\text{O}:\text{N}_2$ ratio

Direct measurement of the terminal products of denitrification, $\text{N}_2\text{O}$ and $\text{N}_2$
Direct measurement of the de-nitrifiers, $nirS$, $nirK$ and $nosZ$ genes

$\text{NO}_3^- \xrightarrow{\text{Nar}} \text{NO}_2^- \xrightarrow{\text{Nir} \ nirS \ nirK} \text{NO} \xrightarrow{\text{Nor}} \text{N}_2\text{O} \xrightarrow{\text{Nos} \ nosZ} \text{N}_2$

- Anaerobic respiration
- Phylogenetically diverse: Bacteria, Archaea, Fungi, Protozoa
Direct measurement of the de-nitrifiers, \textit{nirS}, \textit{nirK} and \textit{nosZ} genes

**Polymerase Chain Reaction (PCR) technique**

Soil Sample \rightarrow Extracted DNA \rightarrow Amplified product visible on gel \rightarrow Amplified gene of interest