

# Benign de-nitrification in the subsurface environment

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\*Presenting on behalf of our students, post-doc and colleagues Mr. Aldrin Rivas, Mr. Ahmed Elwan, Mr. Pete McGowan, Mr. Stephen Collins, Ms. Genevieve Smith, Ms. Heather Martindale, Dr. Uwe Morgenstern, Dr. Neha Jha, Dr. Andrew McMillian, Dr. Andrew Manderson, Dr. Lucy Burkitt, A/Professor David Horne, Professor Mike Hedley, Ms. Abby Matthews, and Dr. Jon Roygard

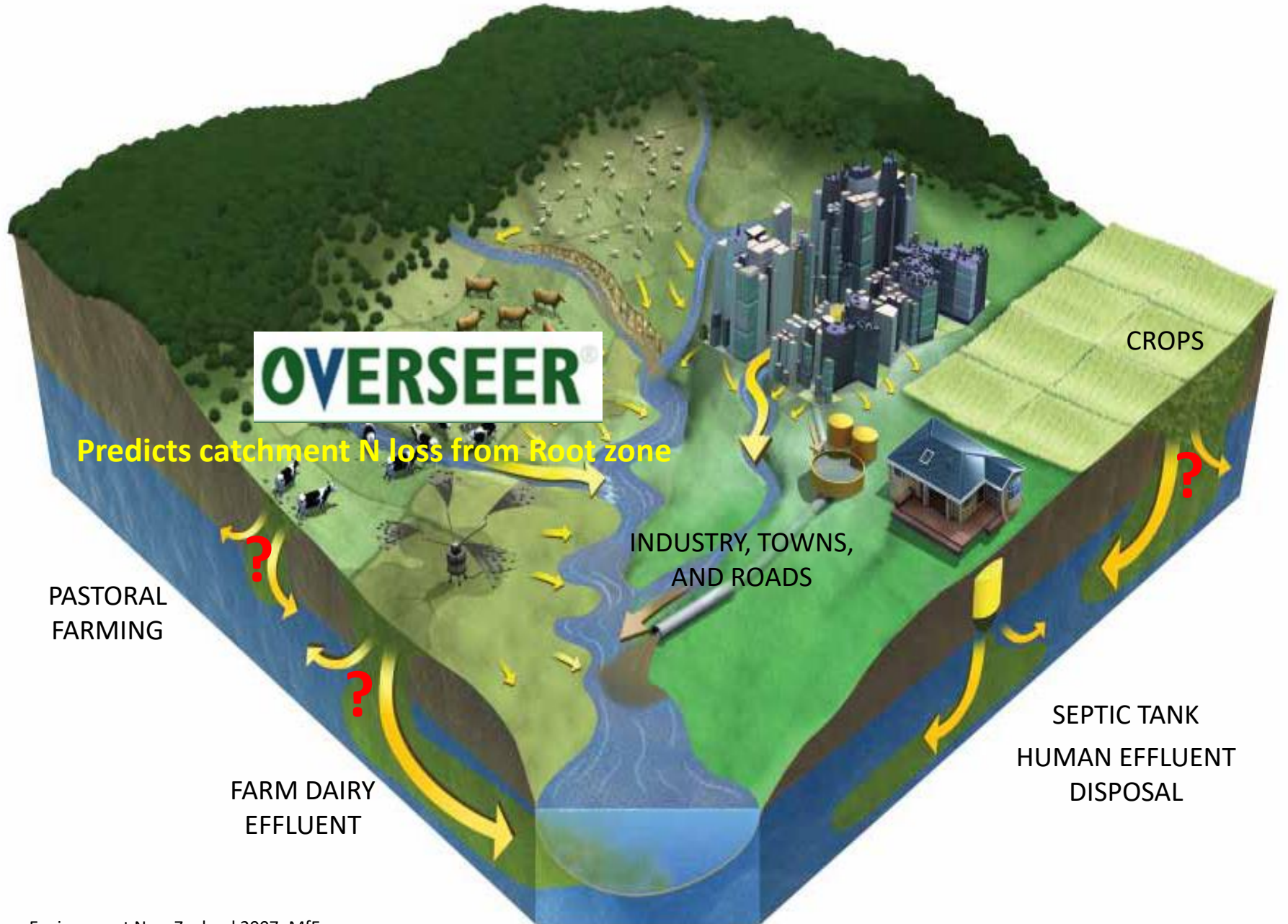


## Periphyton (benthic algae)

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?



Source: Environment New Zealand 2007, MfE.

# Manawatu Catchment @ Upper George

Nitrogen attenuation factor ( $AF_n$ )

$$= (N_{\text{rootzone}} - N_{\text{river}}) / N_{\text{rootzone}}$$

$$= (16.2 - 6.9) / 100$$

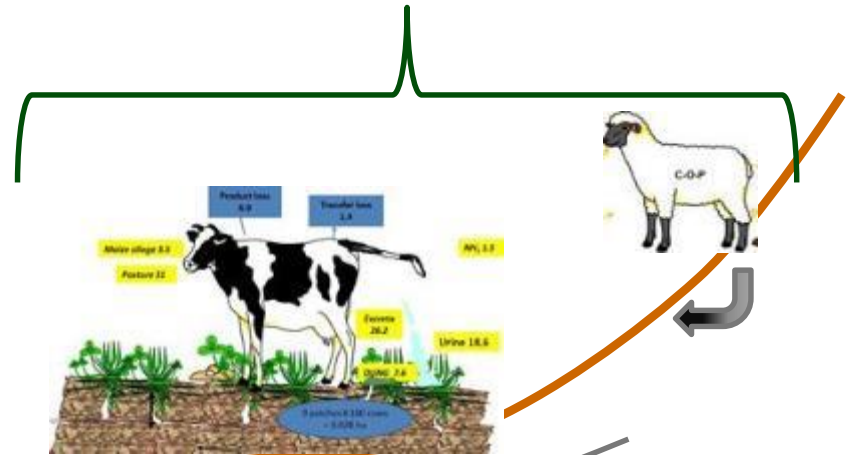
$$= 9.3 / 16.2 = 0.6$$

**Nitrogen assimilative capacity:**

Catchment average ~ 60% of root zone losses

**Root zone N losses (catchment average):**

$N_{\text{root zone}} = 16.2 \text{ kg per ha per year}$



**Hydrology? Biogeochemical processes?**

**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

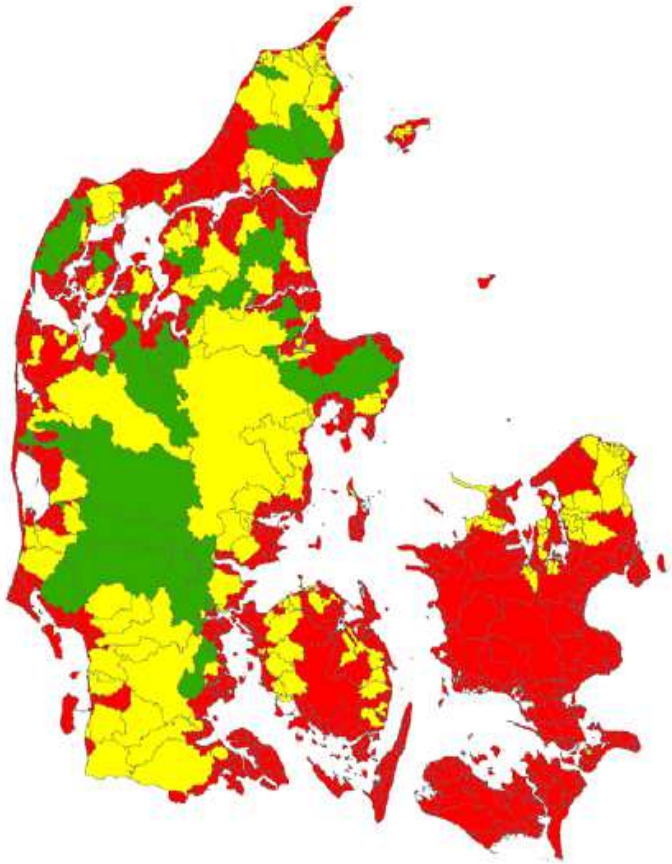
Red < 50 %  
N reduction

## 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: Ernstsens 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



**Landcare Research**  
**Manaaki Whenua**



&

National  
**science**  
Challenges

OUR LAND  
AND WATER

Toitū te Whenua,  
Toiora te Wai

# 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)

200 cm

Suction cups (depth, bgl)

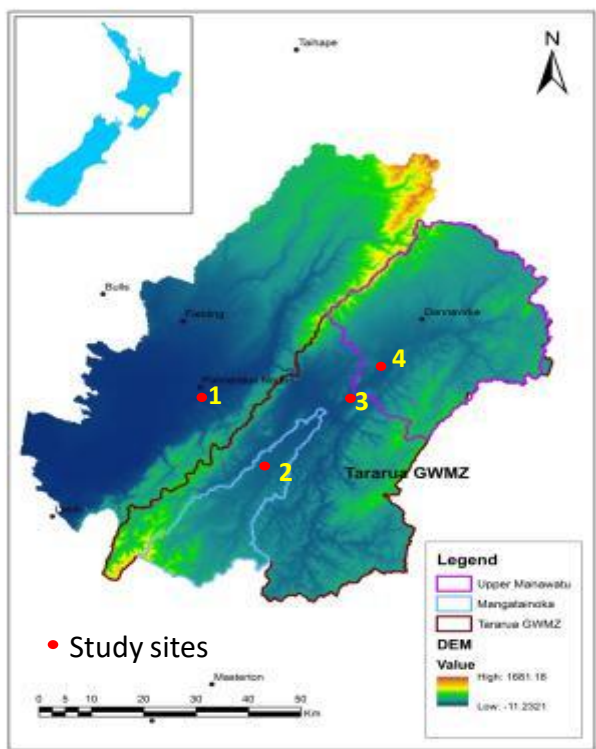
100 cm

60 cm

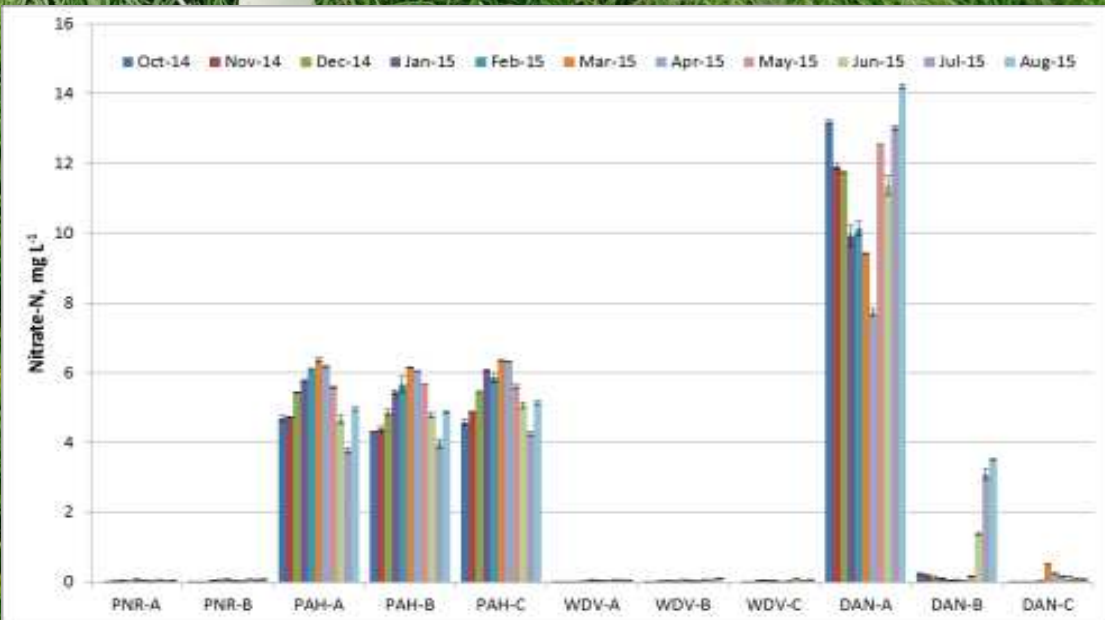
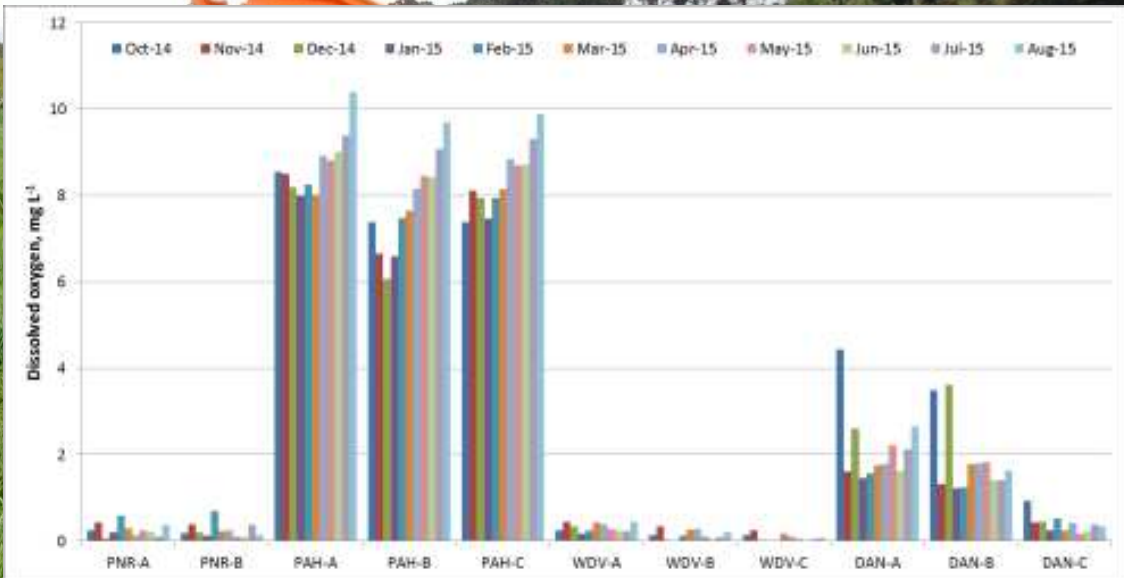
30 cm



# In-field monitoring and observations



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

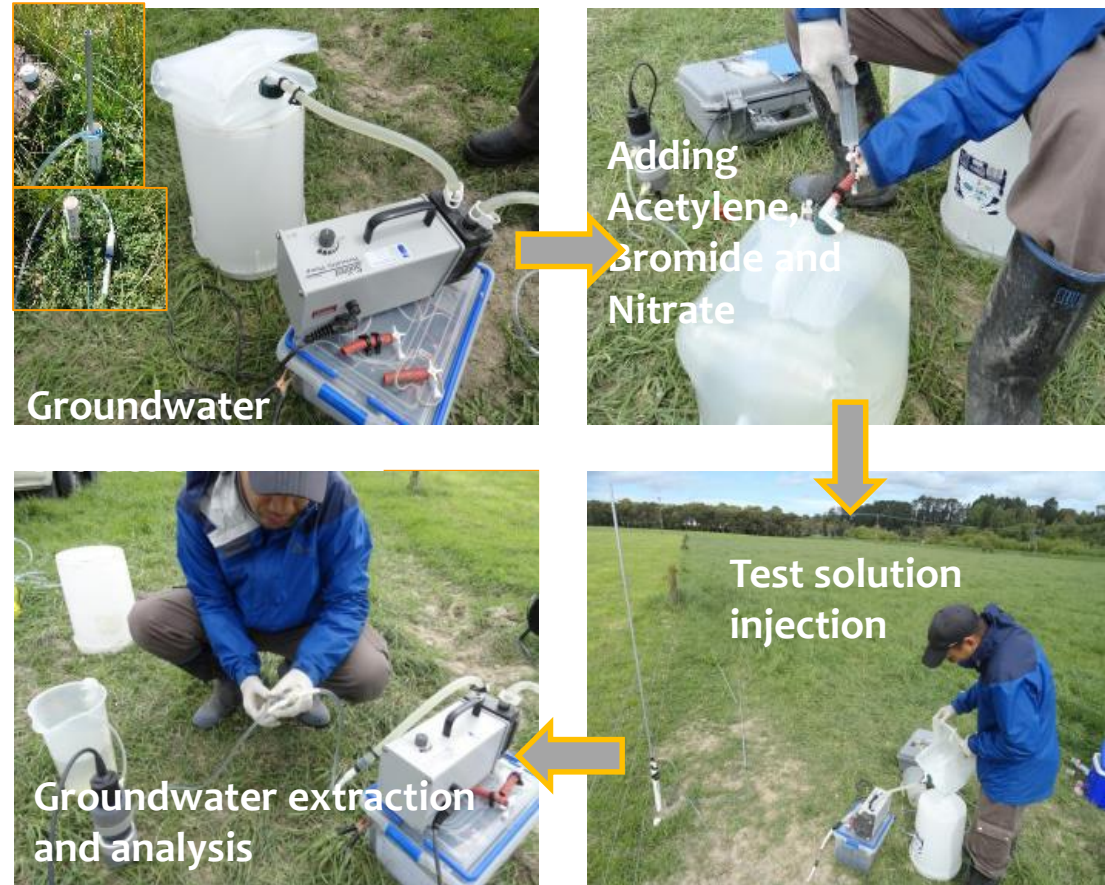


# De-nitrification: the key nitrogen attenuation process

## Methods:

- Lab incubations and in-field 'push-pull' tests
- Isotope tracer techniques
- **Excess N<sub>2</sub>** (being developed by GNS Sciences)
- **Molecular techniques** (being developed by Massey FLRC and Landcare Research )

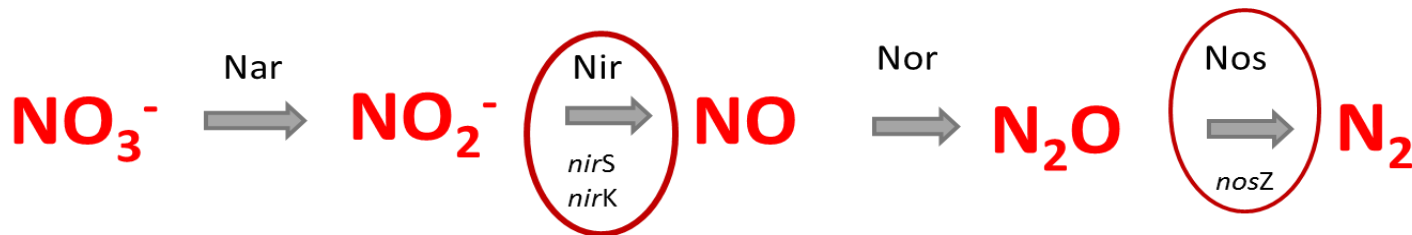
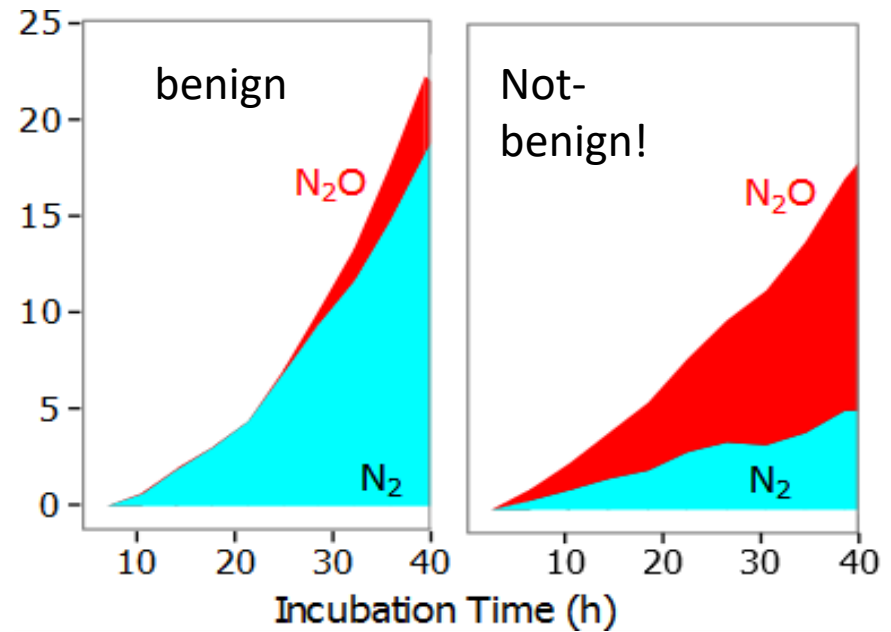
## Single Well 'Push-Pull' Test



# De-nitrification: the key nitrogen attenuation process

## Groundwater de-nitrification? benign or not-benign?

- Direct measurement of the terminal products of denitrification,  $N_2O$  and  $N_2$
- Direct measurement of the de-nitrifiers, *nirS*, *nirK* and *nosZ* genes



# Relationships between nitrogen attenuation and catchment characteristics

Nitrogen attenuation factor ( $AF_n$ ) =  $(N_{\text{rootzone}} - N_{\text{river}}) / N_{\text{rootzone}}$

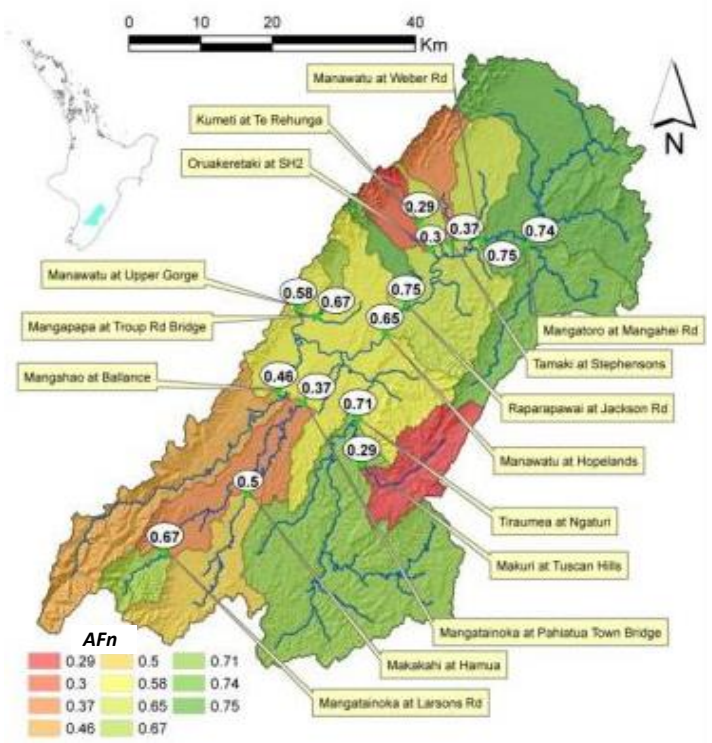
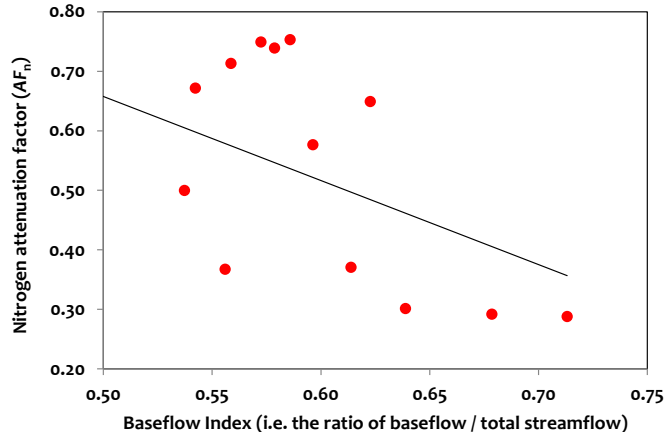


Table 1: Results of linear regression analysis between the  $AF_n$  values and catchments characteristics

Catchment Characteristics	$AF_n$	
	$R^2$	$p$
Well-drained (e.g. soils with drainage class 5) soils*	-0.35	<0.05
Fine textured (e.g. clay loam) soils	0.37	<0.05
Base Flow Index (BFI)	-0.31	<0.05

\*Soils with drainage class 5, in the Fundamental Soil Layer "FSL", are well-drained soils.



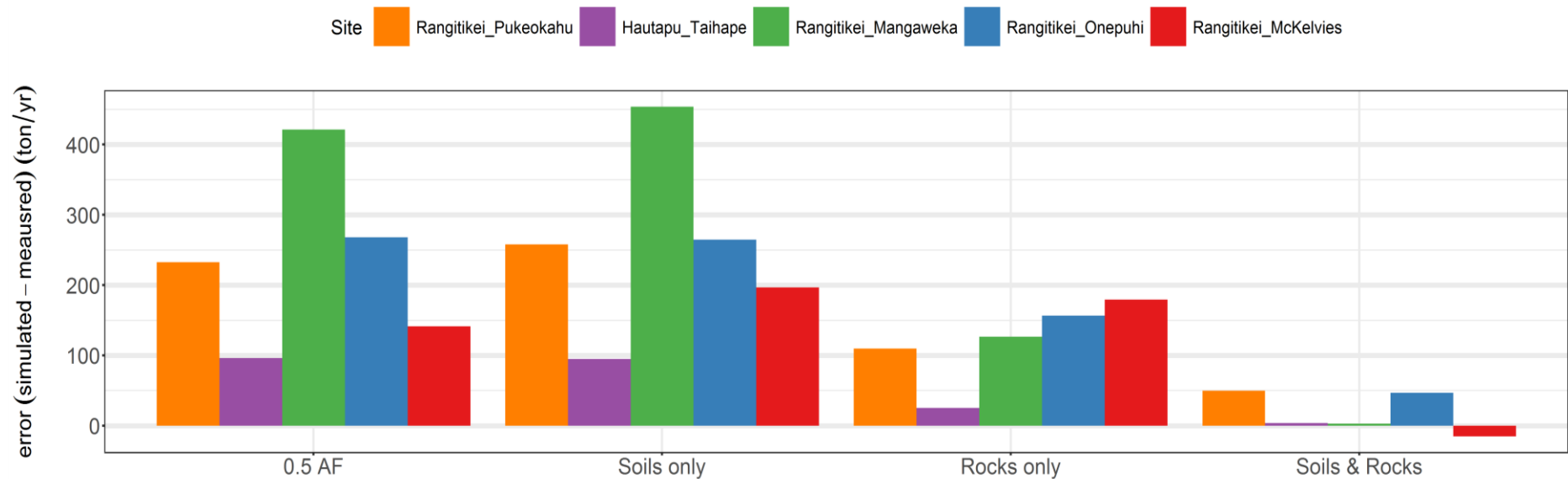
Spatial distribution of the nitrogen attenuation factor for 15 sub-catchments in the Tararua Groundwater Management Zone (TGWMZ) (Elwan et al, 2015).

# Prediction of nitrogen loads in the Rangitikei River

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

$$River\ N\ load\ (ton\ yr^{-1}) = m \sum_{i=1}^n A_i * N_i * (1 - AF_{N_{RT}})(1 - AF_{N_{ST}})$$

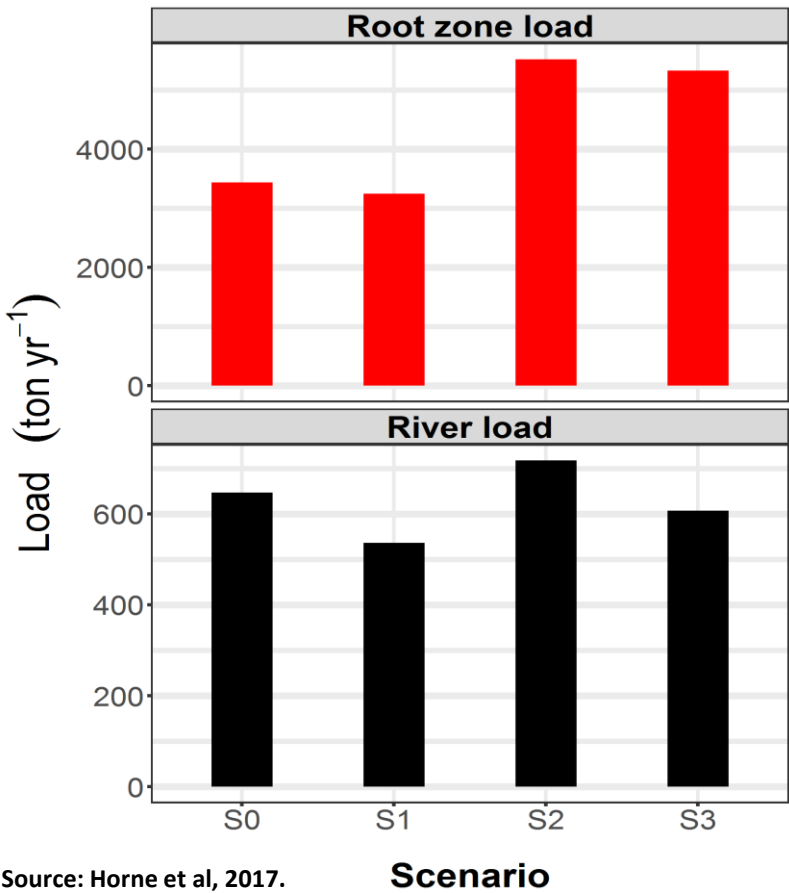
Comparison of predicted vs. measured average annual soluble inorganic nitrogen (SIN) loads in different sub-catchments of the river



Source: Singh et al, 2017.

# 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%

Source: Horne et al, 2017.

# 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



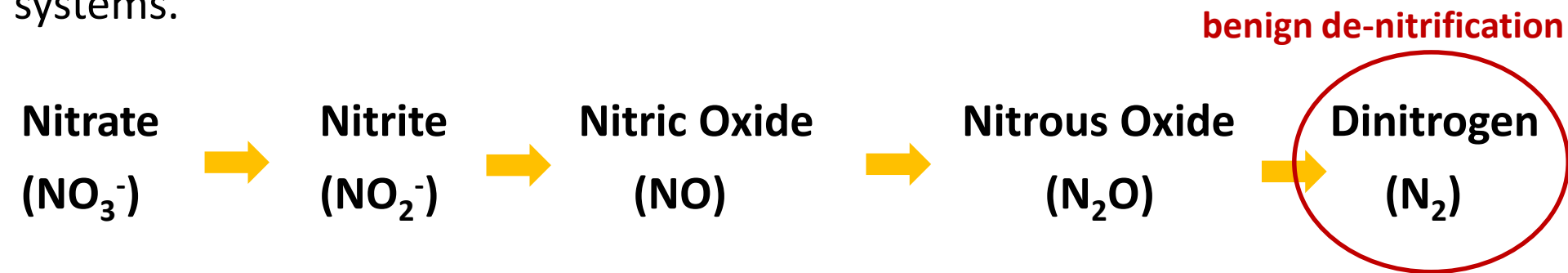
Thank you – Questions  
and suggestions please!

# Supporting Slides



# De-nitrification: the key nitrogen attenuation process

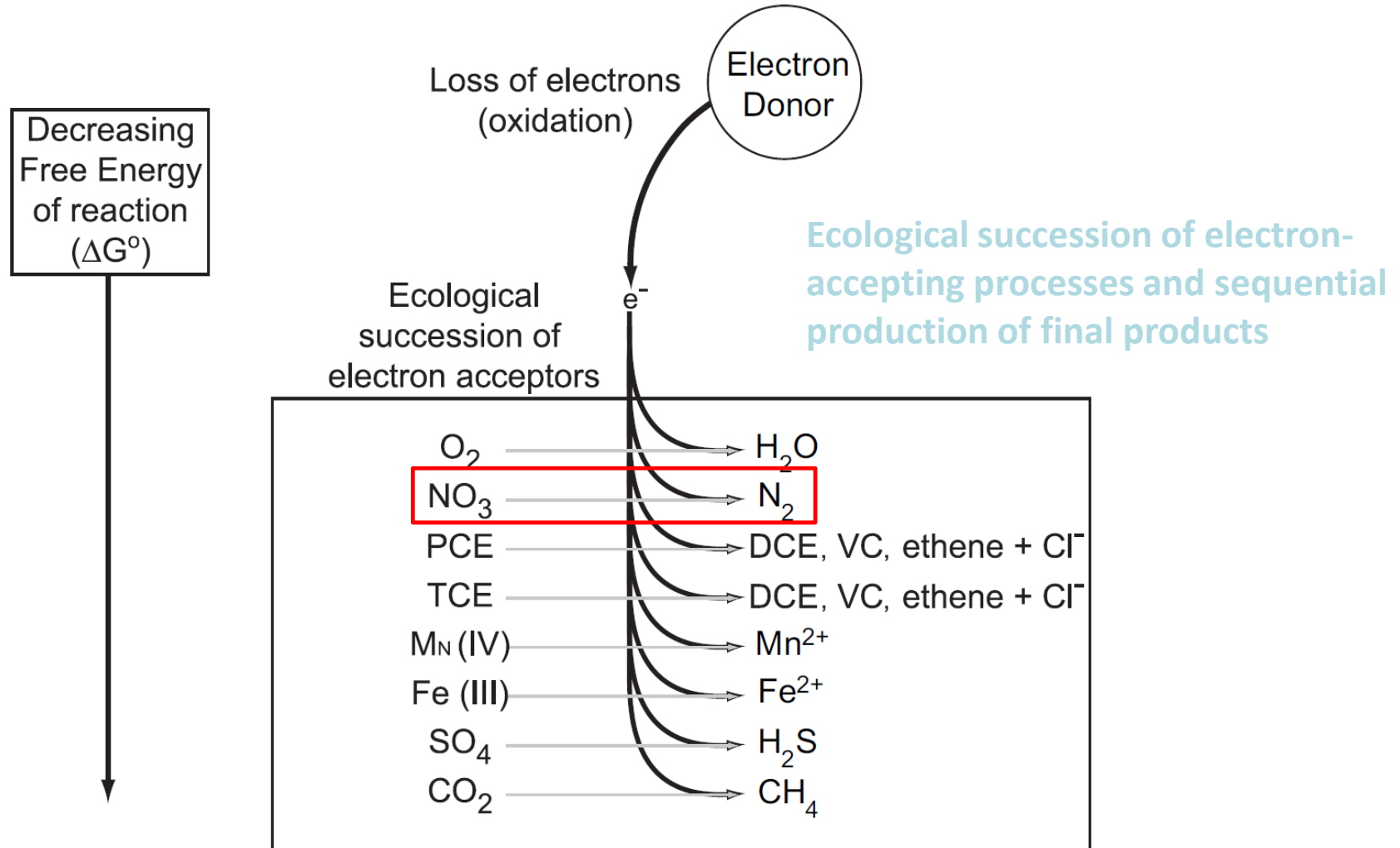
De-nitrification is a biogeochemical process, which converts nitrate-nitrogen to gaseous forms of nitrogen; predominantly to dinitrogen in groundwater systems.



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



Source: McMahon & Chapelle (2008)

# De-nitrification: the key nitrogen attenuation process

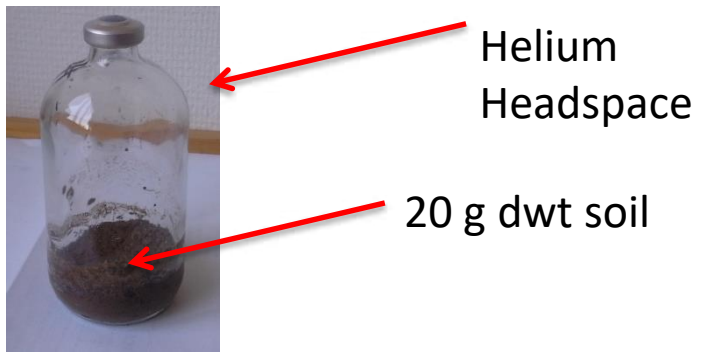
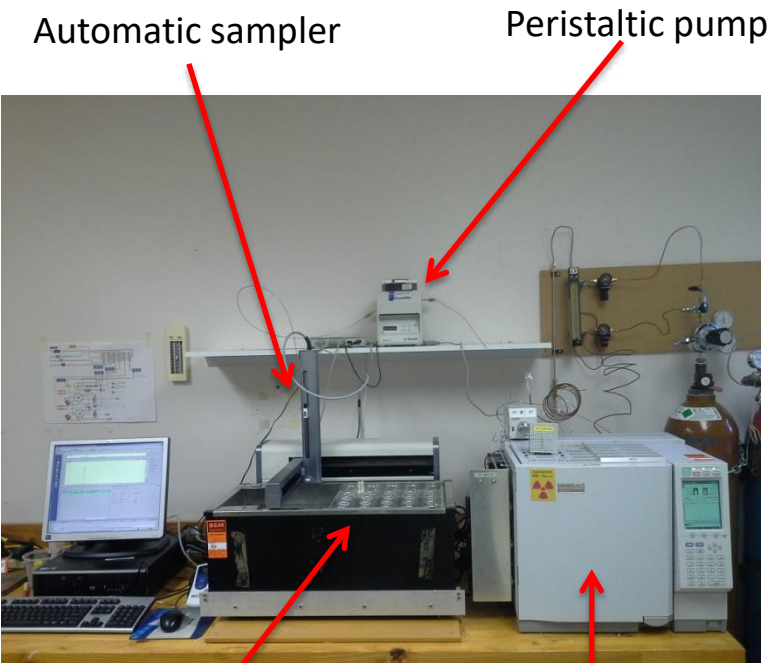
**Table 1**  
**Threshold Concentrations for Identifying Redox Processes in Regional Aquifer Systems**

Redox Process	Water Quality Criteria (mg/L)					Comments
	O <sub>2</sub>	NO <sub>3</sub> <sup>-</sup> -N	Mn <sup>2+</sup>	Fe <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	
Oxic						
O <sub>2</sub> reduction	≥0.5	—	<0.05	<0.1	—	—
Suboxic						
—	<0.5	<0.5	<0.05	<0.1	—	Further definition of redox processes not possible
Anoxic						
NO <sub>3</sub> <sup>-</sup> reduction	<0.5	≥0.5	<0.05	<0.1	—	—
Mn(IV) reduction	<0.5	<0.5	≥0.05	<0.1	—	—
Fe(III)/SO <sub>4</sub> <sup>2-</sup> reduction	<0.5	<0.5	—	≥0.1	≥0.5	—
Methanogenesis	<0.5	<0.5	—	≥0.1	<0.5	—
Mixed						
—	—	—	—	—	—	Criteria for more than one redox process are met

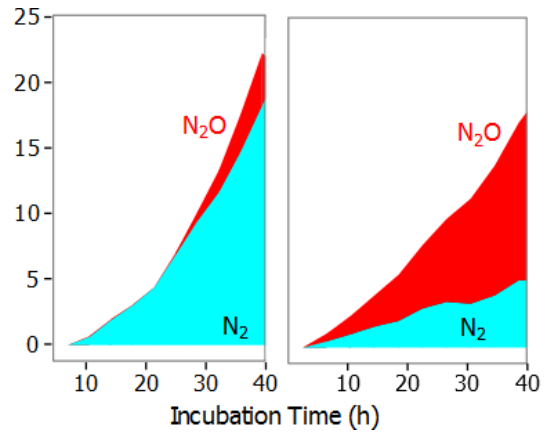
**de-nitrification? benign or not-benign?**

Source: McMahon & Chapelle (2008)

# Direct measurement of the terminal products of denitrification, N<sub>2</sub>O and N<sub>2</sub>

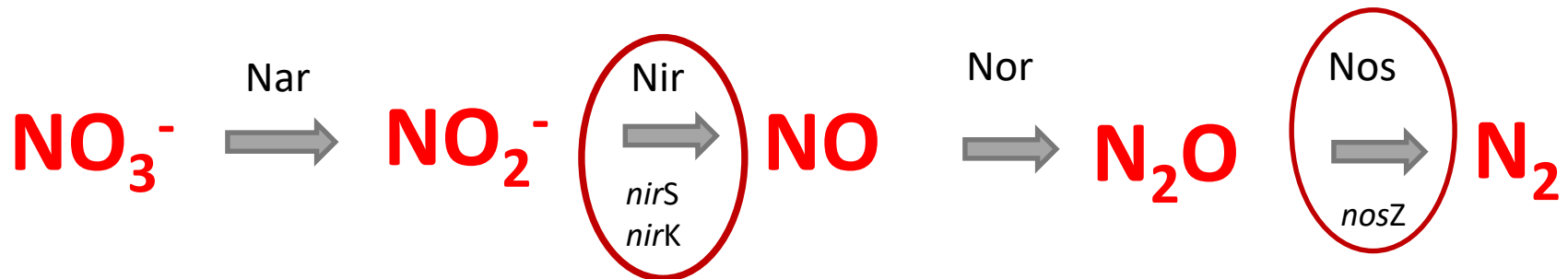


how “benign” the de-nitrification, i.e. calculate the N<sub>2</sub>O:N<sub>2</sub> ratio

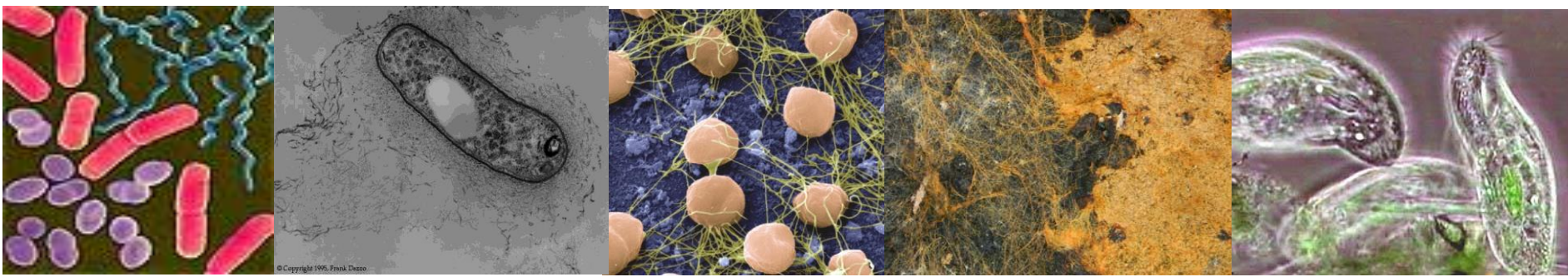


## The Dynamics of Denitrification Gas Chromatograph (DDGC)

# Direct measurement of the de-nitrifiers, *nirS*, *nirK* and *nosZ* genes



- Anaerobic respiration
- Phylogenetically diverse: Bacteria, Archaea, Fungi, Protozoa

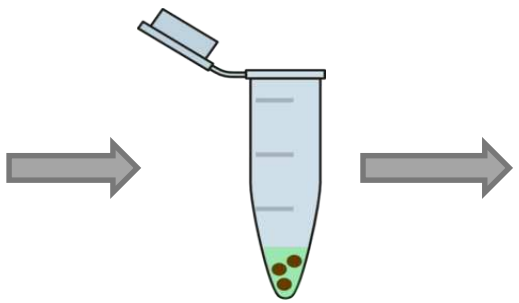


# Direct measurement of the de-nitrifiers, *nirS*, *nirK* and *nosZ* genes

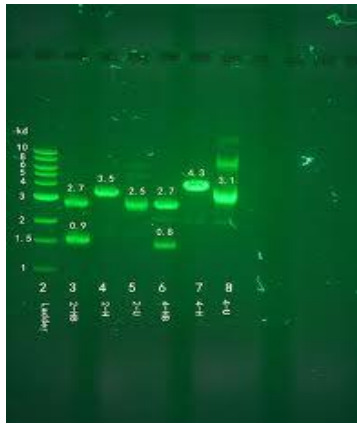
## Polymerase Chain Reaction (PCR) technique



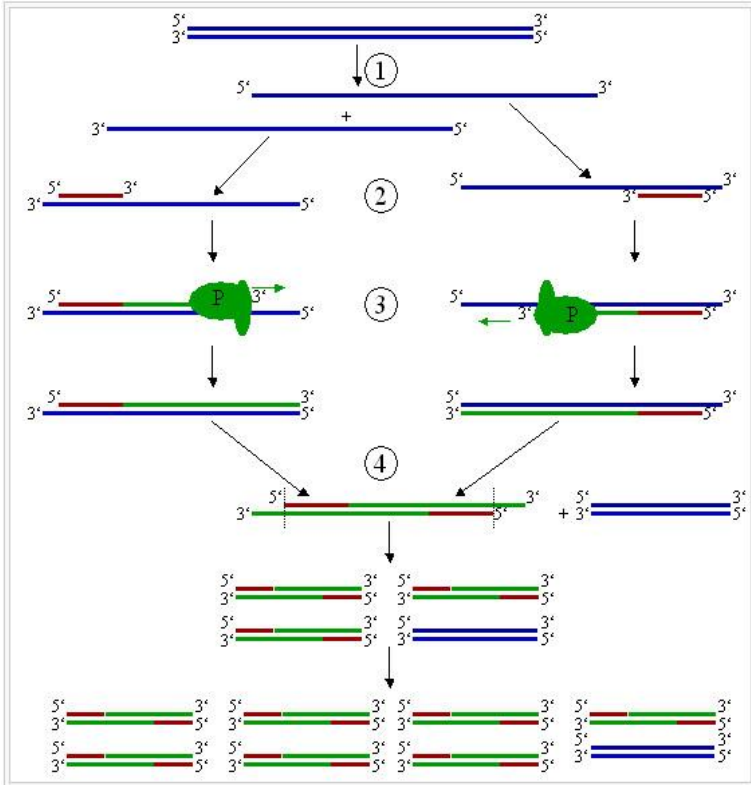
Soil Sample



Extracted DNA



Amplified product visible on gel



Amplified gene of interest