

Denitrification in shallow groundwaters – An ecosystem service or pollution swap?

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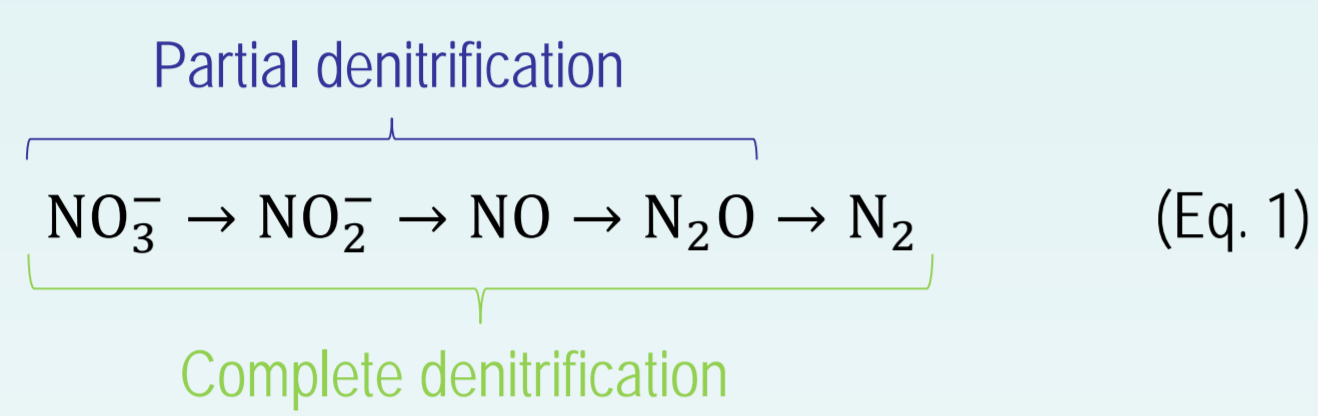
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Introduction

Denitrification in groundwaters has been identified as a key nitrogen attenuation process, where leached NO₃⁻ can be microbiologically reduced to dinitrogen (N₂ – a harmless gas), offering an ecosystem service in terms of water quality protection. However, a partial denitrification can release nitrous oxide (N₂O – a greenhouse gas), resulting in a pollution swap protecting water quality but adding to global warming potential.



The main limiting factors of subsurface denitrification are the presence of suitable bacteria, electron donors, NO₃⁻ and a C source (Korom, 1992; Rivett *et al.*, 2008). In many cases NO₃⁻ inputs exceed subsurface attenuation capacity and NO₃⁻ accumulates. There is still very limited information about the status - **partial** or **complete** - of subsurface denitrification across New Zealand's agricultural catchments and worldwide.

Objectives

- Assess biogeochemical transformation of NO₃⁻ in shallow groundwater at 6 pastoral farms across the Manawatu and Rangitikei River catchments.
- Quantify the products of subsurface denitrification in shallow groundwater through in-field and laboratory measurements.

Methods

We collected a monthly groundwater data set (March – September 2018) of groundwater chemistry and redox parameters and main subsurface denitrification controlling factors. We also conducted push and pull tests at each study site to gain insights into the dynamics and status of subsurface denitrification.

- A Dionex™ Aquion™ IC (ThermoFisher Scientific) was used for the analysis of anions NO₃⁻, sulphate SO₄²⁻, and bromide Br⁻.
- For the analysis of the cations Fe²⁺, Mn²⁺ and Al³⁺ a 4200 MP-AES (Agilent Technologies, Santa Clara, CA USA) was used.
- Dissolved gases N₂O and N₂ were analyzed by a Shimadzu 2010-Plus gas chromatograph system (Shimadzu Corp, Kyoto, Japan) with an electron capture detector (ECD), flame-ionization detector (FID) and thermal conductivity detector (TCD) (McMillan *et al.*, 2014) at the Environmental Chemistry Laboratory, Manaaki Whenua Landcare Research.
- Excess N₂ (end product of subsurface denitrification) was measured by the Membrane Inlet Mass Spectrometry (MIMS) at the National Institute of Water and Atmospheric Research (NIWA) in Wellington.

Table 1: Description of the study sites across Manawatu and Rangitikei River catchments.

Site Code	DF	SC	ARM	SR	BUR	CAM
Area of sampling site	Palmerston North	Santoft	Woodville	Pahiatua	Pahiatua	Dannevirke
Piezometer No.	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
Depth (m, bgl)	5.9, 7.8, 9.0	6.4, 3.4, 5.2	5.3, 5.9, 7.8	4.7, 5.7, 6.7	3.6, 4.3, 6.1	4.8, 2, 7.7
Land use	Dairy	Dairy	Beef/Sheep	Dairy	Dairy	Dairy
Soil type*	Manawatu fine sandy loam	Foxton brown sand-Pukepuke black sand Himitungi sand	Kairangi silt loam and clay loam	Kopua stony silt loam	Kopua stony silt loam	Takapau silt loam
Rock type*	Alluvium	Sand flat	Alluvium	Loess over gravel	Loess over gravel	Loess over gravel

The product of complete subsurface denitrification (N₂) is quantified as Excess N₂ as follows (Weymann *et al.*, 2008):

$$X_{\text{Excess N}_2} = X_{\text{N}_2\text{T}} - X_{\text{N}_2\text{EA}} - X_{\text{N}_2\text{EQ}}$$

X: Molar concentration of each parameter.

N₂T = Total dissolved N₂ in the groundwater sample.

N₂EA = N₂ from excess air.

N₂EQ = Dissolved N₂ in equilibrium with the atmospheric concentration.

- N₂ from excess air

$$X_{\text{N}_2\text{EA}} = (X_{\text{ArT}} - X_{\text{ArEQ}}) * \left(\frac{X_{\text{N}_2\text{atm}}}{X_{\text{Aratm}}} \right)$$

N₂atm = Atmospheric mole fraction of N₂

Aratm = Atmospheric mole fraction of Argon (Ar).

ArT = Total dissolved Ar in the groundwater sample.

ArEQ = Dissolved Ar in equilibrium with the atmospheric concentration.

Results and Discussion

Table 2: Groundwater redox status and process based on the monthly groundwater samples (March-September 2018) of the study sites across the Manawatu and Rangitikei River catchments.

Site	Piezometer	DO	NO ₃ ⁻	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	Redox status	Redox process
		0.5	0.5	0.05	0.1	0.5		
DF	1	0.52	0.11	0.12	2.57	2.81	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
	2	0.27	0.04	0.11	3.59	2.54	Anoxic	Fe(III)/SO ₄ ²⁻
	3	1.40	0.11	0.03	1.61	4.11	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
SC	1	1.00	1.50	0.23	0.60	10.53	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
	2	0.51	0.69	0.44	5.62	4.14	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
	3	0.21	0.04	0.12	3.77	18.38	Anoxic	Fe(III)/SO ₄ ²⁻
ARM	1	0.20	0.02	0.08	3.96	4.62	Anoxic	Fe(III)/SO ₄ ²⁻
	2	0.18	0.02	0.07	3.14	1.70	Anoxic	Fe(III)/SO ₄ ²⁻
	3	0.13	0.02	0.05	0.72	0.36	Anoxic	CH ₄
CAM	1	4.79	6.93	0.10	0.13	11.60	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
	3	0.54	0.06	0.52	0.23	2.70	Mixed	O ₂ -Fe(III)/SO ₄ ²⁻
	SR	1	7.96	3.38	0.02	0.02	5.01	Oxic
SR	2	7.61	3.43	0.02	0.07	4.96	Oxic	O ₂
	3	7.58	3.45	0.02	0.08	4.91	Oxic	O ₂
	BUR	1	3.40	3.17	0.02	0.03	4.34	Oxic
2		4.95	4.88	0.02	0.09	6.14	Oxic	O ₂
3		4.59	6.75	0.02	0.02	6.67	Oxic	O ₂

Groundwater redox status and process (Table 2) were defined based on McMahon and Chapelle (2008) criteria/threshold values for groundwater parameters:

- Mixed sites (DF 1 and 3; SC 1 and 2; CAM 1 and 3) showed O₂-Fe³⁺ and SO₄²⁻ as the main redox process. NO₃⁻ ranged between 0.06 to 6.93 mg·L⁻¹.
- Oxic sites (SR 1, 2 and 3; BUR 1, 2 and 3; and CAM 1 (redox status: mixed) showed NO₃⁻ accumulation ≥ 3 mg·L⁻¹.
- Anoxic sites (DF 2; SC 3; ARM 1, 2, 3 (DO ≤ 0.5 mg·L⁻¹) showed little NO₃⁻ (≤ 0.1 mg·L⁻¹); subsurface denitrification is suggested as the main process.
- Presence of Fe²⁺ (≥ 0.1 mg·L⁻¹) and/or Mn²⁺ (≥ 0.05 mg·L⁻¹) suggest reduction processes occurring at sites DF 1, 2 & 3; SC 1, 2 & 3; ARM 1, 2 & 3; and CAM 3.

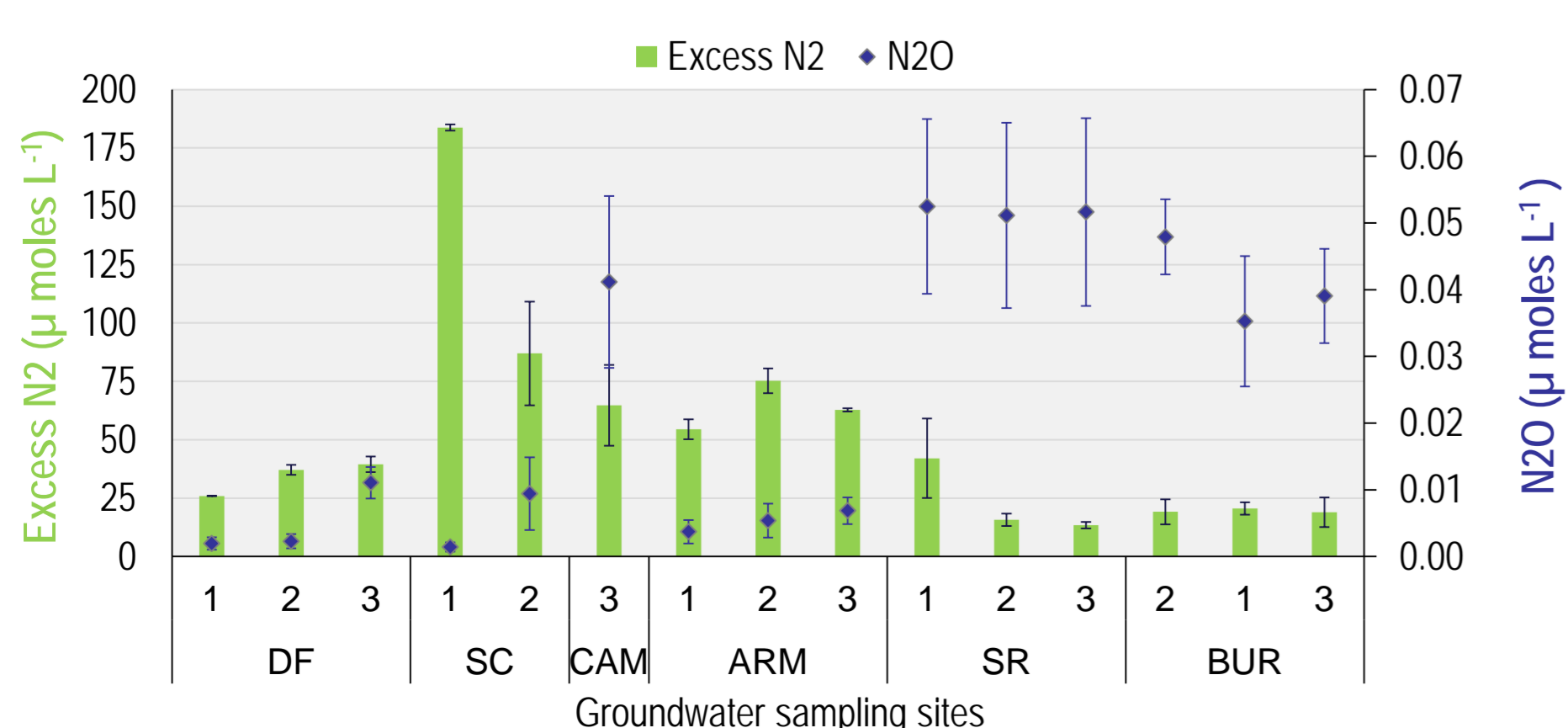


Figure 1: Monthly average of Excess N₂ and N₂O (June, August and September 2018) (n=3 ± SEM) at each site across the Manawatu and Rangitikei River catchments.

- The oxic sites SR 2 and 3; BUR 1, 2 and 3 have less Excess N₂ (≤ 20 μmol·L⁻¹) and higher N₂O concentration (≥ 0.035 μmol·L⁻¹) → indication of **partial** subsurface denitrification.
- The mixed sites DF 1 and 3; and SC 1 and 2 and anoxic sites DF 2; and ARM 1, 2 and 3 have the highest average for Excess N₂ (≥ 25 μmol·L⁻¹) and lower N₂O (≤ 0.02 μmol·L⁻¹) → indication of **complete** subsurface denitrification.
- The CAM 3 (mixed) and SR 1 (oxic) sites have N₂O concentration higher than 0.04 μmol·L⁻¹ and more than 40 μmol·L⁻¹ of Excess N₂ → **micro-sites** within the aquifer can have favorable conditions for complete subsurface denitrification.

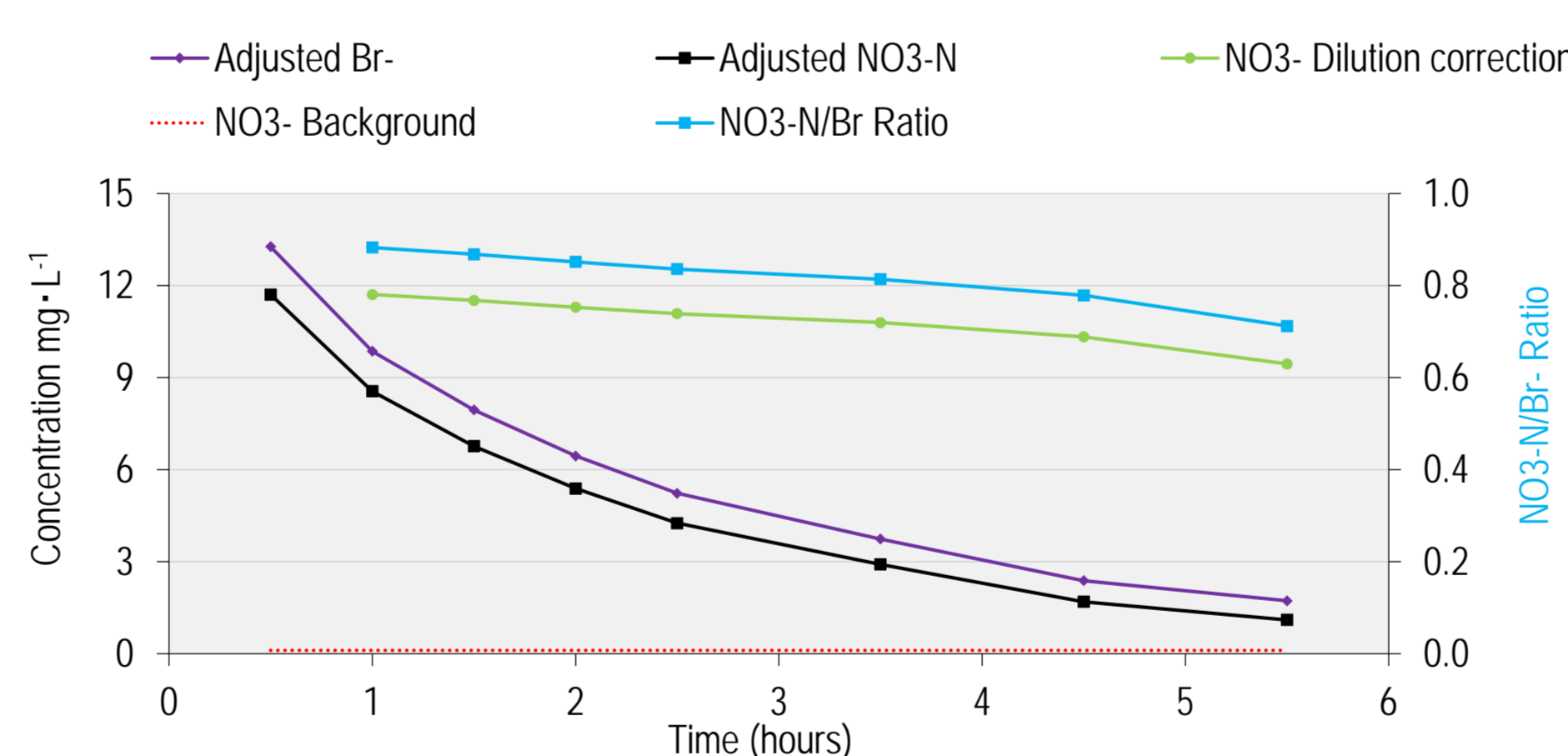


Figure 2: Push and pull test results of adjusted NO₃-N, Br⁻, NO₃⁻ dilution correction, NO₃⁻ background, NO₃⁻/Br⁻ ratio conducted at site DF 3.

If the slope (negative) of the ratio between NO₃-N (reactant) and Br⁻ (tracer) (Fig. 2) is closer to 0, then more NO₃⁻ is being attenuated (CAM > ARM > DF > SR > BUR). Figure 3 shows ratio of Excess N₂ and N₂O measured during the push-pull tests to assess **partial** and **complete** subsurface denitrification.

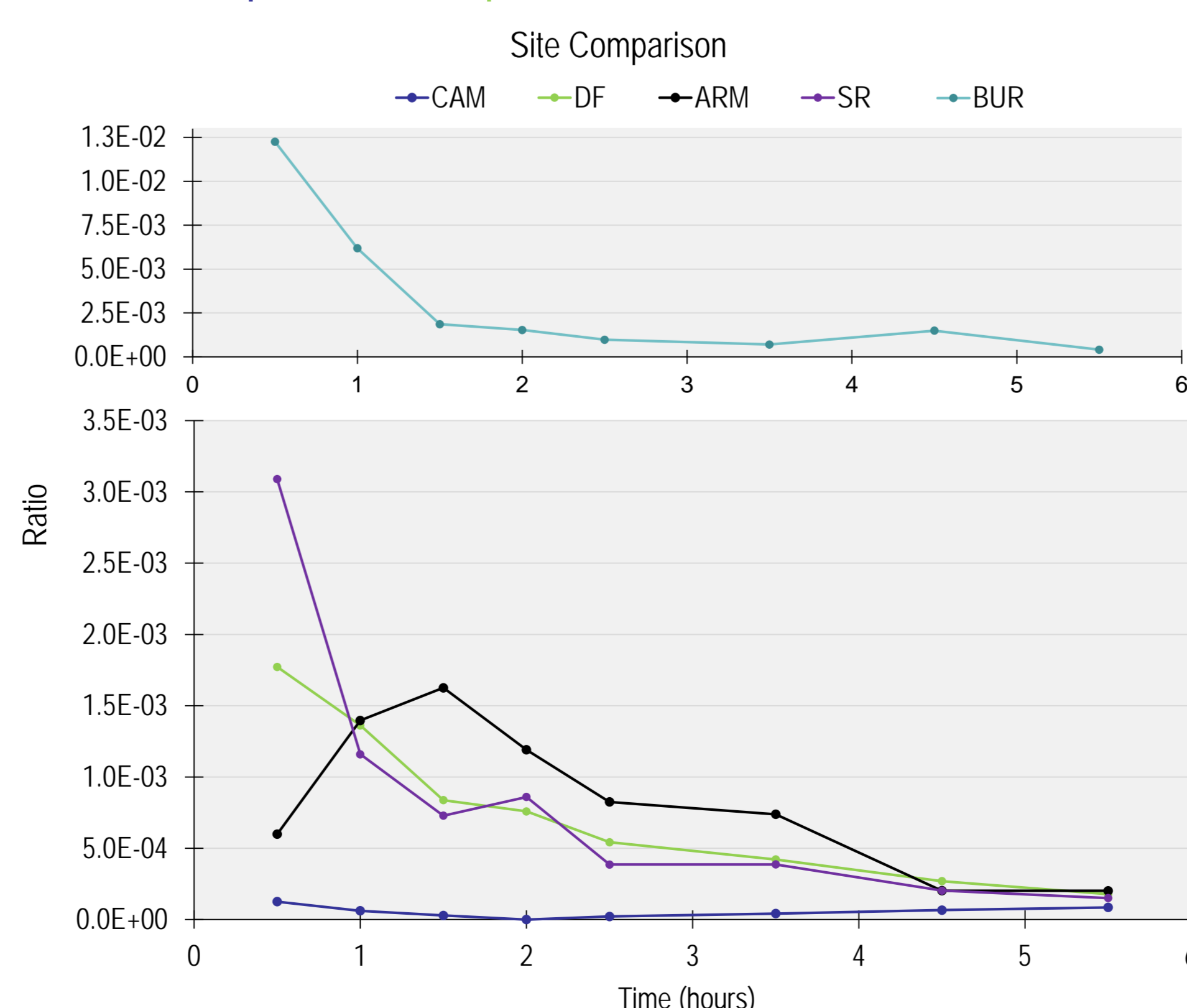


Figure 3: Ratios of N₂O/Excess N₂ + N₂O over push and pull test at the deepest piezometer at sites BUR, DF, CAM, ARM and SR.

- N₂O/Excess N₂ + N₂O ratios (Fig. 3) at DF, ARM, SR and BUR sites indicates both **partial** and **complete** subsurface denitrification process occurring during the push and pull test. However the **complete** reduction of NO₃⁻ is favourable.
- BUR has the highest ratio during the push and pull test, an indication that **partial** denitrification is the predominate process.
- CAM site shows favourable conditions for **complete** subsurface denitrification during the push and pull test. And 406.5 μmol·L⁻¹ of Excess N₂ produced by T5.5 hrs (highest concentration compared with the other sites.)

Table 2: Correlation analysis based on groundwater chemistry and dissolved N gases at all study sites across the Manawatu and Rangitikei River catchments.

	DO	DOC	Fe ²⁺	Mn ²⁺	SO ₄ ²⁻	NO ₃ ⁻	N ₂ O	N ₂	Excess N ₂
DO	*	-0.32	-0.64	-0.51	0.13	0.77	0.36	-0.63	-0.53
DOC	-0.32	*	0.48	0.21	0.58	-0.15	-0.02	0.64	0.59
Fe ²⁺	-0.64	0.48	*	0.36	-0.10	-0.57	-0.28	0.60	0.75
Mn ²⁺	-0.51	0.21	0.36	*	-0.09	-0.41	-0.06	0.58	0.69
SO ₄ ²⁻	0.13	0.58	-0.10	-0.09	*	0.31	-0.07	0.33	-0.07
NO ₃ ⁻	0.77	-0.15	-0.57	-0.41	0.31	*	0.46	-0.60	-0.47
N ₂ O	0.36	-0.02	-0.28	-0.06	-0.07	0.46	*	-0.35	-0.24
N ₂	-0.63	0.64	0.60	0.58	0.33	-0.60	-0.35	*	0.63
Excess N ₂	-0.53	0.59	0.75	0.69	-0.07	-0.47	-0.24	0.63	*

Conclusions

- Subsurface denitrification in shallow groundwaters is spatially variable.
- A **complete** subsurface denitrification appears as predominant process in the mixed and anoxic groundwaters (see sites mixed sites DF 1 and 3; and SC 1 and 2 and anoxic sites DF 2; and ARM 1, 2 and 3).
- A negative correlation was found between Excess N₂ and DO levels and NO₃⁻ concentrations; and a strong correlation with the reduced electron donors Fe²⁺ and Mn²⁺ → **complete** subsurface denitrification.
- A **partial** subsurface denitrification process appears as predominant process in oxic groundwater (see the oxic sites SR 1, 2 and 3 and BUR 1, 2 and 3).
- A positive correlation was found between DO levels and NO₃⁻ and N₂O concentrations → **partial** subsurface denitrification.

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