Dissolved gases as an indicator of denitrification process in shallow groundwater in agricultural landscape

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Presentation structure

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1. *Nitrate attenuation In groundwater*
2. *Experimental design and data analysis*
3. *Results*
4. *Summary*
5. *Conclusion*

1. Nitrate in groundwater

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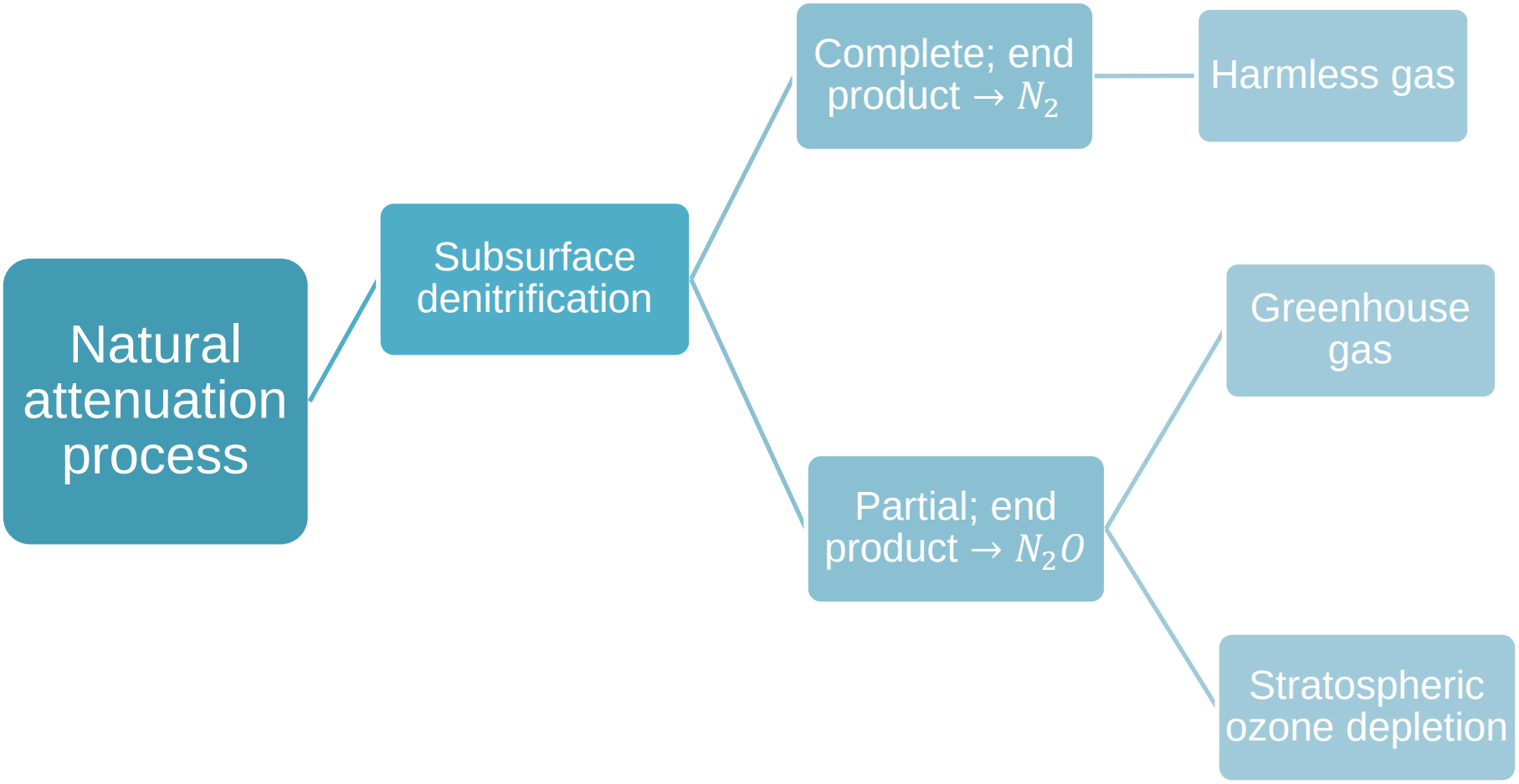

Approach

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Table 1: Location, geological setting and land use of the study sites.

Site Code	DFP		SC		ARM		SR		BUR		CAM	
Area of sampling site	Palmerston North		Santoft		Woodville		Pahiatua		Pahiatua		Dannevirke	
Piezometer Nº, Depth (m, bgl)*	P1	5.9	P1	6.4	P1	5.3	P1	4.7	P1	3.6	P1	4.8
	P2	7.8	P2	3.4	P2	5.9	P2	5.7	P2	4.3	P2	7.7
	P3	9.0	P3	5.2	P3	7.8	P3	6.7	P3	6.1		
Land use	Dairy		Dairy		Beef/Sheep		Dairy		Dairy		Dairy	
Soil type**	Manawatu fine sandy loam		Foxton brown sand-Pukepuke black sand Himitangi sand		Kairange 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	

*Screen depth (m, bgl) = 0.5 m on each piezometer
**Collins et al, 2018, Rivas et al, 2015

2. Experimental design and data analysis

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Methodology and measurements analyzed over 6 months of study and a set of push and pull test at each site during wet season.

Measurements	Methodology	Parameter
Chemical Analysis	Monthly sampling	NO_3^-, Br^-, SO_4^{2-}, Fe^{2+}, DO, DOC
Dissolved gas analysis	Push and Pull Test	N_2O and N_2
Excess N_2	MIMS (NIWA)	N_2 from subsurface denitrification

2. Experimental design and data analysis

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One set of Push and Pull Test was developed in the deepest piezometer at each site.

A 100 L of groundwater was pumped, added a source of nitrate (KNO_3) and a tracer (KBr) to obtain a final concentration of 10 mg (NO_3-N)· L^{-1}.

Samples were collected every 30 minutes for 2.5 hours and then every hour until 5.5 hours of sampling.

Gas chromatograph system (Shimadzu Corp, Kyoto, japan), electron capture detector (ECD), flame-ionization detector (FID) and thermal conductivity detector (TCD) (McMillan *et al.*, 2014).

3. Results

Dissolved organic carbon, dissolved oxygen, iron and nitrate average concentration over 6 months of study (March-September) at each site. Values are given in mg L^{-1}

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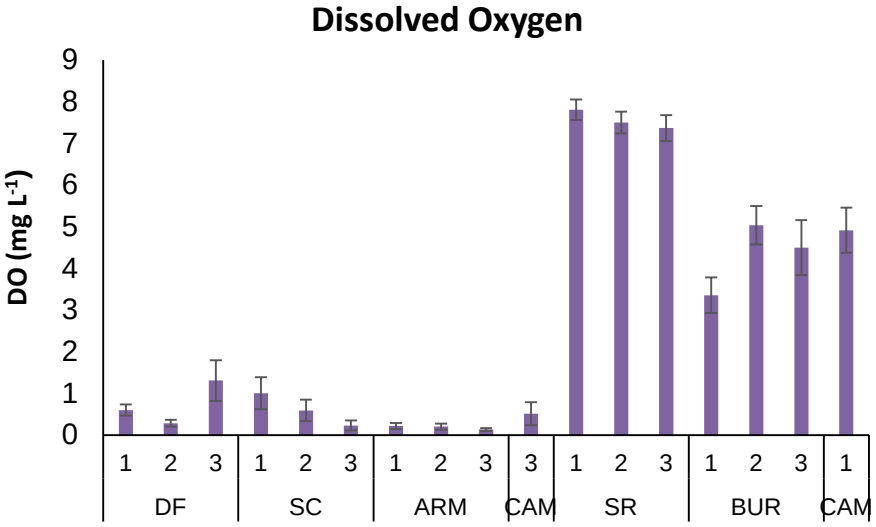

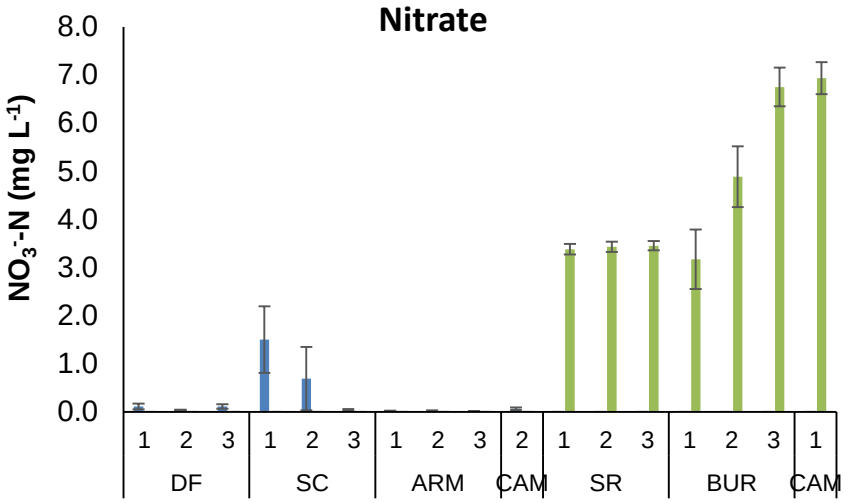

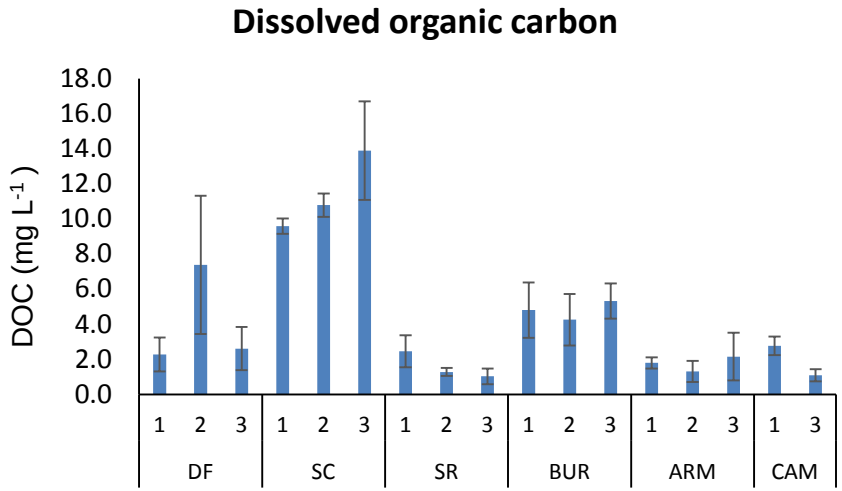

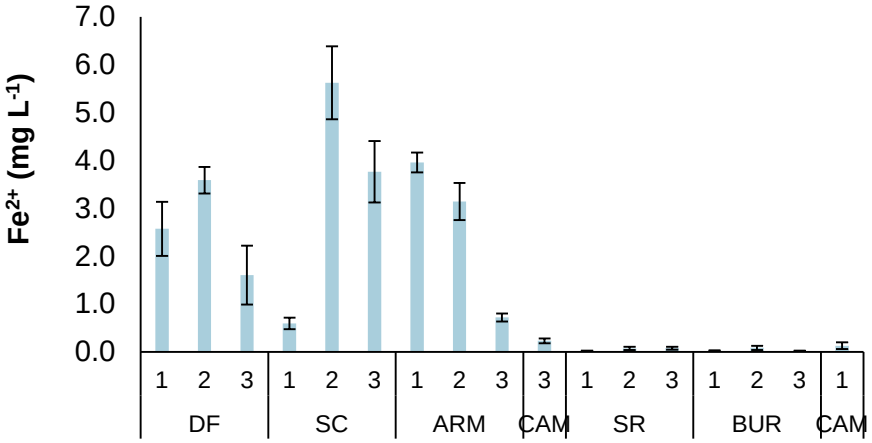

3. Excess N_2 analysis

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- Excess N_2 calculation (Weymann et al, 2008)

$$X_{\mathrm{Excess}N_2} = X_{N_2\mathrm{T}} - X_{N_2\,\mathrm{EA}} - X_{N_2\,\mathrm{EQ}}$$

X: Molar concentration of the parameters.
N_2 T = Total dissolved N_2 in the groundwater sample.
N_2 EA = N_2 from excess air.
N_2 EQ = Dissolved N_2 in equilibrium with the atmospheric concentration.

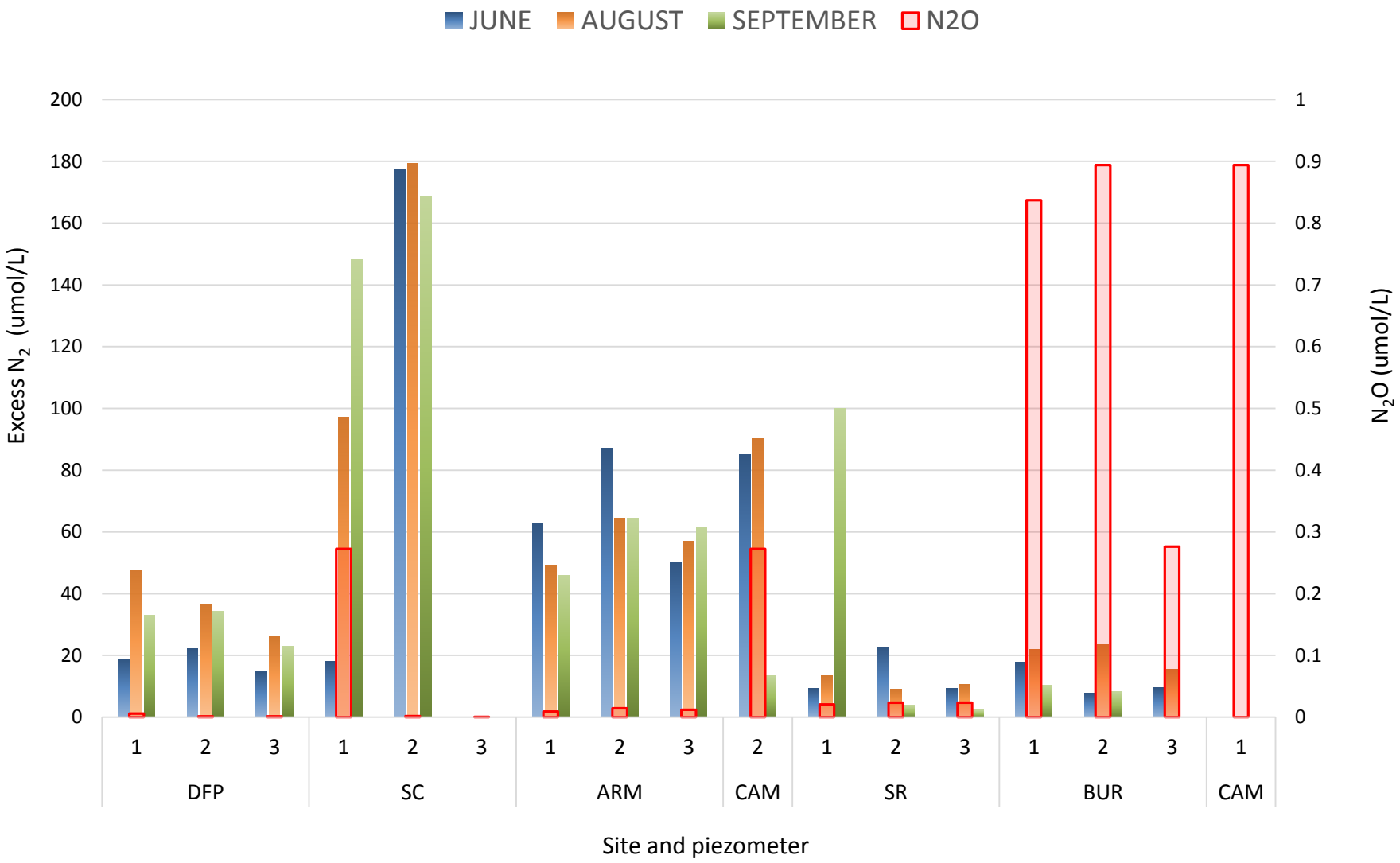
- N_2 from excess air (Weymann et al, 2008)

$$X_{N_2\mathrm{EA}} = \left(X_{\mathrm{Ar\,T}} - X_{\mathrm{Ar\,EQ}}\right) * \left(\frac{X_{N_2\,\mathrm{atm}}}{X_{\mathrm{Ar\ atm}}}\right)$$

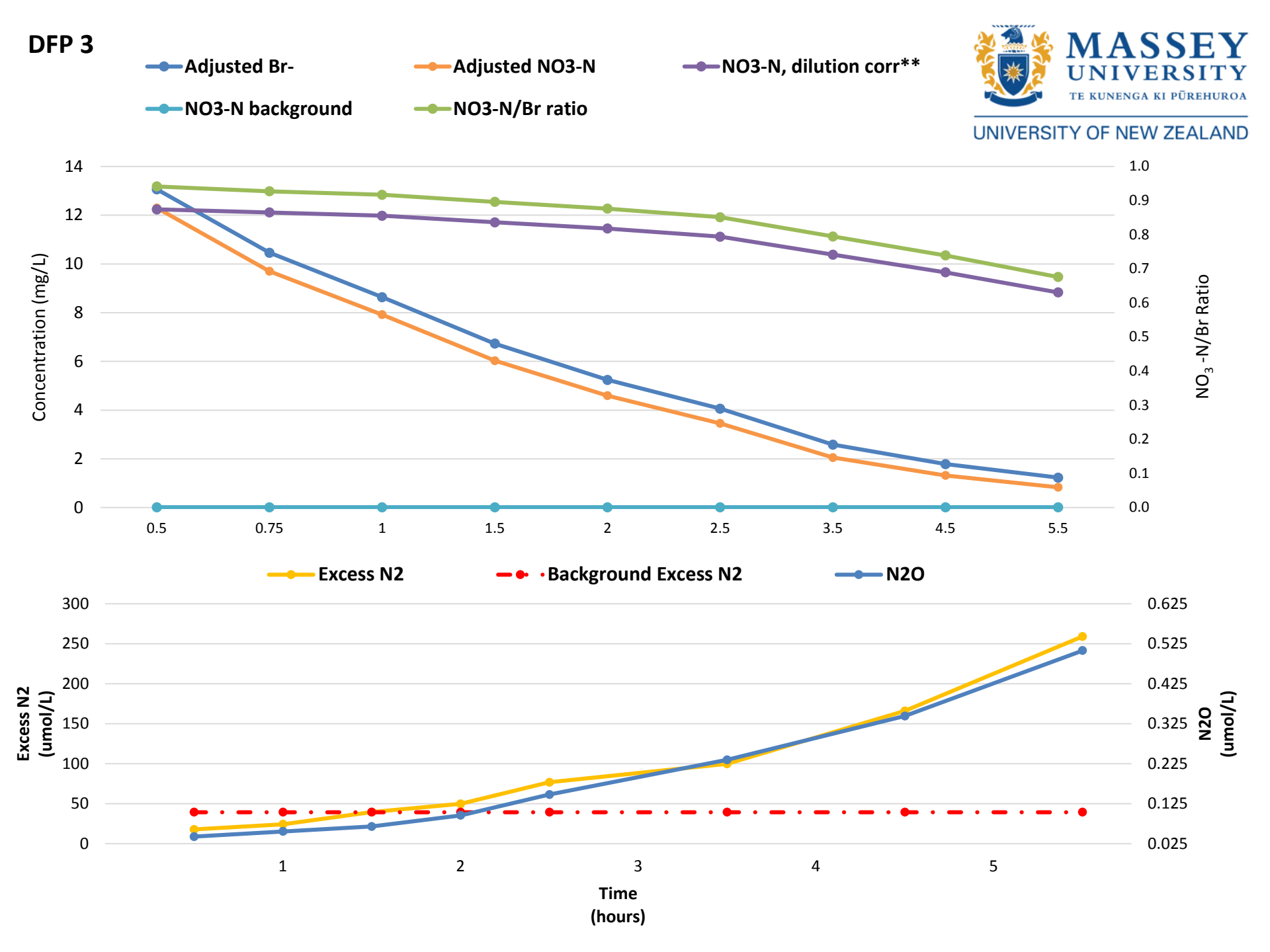
N_2 atm = atmospheric mole fraction of N_2
Ar atm = atmospheric mole fraction of Ar.
Ar T = total dissolved Ar in the groundwater sample.
Ar EQ = Dissolved Ar in equilibrium with the atmospheric concentration

- Uncertainty → Recharge temperature

Monthly values for Excess N_2 (3 months) and N_2O (6 average of months).



DFP 3


Adjusted Br-
Adjusted NO3-N
NO3-N, dilution corr**
NO3-N background
NO3-N/Br ratio
Concentration (mg/L)
NO_3-N/Br Ratio
0
2
4
6
8
10
12
14
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.5
0.75
1
1.5
2
2.5
3.5
4.5
5.5
Excess N2
Background Excess N2
N2O
Excess N2 (umol/L)
N2O (umol/L)
0
50
100
150
200
250
300
0.025
0.125
0.225
0.325
0.425
0.525
0.625
1
2
3
4
5
Time (hours)

4. Summary

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Site	Redox status	Reduced NO_3^- (%)	Total Excess N_2 (umol/L)	N_2O/(Excess N_2 + N_2O)	Type of denitrification
DFP I	Anoxic, NO_3-N, Mn (IV) and Fe (III) reduction	37	259.07 ± 0.79	0.0020	Complete
SC III	Anoxic, NO_3-N, Mn (IV) reduction	1.4	-	-	-
ARM I	Anoxic, NO_3-N, Mn (IV) and Fe (III) reduction	9.8%	166.35 ± 0.55	0.0008	Complete
CAM III	Anoxic, NO_3-N, Mn (IV) reduction	7.3%	406.45 ± 1.36	0.0004	Complete
SR III	Oxic, O2 reduction	51%	202.12 ± 4.47	0.0016	Partial
BUR II	Oxic, O2 reduction	57%	86.93 ± 0.42	0.0064	Partial

Correlation Analysis

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Parameter	DO	DOC	Fe^{2+}	Mn^{2+}	SO_4^{2-}	NO_3^-	N_2O	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_2O	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	*

5. Conclusions

- DFP (I, II, III), ARM (I, II, III), SC (I, II, III), and CAM (III) site present suitable mixed and anoxic condition for complete subsurface denitrification to occur. More concentration of electron donors (Fe^{3+}) and low concentrations of DOC.
- BUR (I, II, III), SR (I, II, III), and CAM (I) site present unsuitable oxic conditions thus, subsurface denitrification is energetically unfavorable.
- Excess N_2 values are high at anoxic sites indicating complete subsurface denitrification and vice verse.
- Oxic sites show increment of N_2O during push and pull test and low excess N_2 (ratio), indicating partial subsurface denitrification.

Acknowledgment

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