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Quantification of denitrification rate in shallow groundwater using the single-well, push-pull test technique

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ABSTRACT

Denitrification has been identified as a significant nitrate attenuation process in groundwater systems. Hence, accurate quantification of denitrification rates is consequently important for the better understanding and assessment of nitrate contamination of groundwater systems. There are, however, few studies that have investigated quantification of shallow groundwater denitrification rates using different analytical approaches or assuming different kinetic reaction models. In this study, we assessed different analytical approaches (reactant versus product) and kinetic reaction (zero-order and first-order) models analysing observations from a single-well, push-pull tests to quantify denitrification rates in shallow groundwater at two sites in the Manawatū River catchment, Lower North Island of New Zealand. Shallow groundwater denitrification rates analysed using the measurements of denitrification reactant (nitrate reduction) and zero-order kinetic models were quantified at 0.42–1.07 mg N L^{-1} h^{-1} and 0.05–0.12 mg N L^{-1} h^{-1} at the Palmerston North (PNR) and Woodville (WDV) sites, respectively. However, using first-order kinetic models, the denitrification rates were quantified at 0.03–0.09 h^{-1} and 0.002–0.012 h^{-1} at the PNR and WDV sites, respectively. These denitrification rates based on the measurements of denitrification reactant (nitrate reduction) were quantified significantly higher (6 to 60 times) than the rates estimated using the measurements of denitrification product (nitrous oxide production). However, the denitrification rate quantified based on the nitrate reduction may provide representative value of denitrification characteristics of shallow groundwater systems. This is more so when lacking practical methods to quantify all nitrogen species (i.e., total N, organic N, nitrite, nitrate, ammoniacal N, nitrous oxide, nitric oxide, and nitrogen gas) in a push-pull test. While estimates of denitrification rates also differed depending on the kinetic model used, both a zero-order and a first-order model appear to be valid to analyse and estimate denitrification rate from push-pull tests. However, a discrepancy in estimates of denitrification rates using either reactant or product and using zero- or first-order kinetics models may have implications in assessment of nitrate transport and transformation in groundwater systems. This necessitates further research and analysis for appropriate measurements and representation of spatial and temporal variability in denitrification characteristics of the shallow groundwater system.

1. Introduction

Agricultural intensification and expansion has driven increase in the use of fertiliser to support food production (Di and Cameron, 2002; Food and Agriculture Organization of the United Nations (FAO), 2015). However, if not used properly, excess nitrogen (N) in agricultural lands could eventually leach and contaminate groundwater and subsequently receiving surface waters and affect their quality by eutrophication and fish poisoning (Di and Cameron, 2002; Puckett et al., 1999). Groundwater systems, however, do not merely act as a pathway for nitrate (NO_3^-) transport and contamination of surface water, but could also transform NO_3^- via biogeochemical processes such as denitrification attenuating the NO_3^- load to surface waters (Jahangir et al., 2012b; Starr and Gillham, 1993; Stenger et al., 2008). A number of studies have

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shown significant attenuation of NO_3^- in groundwater systems (e.g., Jahangir et al., 2013; Seitzinger et al., 2006; Singleton et al., 2007; Tesoriero et al., 2000). Jahangir et al. (2013) found that denitrification in groundwater accounted for the 24 % of N inputs to the land in a grassland site in southeastern Ireland. The leached NO_3^- from the soil profile (beyond the plant root zone) may be reduced 'attenuated' in the subsurface environment by nitrogen transformation processes such as (a) assimilation of nitrate into microbial biomass (immobilisation); (b) assimilatory nitrate reduction; (c) dissimilatory nitrate reduction to ammonium (DNRA); and (d) denitrification (Rivett et al., 2008). Another nitrogen reduction process observed in groundwater is anaerobic ammonium oxidation (anammox), in which ammonium is directly oxidized to reduce nitrite and produce dinitrogen (Smith et al., 2015; Wang et al., 2017). The assimilatory and dissimilatory nitrate reduction processes both reduce NO_3^- into ammonium in soil-water systems (Rütting et al., 2011). However, denitrification is a microbial-mediated transformation of NO_3^- to gaseous oxides (nitric oxide [NO] and nitrous oxide [N_2O]), with nitrogen gas (N_2) as the ultimate end-product (Trudell et al., 1986; Korom, 1992; Rivett et al., 2008). Denitrification could be either heterotrophic or autotrophic depending on the source of electron donor. It is characterised as heterotrophic if electron donor is organic (particularly carbon), whereas autotrophic if electron donor is inorganic (e.g., reduced manganese, ferrous iron, and sulphides) (McMahon and Chapelle, 2008). Thus, a sound understanding of the transport and transformation of NO_3^- in groundwater systems is essential to manage and mitigate any negative impacts of agriculturally-derived NO_3^- on quality of receiving surface water bodies.

Several methods have been developed to assess denitrification processes and quantify in situ denitrification rates in shallow groundwater (Burbery, 2018), e.g. single-well, push-pull test (Jahangir et al., 2013; Istok, 2013; Sanchez-Perez et al., 2003; Addy et al., 2002; Istok et al., 1997), well cluster method (Bragan et al., 1997; Woodward et al., 2009), in situ microcosms (Gillham et al., 1990; Mengis et al., 1999; Starr and Gillham, 1993), in situ mesocosms (Korom et al., 2005, 2012), and multilevel wells (Kellogg et al., 2005; Korom et al., 2012; Zhou et al., 2018). The single-well push-pull test, however, is the most commonly used method allowing cost-effective and less time consuming measurement of in situ denitrification rates in groundwater (e.g., Addy et al., 2002; Istok et al., 1997; Jahangir et al., 2013; Sanchez-Perez et al., 2003; Tesoriero et al., 2000; Well et al., 2003; Eschenbach et al., 2015; Kruisdijk et al., 2022). The applicability of push-pull tests in quantifying in situ denitrification rate hinges on assumptions that (a) the injection solution containing the reactant and conservative tracer is well mixed, (b) reactants and tracers have identical retardation factors and transport properties, (c) reaction rates are homogeneous, and (d) that there is negligible regional groundwater flow, which could potentially drift away a major portion of the injected test solution from the test site (Burbery, 2004; Haggerty et al., 1998; Istok, 2013; Snodgrass and Kitanidis, 1998).

However, accurate quantification of denitrification rates could also be affected by the choice of an analytical approach and kinetic reaction model to analyse the push-pull tests data. There have been different analytical approaches developed to estimate denitrification rates using field data obtained from single-well, push-pull tests (Korom et al., 2012; Sanchez-Perez et al., 2003; Well et al., 2003). These methods depend on the parameter used in the analysis namely, denitrification reactant (nitrate), product (nitrous oxide and/or dinitrogen), or both reactant and product (Istok et al., 1997). The first method using the denitrification reactant, i.e. NO_3^-, is the simplest as the rate can be obtained by analysing changes in concentrations of the reactant (NO_3^-) and the conservative tracer such as bromide (Br) (Istok et al., 1997). The other two methods using the denitrification product such as nitrous oxide (N_2O) or/and dinitrogen (N_2) need additional treatment or the use of stable isotopes to estimate the denitrification rate. For instance, some studies (e.g., Sanchez-Perez et al., 2003; Well et al., 2003; Woodward et al., 2009) added acetylene to inhibit the reduction of the intermediate product N_2O to N_2, enabling estimation of denitrification rate by analysing concentrations of N_2O measured during the test. However, several authors argued the possibility of enhanced denitrification with acetylene as the carbon source in denitrification assays particularly if carbon is limited (Tiedje et al., 1989; Yeomans and Beauchamp, 1982). Other studies (e.g., Schürmann et al., 2003) used isotopically labelled nitrate ($^{15}NO_3^-$), thus enabling them to determine the amount of N_2O and N_2 derived from the reactant (NO_3^-). The use of acetylene or isotope enrichment in push-pull tests enables the estimation of denitrification rate from both the reactant and products of the denitrification process (e.g., Addy et al., 2002; Schürmann et al., 2003). However, there are only a few studies that have used both the denitrification reactant and product (Baker and Vervier, 2004; Istok et al., 1997; Trudell et al., 1986) and assessed their accuracy and implications on quantification of NO_3^- attenuation in shallow groundwater systems.

Moreover, different kinetic models, i.e. zero-order or first-order, have been assumed by several studies in quantifying denitrification rates in groundwater using the push-pull test (e.g., Burbery et al., 2004; Korom et al., 2012; Tesoriero and Puckett, 2011). Enzyme kinetics would be zero-order if conditions are not limited by the reactant concentration (i.e. at high concentrations), or first-order when conditions are limited by the reactant concentration (i.e. at low concentrations) (Tesoriero and Puckett, 2011). The kinetics of denitrification process depends on several factors, e.g., available carbon, temperature, pH, dissolved oxygen, redox potential, NO_3^- concentration, and the presence and activity of denitrifiers (Reddy et al., 1978; Bekins et al., 1998). Existing denitrification studies have generally used either zero-order or first-order kinetics model and did not specify which kinetic model is more appropriate for the analysis (Burbery et al., 2004; Schroth et al., 2001; Tesoriero and Puckett, 2011). Currently, there is no clear objective guidance on which kinetic reaction model is appropriate to analyse the push-pull tests data.

This study evaluated the use of different tracers (denitrification reactant, NO_3^-, or denitrification product, N_2O) and kinetic reaction models (zero-order and first-order) to quantify denitrification rates from single-well, push-pull test data in shallow groundwater aquifers (e.g., $<$10 m below ground level). Moreover, the study compared the single-well, push-pull tests with or without added acetylene to quantify potential effect of acetylene on measurements of shallow groundwater denitrification (Tiedje et al., 1989; Yeomans and Beauchamp, 1982), and to provide indications whether shallow groundwater denitrification is partial/incomplete releasing N_2O or complete releasing N_2 as the final product (Saggar et al., 2013). This is expected to inform further development and potential applications of single-well, push-pull test data to quantify denitrification rates in shallow groundwaters, which may have significant implications for assessment and management of nitrate contamination of the groundwater system.

2. Methods and materials

2.1. Study area and experimental site

Field experiments were conducted at the study sites in the Manawatū River catchment (6000 km^2), located in the lower North Island of New Zealand (Fig. 1). At the time of the study, the catchment land use was dominated by pastoral farming, including sheep and/or beef farms accounting for 58 % and dairy farms 17 %, whereas native cover comprises 17 %, exotic cover 4 %, and cropping a very small percentage ($<$1 %) (Clark and Roygard, 2008). The landform is dominated by the axial mountain ranges (Ruahine and Tararua ranges) traversing the middle of the catchment on a north-south direction with elevation reaching 1600 m above sea level (Bekesi and Mcconchie, 2002). East of the ranges, the broad depression known as the Pahiatua basin is filled with Quaternary sediments forming the aquifers in this part of the catchment (Zarour, 2008). In the west, these deposits are overlain by dunes brought inland from the coast (Bekesi and Mcconchie, 2002).

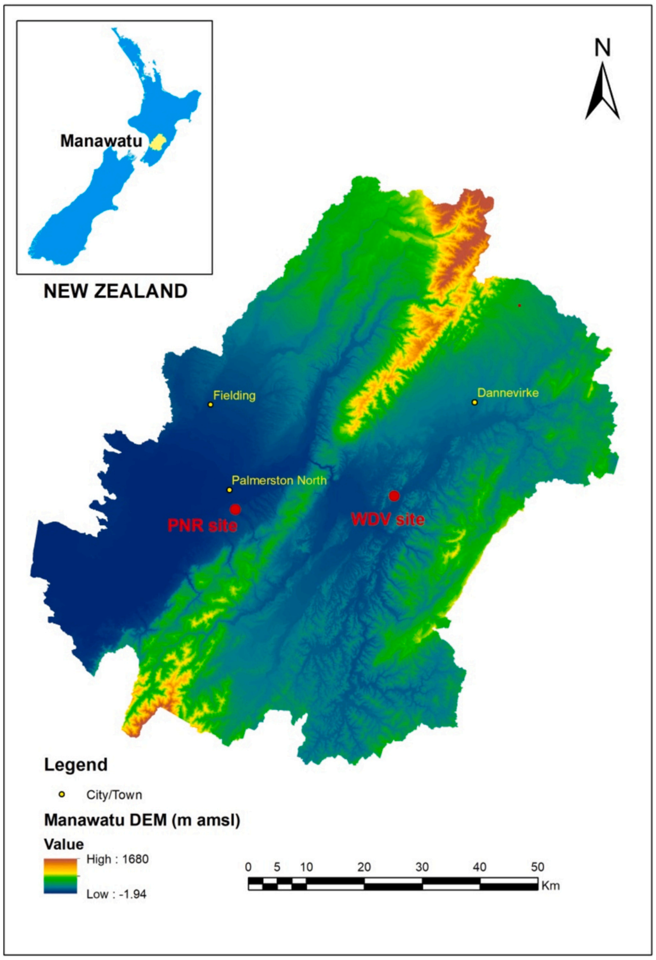

Fig. 1. Manawatū River catchment showing the location of the study sites: Massey University's No. 1 Dairy Farm in Palmerston North (PNR site), and sheep and beef farm near Woodville (WDV site).

The Manawatū river and some of its tributaries have been found with higher concentrations of soluble inorganic nitrogen, exceeding 0.444 g N m^{-3} set as water quality standard for the river (Roygard and McArthur, 2008). A major portion the nitrogen load in the Manawatū River is estimated to originate from diffuse sources, mainly pastoral farming in the catchment (Ledein et al., 2007; Roygard et al., 2012). However, Elwan et al. (2015) found nitrate attenuation capacity (i.e. the difference between the average annual nitrogen leaching from the root zone (soil profile) and the average annual nitrogen load measured in the river) to be highly spatially variable across different subcatchments of the catchment. The catchment has been selected to gain a better understanding of the capabilities of subsurface environment to transport and transform or denitrify NO_3^- and subsequently the vulnerability of groundwater and surface water to NO_3^- contamination. Rivas et al. (2017) found variable redox potential in groundwaters of the eastern parts of the catchment. However, direct measurements and analysis of denitrification processes in the catchment have been lacking.

Two experimental sites; the PNR site and WDV site, were established (Fig. 1) to investigate the ability of the push-pull test to quantify denitrification in shallow groundwater in the catchment. The PNR site was established at the Massey University No. 1 Dairy Farm in Palmerston North in western part of the catchment. This site is characterised as Manawatū fine sandy loam (Weathered Fluvial Recent Soil) underlain by gravel starting at approximately 4.5 m below ground level (bgl). The WDV site was established in the eastern part of the Manawatū catchment near Woodville. Soil at the WDV site is characterised as Kairanga silt loam and clay loam (Recent/Orthic Gley Soil) and is underlain by gravel at approximately 3 m bgl. The sites are yet to be characterised geologically in detail, however the absence of geological details should not be critical to conducting push-pull tests (e.g., Burbery et al., 2004), considering that denitrification rates were estimated using a simplified analytical method that does not require estimates of aquifer physical properties.

2.2. *Piezometer installation*

Two shallow groundwater piezometers were installed at the PNR site at depths of 6.5 m and 7.5 m bgl, whereas three piezometers were installed at the WDV site at depths of 5.0, 6.0, and 7.5 m bgl. The piezometers were made of polyvinyl chloride (PVC) pipes with internal diameter of 28 mm and perforated (5 mm diameter) at the bottom 0.50 m. The perforated portion was covered with 250 μm mesh nylon screen (Rasiah et al., 2003; Zhu et al., 2003) attached with silicon caulking (Well et al., 2003). The piezometers were installed by direct push-probe percussion with a double tube system (Lapham et al., 1997). The piezometers at the PNR site were installed in October 2013, whereas at the WDV site were installed in September 2014. The installed piezometers were initially developed by pumping with a peristaltic pump before the first push-pull tests were conducted.

2.3. *The single-well push-pull tests and analytical methods*

Three push-pull tests (in October 2013, May 2014, and July 2014) were conducted at the PNR test site on the piezometer screened at 6.0–6.5 m bgl, whereas two push-pull tests (in February 2015 and August 2015) at the WDV site on the piezometer screened at 5.5–6.0 m bgl (Table 1). A push-pull pre-test (e.g. Addy et al., 2002; Istok, 2013; Mcphillips et al., 2015; Pauwels et al., 1998) was conducted in July 2013 on another piezometer on the same farm of the PNR site (screened at 5.5 to 6.0 m bgl), to determine the recovery fraction of the conservative tracer and the appropriate volume of groundwater to be extracted for the preparation of the test solution. The first push-pull test at the PNR site was conducted in October 2013, using 40 litres (L) of test solution with added acetylene to measure the denitrification product, N_2O (Sanchez-Perez et al., 2003; Well et al., 2003) (Table 1). The increase in test solution injection volume from 40 L in October 2013 to 100 L in May and July 2014 tests at the PNR site and in both February 2015 and August 2015 tests at the WDV site (Table 1) was intended to "minimise the effect of the slug fringe" (Snodgrass and Kitanidis, 1998) and decrease the "bias from convective and diffusive mixing processes" (Well et al., 2003). At the PNR site, the push-pull test in May 2014 was conducted with the use of acetylene addition (Sanchez-Perez et al., 2003; Well et al., 2003) and the test in July 2014 was conducted without acetylene (Istok et al., 1997; Tesoriero et al., 2000). Data from these experiments were used to assess the effect of acetylene addition on quantification of the denitrification rates (Table 1). Acetylene was used at both tests at the WDV site.

Before each push-pull test, the piezometer was purged with at least three well volumes until the in-field groundwater parameters (temperature, pH, electrical conductivity, and dissolved oxygen) measured with YSI Professional Plus multiparameter probe were stable to ensure the collection of representative groundwater samples (Daughney et al., 2006). Groundwater samples for determination of background concentrations were first collected in triplicates, and then an additional 40–100 L of groundwater was extracted into 20 L collapsible or flexible polyethylene bags (Coleman Water Carrier) to prepare the test solution. Flexible bags or containers have been used in other studies (e.g., Baker and Vervier, 2004; Well et al., 2003), given their advantages such as small quantities of solutes required, operational convenience since they collapse during injection instead of requiring pressured gas to fill the void left by the water pumped into the piezometer, and 'the entire system is closed' minimising losses of solute or exposure to the atmosphere

Table 1
Parameters for the push-pull tests conducted at the two study sites in the Manawatū catchment, New Zealand.

Item	Unit	Massey No. 1 dairy farm (PNR site)			Woodville sheep & beef farm (WDV site)	
		October 2013	May 2014	July 2014	February 2015	August 2015
Br^- (test solution)*	mg L^{-1}	11.06 ± 0.57	12.88 ± 2.60	10.01 ± 0.30	10.59 ± 0.36	10.99 ± 0.16
NO_3^--N (test solution)*	mg L^{-1}	11.23 ± 0.53	12.66 ± 2.20	9.55 ± 0.28	10.73 ± 0.35	11.08 ± 0.15
Test solution volume	L	40	100	100	100	100
Test solution injection rate	L/min	0.95	1.33	1.54	1.82	1.05
Test duration	minutes	225	420	420	420	360
Acetylene used		Yes	Yes	No	Yes	Yes

* Including background concentrations (±stdev); background concentrations for Br^- and NO_3^--N are very low (<0.10 mg L^{-1}) during the tests.

(Istok, 2013).

The extracted groundwater was stored overnight in a temperature-controlled room with the temperature set similar to the groundwater temperature upon collection, approximately 15 °C (except for the October 2013 test, when the test was completed on the same day due to the smaller volume of the test solution). While other studies stored collected groundwater at 4 °C (Addy et al., 2002; Mcphillips et al., 2015; Mehnert et al., 2006), the background water temperature was used in the study to approximate in situ conditions. The low temperature set for overnight storage of groundwater sample could affect the activities of denitrifying microorganisms not just during storage, but also during the test, especially for short duration tests. Several incubation studies even suggested pre-incubation of samples for 24 h to allow for temperature equilibration or acclimatising soil microbes (Barkle et al., 2007; Drury et al., 2008). The test solution was prepared on the site just before injection by adding bromide (KBr) and NO_3^- (KNO_3) to a small container (120 mL × 2) of groundwater which was then transferred back into the test solution containers using a syringe. Acetylene, purified by passing through two traps of concentrated sulphuric acid and one trap of distilled water (Castle et al., 1998), was also added by syringe into the test groundwater solution. The target concentrations (excluding the background concentrations) in the test solution were approximately as follows: 10 mg L^{-1} Br^-, 10 mg L^{-1} NO_3-N, and 50 ml purified acetylene L^{-1} (Mosier and Klemedtsson, 1994; Paramasivam et al., 1999; Well et al., 2003). The use of 10 mg NO_3-N L^{-1} was based on the maximum allowable limit for drinking water (e.g., Burbery, 2004; Mehnert et al., 2006) and close to the estimated average NO_3-N concentrations leaching from dairy farms in New Zealand considering rainfall amounts in the study area (10.8 mg N L^{-1}; Ledgard et al., 2000; Pattle Delamore Partners Ltd, 2013; Singh et al., 2014). The test solution bags were then vigorously shaken to dissolve the substrate and acetylene bubbles and mix the solution properly (Well et al., 2003). Duplicate samples (approximately 50 mL each) from each test solution bag were collected and filtered (0.45 μm) on the site, and frozen at approximately −20 °C until needed for further analysis (e.g. Barns, 2010; Stenger et al., 2008). It must be noted that since NO_3^--N was added in the test solution, the estimated denitrification rates from the push-pull tests may be more appropriately interpreted as denitrification capacity instead of actual denitrification rate.

The test solution was injected at a rate of 0.95 to 1.82 L/min (Table 1) into the piezometer using the injection system by reversing the peristaltic pump (Tesoriero et al., 2000). At completion of the injection of the test solution, extraction of groundwater was commenced and samples were collected periodically (see Addy et al., 2002; Burbery, 2004; Burbery et al., 2013; Istok et al., 1997; Istok, 2013; Schroth et al., 1998; Schürmann et al., 2003; Snodgrass and Kitanidis, 1998; Toda et al., 2002). Groundwater samples were collected from time 0 (right after completion of the test solution injection) (Baker and Vervier, 2004; Istok et al., 1997), and at 15, 30, 60, 90, 120 min, and then hourly up to four or seven hours later (e.g., Baker and Vervier, 2004; Mehnert et al., 2006; Sanchez-Perez et al., 2003). The piezometer was purged prior to each sampling by pumping out approximately 2 L of water to ensure collection of groundwater samples from the aquifer formation surrounding the piezometer (Istok, 2013). Following purging, two sets of groundwater samples were collected at each sampling time. First, triplicate of approximately 50 mL samples were field-filtered with a 0.45 μm syringe filter and collected in polyethylene bottles for the measurement of reactant (NO_3^-) and conservative (bromide) tracer. Second, duplicate samples of 120 mL (in October 2013 and May 2014 tests at the PNR site) or 180 mL (in July 2014 test at the PNR site and at both tests at the WDV site) were collected for the extraction and analysis of dissolved nitrous oxide (N_2O) gas. Groundwater samples for dissolved gas were collected by syringe through a t-type Luer-lock mini valve to avoid sample exposure to air (Addy et al., 2002; Well et al., 2003) and transferred into evacuated vacuum pouches (100x285mm, gauge 70 μm Cas-Pak) for further analysis. The collected samples were transported in a chilly bin with ice (Daughney et al., 2006). The collected samples for hydrochemical analysis were frozen until analysis (e.g. Barns, 2010; Stenger et al., 2008); whereas, the collected samples for N_2O measurements were kept chilled at 4 °C until the gas extraction, which was done within 24 h of groundwater collection. To extract dissolved N_2O gas from the collected water samples, the phase equilibrium headspace extraction method (Addy et al., 2002; Lemon and Lemon, 1981) was adapted in which 50 mL (in October 2013 and May 2014 test samples from the PNR site) or 60 mL (in July 2014 test samples from the PNR site and both tests at the WDV site) of N_2 were added to create a headspace in the collection pouches. The collection pouches were then placed on a shaker for 1.5 h at 200 rpm under 20 °C. After shaking, 25 mL of gas samples were removed from each pouch and placed into 12 mL glass vials (Labco Exetainer) for analysis by a gas chromatograph. The use of a larger groundwater sample for dissolved gas extraction, i.e. 180 mL in all the other tests compared to 120 mL in October 2013 and May 2014 tests at the PNR site, was presumed to increase the accuracy of dissolved N_2O measurements.

The collected groundwater samples were analysed for NO_3^--N and Br^- concentrations by ion chromatography (Lachat Instruments IC5000 Ion Chromatograph), whereas ammonium-N (NH_4^+-N) was measured by continuous flow analysis (Technicon® AutoAnalyzer II). In the groundwater samples collected at the PNR site, dissolved organic carbon (DOC) concentrations were determined by potassium dichromate wet oxidation and titration (method 5220B, (Rice et al., 2012)), but with some adjustments: using 10 mL sample, 20 mL H_2SO_4 with 5 g Ag_2SO_4 L^{-1}, and 10 mL 0.025 N $K_2Cr_2O_7$ in digestion, and 0.01 N ferrous ammonium sulphate for titration), whereas DOC concentrations in the samples collected at the WDV site were determined by measuring absorbance with a spectrophotometer (wavelength = 660 nm) (Chibuike et al., 2021). The collected gas samples were analysed for N_2O with a Shimadzu Gas Chromatograph (GC) 17 A (Japan) which has a ^{63}Ni-electron capture detector.

2.4. *Quantification of denitrification rate*

The tracer concentrations from samples were first analysed and corrected for dilution and/or advection to measure changes in the reactant (i.e. NO_3^--N) or product (i.e. N_2O—N) during the tests. The measured NO_3^--N concentrations were corrected by multiplying with a dilution factor (DF) calculated as the ratio of the average initial concentration of the conservative tracer Br^- in the test solution and its concentrations measured at the respective samplings during the test. The measured concentrations of N_2O-N were first corrected for the amount of N_2O-N dissolved in groundwater during the phase equilibrium headspace extraction, similar to the procedure used in denitrification assays with soil samples in solution (Hill et al., 2000; Sanchez-Perez et al., 2003; Well et al., 2003). Thereafter, the amount of N_2O-N produced per sampling was corrected for dilution and/or advection based on the measured concentrations of the conservative Br^- tracer (Sanchez-Perez et al., 2003; Well et al., 2003). The corrected N_2O-N concentration was computed in the same manner as described above for the NO_3^--N concentrations.

The dilution corrected NO_3^--N and N_2O-N concentrations were used to quantify denitrification rate by analysing the decrease in the reactant (NO_3^--N) and/or the increase in the product (N_2O—N) (Istok, 2013; Istok et al., 1997). Further, denitrification rate was quantified assuming different kinetic models, i.e. the zero-order or first-order kinetics (see Table 2).

A review of existing studies suggests several models developed and used to quantify denitrification rate based on the reactant (NO_3^--N) or the product (N_2O—N) (Table 2). This study assessed only the most common models used for quantification of denitrification rate using either the denitrification reactants or the products (see Table 2, including the relevant references). Particular attention was paid to ensure that this assessment included models that were applicable for both the reactant and product. For instance, for estimation of denitrification rate assuming zero-order kinetics, the model of Trudell et al. (1986) based on the reactant and the model of Sanchez-Perez et al. (2003) based on the product were included in the assessment (Table 2). Both models quantify denitrification rate based on the slope of the line tangent to the regression curve of the data. For estimation of denitrification rate assuming first-order kinetics, the model of Haggerty et al. (1998) for the reactant (Eq. (4), Table 2), and the model of Schürmann et al. (2003) for the product (Eqs. (11)–(13), Table 2) were both included, as the latter is a modification of the former for product-based estimates (Table 2).

In this study, using the concentrations of the reactant (NO_3-N), the zero-order denitrification rate was quantified using three commonly used models: a regression line of dilution corrected NO_3-N, noted as Zero-order 1 model (Baker and Vervier, 2004; Istok, 2013; Korom et al., 2012; Tesoriero et al., 2000); a tangent line to the curve approximating dilution corrected NO_3-N, noted as Zero-order 2 model (Trudell et al., 1986); and the method by Snodgrass and Kitanidis (1998), noted as Zero-order 3 model (Table 2). Using the concentrations of the product (N_2O), the zero-order denitrification rate was quantified using the method of Sanchez-Perez et al. (2003), noted as Zero-order 4 model (Table 2). Using the concentrations of the reactant (NO_3-N), the first-order denitrification rates were quantified by applying three models namely, First-order model 1 (Haggerty et al., 1998), First-order model 2 (Snodgrass and Kitanidis, 1998), and First-order model 3 (Korom et al., 2005, 2012) (Table 2). The first-order denitrification rate was also quantified by adapting Haggerty et al. (1998) model for analysis of the denitrification product (N_2O) (Schürmann et al., 2003), noted as First-order 4 model (Table 2).

3. Results and discussion

3.1. Push-pull test results

Table 3 summarizes the background characteristics of shallow groundwater measured during the push-pull tests at the two study sites. At the PNR site, the measured background groundwater characteristics were similar during the three tests except for sulphate (SO_4^{2-}) concentration in July 2014 test (Table 3), which could indicate anthropogenic sources (e.g. fertilisers) due to recharge in the winter season

Table 2

Summary of different models for estimating zero-order (*r*) or first-order (*k*) denitrification rate from single-well push-pull test data.

Tracer	Kinetic model	Approach and/or formula	References
Reactant	Zero-order	$r = \frac{C_{dc}^{i} - C_{dc}^{f}}{T}$ (Eq. (1))	Toda et al., 2002
		Rate (*r*) based on best-fit slope of regression line of C_{dc} against time	Baker and Vervier, 2004; Istok, 2013; Korom et al., 2012; Tesoriero et al., 2000 *(Zero-order 1)*
		Rate (*r*) based on the slope of tangent line to the regression curve approximating C_{dc} plotted against time	Trudell et al., 1986 *(Zero-order 2)*
		$r = \frac{M_{r.inj} - M_{r.ext}}{V_{inj} \times RT_{ave}}$ (Eq. (2))	Istok et al., 1997; Mehnert et al., 2006
		Rate (*r*) based on the slope of the transformation of the reactive solute concentration, $C_r(t)$, plotted against time $C_r(t) = C_r^0\left(\frac{C_r^m(t)}{C_r^0} - \frac{C_t^m(t)}{C_t^0} + 1\right)$ (Eq. (3))	Snodgrass and Kitanidis, 1998 *(Zero-order 3)*
	First-order	$ln\left(\frac{C_r^*(t)}{C_t^*(t)}\right) = ln\left[\frac{\left(1 - e^{-kt_{inj}}\right)}{kt_{inj}}\right] - kt$ (Eq. (4))	Haggerty et al., 1998 *(First-order 1)*
		$ln\left(\frac{C_r^*(t)}{C_t^*(t)}\right) = ln\frac{C_{dc}}{C_r^0} = -kt$ (Eq. (5))	Korom et al., 2005, 2012 *(First-order 3)*
		$ln\left(\frac{C_r^m(t)}{C_t^m(t)}\right) = ln\left(\frac{C_r^0}{C_t^0}\right) - kt$ (Eq. (6))	Snodgrass and Kitanidis, 1998 *(First-order 2)*
Product	Zero-order	Rate (*r*) based on best-fit slope of regression line of C_{dc} against time	Baker and Vervier, 2004
		Rate (*r*) based on the slope of tangent line to the regression curve approximating C_{dc} plotted against time	Sanchez-Perez et al., 2003; Trudell et al., 1986 *(Zero-order 4)*
		$r = \frac{C_{dc}(t) - C_p(t-1)}{dt}$ (Eq. (7)) $C_{dc}(t) = \frac{C_p(t) - C_p^0 * [1 - F_{dil}]}{F_{dil}}$ (Eq. (8)) $F_{dil} = \frac{C_t^*(t)}{C_t^*(t-1)}$ (Eq. (9))	Well et al., 2003
		$r = \frac{M_{p.ext}}{V_{inj} \times RT_{ave}}$ (Eq. (10))	Istok et al., 1997
	First-order	Adapted Eq. (4), replacing the left-side term with an expression for products as below: $\frac{C_r^*}{C_t^*} = 1 - \frac{C_p^*}{C_t^*}$ (Eq. (11)) $C_p^* = \frac{C_p}{C_r^0}$ (Eq. (12)) $C_p = C_r^0\left(1 - e^{-kt}\right)$ (Eq. (13))	Schürmann et al., 2003 *(First-order 4)*

Note: C_{dc}^{i} is the initial dilution-corrected concentration of the reactant; C_{dc}^{f} is the final dilution-corrected concentration of the reactant; T is the duration of the extraction or ‘pull’ phase; C_{dc} is the dilution-corrected concentration of either the reactant (nitrate) or product (e.g., nitrous oxide); $M_{r.inj}$ is the mass of the injected reactant; $M_{r.ext}$ is the mass of the extracted reactant; $M_{p.ext}$ is the mass of the product formed; V_{inj} is the test solution injection volume; RT_{ave} is the mean residence time for the test solution; C_r^0 and C_t^0 are the injection solution concentrations of the reactive and conservative tracer, respectively; $C_r^m(t)$ and $C_t^m(t)$ are the measured concentrations of the reactive and conservative tracer, respectively, during the 'pull' phase at time t; $C_r^*(t)$ and $C_t^*(t)$ are relative concentrations (ratio of concentration measured at time t and concentration of the injected solution) of the reactant and the conservative tracer, respectively; t_{inj} is the duration of injecting the test solution; C_p is the concentration of the denitrification product; C_p^0 is the background concentration of the denitrification product; F_{dil} is a dilution factor.

Table 3
Background characteristics of shallow groundwater measured during the assessment of push-pull tests conducted at the two study sites in the Manawatū catchment, New Zealand.

Parameter	Unit	Massey No. 1 dairy farm (PNR site)			Woodville sheep & beef farm (WDV site)	
		October 2013	May 2014	July 2014	February 2015	August 2015
Depth to water (bgl)	m	4.29	4.65	4.71	3.96	3.05
Temperature	°C	14.6	15.7	15.1	14.4	13.9
Dissolved oxygen	mg L^{-1}	0.40	0.45	0.44	0.22	0.37
SPC	μS cm^{-1}	234.6	228.9	255.9	415.0	424.7
pH		6.25	5.89	5.82	6.30	6.31
ORP (Eh)	mV	188.9	243.7	253.5	94.5	68.7
Br^-	mg L^{-1}	0.099	0.099	0.080	0.08	0.15
NO_3^--N	mg L^{-1}	0.049	<0.01	<0.01	<0.01	0.02
NO_2^--N	mg L^{-1}	<0.003	<0.003	<0.003	<0.003	<0.003
DOC	mg L^{-1}	3.55	3.81	n/a	1.24	1.72
Cl^-	mg L^{-1}	19.10	22.16	20.51	29.98	36.19
SO_4^{2-}	mg L^{-1}	5.57	6.17	22.38	25.04	3.39

Note: Except for field measured parameters (temperature, DO, pH, SPC, ORP), values presented are averages of three replicates. bgl – below ground level, DO – dissolved oxygen, DOC – dissolved organic carbon, SPC – specific conductance or electrical conductivity, ORP – oxidation-reduction potential.

(June–August). The background concentrations of NO_3^--N and NO_2^--N were measured at very low concentrations (<0.05 mg L^{-1}). Low concentrations of dissolved oxygen (DO) indicate the presence of reduced groundwater at the site. The oxidation reduction potential (*ORP*) measured with an Ag/AgCl reference electrode were converted to *Eh* values (i.e., with respect to standard hydrogen electrode) by adding 200 mV to the measured values (Rice et al., 2012). The *Eh* values at the PNR site were quantified higher in May 2014 (243.7 mV) and July 2014 (253.5 mV) tests, which could be due to groundwater recharge during the late autumn (May) and winter seasons (June–August). However, the measured ORP values suggested reduced groundwater conditions (<250 mV; Thayalakumaran et al., 2008). Coupled with significant amounts of DOC values (Table 3), this suggests a high potential for denitrification to occur at the PNR site. This is supported by measured low concentrations of NO_3^- (<0.05 mg N L^{-1}), despite the study site being located on a dairy farm with sandy loam soil (Singh et al., 2014). At the WDV site, the measurement of low DO concentrations (0.22–0.37 mg L^{-1}) and ORP (*Eh* of 68.7–94.5) suggests groundwater conditions favorable denitrification. This is also reflected in very low NO_3^- concentrations ($\leq$ 0.02 mg L^{-1}). However, the lower DOC content (1.24–1.72 mg L^{-1}) at the WDV site could indicate lower potential for denitrification to occur compared to the PNR site. However, this comparison did not account for other potential electron donors (e.g., Fe(II) and Mn(II) (Thayalakumaran et al., 2008; Istok, 2013), which we did not measure during the experiments. Later, Jha et al. (2018) measured a relatively higher Fe(II) content, ranging from 0.60 to 4.02 mg L^{-1} at the WDV (Woodville) and PNR (Palmerston North) sites. This supports a microbial nitrate reduction coupled with oxidation of Fe(III), as potential electron donor to support denitrification in groundwater at the study sites (Rivett et al., 2008; Thayalakumaran et al., 2008).

Figs. 2 and 3 show the measurements of push-pull tests conducted on three occasions at the PNR site and on two occasions at the WDV site, respectively. At the PNR site, all three push-pull tests measured a quick decrease in NO_3^--N and Br^- concentrations from about 10 mg L^{-1} (at $t=0$) to less than 2 mg L^{-1} within 7 h (at $t=7$). A relatively faster decrease in NO_3^--N and Br^-concentrations were observed in the October 2013 test, which could be attributed to the smaller volume of test solution used (40 L). A larger deviation in the measured NO_3^--N and Br^- concentrations (shown by the error bars) was apparent in the early stages of the pull phase, with much lower deviation in the later stages (Fig. 2). This was also observed at the WDV site (Fig. 3) and could be due to mixing of the injected test solution with the resident groundwater around the test piezometer. The measured concentrations of the push-pull test tracers consistently showed a decrease of NO_3^--N /Br^- ratio at the two sites (although a relatively smaller decrease at the WDV site), indicating that NO_3^--N decreased more than Br^- during the tests. This suggests NO_3^- attenuation processes such as denitrification occurring in the shallow groundwater during the tests. This is also supported by the observed trend of increasing N_2O-N production during the tests (Figs. 2a2, b2, c2; 3a2, b2). It should be noted that these N_2O-N values shown in Figs. 2 and 3 have not yet been corrected for diffusion and/or advection transport that might have diluted N_2O-N produced during the tests. The plots of dilution-corrected N_2O concentrations measured during the tests are shown in the Figs. S7 and S8 (in the Supplementary Materials).

Fig. 4 reproduces the dilution-corrected concentrations of NO_3^--N, NO_2^--N and N_2O-N observed during the May 2014 test at the PNR site. As more NO_3^--N was lost, as shown by decreasing dilution-corrected NO_3^--N concentration, more NO_2^--N and N_2O-N were produced. The background concentrations of NO_2^--N were found to be below the detection limit (<0.003 mg N L^{-1}) in all tests (Table 3), but significant amounts were subsequently observed during the May 2014 and July 2014 tests (up to 0.207 and 0.090 mg N L^{-1}, respectively) at the PNR site. This further confirms the occurrence of denitrification, with NO_2^--N being produced as an intermediate product of the process (Appelo and Postma, 2005; Rivett et al., 2008). The concentrations of N_2O—N, deemed as the terminal product of denitrification process with the use of acetylene, increased during the duration of the tests confirming the occurrence of denitrification at the test site (Fig. 4).

3.1.1. *Effect of acetylene on nitrous oxide concentrations during the push-pull tests*

The effects of acetylene on N_2O-N concentrations produced during the May and July 2014 tests at the PNR site are highlighted in Fig. 5. A linear trend on increase in N_2O-N concentrations was observed in the May 2014 test (with acetylene), but not in the July 2014 test (without acetylene). In the July 2014 test, the measured N_2O-N concentrations showed an initial increase (up to the 4th hour) and then plateaued afterwards (Fig. 5). This put in contrast to a steadily rise of N_2O-N concentrations measured during the May 2014 test (with acetylene). This contrast in the measured concentrations of N_2O-N during the May 2014 test (with acetylene) and July 2014 test (without acetylene) indicates the possibility of N_2O conversion to N_2 in denitrification process during the July 2014 test. Although N_2 measurements are needed to confirm this, the apparent conversion of N_2O to N_2 in the July 2014 test suggests the potential of complete denitrification in shallow groundwater as observed in other studies (e.g., Jahangir et al., 2012a). Later, Jha et al. (2018) measured a relatively higher concentrations of dissolved N_2 in the reduced groundwater samples (including the WDV, Woodville and the PNR, Palmerston North) sites, as compared to the oxidized groundwater samples in the study area. The potential for complete subsurface denitrification underlines the significance of NO_3^-

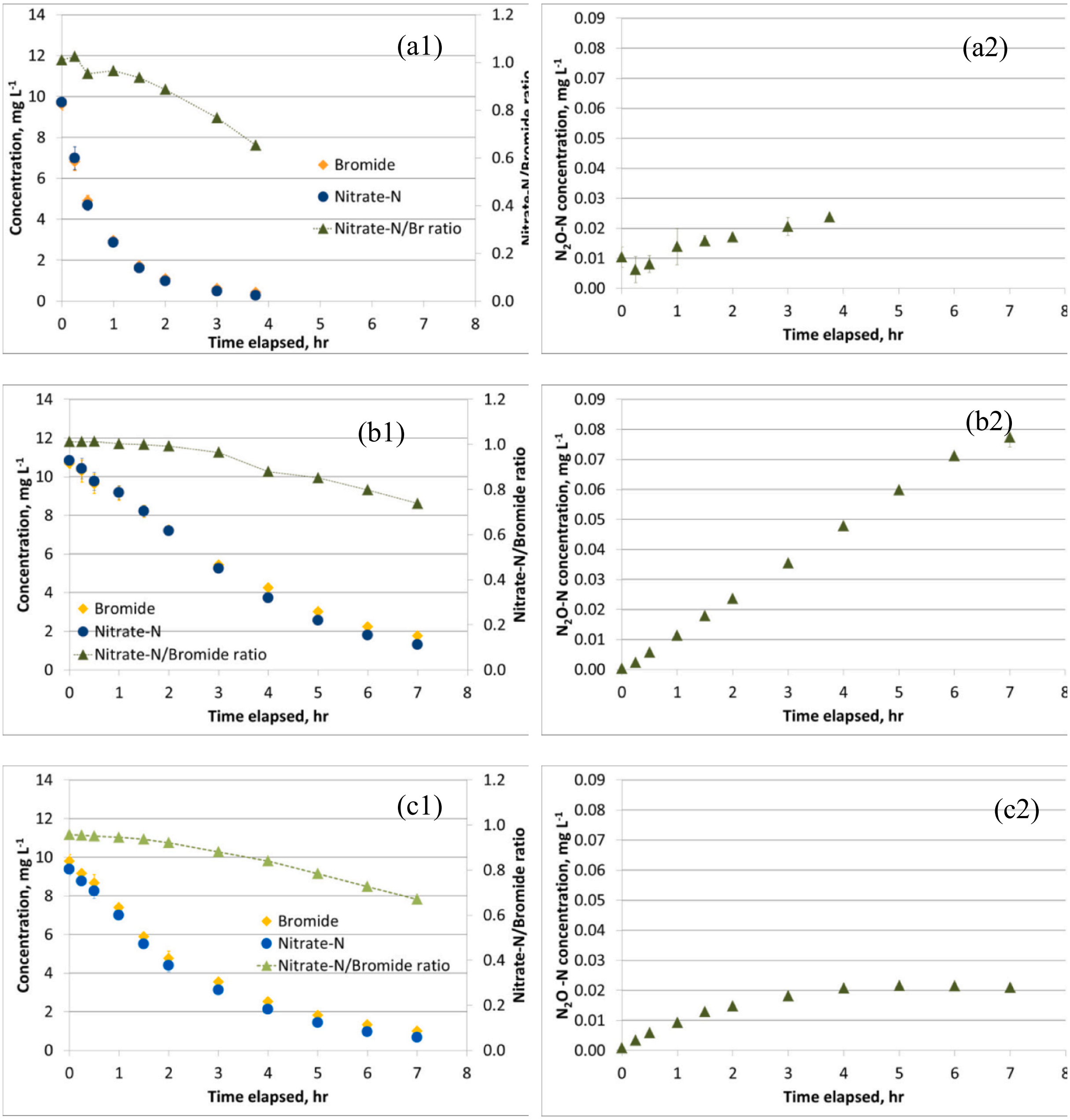

Fig. 2. Concentrations of (1) nitrate-N and bromide, and (2) nitrous oxide-N during the push-pull test conducted in (a) October 2013, (b) May 2014, and (c) July 2014 at the Massey No. 1 Dairy Farm, Palmerston North, New Zealand (PNR site). Error bars represent standard deviations of the sampling replicates. Volume of test solution – 40 L (Oct 2013) and 100 L (May 2014 and July 2014).

attenuation in shallow groundwater systems in the “long-term improvement” of water quality. In case of complete denitrification, the produced dinitrogen gas (N_2) is unlikely to be converted back to NO_3^- within the system (Starr and Gillham, 1993). However, a choice of using either the denitrification reactant or product, and different kinetic reaction (zero-order and first-order) models appear to influence an accurate quantification of denitrification rate from the push-pull tests.

3.2. Zero-order denitrification rates

Tables 4 and 5 summarise the zero-order denitrification rates quantified based on the reactant (NO_3^--N) or product (N_2O—N), respectively, during the push-pull tests. The Supplementary Figs. S1 to S8 plot quantification of zero-order dentification rates using different methods analysing the reactant (NO_3^--N) or product (N_2O—N) concentrations measured during the push-pull tests. The average (mean) rate of the Zero-order 2 model was estimated from the average of rates computed from the slopes at sample times and in between, minimum (min) rate was obtained from the tangent line with the least slope, maximum (max) rate from the tangent line with the largest slope (at the last sampling time), and the max interval rates from the slope of the tangent line drawn in the middle of the sampling interval with maximum variation or gradient (at the last sampling interval). These rates showed that the estimated Zero-order 2 denitrification rates (Tables 4 and 5) vary depending on which point of the curve the tangent line is drawn (S3 and S4).

The zero-order denitrification rates, based on the measured concentrations of NO_3^--N as the denitrification reactant, estimated from the Zero-order 1 model or linear regression methods (Baker and Vervier, 2004; Istok, 2013; Korom et al., 2012; Tesoriero et al., 2000) were in the

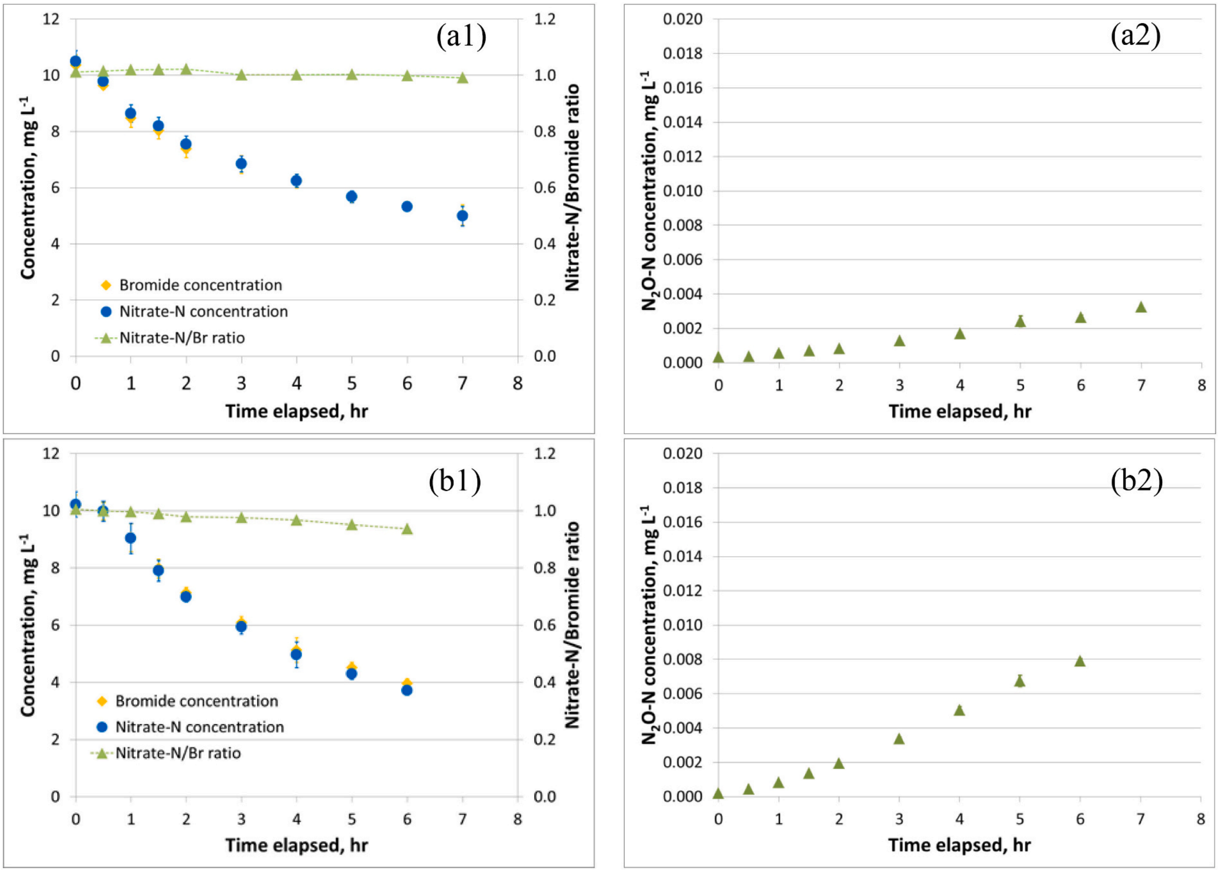

Fig. 3. Concentrations of (1) nitrate-N and bromide, and (2) nitrous oxide-N during the push-pull test conducted in (a) February 2015 and (b) August 2015 at a sheep and beef farm near Woodville, New Zealand (WDV site). Error bars represent standard deviations of the sampling replicates. Volume of test solution 100 L.

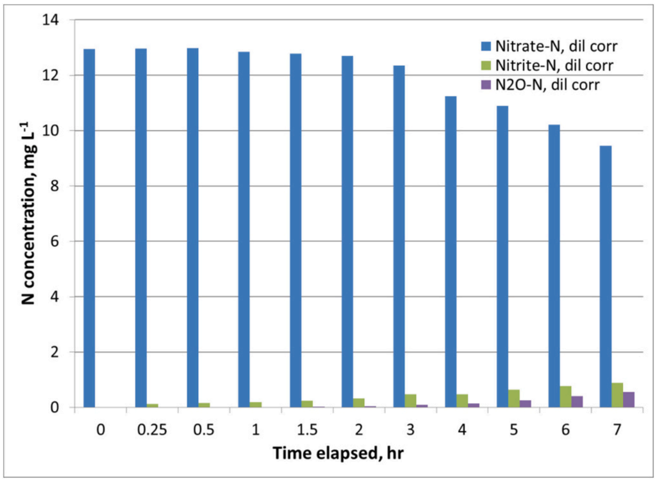

Fig. 4. Concentrations of different forms of nitrogen in groundwater samples collected during the push-pull test conducted in the May 2014 at the Massey No. 1 Dairy Farm, Palmerston North, New Zealand (PNR site).

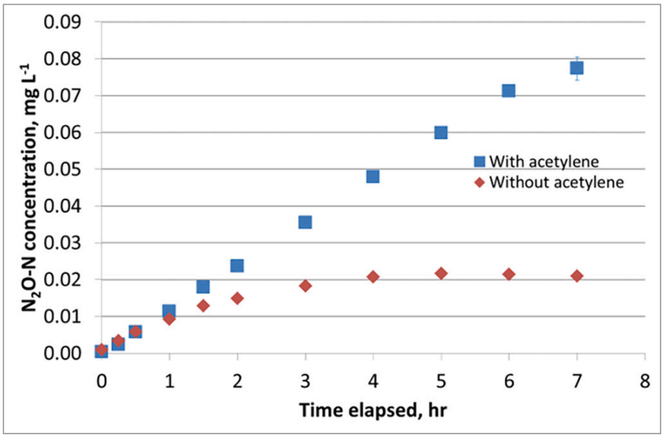

Fig. 5. Nitrous oxide concentrations (uncorrected for dilution) during the push-pull tests conducted in May 2014 (with acetylene) and July 2014 (without acetylene) at the Massey No. 1 Dairy Farm, Palmerston North, New Zealand. Error bars represent standard deviations of the sampling replicates. The volume of test solution for both tests was 100 L.

range of 0.44–1.07 and 0.05–0.12 mg N L^{-1} h^{-1} at the PNR and WDV sites, respectively (Table 4). A similar range of denitrification rates were obtained using the Zero-order 2 model following Trudell et al. (1986) with mean zero-order denitrification rates of 0.41–0.95 and 0.05–0.12 mg N L^{-1} h^{-1} at the PNR and WDV sites, respectively (Table 4). These zero-order denitrification rates are also comparable to the reported zero-order denitrification rates in the literature using the push-pull test technique (0.01–1.12 mg N L^{-1} h^{-1}) (Addy et al., 2002; Istok et al., 1997; Starr and Gillham, 1993; Toda et al., 2002; Trudell et al., 1986; Well et al., 2003). On the other hand, the Zero-order 3 model, as per Snodgrass and Kitanidis (1998), resulted into relatively lower zero-order denitrification rates of 0.01–0.12 and 0.026–0.032 mg N L^{-1} h^{-1} at the PNR and WDV sites, respectively (Table 4). Moreover, the zero-order denitrification rates obtained by the Zero-order 3 model do not seem to follow the trend as estimated by the other models as shown above. For instance, with the first two models, the Zero-order 1 and Zero-order 2

Table 4
Estimates of denitrification rate by different models based on zero-order and first order-kinetics using denitrification reactant (nitrate-nitrogen) measured during the push-pull tests conducted at the two study sites in the Manawatū catchment, New Zealand.

Push-pull test	Estimated denitrification rate					
	Zero-order 1 (several references)*	Zero-order 2 (Trudell et al., 1986)	Zero-order 3 (Snodgrass and Kitanidis, 1998)	First-order 1 (Haggerty et al., 1998)	First-order 2 (Snodgrass and Kitanidis, 1998)	First-order 3 (Korom et al., 2005, 2012)
PNR site						
October 2013	-1.07 mg N L^{-1} h^{-1}	Mean: -0.95 mg N L^{-1} h^{-1} Min (0.5 h): -0.03 Max (3.75 h): -2.08 Interval (3.25 h): -1.77	-0.01 mg N L^{-1} h^{-1}	-0.08 h^{-1}	-0.10 h^{-1}	-0.10 h^{-1}
May 2014	-0.56 mg N L^{-1} h^{-1}	Mean: -0.52 mg N L^{-1} h^{-1} Min (0.5 h): -0.26 Max (7.0 h): -0.87 Interval (6.5 h): -0.82	-0.112 mg N L^{-1} h^{-1}	-0.03 h^{-1}	-0.03 h^{-1}	-0.03 h^{-1}
July 2014	-0.44 mg N L^{-1} h^{-1}	Mean: -0.41 mg N L^{-1} h^{-1} Min (0.5 h): -0.20 Max (7.0 h): -0.68 Interval (6.5 h): -0.64	-0.04 mg N L^{-1} h^{-1}	-0.03 h^{-1}	-0.04 h^{-1}	-0.04 h^{-1}
WDV site						
February 2015	-0.05 mg N L^{-1} h^{-1}	Mean: -0.05 mg N L^{-1} h^{-1} Min (0.5 h): -0.04 Max (7.0 h): -0.05 Interval (6.5 h): -0.05	-0.03 mg N L^{-1} h^{-1}	-0.002 h^{-1}	-0.002 h^{-1}	-0.002 h^{-1}
August 2015	-0.12 mg N L^{-1} h^{-1}	Mean: -0.12 mg N L^{-1} h^{-1} Min (0.5 h): -0.09 Max (6.0 h): -0.15 Interval (5.5 h): -0.15	-0.03 mg N L^{-1} h^{-1}	-0.01 h^{-1}	-0.01 h^{-1}	-0.01 h^{-1}

* References: Baker and Vervier, 2004; Istok, 2013; Korom et al., 2012; Tesoriero et al., 2000.

Table 5
Estimates of denitrification rate by different models based on zero-order and first order-kinetics using denitrification product (nitrous oxide-nitrogen) measured during the push-pull tests conducted at the Palmerston North (PNR) and Woodville (WDV) sites in the Manawatū catchment, New Zealand.

Push-pull test site	Estimated denitrification rate	
	Zero-order 4 (Sanchez-Perez et al., 2003)	First-order 4 (Schürmann et al., 2003)
PNR site		
October 2013	Ave: 0.17 mg N L^{-1} h^{-1} Max interval: 0.29	0.009 h^{-1}
May 2014	Ave: 0.07 mg N L^{-1} h^{-1} Max interval: 0.18	0.004 h^{-1}
WDV site		
February 2015	Ave: 0.001 mg N L^{-1} h^{-1} Max interval: 0.002	0.0001 h^{-1}
August 2015	Ave: 0.003 mg N L^{-1} h^{-1} Max interval: 0.006	0.0002 h^{-1}

Note: No denitrification rate was estimated based on the denitrification product (nitrous oxide-nitrogen) for the July 2014 test at the PNR site as acetylene was not used in the push-pull test.

denitrification rates were found to be highest in the October 2013 test, then in the May 2014 test, and lowest in the July 2014 test at the PNR site. However, the Zero-order 3 based on Snodgrass and Kitanidis (1998) quantified highest zero-order denitrification rate in the May 2014 test, followed by the July 2014 test and the October 2013 test. It is apparent that the way the dilution was accounted for in the calculation of denitrification rates, as with the Zero-order 1 and 2 vs the Zero-order 3, has implications for quantification of the zero-order denitrification rates using the single-well, push-pull test data (Table 4).

In considering results of Zero-order 1 and Zero-order 2 models based on the reactant (NO$_3^-$-N), which have comparable results, the denitrification rate was quantified higher in the October 2013 test and lower in the May and July 2014 tests at the PNR site (Table 4). The apparent decrease in denitrification rates in the May 2014 and July 2014 tests is not unique considering the different time for the tests (e.g., Korom et al., 2012). Possible factors for this decrease in denitrification rates in May 2014/July 2014 tests may include an increase in ORP (*Eh*) and a slight decrease in *pH* values (Table 3). At the WDV site, denitrification rate in February 2015 was lower than in August 2015 (Table 4). However, this difference may not be of particular importance considering the low denitrification rate and lack of any difference in *pH*, DO and DOC in groundwater samples at the study site.

Using denitrification product (N$_2$O—N) and following the Zero-order 4 model (Sanchez-Perez et al., 2003) (Table 2), the zero-order denitrification rates obtained at the PNR site were 0.17 and 0.07 mg N L^{-1} h^{-1} in October 2103 and May 2014, respectively, whereas at the WDV site the denitrification rates were quantified lower at 0.001 and 0.003 mg N L^{-1} h^{-1} in February and August 2015, respectively (Table 5). These rates are generally comparable to the zero-order rates of 0.006–1.97 mg N L^{-1} h^{-1} estimated by other studies using the denitrification product (Sanchez-Perez et al., 2003). Note that a zero-order denitrification rate based on the product (N$_2$O—N) measurements could not be estimated for the July 2014 test at the PNR site as acetylene was not used in this test and thus N$_2$O-N could not be considered as the terminal product of the denitrification process (Table 1). However, interestingly, the zero-order denitrification rates based on the measured reactant N_3O-N concentrations were quantified 6 to 50 times higher than the denitrification rates estimated based on the measured product N_2O-N concentrations during the push-pull tests (Tables 4 and 5). This discrepancy in the estimates of denitrification rates is further discussed later in Section 3.4 (below) comparing the denitrification rates obtained using the reactant (NO_3^--N) and product (N_2O—N).

3.3. First-order denitrification rates

Tables 4 and 5 summarise the first-order denitrification rates quantified based on the reactant (NO_3^--N) or product (N_2O—N), respectively, during the push-pull tests. The Supplementary Figs. S9 to S14 plot quantification of the first-order dentification rates using different methods analysing the reactant (NO_3^--N) concentrations measured during the push-pull tests. Following Haggerty et al. (1998) (First-order 1 model), Supplementary Figs. S9 and S10 show the plots for estimates of first-order denitrification rate based on the reactant during the tests at the PNR and WDV site, respectively. In Haggerty et al. (1998), forcing y to a certain value at time $t = 0$ assumes that a similar reduction rate is in effect to reduce NO_3^- during injection and thus less NO_3^- was expected at the end of injection. This consequently results in the plot line starting (at $t = 0$) a bit lower than the sample data (S9 and S10).

However, analysing the measured concentrations of (NO_3^--N) as the reactant, the estimated first-order denitrification rates were quantified generally comparable among the three models for each of the push-pull test conducted (Table 4). The quantified first-order denitrification rates were in the range 0.03–0.01 h^{-1} and 0.002–0.01 h^{-1} at the PNR and WDV sites, respectively (Table 4). The first-order denitrification rates obtained at the WDV site were in the range of observed first-order rates in a few similar studies conducted elsewhere (0.001–0.02 h^{-1}) (Burbery et al., 2013; Korom et al., 2012), whereas the rates at the PNR site were greater (0.03–0.10 h^{-1}). Kruisdijk et al. (2022) estimated first-order denitrification from 0.1 – >1 d^{-1} from their push-pull tests during aquifer storage and recovery of drainage water from agricultural land in the North-Western part of the Netherlands. However, it is difficult to assess the first-order rates obtained in this study in terms of the different groundwater environments given the limited studies that quantify denitrification in shallow groundwater.

The main difference between the model of Haggerty et al. (1998), (First-order 1) and that of Snodgrass and Kitanidis (1998) (First-order 2) and Korom et al., 2005, 2012 (First-order 3) is that the latter models do not assume NO_3^- reduction during injection phase of the push-pull test. Therefore, Snodgrass and Kitanidis (1998) (First-order 2) and Korom et al. (2005, 2012) (First-order 3) models may not be appropriate for push-pull tests with long injection duration and highly conducive denitrification environment in which NO_3^- reduction may be significant and quick during the injection period. However, they could be suitable for short injection duration such as in this study, as supported by the comparable estimates of the first-order dentification rates by the models (Table 4).

As the zero-order denitrification rates, the first-order denitrification rates were quantified relatively higher (0.08–0.10 h^{-1}) during the October 2013 test as compared to the July 2014 and May 2014 tests (0.03–0.04 h^{-1}) at the PNR site (Table 4). Moreover, a lower first-order denitrification rate was observed at the WDV site in February 2015 (0.002 h^{-1}) compared to August 2015 (0.01 h^{-1}) (Table 4). The model of Schürmann et al. (2003) (First-order 4) was applied to quantify first-order denitrification rates based on measurements of denitrification product (N_2O—N) during the push-pull tests. The estimated first-order denitrification rates based on the product (N_2O—N) were also measured higher (0.009 h^{-1}) during the October 2013 test as compared to the July 2014 tests (0.004 h^{-1}) at the PNR site (Table 5). These rates are comparable to the results (0.0079–0.01 h^{-1}) from limited studies using the same model (Schürmann et al., 2003). However. the first-order denitrification rates were quantified relatively lower at the WDV site (0.0001–0.0002 h^{-1}) (Table 5). Nevertheless, a greater first-order denitrification rate was also estimated for the February 2015 test compared to the August 2015 test (Table 5). However, as the results of using zero-order models, the first-order denitrification rates estimated using the measurements of N_3O-N as the denitrification reactant were quantified 8 to 11 times higher at the PNR site; and 20 to 60 times higher at the WDV site, as compared to the first-order denitrification rates estimated based on the measurements of N_2O-N as the dentification product (Tables 4 and 5).

3.4. Comparison of denitrification rates obtained using denitrification reactant (NO_3^--N) and product (N_2O—N)

Denitrification rate estimates were found to vary depending on which tracer is measured and used (e.g. the reactant (NO_3^--N) or product (N_2O—N)) (Tables 4 and 5). The denitrification rates based on the NO_3^--N reductions were quantified much higher (6 to 60 times) than the rates based on the N_2O-N production during the push-pull tests. This discrepancy in denitrification rate estimation has also been observed in soil denitrification assays (Yu et al., 2008). Fig. 4 shows the dilution-corrected concentrations of NO_3^--N, NO_2^--N and N_2O-N observed during the May 2014 test at the PNR site. In this test, from the fourth hour of the ‘pull’ phase, the sum of NO_2^--N and N_2O-N accounted for approximately 40 % of the NO_3-N reduced. While ammonium-N concentrations were not measured in the samples from the push-pull test conducted in May 2014, measurements obtained for the October 2013 test at the same site showed very low ammonium-N concentrations (<0.08 mg N L^{-1}; mostly <0.05 mg N L^{-1}). Thus, it is unlikely that dissimilatory NO_3^- reduction to ammonium (DNRA) was a significant process for the reduction of NO_3^--N in shallow groundwater at the study site. DNRA and denitrification could occur under similar conditions, low *DO* (dissolved oxygen) and *Eh* (redox potential) environment. However, DNRA is a favored process when electron donors such as dissolved carbon are more abundant relative to NO_3^--N supplies (Korom, 1992; Thayalakumaran et al., 2008; Rütting et al., 2011). Rütting et al. (2011) specified the carbon: nitrate-N ratio of 12 as the threshold for the significant occurrence of DNRA which was based on a study on paddy soils in China and Australia. In this study, the ratio of dissolved organic carbon: nitrate-N in the push-pull tests (Tables 1 and 3) was relatively lower than the threshold suggested for the significant occurrence of DNRA (Rütting et al., 2011). Also, several studies have indicated occurrence of denitrification but not of other processes like DNRA in shallow groundwaters under pastoral soils in New Zealand (Stenger et al., 2008; Clague et al., 2013). However, the amounts of NO_2^--N, N_2O-N and ammonium-N concentrations combined in the samples could not account for the total NO_3^--N lost during the push-pull test (Fig. 4). It is therefore possible that, apart from denitrification and DNRA, there may be other processes involved such as accumulation of microbial biomass and/or potentially incomplete inhibition of N_2O conversion to N_2 by the acetylene used during the tests (Starr and Gillham, 1993; Groffman et al., 2006; Qin et al., 2012).

Few studies have investigated estimates of denitrification rates using both NO_3^- reduction and N_2O production. While Gillham et al. (1990) found an increase in N_2O-N corresponding to NO_3^--N lost, other studies did not provide conclusive explanations of the discrepancies between the denitrification rates obtained based on NO_3^--N reduction and N_2O-N production (e.g. Istok et al., 1997; Starr and Gillham, 1993). Schürmann et al. (2003) measured first-order denitrification rates (based on Haggerty et al., 1998) from reactants and products ($N_2 + N_2O$) using ^{15}N-labelled NO_3^- in push-pull tests. They also measured nitrite and ammonium concentrations, and conducted a mass balance based on recovery (relative) values and accounted for the portion of NO_3^- lost from products. They attributed unaccounted NO_3^- losses to other processes, such as abiotic NO_3^- consumption, DNRA (based on NH_4^+ increase; although this minor process was unlikely to affect the mass balance) and assimilatory NO_3^- reduction (from ^{15}N recovered in suspended biomass; although this was not quantified) based on ^{15}N isotope analyses. It seems, therefore, that without measuring all the other species of N in both water and sediment samples during the push-pull test (e.g., NO_3^--N, nitrite-N, ammonium-N, organic-N, N_2O—N, NO-N, N_2—N), the denitrification rate estimates remain indicative and not absolute in groundwater systems.

Nevertheless, given the complexity in ascertaining the complete inhibition of nitrous oxide reduction (Starr and Gillham, 1993) and uncertainties in capturing all the nitrous oxide produced in-situ in push-pull tests adopting the acetylene inhibition method (Groffman et al., 2006; Qin et al., 2012), the denitrification rate quantified based on the reactant (NO_3^--N) may provide a representative value of the denitrification characteristics of shallow groundwater. This is reasonable given that the limited number of studies that assessed possible processes influencing the reduction of nitrate in groundwaters do not indicate significant contribution from other NO_3^- attenuation processes (Starr and Gillham, 1993; Schürmann et al., 2003; Stenger et al., 2008; Jahangir et al., 2012a, 2012b; Clague et al., 2013).

3.5. *Comparison of denitrification rates obtained by zero-order and first-order kinetic models*

Denitrification rates are typically considered to be dependent on the substrate (NO_3^-) at low concentrations, approximating first-order kinetics, and independent on substrate at higher concentrations, approximating zero-order kinetics (Tesoriero and Puckett, 2011). While the first-order rate estimates may be adequate to describe the NO_3^- reduction processes in low concentrations (Burbery and Wang, 2010), studies have identified varying threshold concentrations where the transition from zero-order to first-order kinetics was observed to occur (Bowman and Focht, 1974; Knowles, 1982; Starr and Gillham, 1993; Yu et al., 2008). For instance, Tchobanoglous et al. (2014) stated that “the effect of the NO_3^- concentration on substrate utilisation rate is only at concentrations below 0.10 to 0.20 mg of NO_3 L^{-1}”, much lower than the threshold of 1.0 to 1.5 mg of NO_3 L^{-1} observed by Bowman and Focht (1974).

The differing threshold NO_3^- concentrations for the transition between zero-order and first-order kinetics could be because other factors influence the denitrification process. These include the availability of an electron donor and suitable denitrifier populations (Bekins et al., 1998; Bowman and Focht, 1974), not to mention the required low concentration of dissolved oxygen or anoxic conditions. These site-specific factors (denitrifier population, electron donor, dissolved oxygen, etc.) may be addressed by the use of a half-saturation constant as a location-specific parameter assuming no-growth Monod or Michaelis-Menten kinetics. “The half-saturation constant is the concentration of substrate at which the transformation rate is half the maximum value” (Bekins et al., 1998). First-order kinetics is considered in play when substrate concentration is much less than the half-saturation constant (Bekins et al., 1998). Bekins et al. (1998) and Counotte and Prins (1979) presented ways to estimate the half-saturation constant by assuming constant microbial biomass, justified considering the insignificant change observed in the microbial population even after prolonged exposure (Bekins et al., 1998).

However, this study attempted to estimate the half-saturation constant for the push-pull tests following the method of Counotte and Prins (1979), using the time-series NO_3^--N concentration data observed during the May 2014 push-pull test at the PNR site. A high half-saturation constant of 4.0 mg N L^{-1} was obtained using NO_3^--N concentrations uncorrected for dilution, whereas a negative value using the dilution-corrected NO_3^--N concentrations measured during the test. There are several reasons that could point out that the methods for estimating half-saturation constant (Counotte and Prins, 1979; Bekins et al., 1998) may not be directly applicable for the push-pull test data collected from an open system. The methods of Bekins et al. (1998) and Counotte and Prins (1979) for estimating half-saturation constant are basically based on closed-system incubation in which the decrease in substrate concentration was solely due to microbial activities. On the other hand, the NO_3^--N concentration data of the push-pull test are significantly influenced by the dilution of NO_3^--N in groundwater during the test. The use of NO_3^--N concentrations uncorrected for dilution would imply that the decrease in concentrations were due only to microbial activity and the effect of dilution being disregarded, hence would result to an erroneous half-saturation constant. On another hand, using the dilution-corrected NO_3^- concentrations would mean using high NO_3^--N concentrations in the estimation of a half-saturation constant. This misrepresents the actual conditions (low NO_3^- concentration at later stages of the test) that influence the microbial activity, and subsequently the estimation of half-saturation constant. Moreover, the increasing instantaneous zero-order denitrification rate with time observed in this study following Trudell et al. (1986) indicated higher denitrification rates measured at the later stage of all the tests when NO_3^- concentrations had already gone down (Tables 4 and 5; Figs. S3, S4, S7 and S8). This is contrary to the Michaelis-Menten or Monod model in which a reaction rate is expected to be higher at higher substrate concentration. This could be another reason that a reasonable half-saturation constant could not be estimated with the push-pull test data. Kruisdijk et al. (2022) also noted the Monod kinetic parameters (*Vmax*, the maximum rate constant, and *Ks*, the half-saturation concentration) could not be accurately determined from their push-pull tests data during an aquifer storage and recovery of drainage water from agricultural land in the North-Western part of the Netherlands. They noted “the measurements were unequally distributed over the pseudo zero- and first-order part, which resulted in an insufficient number of measurements for an accurate fit (Kruisdijk et al., 2022).” Further research is required in evaluating different approaches to estimate the Monod kinetic parameters (*Vmax* and *Ks*) from the push-pull test data. However, developing a method to estimate half-saturation constant in short-term push-pull test, where dilution influences concentrations of reactant and tracers is beyond the scope of this study.

Several authors have used other assessment methods such as residual some of squares (RSS) (Liao et al., 2012) and coefficient of determination (R^2) (Korom et al., 2005, 2012) to determine which model is more appropriate for their data. These performance statistics were determined for the denitrification rates estimated using the reactant only (Table 6), considering the outcome of comparison with results using the denitrification product (Section 3.4). However, no metrics could be estimated for the zero-order rates that were estimated using tangent lines to the curve using Trudell et al. (1986) (Zero-order 2 model) as the rates vary depending on the location of the tangent line. While zero-order models have larger RSS values than the first-order models (Table 6), this difference is immaterial and could not be used to compare between the two types of kinetic models because RSS is unit dependent and the units for zero-order and first-order models are not similar. Generally, comparable R^2 were obtained for all the models assessed, except for odd values in a couple of instances (e.g., the Zero-order 3 model, PNR site, Oct 13 [$R^2 = 0.03$]; the First-order 1 model, WDV site, Feb 15 [$R^2 = 0.329$]) (Table 6). Disregarding these two low R^2 values, the Zero-order 1 model gave R^2 values of 0.93–0.98 and 0.80–0.98 at the PNR and WDV sites, respectively; and the Zero-order 3 model gave R^2 of 0.82–0.90 and 0.73–0.91, respectively. The First-order 1 model gave R^2 of 0.73–0.85 and 0.94, at the PNR and WDV sites, respectively; and the First-order 2 and 3 models gave similar R^2 of 0.82–0.93 and 0.58–0.98, respectively. Thus, it appears that, based on these model performance metrics, the use of either zero-order or first-order kinetics appears reasonable to estimate the denitrification rate for using the push-pull test data. However, these established methods for estimating denitrification rates with zero-order or first-order kinetic models use different terms to account for the effect of dilution on NO_3^- concentrations in estimating the denitrification (NO_3^- reduction) rate (Table 2). Methods used to estimate zero-order rates used a dilution factor which is a ratio of tracer (e.g., bromide) concentration of the injection solution to the tracer concentration at time of measurement (Sanchez-Perez et al., 2003; Trudell et al., 1986). On the

Table 6

Comparison of different models assuming zero-order or first-order kinetics for the push-pull tests conducted at Massey No. 1 dairy farm, Palmerston North (PNR site) and at a sheep and beef farm near Woodville (WDV site) in the Manawatū catchment, New Zealand.

Approach/method	Residual sum of squares, RSS					Coefficient of determination, R^2				
	PNR site			WDV site		PNR site			WDV site	
	Oct 13	May 14	Jul 14	Feb 15	Aug 15	Oct 13	May 14	Jul 14	Feb 15	Aug 15
Reactant-based models										
Zero-order 1	0.6786	0.4753	0.1837	0.0221	0.0080	0.927	0.965	0.978	0.805	0.980
Zero-order 2*	–	–	–		–	–	–	–		
Zero-order 3	0.0704	0.0839	0.0207	0.0106	0.0060	0.030	0.903	0.824	0.726	0.906
First-order 1	0.0248	0.0341	0.0224	0.0005	0.0002	0.851	0.728	0.853	0.329	0.944
First-order 2	0.0163	0.0229	0.0113	0.0012	0.0127	0.902	0.817	0.926	0.576	0.977
First-order 3	0.0163	0.0229	0.0113	0.0004	0.0001	0.902	0.815	0.926	0.576	0.977

Note: *No performance statistics computed as the estimated rates were variable based on the tangent of the curve approximating the data; similarly with rates estimated using the denitrification product.

other hand, established methods for estimating first-order rates by Haggerty et al. (1998) used the ratio of the relative concentrations of NO_3^- (ratio of measured concentration with the injection solution concentration) and tracer (e.g., bromide). As a result of this difference in representing the ‘y’ component of the regression line, both zero-order or first-order kinetic models may yield satisfactory R^2 results for both kinetic models, as has been observed in other studies (Korom et al., 2012; Tesoriero and Puckett, 2011). However, use of either zero-order or first-order denitrification rates may have impact on assessment of NO_3^- transport and transformation in groundwater systems. Quantification of the effects of the denitrification rates based on either the reactant (NO_3^-N) or product (N_2ON), and the zero-order or first-order kinetics (Tables 4 and 5), such as in assessment of NO_3^- delivery from groundwater to receiving surface water, is beyond the scope of this study and a subject of further study.

4. Conclusions

The single-well, push-pull tests offered practical method to quantify denitrification rates in shallow groundwater at the study sites. The use of acetylene in the push-pull tests reinforced the evidence of denitrification by facilitating measurement of the denitrification product in the form of nitrous oxide (N_2O—N). Also, a comparison of N_2O-N concentrations measured during the push-pull test with acetylene (May 2014 test at the PNR site) and without acetylene (July 2014 test at the PNR site) indicates the potential of partial or complete denitrification in shallow groundwater as observed in the study.

However, the denitrification rates estimated based on the measurements of denitrification reactant (NO_3^- reduction) were quantified much higher (6 to 60 times) compared to the rates estimated based on the measurements of denitrification product (nitrous oxide production). These differences may be attributed to other nitrogen transformation processes such as dissimilatory NO_3^- reduction to ammonium (DNRA), assimilatory NO_3^- reduction, and/or incomplete inhibition of nitrous oxide reduction by addition of acetylene during the tests. It seems, therefore, that without measuring all the other species of N in both water and sediment samples during the push-pull test (e.g., NO_3^--N, nitrite-N, ammonium-N, organic-N, N_2O—N, NO-N, N_2—N), the denitrification rate estimates remain indicative and not absolute values in groundwater systems. Nevertheless, given that previous studies that attempted to measure the other species of N during a test found that other processes mentioned above are not significant compared to the reduction by the denitrification process, the denitrification rate quantified on the basis of the reactant (NO_3^- reduction) may provide representative value of denitrification characteristics of shallow groundwater.

This study attempted to resolve the question on which kinetic model (zero- or first-order) should be used in estimating denitrification rates from the push-pull test data, but the results obtained appear short of providing definitive answers. However, a statistical comparison calculating as residual some of squares (RSS) and coefficient of determination (R^2) of the denitrification data of the five push-pull tests conducted at the two study sites in this study showed that either a zero-order or a first-order model may be valid for quantification of denitrification in shallow groundwater using the push-pull tests. However, a choice of application of different zero-order and first-order models resulted into a range of denitrification rate values based the push-pull test data. Application of four zero-order kinetic models quantified the zero-order denitrification rates at 0.42–1.07 mg N L^{-1} h^{-1} and 0.05–0.12 mg N L^{-1} h^{-1} at the Palmerston North (PNR) and Woodville (WDV) sites, respectively. Application of three first-order kinetic models, the first-order denitrification rates were quantified at 0.03–0.09 h^{-1} and 0.002–0.012 h^{-1} at the PNR and WDV sites, respectively. This variability in quantification of denitrification rates may have implications in the representation of spatial and temporal variability of denitrification characteristics of the shallow groundwater system, including in groundwater simulation models of nitrate transport and attenuation to receiving surface waters. This uncertainty and variability in denitrification rates estimated by zero-order or first-order kinetics models and push-pull tests conducted at different spatial and temporal scales needs further research to inform appropriate scale of denitrification rate measurements and simulation of nitrate transport and transformation processes in shallow groundwater systems.

CRediT authorship contribution statement

Aldrin Rivas: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ranvir Singh:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **David Horne:** Writing – review & editing, Supervision, Conceptualization. **Jonathan Roygard:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Abby Matthews:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Michael Hedley:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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