

THE EFFECT OF SOIL TYPE AND SLOPE ON THE DISSOLVED ORGANIC CARBON CONCENTRATION AND DENITRIFICATION CAPACITY OF A HILL COUNTRY SUB-CATCHMENT

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Abstract

Characterising the dissolved organic carbon (DOC) concentration and denitrification capacity of the varying soils and slopes in hill country is important in order to manage the leaching and availability of nitrate in ground and surface waters.

There is a pressing need to assess soil types (soil series) and slopes within a farm or catchment, in terms of their denitrification capacity, as this knowledge will allow more accurate and equitable allocation of nitrogen (N) loss restrictions, should they apply to hill country in the future.

This study investigated the DOC concentration and denitrification capacity of the soils and slope classes of a sub-catchment within a hill country farm, located in Palmerston North, New Zealand. Fifty locations comprising of 2 soil orders (Pallic, Brown), 8 soil types (grouped into 3 drainage classes) and 3 slope classes were sampled from different soil depths down to 1 m.

The results suggest that compared to slope, soil type may have a greater effect on denitrification within the sub-catchment. The soil with the highest DOC concentration and moisture content (Ramiha soil) had the highest denitrification capacity. This soil had andic soil properties and thus a higher soil organic carbon (C) content compared to the other soil types. This suggests that farms and catchments with this specific soil type may have a greater capacity to attenuate N losses to the environment.

Introduction

The contrasting micro-topographical units within hill country landscapes lead to spatial variability in the distribution of nitrate within hill country. Although nitrate accumulation generally occurs at lower slope regions, due to animal grazing and resting habits (Bowatte, 2003; Crofoot *et al.*, 2010; Hickson *et al.*, 2016), the denitrification capacity of the specific soils within this region determines the amount of nitrate leached to groundwater.

In most cases, well-drained soils have a greater tendency to leach more nitrate compared to poorly-drained soils, while poorly-drained soils tend to have a higher denitrification capacity, mainly due to the abundance of oxygen-limiting conditions (high soil moisture). When soils

with varying drainage capability occur on a particular micro-topographical unit/region, there will be spatial variability in the denitrification capacity within that region. Understanding how the interaction between slope and drainage affect denitrification and therefore the leaching and availability of nitrate, will assist regulators to accurately assess hill country landscapes in terms of their capacity to attenuate nitrogen (N) and limit the contamination of water bodies.

Previous studies on denitrification have shown that the availability of dissolve organic carbon (DOC) is an important factor that limits denitrification below the surface soil (Yeomans *et al.*, 1992; McCarty and Bremner, 1993; Jahangir *et al.*, 2012). Knowledge of the DOC concentration of the various soil and slope combinations in hill country landscapes will help in the prediction of their denitrification capacity, which in turn will help in effective nutrient management for improved water quality.

Although a number of New Zealand studies have examined the effect of slope and soil drainage on denitrification in hill country landscapes, these studies have focussed on either nitrous oxide (N₂O) emissions from the top soil, i.e. ≤ 30 cm depth, or the study of hill country denitrification from a regional and national perspective (Hoogendoorn *et al.*, 2011; Luo *et al.*, 2013; Saggar *et al.*, 2015). Information on subsurface denitrification in hill country as affected by soil type and slope is therefore absent, to the best of our knowledge. Thus, this study was designed to investigate the effect of soil type (drainage) and slope on DOC concentration and denitrification capacity of surface and subsurface soils in a hill country sub-catchment. It adopts a farm-specific approach to take into account the spatial variability that exists within a farm, for effective nitrate and water quality management at the farm level.

Materials and methods

Site description

The study took place at Massey University's Agricultural Experiment Station, Tuapaka, which is a sheep and beef cattle farm located about 15 km north-west of Palmerston North, lower North Island, New Zealand (40°21'20.1"S, 175°44'19.6"E). The farm has a humid temperate climate with an annual average rainfall of 1100 mm, and predominantly dry summers (Massey University, 2016) . It is about 470 ha in size and comprises of relatively flat areas at lower elevations (50-100 m), to hilly and steep slopes at higher elevations (360 m) (Hedley *et al.*, 2014). Nine different soil types (soil series) and some variants of these series are present on the farm; these soils have been described by Pollok and McLaughlin (1986).

Experimental design and sample collection

A previous experiment on Tuapaka farm (Hedley *et al.*, 2014) investigated the total carbon (C) content of 50 locations, from lowest to highest elevation, within a sub-catchment in the farm. In the present study, which took place during spring (November 2016), these 50 locations were resampled at 3 soil depths (0-30, 30-60, 60-100 cm), using a soil core of ca. 4 cm in diameter. The soil samples were kept cool, transported to the laboratory and stored below 4°C for subsequent analyses.

Eight different soil types belonging to 2 soil orders (Pallic, Brown) were within the sampled sub-catchment, and these soils were distributed across 3 slope classes as described by Hoogendoorn *et al.* (2011), i.e. low (1-12°), medium (12-25°) and high (> 25°) slopes

(Figure 1). The soil types were grouped into 3 soil drainage classes, i.e. poorly-drained, imperfectly-drained and well-drained. A combination of the soil drainage and slope classes gave rise to 5 treatments as follows: Poor/Low, Imperfect/Medium, Imperfect/High, Well/Medium and Well/High (Table 1). The soil parent materials are briefly described in Table 2.

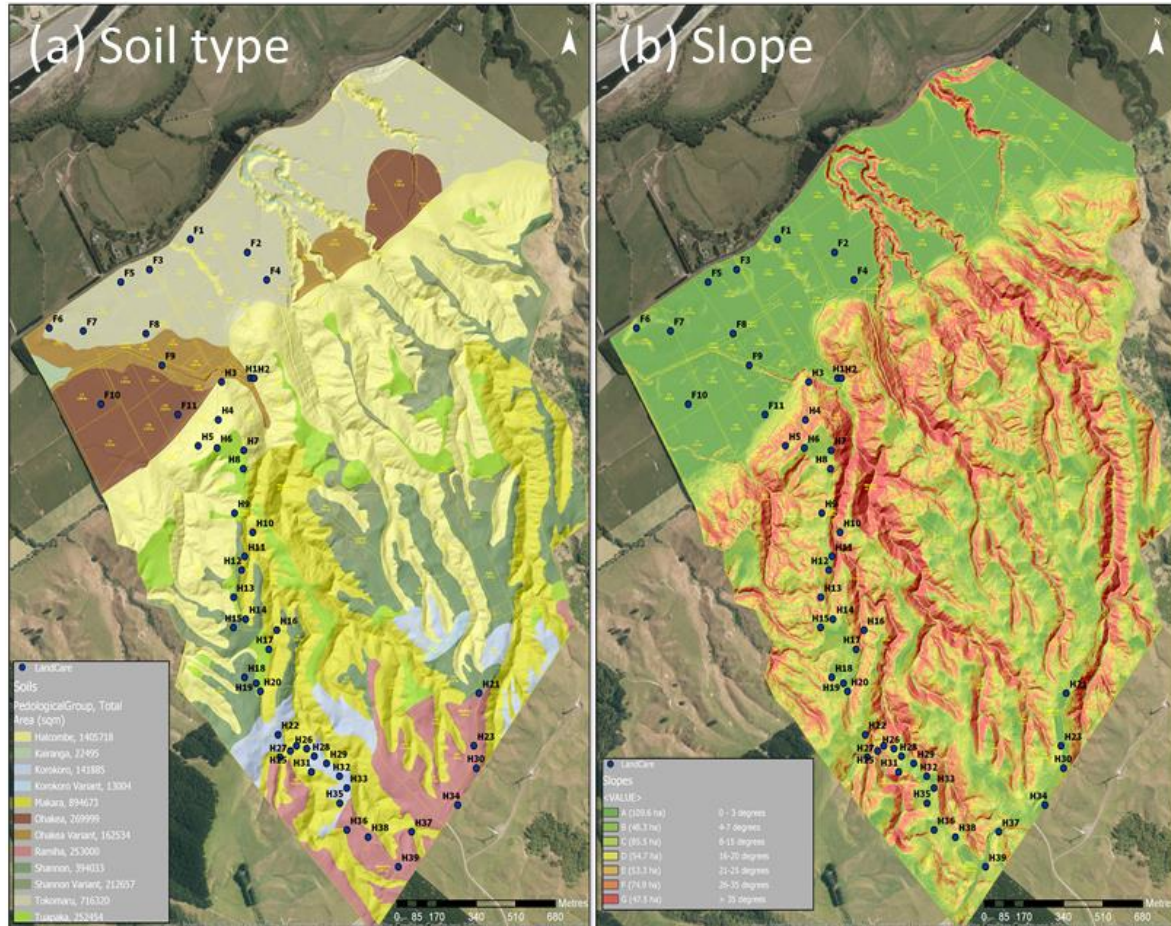


Figure 1: Maps showing the different soil types and slopes within the sampled sub-catchment. Blue dots represent the sampled locations.

Table 1: Soil drainage and slope classes of the sub-catchment

Soil name	Number of observations (n)	Soil drainage Class	Slope Class	Treatment
Tokomaru	8	Poorly-drained	Low	Poor/Low
Ohakea	3	Poorly-drained	Low	Poor/Low
Shannon	2	Imperfectly-drained	Medium	Imperfect/Medium
Tuapaka	8	Imperfectly-drained	Medium	Imperfect/Medium
Halcombe	5	Imperfectly-drained	High	Imperfect/High
Korokoro	5	Well-drained	Medium	Well/Medium
Ramiha	7	Well-drained	Medium	Well/Medium
Makara	12	Well-drained	High	Well/High

Slope class = Low: 1-12°; Medium: 12-25°; High: > 25°

Table 2: Brief description of soil parent material

Soil name	New Zealand soil order	Soil description (Pollok and McLaughlin, 1986)
*Tokomaru	Pallic soil	The soil is formed from loess, sometimes with the addition of loessial and sandy materials that contain the Aokautere Ash, at depth. It is characterised by medium textured topsoil. It possesses a fragipan, or compacted horizon, at depth. A thick, highly mottled, fine-textured subsoil lies above the fragipan.
*Ohakea	Pallic soil	This soil is formed from loess interbedded with lenses of redeposited loessial material, sand and gravel that lacks the Aokautere Ash.
Shannon	Pallic soil	It is formed from loess overlying marine sand. The profile lacks a morphologically distinct eluvial horizon and possesses mottled subsoil.
Tuapaka	Pallic soil	It is formed from loess overlying marine sands and gravels. It is characterised by a morphologically distinct eluvial horizon, with strongly mottled subsoil, commonly with clay skins.
Halcombe	Pallic soil	The soil is formed from a variety of parent materials. The primary parent material is loess, with deposits of underlying sand, conglomerate and tephra. It is characterised by generally mottled subsoil.
Korokoro	Brown soil	This soil is formed from loess (< 1 m thick) overlying greywacke bedrock. Its subsoil gives a weak to moderate positive response to the field test for allophane, indicating the presence of volcanic ash in the loess that overlies the greywacke base.
Ramiha	Brown soil	It is formed from a mixture of loess and volcanic ash. It contains allophane as the principal clay mineral.
Makara	Brown soil	This soil is formed essentially out of greywacke.

*These soils are located on flat topography and receive higher rates of lime and fertiliser compared to the other soils within the farm.

Laboratory analyses

DOC concentration

Ten grams of fresh soil sample was extracted with 25 mL deionised water (1:2.5 v/v) at room temperature by shaking in a 50 mL extraction tube, on a rotatory shaker for 1 h. The agitated sample was subsequently centrifuged at 5000 rpm for 10 min and filtered with Whatman No. 41 filter paper. Thereafter, the filtered sample was centrifuged at 5000 rpm for 2 h (this second centrifugation separated more particulate organic matter than a 0.22 and 0.45 μm filter, on a sub-set of 10 samples). The centrifuged sample was decanted and analysed for DOC concentration.

The concentration of DOC in the extract was determined by the dichromate semi-automated method described by O'Dell (1993), with some modification as follows: 10 mL of the extract was pipetted into a 100 mL digestion tube to which 2 grains of anti-bumping granules, 1.5 mL of digestion solution (5.1 g $\text{K}_2\text{Cr}_2\text{O}_7$ + 84 mL conc. H_2SO_4 + 16.7 g HgSO_4 + 500 mL deionised water) and 10 mL of catalyst solution (5 g AgSO_4 + 500 mL conc. H_2SO_4) were added consecutively. The solution was mixed with a vortex mixer, covered with a glass funnel and placed on a thermostatically controlled (150°C) digestion block for 2 h. After digestion, the solution was allowed to cool at room temperature, made up to 25 mL with deionized water and mixed with a vortex mixer. The absorbance of the sample solution was read at a wavelength of 420 nm with a Philips PU 8625 UV/VIS spectrophotometer (Biolab Scientific Ltd.) and DOC concentration was obtained by plotting a calibration curve, using potassium hydrogen phthalate (KHP) as a standard.

Denitrification capacity

Denitrification enzyme activity (DEA) was used to determine the denitrification capacity of the soil. This was carried out via the acetylene inhibition method, while using the vacuum pouch technique described by Rivas *et al.* (2014). In brief, this analysis was performed as follows: twenty grams of fresh soil (dry weight equivalent) was weighed into a polyethylene pouch (10 x 28.5 cm) fitted with a luer-lock valve. The pouch was heat sealed and subsequently vacuumed with a syringe via the luer-lock valve. The vacuumed pouch was then flushed with 50 mL of dinitrogen (N_2). Thereafter, 20 mL of acetylene, 20 mL of DEA solution (containing 50 μg NO_3^- -N g^{-1} dry soil and 10 ppm chloramphenicol) and 180 mL of N_2 were consecutively placed inside the pouch via the luer-lock valve. The pouch/sample was incubated in the dark at 20°C, on a rotary shaker (160 rpm). Gas samples (25 mL) were collected from the pouch at two hour intervals, i.e. 0 (initial gas sample before incubation), 2, 4 and 6 h of incubation. The gas sample was compressed into a 12 mL vac-vial for subsequent nitrous oxide (N_2O) analysis via the Shimadzu Gas Chromatograph (GC) machine. After this analysis, the denitrification capacity of the soil was calculated from the slope of N_2O concentration and incubation time, divided by the mass of dry soil.

Properties of water-extracted soil

Nitrate concentration in the extracts was determined by continuous flow analysis (Technicon® AutoAnalyser II). Ammonium concentrations were negligible (< 0.1 mg kg^{-1}) and hence were not reported. The pH of the extract was read with a table-top standard pH meter (Meter Lab®) and the concentrations of dissolved aluminium (Al), iron (Fe) and manganese (Mn) were read with a 4200 Microwave Plasma-Atomic Emission Spectrometer – MP-AES (Agilent Technologies).

Selected soil chemical properties

Soil samples were analysed for their total C and N concentrations using the elemental® (vario MICRO cube). In order to have a better understanding of the properties of the soil types, sodium pyrophosphate and acid ammonium oxalate extractions/analyses were also performed as described Blakemore *et al.* (1987). The gravimetric soil moisture content was also determined and hence nutrient concentrations were corrected to oven-dry soil basis.

Statistical analyses

Analysis of Variance (ANOVA) with Tukey comparison procedure ($p = 0.05$) was used to detect for differences between treatment means. The relationship between denitrification capacity and other measured soil/water-extract parameters was determined with the Pearson correlation technique; and multiple regression analysis with the best subsets option was used to identify the best predictors of the denitrification capacity of the soil. All analyses were carried out with Minitab statistical software (17.2.1 Minitab, Inc.).

Results

Description of soil chemical properties

Compared to the other soils, Tokomaru and Ohakea (Poor/Low, i.e. poorly-drained soils at low slopes) had the lowest total C concentration (17 g kg^{-1} at the surface 30 cm) (Table 3). These soils also had the highest pH (6.1-7.1 at the surface soil). Conversely, Ramiha soil (Well/Medium) had the highest total C concentration (55 g kg^{-1} at the surface 30 cm), consistent with its andic properties ($\text{Al}_o + \frac{1}{2}\text{Fe}_o > 10 \text{ g kg}^{-1}$ in the top 60 cm of the soil profile). As expected, total C, N and exchangeable C (sodium pyrophosphate-extractable C, C_p) decreased with soil depth, with C_p generally being 1/3 of total C in the surface 30 cm of the soils.

Table 3: Selected soil chemical properties

Soil name	Soil depth (cm)	pH	Total C (g kg ⁻¹)	Total N (g kg ⁻¹)	C _p (g kg ⁻¹)	Al _p (g kg ⁻¹)	Fe _p (g kg ⁻¹)	Al _o (g kg ⁻¹)	Fe _o (g kg ⁻¹)	Si _o (g kg ⁻¹)	Total C/Total N	C _p /Total C	Al _p /Al _o	Al _o +1/2Fe _o (g kg ⁻¹)
Tokomaru	0-30	7.10	17.3	1.82	5.56	0.95	2.75	1.62	2.39	1.25	9.51	0.32	0.59	2.82
	30-60	6.86	3.3	0.65	1.72	0.66	1.72	2.00	3.19	0.66	5.08	0.52	0.33	3.60
	60-100	6.73	1.1	0.47	0.95	0.57	1.30	2.32	2.54	3.68	2.34	0.86	0.25	3.59
Ohakea	0-30	6.07	16.7	1.53	5.58	0.78	3.13	1.80	5.23	2.17	10.92	0.33	0.43	4.42
	30-60	6.08	5.2	0.69	2.34	0.53	3.80	1.78	4.78	1.32	7.54	0.45	0.30	4.17
	60-100	5.99	1.0	0.24	0.84	0.55	1.94	1.26	3.85	3.58	4.17	0.84	0.44	3.19
Shannon	0-30	4.63	29.3	2.50	8.45	1.49	5.35	2.33	3.66	0.09	11.72	0.29	0.64	4.16
	30-60	4.49	8.5	1.20	3.11	1.11	3.97	3.24	3.79	0.67	7.08	0.37	0.34	5.14
	60-100	4.35	3.4	0.99	1.38	3.31	1.75	3.04	1.77	0.89	3.43	0.41	1.09	3.93
Tuapaka	0-30	5.29	27.2	2.88	7.87	1.38	4.80	2.34	4.00	1.03	9.44	0.29	0.59	4.34
	30-60	5.26	6.9	1.38	1.91	0.70	2.96	2.12	3.23	2.56	5.00	0.28	0.33	3.74
	60-100	5.01	3.7	1.04	1.18	0.78	1.37	2.81	2.52	2.96	3.56	0.32	0.28	4.07
Halcombe	0-30	5.84	19.9	1.96	5.81	0.60	2.14	1.58	5.41	1.58	10.15	0.29	0.38	4.29
	30-60	5.95	6.7	1.23	2.01	0.68	3.34	2.32	3.54	0.77	5.45	0.30	0.29	4.09
	60-100	5.85	3.5	0.82	1.40	1.04	2.50	2.40	2.30	1.77	4.27	0.40	0.43	3.55
Korokoro	0-30	5.09	25.3	2.59	11.79	1.60	8.83	2.41	3.64	1.56	9.77	0.47	0.66	4.23
	30-60	5.02	11.0	1.43	5.90	1.71	8.97	4.97	3.66	3.03	7.69	0.54	0.34	6.80
	60-100	5.00	4.5	1.01	2.82	2.18	6.24	5.14	2.87	3.91	4.46	0.63	0.42	6.58
Ramiha	0-30	5.07	54.6	4.83	14.22	6.67	7.74	8.17	7.63	1.87	11.30	0.26	0.82	11.99
	30-60	4.89	24.3	2.47	12.12	5.36	8.17	8.54	8.86	0.60	9.84	0.50	0.29	12.97
	60-100	5.18	6.3	1.20	3.36	2.00	4.08	5.61	8.56	6.39	5.25	0.53	0.36	9.89
Makara	0-30	5.71	24.4	2.28	8.64	2.05	6.47	2.92	3.48	1.58	10.70	0.35	0.70	4.66
	30-60	5.53	8.5	1.29	3.49	1.72	5.55	3.83	4.33	1.53	6.59	0.41	0.45	6.00
	60-100	5.42	3.3	0.97	2.04	1.33	4.21	2.44	2.07	2.23	3.40	0.62	0.55	3.48

Subscript p: sodium pyrophosphate extracts; subscript o: acid ammonium oxalate extracts; values for Al_p/Al_o are molar ratios.

Variations in DOC concentration

The DOC concentrations of the treatments generally decreased with increasing soil depth (Figure 2). These concentrations were similar in the surface 30 cm of the soil. Further down the profile (30-60 cm), however, the Well/Medium treatment had significantly ($p \leq 0.05$) higher DOC than all other treatments. A similar trend was observed within 60-100 cm soil depth, where the Poor/Low treatment had significantly ($p \leq 0.05$) lower DOC concentration compared to the other treatments.

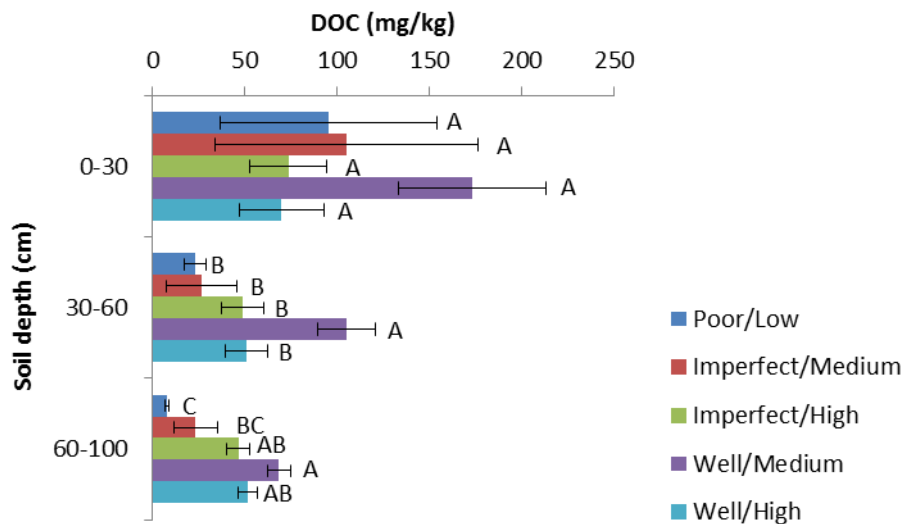


Figure 2: Variations in DOC concentration as influenced by soil drainage and slope classes. Different letters denote significant difference within treatments, for a particular soil depth ($p \leq 0.05$). Error bars are standard error of the mean.

Variations in denitrification capacity

There was > 50% greater denitrification in the surface 30 cm of the soil compared to other soil depths (Figure 3). However, significant ($p \leq 0.05$) differences in denitrification capacity were only observed within 30-60 cm of the soil profile, with higher denitrification occurring in the Well/Medium treatment compared to the Imperfect/Medium and Well/High treatments.

When soil type and slope were considered separately (Figure 4), the Ramiha soil had significantly ($p \leq 0.05$) higher denitrification compared to the other soil types, in the surface 60 cm of the soil profile. No significant differences within slope classes were observed at this soil depth.

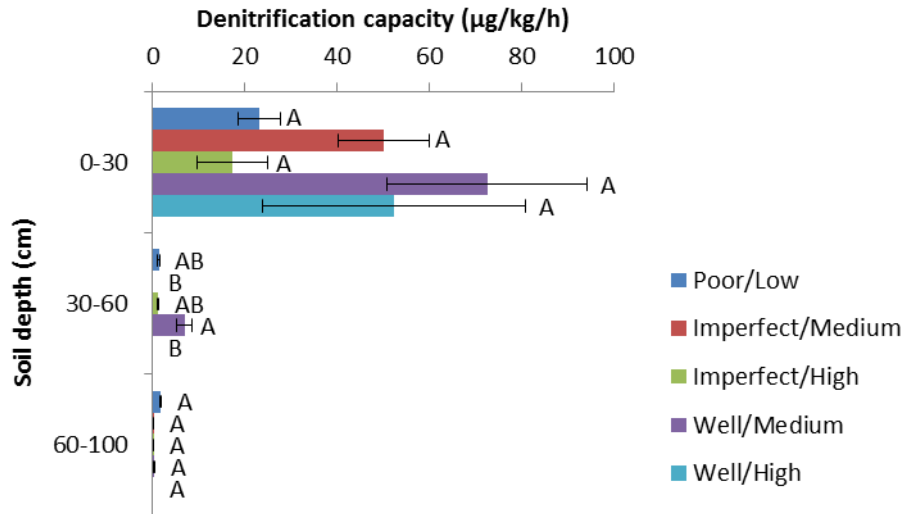


Figure 3: Variations in denitrification capacity as influenced by soil drainage and slope classes. Different letters denote significant difference within treatments, for a particular soil depth ($p \leq 0.05$). Error bars are standard error of the mean.

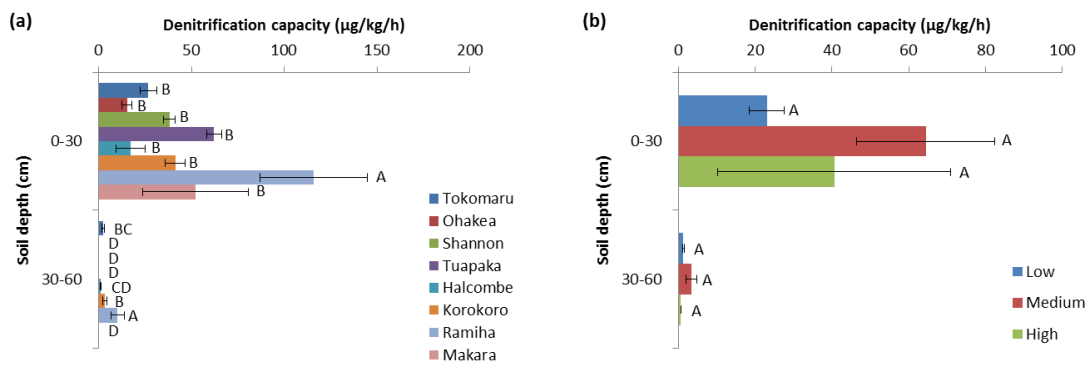


Figure 4: Denitrification capacity of the (a) soil types and (b) slope classes. Different letters denote significant difference within soil types/slope classes, for a particular soil depth ($p \leq 0.05$). Error bars are standard error of the mean.

Variations in soil moisture content

There were no significant ($p \leq 0.05$) differences in the soil moisture content of the treatments at the surface 30 cm of the soil (Figure 5). Further down the profile (30-60 cm), however, the moisture content of the Well/Medium treatment was significantly higher than that of the other treatments.

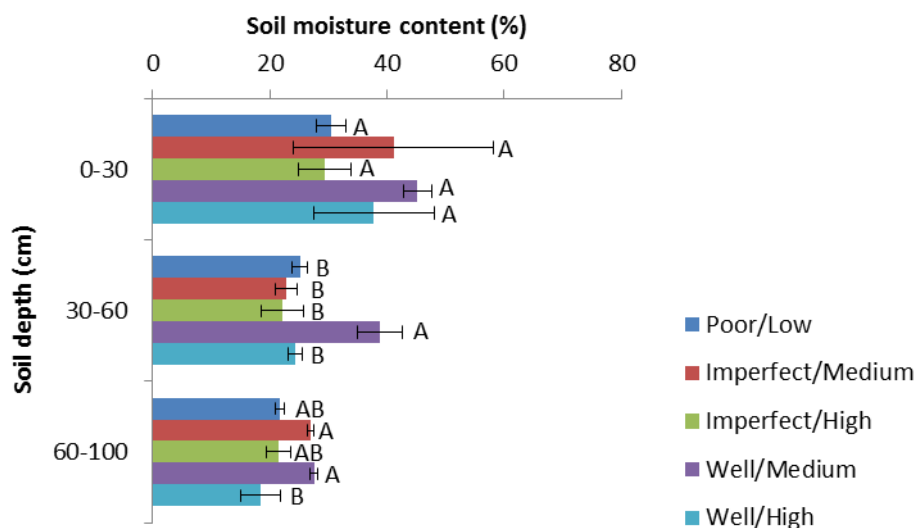


Figure 5: Variations in gravimetric soil moisture content as influenced by soil drainage and slope classes. Different letters denote significant difference within treatments, for a particular soil depth ($p \leq 0.05$). Error bars are standard error of the mean.

Relationship between denitrification capacity and soil parameters

Significant positive correlation existed between denitrification capacity and the following parameters: soil moisture content, DOC and dissolved Mn (Table 4). Compared to the other parameters, soil moisture had the strongest relationship ($r = 0.86$; p -value = 0.000) with denitrification capacity. There was scarcely any correlation between denitrification capacity and pH, though a positive trend was observed. Negative and non-significant ($p \leq 0.05$) correlations existed between denitrification capacity and three other parameters, i.e. nitrate, dissolved Al and Fe. Multiple regression analysis with the best subsets option showed that soil moisture content and DOC were the best predictors of the denitrification capacity of the soil (adjusted $R^2 = 74\%$; p -value = 0.000).

Table 4: Correlation and regression values between denitrification capacity and soil properties

	Soil moisture content	DOC	pH	Nitrate	Dissolved Al	Dissolved Fe	Dissolved Mn
Correlation results							
<i>r</i>	0.863	0.591	0.082	-0.107	-0.136	-0.167	0.440
<i>p</i> -value	0.000	0.003	0.709	0.626	0.537	0.445	0.036
Regression equation:	Denitrification capacity = $-60.5 + 2.4 \text{soil moisture content} + 0.1 \text{DOC}$ (adjusted $R^2 = 74\%$; p -value = 0.000)						

n = 23

Discussion

The soil type and slope of the sampled sub-catchment are intricately linked (i.e. specific soil types occur on specific slope, e.g. Tokomaru soil occurred only on low slope), hence the effect of slope on denitrification was masked in this study, as evidenced by the absence of significant differences in the denitrification capacity of the slope classes. On the other hand, the effect of soil type on denitrification was dominant, mostly due to the soil parent material/composition and not the drainage class *per se*. For instance, a number of studies have reported higher denitrification occurring on poorly-drained soils compared to well-drained soils primarily due to higher moisture retention in the poorly-drained soils which creates anoxic conditions that favour denitrifiers (Gambrell *et al.*, 1975; Schnabel and Stout, 1994; Morales *et al.*, 2015). In the present study, however, higher denitrification occurred in the well-drained soils (Well/Medium treatment only) compared to the poorly-drained soils. This is mainly because the Well/Medium treatment contained the Ramiha soil which has a high content of short-range order constituents such as allophane and thus a higher capacity to store C (Dahlgren *et al.*, 2004). The total C (and to some extent the DOC) of the Ramiha soil was 2-3 times higher than that of the other soil types (Table 3). This explains why it had a higher denitrification capacity compared to the other soil types. It should be noted that nitrate concentrations of this soil at depth were not significantly larger than those in the other soils studied (data not shown). Overall, the results obtained imply that the Ramiha soil plays an important ecosystem function in terms of nitrate attenuation in landscapes and this should be taken into account when making N loss restrictions for hill country farms.

Soil sampling was carried out during spring, i.e. when most soils were wet, hence the absence of significant differences in soil moisture within the surface 30 cm of the soil. However, multiple regression analysis showed that soil moisture content was a good predictor of the soil denitrification capacity in this study. This relationship between soil moisture and denitrification highlights the important influence wetlands (which are prevalent in hill country farms) could have on nitrate attenuation within hill country landscapes and therefore calls for further research to improve understanding of the contribution of wetlands (soil moisture) to denitrification within hill country farms.

The denitrification rates obtained in the current study are lower than those obtained in a similar study (no added C source in DEA assay) on a New Zealand dairy farm (Luo *et al.*, 1998). This is mainly because dairy farms are more intensively managed, and thus, contain more substrate for denitrification compared to hill country farms. Comparing the present study with most other New Zealand pastoral studies (on both hill country and dairy farms) would be misleading since most of these studies involved the addition of an artificial C source in the DEA assay (Jha *et al.*, 2012; Bishop *et al.*, 2014; Rivas *et al.*, 2014). However the notable reduction in denitrification with increasing soil depth obtained in this study, compares well with the findings of these New Zealand studies.

Conclusion

Greater denitrification occurred in the Well/Medium treatment mainly due to its higher DOC concentration (and moisture content) resulting from the presence of Ramiha soil. This soil had the highest soil organic C concentrations, which is associated with the presence of short-range order constituents. Since nitrate concentrations at depth in Ramiha soil were not larger than those of the other soils, it can be deduced that this soil could play an important role in nitrate attenuation in farms where they occur and thus should be accounted for if N loss restrictions are introduced for hill country landscapes.

Acknowledgements

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