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NITRATE ATTENUATION CAPACITY OF A HILL COUNTRY SEEPAGE WETLAND AND ADJACENT DRY AREAS AS INFLUENCED BY THE CONCENTRATION AND CHEMISTRY OF DISSOLVED ORGANIC CARBON

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Abstract

Naturally occurring seepage wetlands in hill country agricultural landscapes have the potential to reduce nitrate leaching through denitrification. However, the effect of dissolved organic carbon (DOC) concentration and chemistry on the denitrification capacity of these seepage wetlands relative to adjacent dry areas in the landscape have not yet been assessed. This study investigated the denitrification capacity, and DOC concentration and chemistry, of a seepage wetland and adjacent dry areas within a hill country paddock located near Palmerston North, New Zealand. Soil samples were collected in November 2017 from different soil depths down to 100 cm. The results showed that the denitrification capacity of the seepage wetland within the 0-30 and 30-60 cm depths was 7 and 69 times greater, respectively, than that of the adjacent dry areas. The DOC concentration of the seepage wetland was 4-5 times greater than that of the dry areas within the surface 60 cm soil depth. This higher DOC concentration and the presence of readily-decomposable (lower molecular weight) DOC in the seepage wetland contributed to its higher denitrification capacity. The contrasting nitrate attenuation capacities of the hill country seepage wetland versus that of dry areas highlights the potentially important contribution of seepage wetlands to attenuate nitrate and thus improve water quality. It also suggests that contrasting management practices (such as maintaining/enhancing DOC levels) are required for these distinct landscape features, if nitrogen loss restrictions are imposed on hill country farms in the future.

Introduction

Pastoral seepage wetlands are flat and boggy areas (usually < 5000 m^2) that are often located close to streams. They are comprised of unconsolidated soils, and because they are usually grazed by farm animals, they are sometimes drained by farmers to reduce the risk of animals becoming mired (Tanner *et al.*, 2015). Seepage wetlands have the capacity to reduce more than 75% of nitrate losses to water bodies (Rutherford *et al.*, 2018). Thus, they help to improve water quality in agricultural catchments.

Denitrification is an important nitrate attenuation process in seepage wetlands. It is strongly influenced by the concentration of dissolved organic carbon (DOC) (Peterson *et al.*, 2013). However, the contribution of DOC to denitrification in New Zealand hill country seepage wetlands is yet to be investigated. In addition, comparisons between the denitrification capacity of seepage wetlands and adjacent dry areas within hill country farms are absent in literature. Such assessments are necessary as they could provide information needed to account for and enhance the nitrate attenuation capacity of seepage wetlands, which will ultimately result in improved water quality management in hill country landscapes. This will also provide hill country farmers with a flexible management response to regional council nutrient regulations.

The objectives of this study were to: (i) compare the DOC concentration of a hill country seepage wetland to that of adjacent dry area soils; and (ii) determine the differences in the denitrification capacities of these contrasting landscape features, and relate the differences (if any) to DOC and other soil properties.

Materials and methods

Study site

The experiment was carried out at Massey University's Agricultural Experiment Station, Tuapaka, a sheep and beef cattle hill country farm located near Palmerston North, New Zealand (40°21'20.1"S, 175°44'19.6"E). Research activity was confined to one paddock in the farm (Figure 1), which comprised of three dry area soils, namely Korokoro, Makara and Ramiha, all classified as Brown soils. The seepage wetland within the paddock is dominated by a Gley soil developed from a colluvium of the Makara soil and an alluvium of the Ramiha/Korokoro soils.

Vegetation in the paddock is primarily browntop (*Agrostis capillaries* L.) and perennial ryegrass (*Lolium perenne* L.), with rushes (*Juncus edgariae* L.) occurring in the seepage wetland.

Sampling strategy

Three sites were sampled for each soil type (Figure 1). Six and twelve replicate soil cores were sampled from each seepage wetland and dry area site, respectively. Soil was sampled from depths of 0-30, 30-60 and 60-100 cm. Soil sampling was carried out in November 2017.

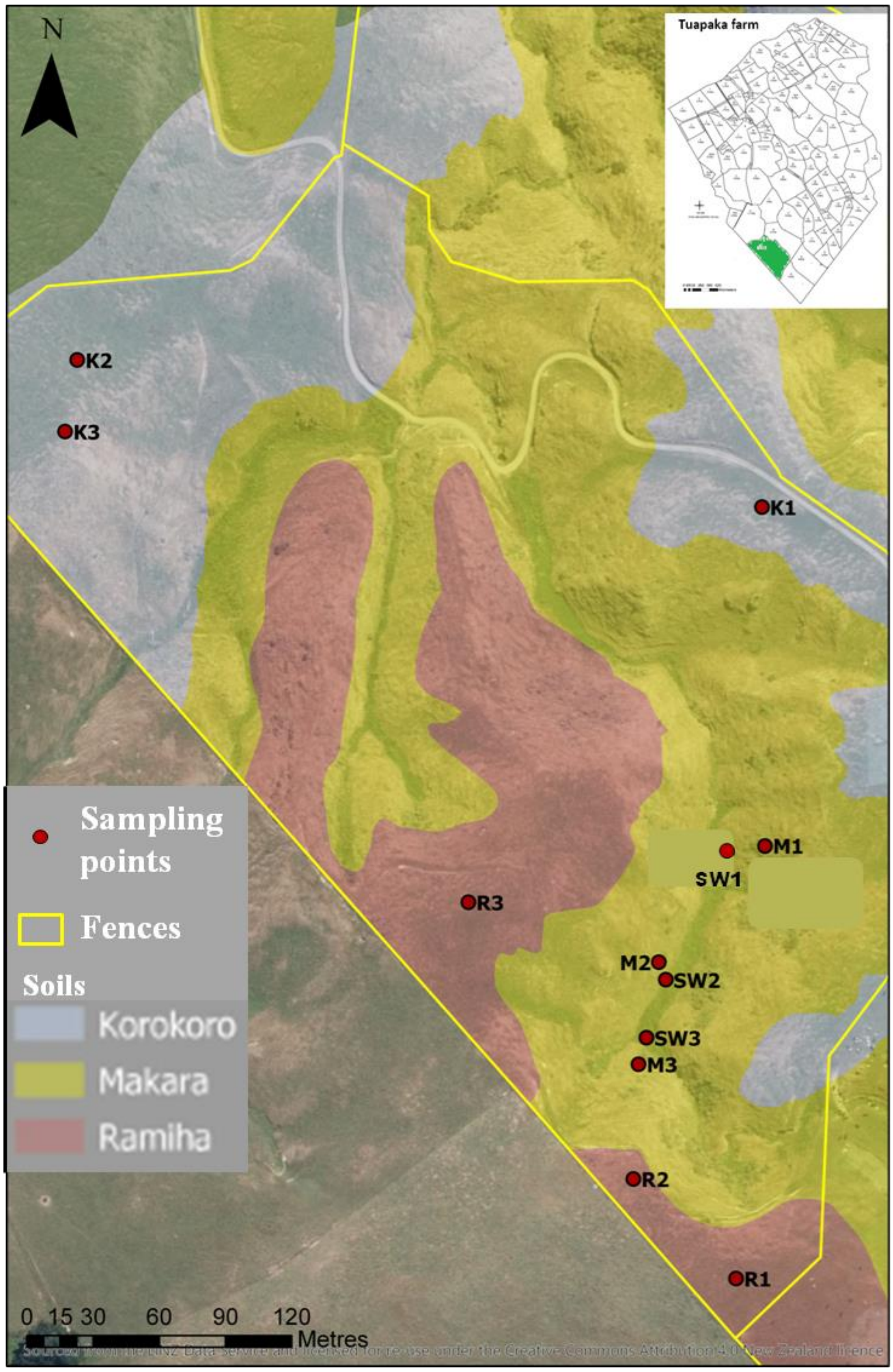

Figure 1. Map of sampled paddock within Tuapaka farm and associated soil types. *K: Korokoro dry area; M: Makara dry area; R: Ramiha dry area; SW: seepage wetland. Numbers represent the different sites for the seepage wetland and each dry area soil.*

Soil analyses

DOC in the soil sample was extracted with deionised water (1:2.5 wt/v). After extraction, DOC concentration was determined with the TOC analyser (Shimadzu TOC-L). DOC chemistry was determined via the sUVa index (absorbance measured at 254 nm divided by DOC concentration in mg L^{-1}), the E2/E3 index (ratio of absorbance measured at 250 nm and

365 nm), and the E4/E6 index (ratio of absorbance measured at 465 nm and 665 nm). Denitrification capacity was determined by measuring the denitrification enzyme activity as reported by Chibuike *et al.* (2019).

Statistical analyses

Analysis of Variance (ANOVA) with Tukey comparison procedure was performed on measured parameters to detect significant differences in treatment means. The Pearson correlation technique was used to compare the relationship between denitrification capacity and other soil properties. All statistical analyses were performed with Minitab software (17.2.1 Minitab, Inc.).

Results and discussion

DOC concentration of the seepage wetland and dry area soils

The seepage wetland soil had significantly ($p \leq 0.05$) higher DOC concentration compared to the dry area soils (Figure 2). “Between site” DOC variability, in the surface 30 cm soil depth, was higher in the seepage wetland (CV > 50%) compared to the dry areas (CV ≤ 21%). This higher DOC variability in the seepage wetland was attributed to the differences in soil moisture content of the three sites, and spatial variation in the deposition of dung and urine across the sites.

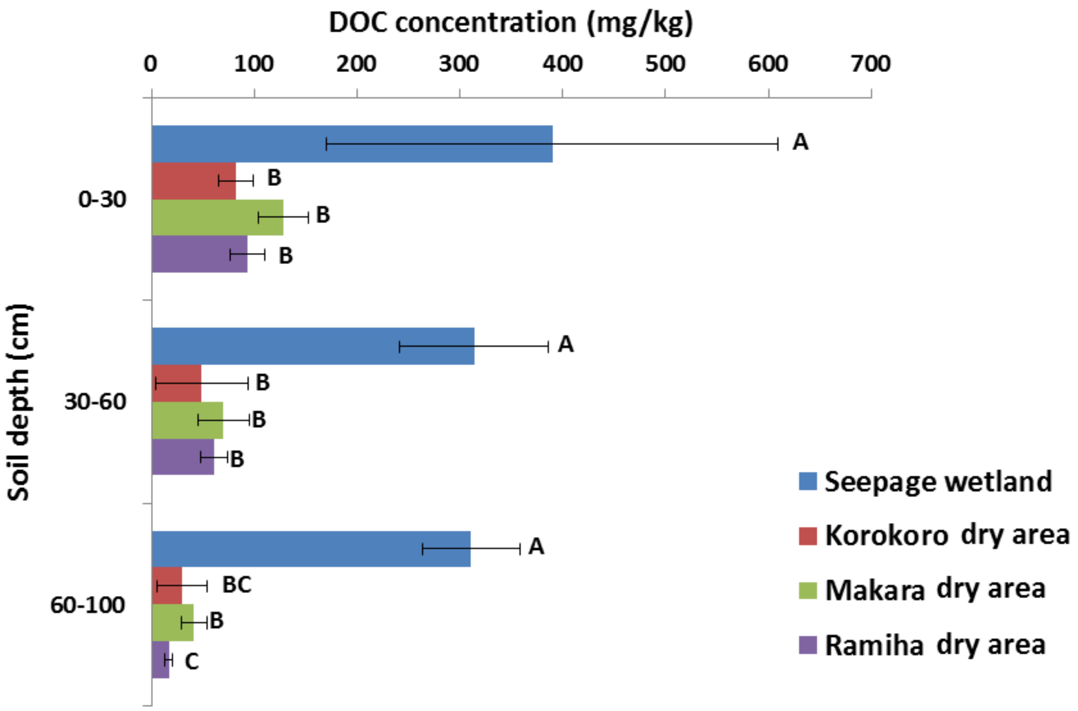

Figure 2. DOC concentration of the seepage wetland and dry area soils. *The values represent the mean value of the three sites for each soil. Different letters indicate significant ($p \leq 0.05$) difference between soils for a particular soil depth. Error bars are standard error of the mean. Number of observations (n) = 18 for the seepage wetland soil, and 36 for each dry area soil.*

Denitrification capacity of the seepage wetland and dry area soils

Due to similarity in the DOC concentration of the dry area soils (Figure 2), all other comparisons (denitrification capacity and other soil properties) were made between the seepage wetland and only one dry area soil, i.e. the Makara dry area soil because it was closest to the seepage wetland (Figure 1). For these comparisons, three soil cores were randomly selected from each sampled site of the seepage wetland and Makara dry area.

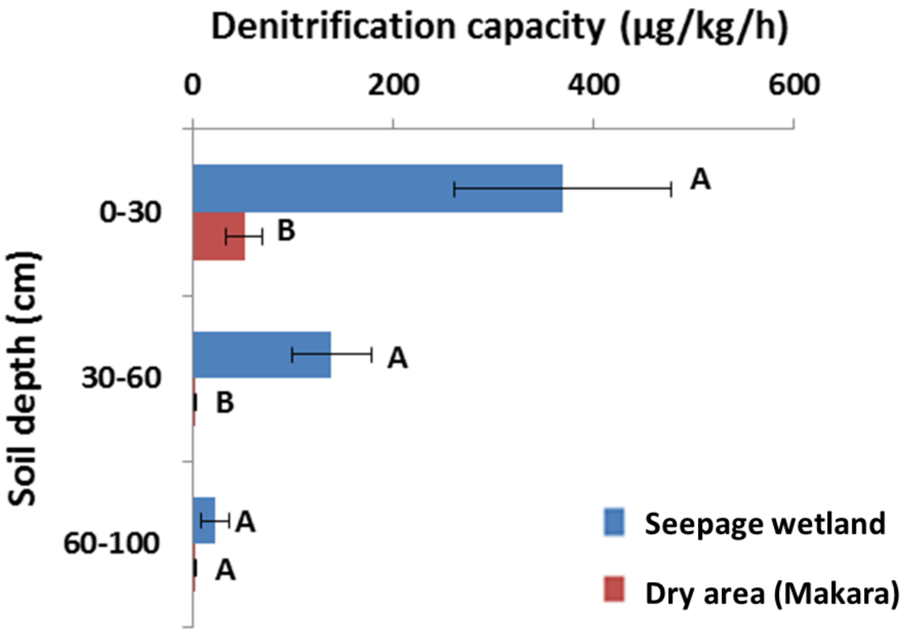

Figure 3. Denitrification capacity of the seepage wetland and dry area soils. *Different letters indicate significant ($p \leq 0.05$) difference between soils for a particular soil depth. Error bars are standard error of the mean ($n = 9$).*

The denitrification capacity of the seepage wetland was significantly ($p \leq 0.05$) higher than that of the dry area within the surface 60 cm soil depth (Figure 3). Denitrification capacity decreased with soil depth, due to a reduction in substrate (DOC) availability and vertical mixing (which promotes the transport of nitrate to denitrifying microbes) (Rutherford *et al.*, 2018).

Nitrate attenuation as influenced by other soil properties

Table 1 shows selected soil properties of the seepage wetland and dry area soils in relation to nitrate attenuation. The seepage wetland soil had lower aromaticity in DOC, indicating the presence of a more decomposable fraction of DOC compared to the dry area soil. Therefore, it is possible that the higher DOC in the seepage wetland was preferred by denitrifying microbes, which (in addition to its higher moisture content and hence more reduced condition) could have contributed to its higher denitrification capacity compared to the dry area.

The seepage wetland soil had higher pH due to its more reduced condition (lower E_h). This reduced condition indicates a decrease in oxygen concentration which could have promoted denitrification. The higher Mn^{2+} and ammonium concentrations in the seepage wetland suggests that other nitrate attenuation processes such as Mn^{2+} oxidation and dissimilatory nitrate reduction to ammonium (DNRA) could be taking place within the seepage wetland (Luther *et al.*, 1997; Rütting *et al.*, 2011), but more detailed research would be required to confirm this assumption.

Table 1. Soil properties in relation to nitrate attenuation

Soil properties	Seepage wetland	Dry area (Makara)
DOC chemistry	Lower aromaticity	Higher aromaticity
pH	Higher (5.6-7.1)	Lower (5.0-6.3)
E_h	Lower (0.20-0.38 V)	Higher (0.31-0.44 V)
Mn^{2+}	Higher (~ 1.0 mg kg^{-1})	Lower (~ 0.5 mg kg^{-1})
Ammonium	Higher (1.0-9.0 mg kg^{-1})	Lower (0.6-4.0 mg kg^{-1})
Nitrate	< 1.0 mg kg^{-1}	< 1.0 mg kg^{-1}

Significant ($p \leq 0.10$) correlations were observed between denitrification capacity and the following soil properties: soil moisture and Mn^{2+} ($r = 0.5$), DOC concentration and ammonium ($r = 0.3$), and DOC chemistry ($r = -0.3$).

Conclusion

Hill country seepage wetlands have higher nitrate attenuation capacity compared to surrounding dry areas. Soil moisture, and the concentration and chemistry of DOC influence the denitrification capacity of seepage wetlands. These areas have the potential to improve water quality; thus, the extent of seepage wetlands on hill country farms needs to be measured and preserved/enhanced in order to achieve environmental objectives. The identification and management of seepage wetlands may also provide hill country farmers with flexibility in relation to future nutrient loss regulations.

Further research in the following areas would be required to aid in the effective management of hill country seepage wetlands for improved water quality outcomes: (i) factors influencing the spatial variation in DOC and denitrification capacity of seepage wetlands, (ii) seasonal *in-situ* measurements of denitrification capacity, (iii) other pathways of nitrate attenuation besides denitrification, (iv) monitoring of streamflow and nitrate/ammonium concentrations into and out of the seepage wetlands.

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