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SPATIAL AND TEMPORAL VARIABILITY OF GROUNDWATER CHEMISTRY AND REDOX CONDITIONS IN AN AGRICULTURAL LANDSCAPE

Stephen Collins[1,2], R Singh[1], A Rivas[1,3], D Horne[1] and J Roygard[2]

[1]Fertilizer & Lime Research Centre, Massey University, Palmerston North
[2]Horizons Regional Council, Palmerston North
[3]Lincoln Agritech Ltd, Hamilton

E-mail: Stephen.Collins@horizons.govt.nz

Abstract

Nitrate-N (NO_3-N) leaching from agricultural soils is a key concern for contamination of surface and groundwaters in sensitive agricultural catchments. Leached NO_3^- from agricultural soils can be attenuated by biogeochemical processes such as denitrification, which occurs under favourable hydrogeochemical (redox) conditions in the subsurface environment (beyond the root zone). However, we have very limited information available on the occurrence and variability of groundwater chemistry and redox conditions in our sensitive agricultural catchments.

We collated and analysed a large set of groundwater observations (150+ wells) to identify spatial and temporal variations in groundwater chemistry and redox conditions in the Horizons Region. The collected groundwater dataset was comprised of one-off groundwater surveys and repeated (temporal) observations at the selected groundwater monitoring sites. Using the framework and threshold concentrations of groundwater redox species (McMahon & Chapelle, 2008), the collected groundwater samples were assessed for their dominant groundwater redox conditions and processes. Further, a range of hydrogeological characteristics such as soil texture, drainage class, and underlying geology associated with the sampling sites were identified and analysed for their influence on the spatial and temporal variability of the groundwater redox conditions and processes.

Our analysis suggests highly spatially-variable but generally temporally-stable groundwater redox conditions in the study area. In addition, soil drainage class seemed to be a good predictor of groundwater redox conditions, independent of what rock type the soils had developed on (i.e. alluvium, gravel or loess). The more well-drained soils tended to be more oxic (dissolved oxygen > 1 mg/L), whereas the more poorly-drained soils tended to be more anoxic (dissolved oxygen < 1 mg/L). This had clear implications for groundwater NO_3-N, with elevated concentrations found in the well-drained soils compared with their more poorly-drained counterparts. Interestingly, the coastal sand country of the study region has mostly anoxic (reducing) groundwater conditions, likely due to the abundance of dissolved iron found in the groundwater.

This observed variability in groundwater chemistry and redox conditions highlight the influence of different landscape characteristics on the transport and potential for NO_3-N attenuation in the subsurface environment. Further research focused on a better understanding,

quantification and mapping of these influences will help inform the design of targeted and effective mitigation measures for improved water quality in sensitive agricultural catchments.

Keywords: Agriculture; Water quality; Nitrate attenuation; Nutrient management; New Zealand

Introduction

Nitrate-N (NO_3-N) is a key freshwater contaminant in agricultural catchments worldwide. Its soluble nature means it leaches easily through agricultural lands, from the root zone, to groundwater and eventually to surface waters. Elevated levels of NO_3-N potentially causes the growth of nuisance algae that affects freshwater ecology and aquatic life in surface waters. However, NO_3-N leached from the soil profile (from the root zone) can be attenuated by natural biogeochemical processes occurring in its flow pathways from land to waters. The primary means of NO_3-N attenuation is through denitrification, the chemical reduction of NO_3-N to N_2 through several intermediate compounds (Korom, 1992). Subsurface denitrification in groundwaters has shown to be an effective removal pathway for agriculturally-sourced NO_3-N (Collins et al., 2017). However, it relies on a specific set of environmental conditions for the microbially facilitated reactions to occur, e.g. low oxygen environment, availability of electron donors such as dissolved organic carbon, reduced inorganic iron and sulphur compounds (Rivett et al., 2008). In groundwater, these conditions are broadly described as 'reducing', and generally exist in contrast to 'oxidising' conditions where NO_3-N typically does not get attenuated. Reducing and oxidising (redox) conditions are known to vary spatially in a landscape, but the reasons for this variability are little known. It is also unknown to what extent these conditions are stable over time in subsurface environments.

The Manawatū-Whanganui (Horizons) Region of New Zealand is agriculturally diverse, with land use including sheep and beef; dairy farming; horticulture; cropping; and grazing. These land uses take place on a variety of equally diverse landscapes including hill country; sand country; alluvial plains; and terrace plains. Among these landscapes are a range of soil types and rock types, each with their own qualities and limitations, such as soil drainage or erosion susceptibility. Intensive agriculture such as dairy farming and cropping has generally tended towards the flatter alluvial plains, terrace plains or sand country, whereas the less intensive agriculture such as sheep and beef farming takes place on hill country. This is due to greater versatility generally offered by flatter landscapes that score a higher grade under the country's Land Use Classification (LUC) scheme (where Class 1 is highly versatile and Class 8 has an extremely low versatility). Local regulation (Manawatū-Whanganui Regional Council, 2014) recognises the 'natural capital' potential of these LUC classes and allows for a higher permissible level of nitrogen leaching on Class 1 soils, with a reducing leaching maximum for subsequent LUC classes (Class 2 – Class 8). However, while this form of regulation is not strictly 'horizontal' in its approach, it does not assess or recognise the land's potential to attenuate NO_3-N, therefore it could be considered horizontal to some degree.

An alternative approach would be to consider the natural NO_3-N attenuation capacities of different land units (combinations of soils and rock types, groundwater chemistry and redox status) and guide land use activities based on these environmental qualities of landscapes. Environmental outcomes would be improved if areas of high NO_3-N attenuation capacity were used for more intensive purposes such as dairy cow grazing, thereby attenuating much of the NO_3-N being leached. On the other hand, areas with a lower capacity to attenuate NO_3-N would be more suitable to less intensive uses such as cut & carry, selective grazing, duration controlled grazing to reduce NO_3^- losses from agricultural lands to receiving waters. Recently, Elwan et al. (2015) and Singh et al. (2017) has developed a preliminary hydrogeochemical based model to assess spatially variable NO_3-N attenuation potential of different land units across the Tararua and Rangitīkei catchments in the Horizons Region. They estimated the proportion of nitrogen attenuated in a sub-catchment based on the river N loads versus what is thought to be leaching from the root zone below the various land uses within those sub-catchments. They defined this as the nitrogen attenuation factor (AF_N), calculated as the root zone N losses minus the river N load and divided by the root zone N loss in the sub-catchment. Their estimates of AF_N across Tararua sub-catchments varied from 0.29 to 0.75, demonstrating how diverse the range of NO_3-N attenuation capacities can be within a single catchment. Although it is useful to view the spatial variability of NO_3-N attenuation at the sub-catchment level, it does not provide the ability to efficiently manage land use at that scale. This is because subsurface redox conditions (and therefore the AF_N) are expected to be more variable within a sub-catchment.

What is needed, is to identify those landscape characteristics that give rise to variable subsurface redox conditions, and then map the spatial extent of those conditions based on the influencing landscape characteristics. This aims to provide a view of potential NO_3-N attenuation capacities of different land units across the sub-catchment scale. To achieve this, it is first necessary to examine how groundwater redox conditions vary spatially and determine the temporal stability of these conditions over time in the study region. The spatial variability of groundwater redox conditions has previously been assessed for the Horizons Region (PDP, 2013; Morgenstern et al., 2017; PDP, 2018). However, this has been done with sparsely available groundwater observations. Moreover, there is yet no study assessing temporal stability of groundwater redox conditions across the Horizons Region. In addition, there is very limited information of how different hydrogeological settings influence spatial and temporal variations of groundwater redox conditions in the Region. Therefore, the main objectives of this study were to: (1) determine the spatial variability of groundwater redox conditions in the Horizons Region; (2) determine the temporal stability of those conditions; and (3) explore the relationship between groundwater chemistry conditions and landscape characteristics such as soil texture, drainage and underlying geology types.

Materials and Methods

We complied of a large dataset of existing groundwater observations across the lower part of Horizons Region (Figure 1). Groundwater samples used in this analysis were gathered from two main sources: Horizons Regional Council, as part of their State of the Environment monitoring programme or catchment investigations; and Massey University, as part of their research programme on land use and water quality effects across the Tararua and Rangitīkei catchments. These datasets contain sites that were either sampled only once (i.e. a single data point), or sites that had been sampled more than once (i.e. temporally). In total, there were 167 sites with groundwater data, of which 86 had a single data point, and 81 had more than one sample result.

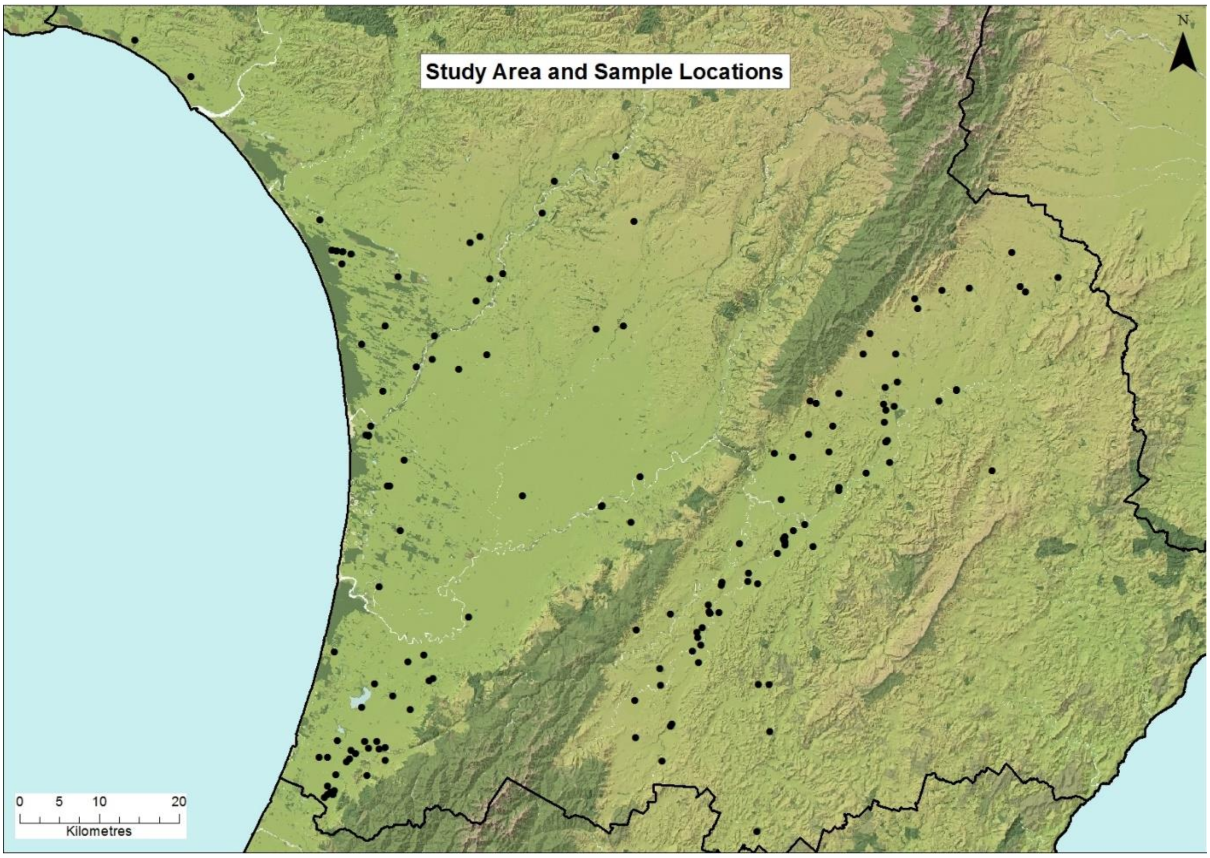

Figure 1: Location of groundwater observations points across the lower Horizons Region.

The collected groundwater chemistry data was analysed to determine whether a site has oxidised or reduced groundwater in its hydrochemical nature. A simple methodology (as a Microsoft Excel tool) developed by McMahon & Chapelle (2008) was used to determine the groundwater redox category and redox process. It requires five groundwater chemistry parameters, including dissolved oxygen (O_2, hereafter known as DO), NO_3-N, dissolved manganese (Mn^{2+}), dissolved iron (Fe^{2+}), and sulphate (SO_4^{2-}). A range of threshold concentrations for each parameter is given to determine (a) the redox category (oxic/suboxic/anoxic/mixed); and (b) the redox process (NO_3-N reduction, iron reduction, manganese reduction etc.). Of most importance to this analysis was to determine the redox category, as it explains in broad terms whether NO_3-N can potentially be reduced within the groundwater system.

For both datasets (spatial and temporal), each sample had at least DO and NO_3-N to determine the redox category, however most samples had the full suite of five parameters required to determine the dominant redox process as well. Where individual results of any parameter were below the detection limit, the detection limit was halved to provide a numeric value to perform the analysis.

In determining the spatial variability of groundwater redox conditions, sites with a single sample were simply included and used in the assessment. For sites with more than a single sample (temporal data), the median value was calculated for all of a site's results for each parameter and the median value was used in the redox assessment. The resulting categories were simplified to be binary, either oxidising or reducing (including suboxic). 'Mixed' determinations were assigned to their dominant category. To determine a site's temporal stability (for sites that had more than a single measurement), each individual sample for a site was assessed for its redox condition, and the dominant redox condition was expressed as a percentage of the time this was observed.

Two national datasets were used to explore the relationship between groundwater chemistry conditions and landscape characteristics: the New Zealand Land Resource Inventory (NZLRI) and the New Zealand Fundamental Soil Layer (FSL). The NZLRI maps the soil and land resources at the national scale. It includes five key physical soil and land resource factors that drive land use capability: soil, rock type, slope, presence and severity of erosion, and vegetation (Lynn et al., 2009). The FSL contains spatial information for 16 key soil attributes, which fall broadly into three groups: soil fertility/toxicity, soil physical properties, and topography/climate. The NZLRI makes a distinction between the surficial rock type and the underlying rock type. This analysis uses the underlying rock type information as a better representation of the general geology of a site. The FSL provided information on soil texture and drainage class at each site.

Results

Spatial variability

Figure 2 shows spatially variable groundwater redox conditions throughout the study area. Of the 167 sites used in this analysis, 82 were classified as reduced groundwater and 85 were classified as oxidised groundwater. Figure 2 shows that the western part of the study area are primarily reduced groundwaters, the south western area being primarily oxidised groundwaters, and the eastern area being both reduced (anoxic) and oxidised groundwaters. These findings are largely consistent with previous groundwater redox assessments of the region (PDP, 2013; Morgenstern et al., 2017; PDP, 2018). The dataset Morgenstern et al. (2017) used was paired with groundwater age tracer data, enabling the comparison of groundwater redox conditions with the groundwater's mean residence time (MRT). They found that groundwater DO concentrations generally decreased with an increase in the groundwater age, with younger groundwater tending to be more oxidising and older groundwater tending to be more reducing. The opposite was observed for Fe^{2+}, CH_4 and NH_4, which generally increased with increasing groundwater age and were primarily reducing.

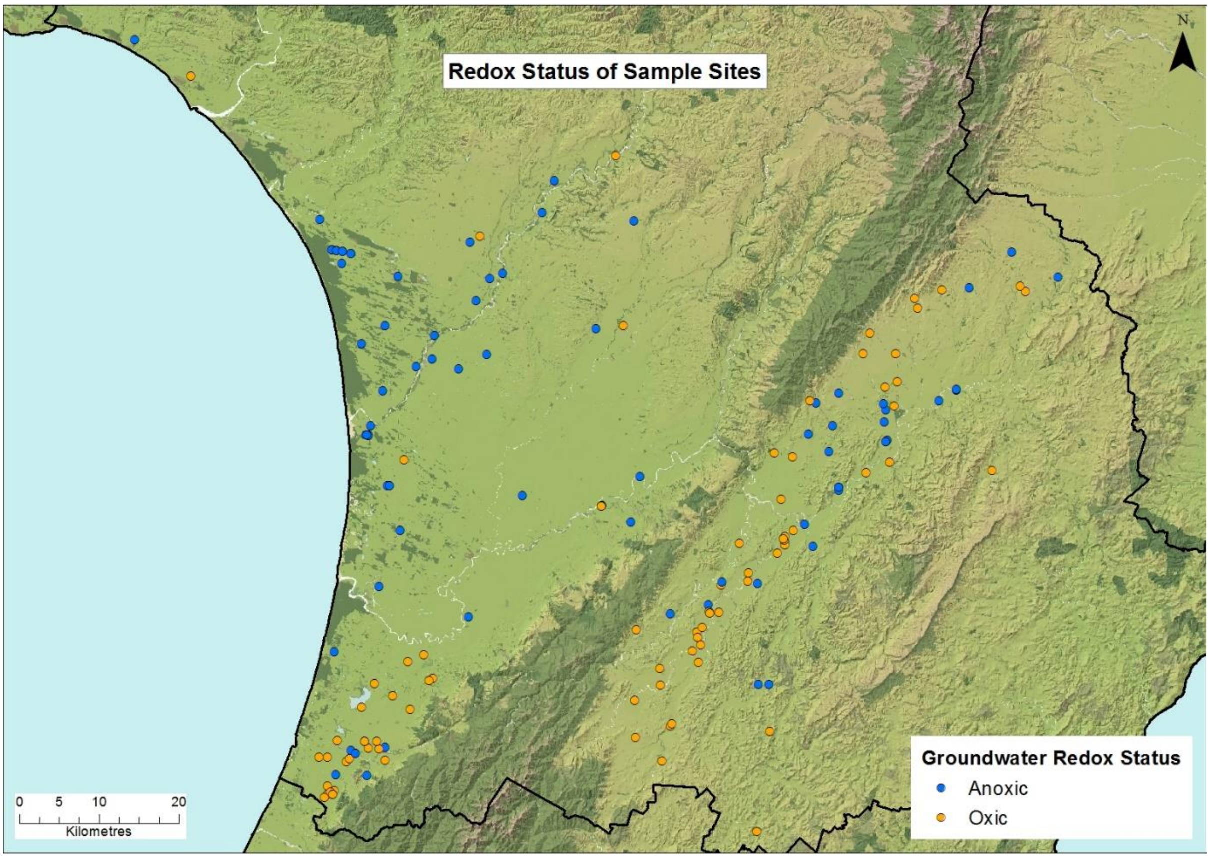

Figure 2: Spatial variability of groundwater redox conditions across the lower Horizons Region.

Temporal stability

With the spatial variability of groundwater redox conditions established, how stable are these conditions over time? There were 81 sites in this analysis that had temporal data, i.e. where there was more than one groundwater sample for the same site. Of these 81 sites: 80% were stable 100% of the time; 83% were stable > 90% of the time; 88% were stable > 75% of the time. Only 11% of sites were stable 50% of the time. Figures 3 and 4 provide an example of groundwater redox stability and variability, respectively, at two groundwater sampling sites in the study region. Overall, 89% of the reducing sites and 79% of the oxidising sties were stable 100% of the time. This suggests, in general, temporally stable groundwater redox conditions at the study sites.

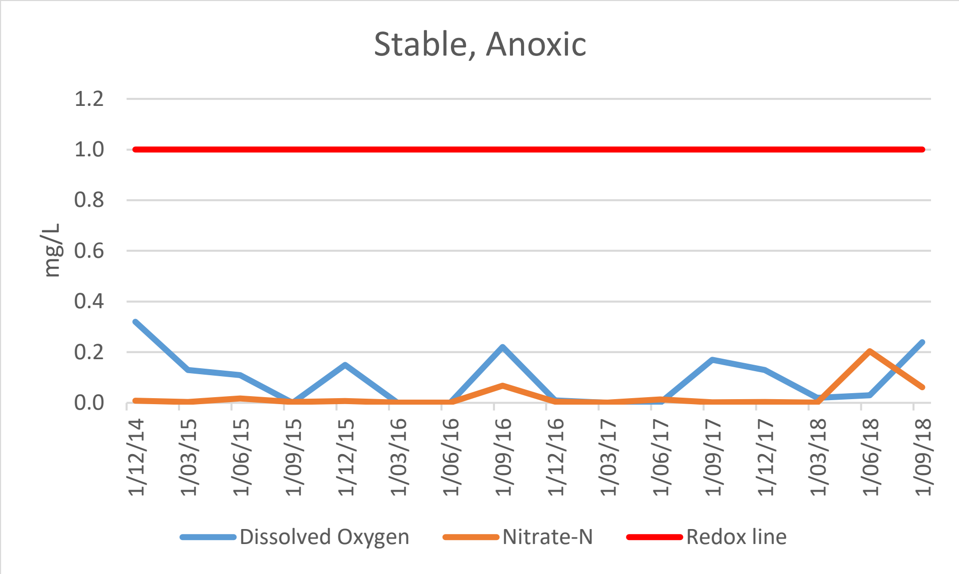

Figure 3: An example of temporal stability of groundwater redox conditions in the study area.

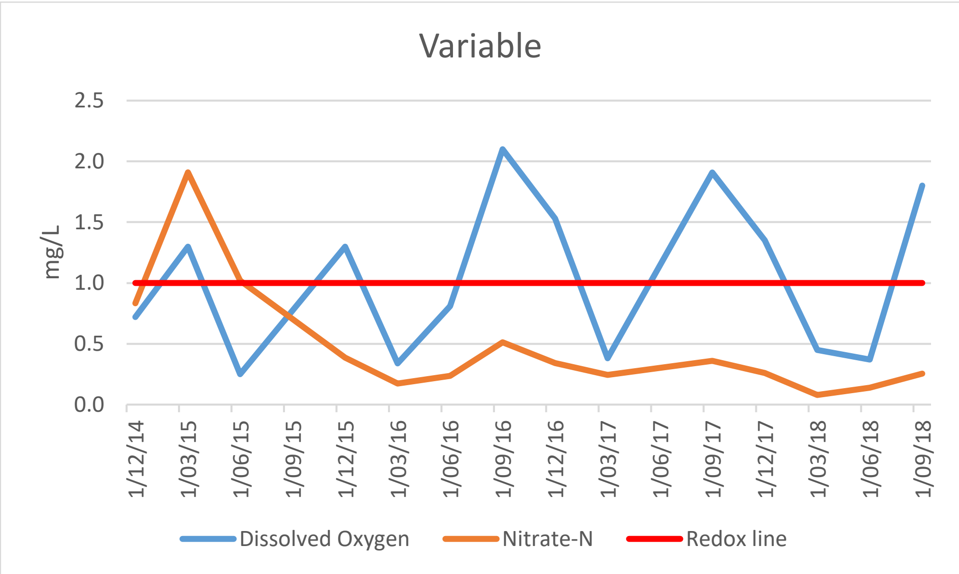

Figure 4: An example of temporal variability of groundwater redox conditions in the study area.

Relationship to landscape characteristics and groundwater hydrochemistry

An assessment of relationships between groundwater hydrochemistry and landscape characteristics involved a comparison of DO, NO_3-N and other redox species with rock type, soil drainage and texture. Figure 5 shows variation in groundwater redox species across the four main rock types in the study being alluvium, gravel, loess and wind-blown sand. There were several other rock types that made up a small minority of sites (nine), and these were excluded. Wind-blown sand has the lowest median and average concentrations of DO and NO_3-N compared with the other rock types. Most of the DO data in the wind-blown sand environment also sits below the 1 mg/L threshold for NO_3-N reduction, so most of these sites are likely to be reducing. The remaining rock types have a much larger range in DO and NO_3-

N concentrations compared to the wind-blown sand. However, the alluvium also has median DO concentrations near the redox threshold of 1 mg/L (Figure 5), making some of these sites reducing/anoxic, thereby supporting the low median NO_3-N concentrations at the sites associated with the alluvium rock type. The gravel and loess rock types have higher median and average DO and NO_3-N concentrations than the alluvium and wind-blown sand rock types, notably having DO concentrations above the redox threshold and associated elevated NO_3-N. Manganese is low throughout all rock types, but iron is especially elevated throughout the wind-blown sands. This is probably further supporting denitrification as reduced iron can act as an electron donor in place of carbon (Korom, 1992).

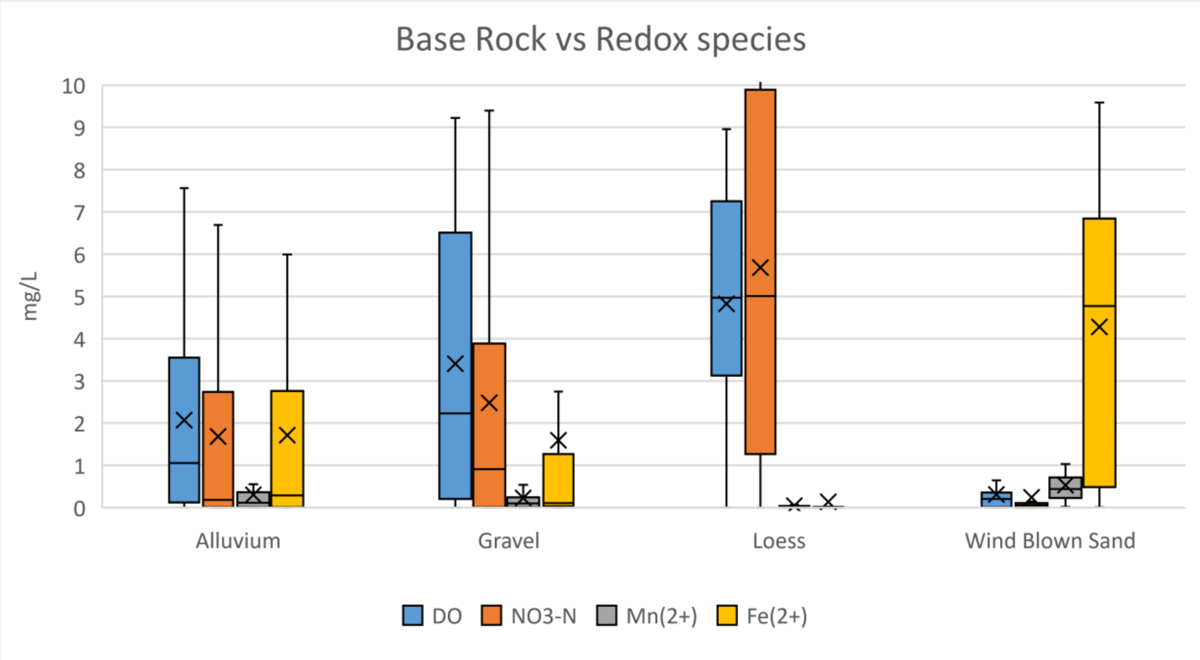

Figure 5: Variation of groundwater redox species observations under different geology (rock) types in the lower part of Horizons Region.

Soil drainage classes were described as poorly drained, imperfectly drained and well-drained as derived from the FSL. For poorly drained soils, these were a combination of very poorly drained and poorly drained soils; similarly, the well-drained soils are a combination of moderately well and well-drained soils. Figure 6 shows the influence of a combination of soil drainage and rock types (rock types divided by soil drainage class) on groundwater DO measurements across the study area. Again, the wind-blown sand has the lowest range of values among the soil drainage classes, with both median and average DO values below the 1 mg/L threshold. Among the other rock types, it was the well-drained soils for each rock type that had the highest values of DO. A similar picture arises for NO_3-N (Figure 7), where the wind-blown environment had the lowest values across all soil drainage classes. Loess had the highest median and average NO_3-N values for their well-drained soils.

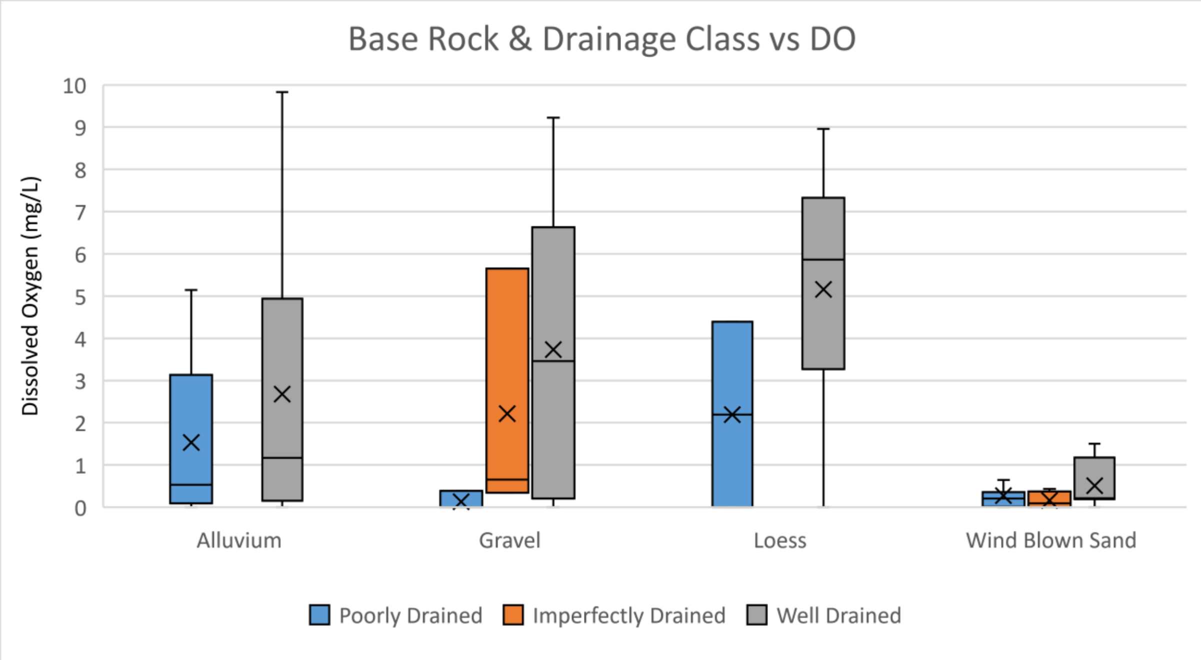

Figure 6: Variation of groundwater dissolved oxygen observations under different soil drainage classes and geology (rock) types in the lower part of the Horizons Region.

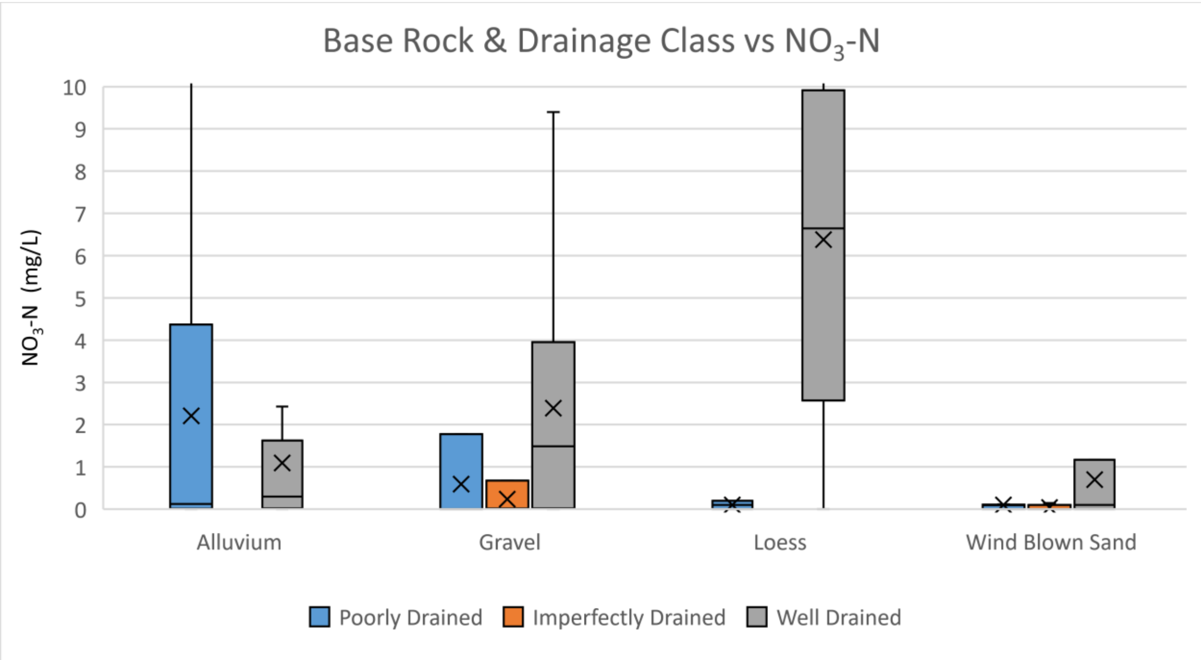

Figure 7: Variation of groundwater NO_3-N observations under different soil drainage classes and geology (rock) types in the lower part of the Horizons Region.

Soil texture was regrouped from their soil descriptions in the FSL and described according to Rivas et al. (2017) as fine, medium and coarse. The fine texture class included heavy silt loam, silt loam & clay loam, and silt loam; the medium texture class included sandy loam & silty loam, and silt loam/sandy loam; and the coarse texture class included sand, sand and stony gravel, and stony loam. Figures 8 and 9 shows how soil texture varies with rock type for DO and NO_3-N, respectively. The wind-blown sand was classed exclusively as a coarse texture, while the loess rock type was classed exclusively as a fine texture. The two rock types had opposing results, where the wind-blown sand environment had low DO and NO_3-N, and the loess environment had the highest DO and NO_3-N levels. The alluvium and gravel rock types both had a range of soil textures; however, their DO and NO_3-N concentrations behaved differently. For the alluvium, it was the coarse texture soils that had the highest DO and NO_3-N, yet for gravel it was the fine texture soils that had the highest DO and NO_3-N.

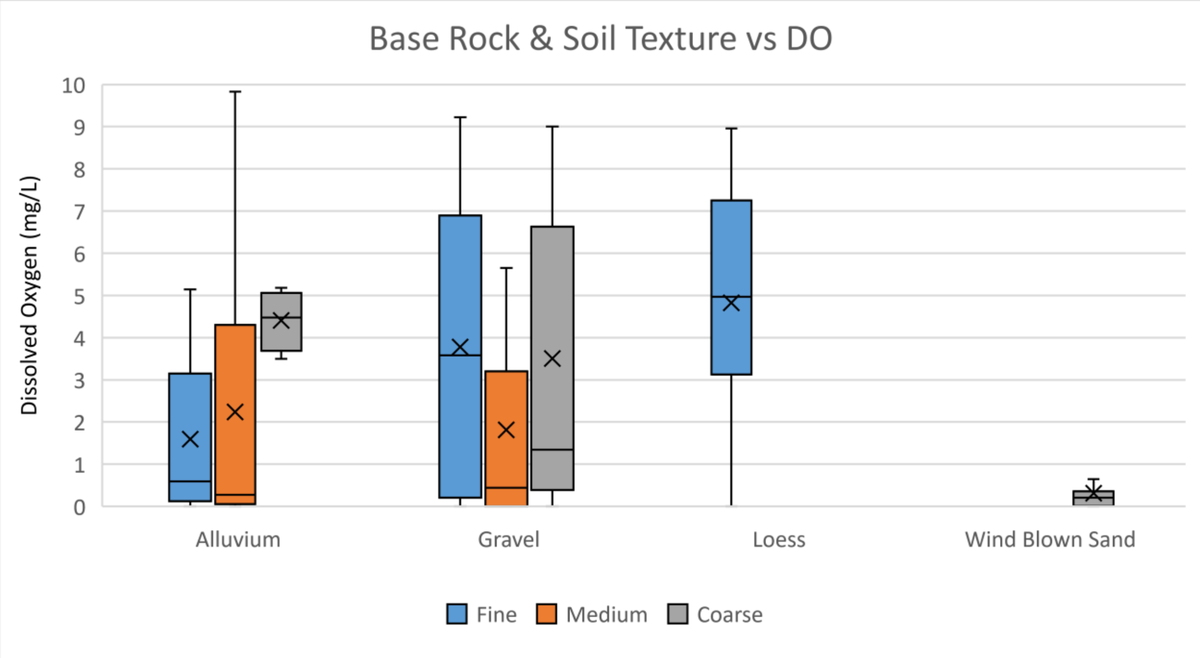

Figure 8: Variation of groundwater dissolved oxygen observations under different soil texture and geology (rock) types in the lower part of the Horizons Region.

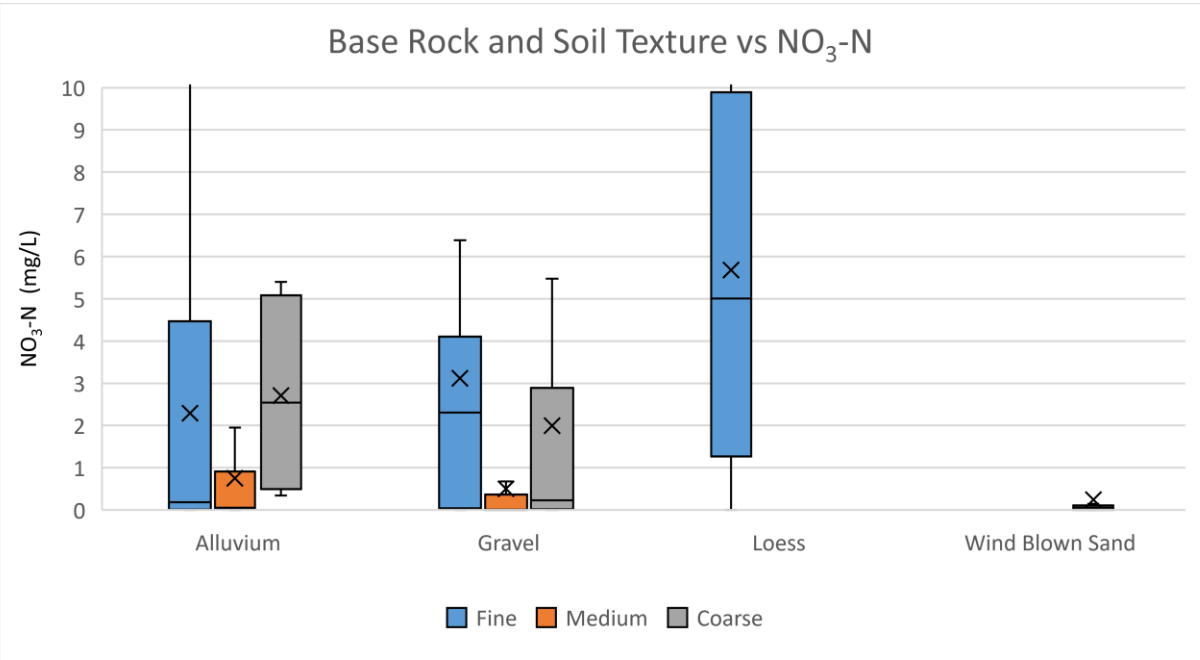

Figure 9: Variation of groundwater NO_3-N observations under different soil texture classes and geology (rock) types in the lower part of the Horizons Region.

Discussion and Conclusion

Groundwater redox conditions were found to be spatially variable throughout the region, though broadly consistent with similar analyses previously performed. The western side of the region has dominant reducing (lower Manawatū and lower Rangitīkei catchments) and oxidising (Horowhenua) conditions with isolated areas of alternative redox processes occurring within them. The eastern (Tararua) side of the region reveals a greater complexity in the spatial distribution of groundwater redox conditions. Interestingly, both groundwater reducing and oxidising conditions are present within short distances of each other and this occurs throughout the eastern area. Landscape variation may be having a stronger effect in this eastern side of the catchment, as compared with the western side, where spatial redox variation exists but over greater distances. Speculation about what the driving force behind this spatial variation in groundwater redox conditions appears in some way linked with the landscape, and the effect it has on general groundwater hydrology and hydrochemistry. These relationships were explored in this paper, comparing rock and soil types as they relate to groundwater chemistry and redox conditions as observed in the study area.

There were four primary rock types identified in the study area, alluvium, gravel, loess and wind-blown sand. Each rock type had distinct hydrochemical outcomes, but the wind-blown sand and loess types had the greatest distinction between each other (Figure 5). The wind-blown sand contains naturally occurring iron, likely a result of sand of volcanic origin being driven onshore by the prevailing NW wind direction (Brathwaite et al., 2017). This appears to have given it some capacity to reduce DO and other oxygen-bearing compounds (NO_3-N etc.) with the result that DO and NO_3-N are both comparatively low. This compares sharply with the loess type, starved of natural inputs of iron, and perhaps other types of electron donors such as dissolved organic carbon, with resulting high DO and NO_3-N in groundwater. Alluvium and gravel had similar outcomes and placed between loess and wind-blown sand in terms of DO and NO_3-N concentrations in groundwater.

Soil drainage class appears to be the most consistent indicator of groundwater DO and NO_3-N outcomes when compared with the rock type. For groundwater DO, all rock type environments appear to have a higher concentration in the well-drained soil areas, than their imperfectly and poorly-drained alternatives. This fits with expectations that well-drained soils should generally have high DO (compared with their imperfectly or poorly-drained counterparts) because they allow more recent and faster recharge of water to infiltrate the soil and aquifer materials. Recent recharge water has a higher DO concentration than older water because it has more recently been in contact with the atmosphere. The Tararua and Horowhenua areas have considerably lower groundwater MRTs compared with the lower Manawatū and Rangitīkei catchments (Morgenstern et al., 2017), suggesting higher recharge and infiltration rates in these areas.

Soil texture appears to be a less consistent indicator of groundwater DO and NO_3-N outcomes. While wind-blown sand and loess soils had exclusive textures (coarse and fine, respectively), the alluvium and gravels had a range of soil textures that had developed on them. However, for the alluvium and gravels, DO and NO_3-N concentrations were observed to have opposing outcomes. For fine textures, alluvium had lower DO and NO_3-N concentrations and gravels had higher DO and NO_3-N. Whereas for coarse textures, alluvium had higher DO and NO_3-N concentrations and gravel had lower DO and NO_3-N. These results suggest soil texture, as classified by the FSL, may have little to do with groundwater hydrochemical properties (DO and NO_3-N at least), or that it may be masked by other hydrochemical properties operating, such as the abundance of Fe^{2+} in the sand country. How exactly it is that soil texture influences groundwater redox conditions requires further investigation.

Despite the spatial variation, it is evident from our analysis that groundwater redox conditions are generally stable over time in the study region. There are some sites that may vary on a seasonal basis or otherwise, but in general groundwater redox conditions are stable. Hence, groundwater redox conditions can be expected to be stable in places where we have no temporal data or any data at all. This supports that limited temporal groundwater observations could be applicable to map spatial and temporal variation of groundwater redox conditions in the study area.

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