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Redox Characteristics of Shallow Groundwater in the Tararua Ground Water Management Zone

A thesis presented in partial fulfilment of the requirements for the degree of Master of Science in Earth Science

at Massey University, Manawatū, New Zealand

Peter Grant McGowan

2018
Abstract

Groundwater redox conditions have a major influence on transport and transformation of nutrients such as nitrate from farms to rivers and lakes. This study focused on measurement and analysis of chemical and physical characteristics of groundwater to determine the spatial distribution of redox characteristics across the Tararua Ground Water Management Zone in the Manawatu River catchment. The influence of catchment characteristics such as soil texture and drainage, and rock type have on groundwater chemistry and its redox characteristics across the Tararua GWMZ is investigated using multivariate statistical analysis.

Existing geographical information was collated and analysed to map spatial distributions of landuse, soil characteristics and lithologies across the study area. This information was utilised to identify potential site locations for sampling and analysis of shallow groundwater in the Tararua GWMZ. A direct-push system capable of penetrating a range of substrates including deep, imbricated, and coarse gravels was developed. Using this system, shallow groundwater samples were recovered from contrasting hydrogeological settings, areas where water wells are rarely installed; such as along the margins of the axial ranges, and from areas considered not to have groundwater; e.g. the mudstone country on the east of the Tararua District.

Data collected with the direct-push method was combined with similar data collected from existing wells by Rivas et al. (2017) and classified according to redox status. The data was subjected to multivariate statistical assessment using Hierarchical Cluster Analysis to determine the water type, and Principle Component Analysis to determine the influence of discrete catchment characteristics on redox reactions occurring in shallow groundwater of the Tararua GWMZ.
The in-field and chemical analysis revealed significant variation of groundwater quality parameters and redox characteristics across the Tararua GWMZ. The regional trend was for reducing conditions in gravel aquifers in the north western areas of the Tararua GWMZ and oxidising in gravel aquifers of the south western; although statistically significant variations of redox characteristics is also recognised within these areas. Groundwater samples were collected from mudstone where little, if any, groundwater research has been conducted previously. Groundwater characteristics from mudstone are generally classified as anoxic and strongly reducing, with very high specific conductivity and analyte levels such as bromide, chlorine, sodium, fluorine, dissolved inorganic carbon and magnesium. Identifying the influence of discrete catchment characteristics on groundwater chemistry and redox characteristics was complex and difficult to quantify. Extrapolation of the principal component inferred to be associated with redox characteristics provides a useful means to evaluate the influence of discrete catchment characteristics on redox conditions in shallow groundwater of the Tararua GWMZ. The direct-push method provided an opportunity to compare groundwater chemistry between samples collected proximal and distal to production wells. Statistically significant differences in redox related parameters such as DOC, Eh, Fe\(^{2+}\), Mn\(^{2+}\), NH\(_4\)-N, and NO\(_2\)-N were detected in groundwater samples collected from existing wells compared to groundwater samples collected with the direct-push method. Factors contributing to this effect were explored but found to be difficult to isolate.
Acknowledgements

Massey University is an amazing institution, without the extramural program and financial support via generous scholarships I would have never been able to complete this thesis. I would also like to thank Horizons Regional Council who provided generous financial support for the analysis of my groundwater samples. I sincerely appreciate the confidence my supervisors placed in me to progress and develop my thesis as I saw fit; yet were always there to provide incisive direction when necessary, thank you Ranvir and Alan.

I gratefully acknowledge the farmers who kindly granted permission for me wander on their land and poke holes through their pasture. Nitrate contamination of groundwater, particularly for the dairy industry is a hot topic at present, yet the farmers were welcoming and keen to establish what was happening on a local and regional basis.

Sincere thanks must go to Terrance from Perry Geotech who kindly provided expensive drill rods for the project and never blinked an eye when I lost an entire string down a hole...twice. Also to David Feek who's technical, engineering and problem solving abilities were outstanding, and his mordant comments on my fieldwork aspirations never failed to jolt me back to reality.

I also would like thank my close friends, Shaun and Fiona, and Bruce and Debbie who over a beer and dinner would often quietly sit and listen to my ramblings of experiences and newfound geological knowledge. I could see your eyes, glazed at times, but never closed, thank you.

My very dear mentor and friend, Monty Blomfield guided and supported me over the last 25 years for which I am eternally grateful. Unashamedly from the “old school” Monty taught me so much and encouraged me to take the plunge into academia. Our many fishing and hunting adventures were awesome, but simply spending time in his presence counted more than anything; more so now that he has passed on.
Over the course of my studies both my parents also passed away. Truly wonderful parents and friends, they always encouraged me to remain positive, develop an enquiring mind, look for the good in everyone, and enjoy life’s every moment. I feel so sad that they weren’t able to see to where my journey has led.

To our children Krystie, Jarrad, and Ryan, you guys are simply the most amazing young people, and if you ever agree to go in the car with me again, I promise not to hold you hostage and waffle on about subduction, obduction, rocks, minerals, plate tectonics, back arc volcanism, turbidites, ultramafics, ophiolites, hydrothermal alteration, mineralization, aquifers, hydraulic conductivity, etc. etc. etc.

Finally I would like to thank my wonderful wife Julie for putting up with me over these long years. I may have been a tad temperamental on the odd occasion, and living apart for 2 ½ years was very difficult for both of us. But you understood that although times were tough, I was following my dream and you never complained. Thank you so much, I will make it up to you.
Frontispiece: The Mangatewainui Stream. This image captures the essence of the Tararua GWMZ; swift flowing streams, vast quantities of greywacke gravels, and tectonically deformed marine sediments that underlie shallow gravel aquifers often mantled with a veneer of loess.
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# List of Abbreviations and Acronyms

**Major Inorganic Constituents**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>units</th>
<th>Parameter Name</th>
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<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>mg L(^{-1})</td>
<td>Dissolved calcium</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>mg L(^{-1})</td>
<td>Dissolved chlorine</td>
</tr>
<tr>
<td>DIC</td>
<td>mg L(^{-1})</td>
<td>Dissolved inorganic carbon</td>
</tr>
<tr>
<td>DOC</td>
<td>mg L(^{-1})</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>mg L(^{-1})</td>
<td>Dissolved bicarbonate</td>
</tr>
<tr>
<td>K(^+)</td>
<td>mg L(^{-1})</td>
<td>Dissolved potassium</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>mg L(^{-1})</td>
<td>Dissolved magnesium</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>mg L(^{-1})</td>
<td>Dissolved sodium</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>mg L(^{-1})</td>
<td>Dissolved silica</td>
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**Minor Inorganic Constituents**

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<td>As</td>
<td>mg L(^{-1})</td>
<td>Dissolved arsenic</td>
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<tr>
<td>B</td>
<td>mg L(^{-1})</td>
<td>Dissolved boron</td>
</tr>
<tr>
<td>Br</td>
<td>mg L(^{-1})</td>
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<td>Cd</td>
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<td>Dissolved carbon dioxide (gas)</td>
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<td>F(^-)</td>
<td>mg L(^{-1})</td>
<td>Dissolved fluoride</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>mg L(^{-1})</td>
<td>Dissolved Iron; ferrous (oxidation state ‘2)</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>mg</td>
<td>Iron; ferric (oxidation state ‘3)</td>
</tr>
<tr>
<td>HS(^-)</td>
<td>mg L(^{-3})</td>
<td>Dissolved bisulphide</td>
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<td>H(_2)S</td>
<td>mg L(^{-1})</td>
<td>Dissolved hydrogen sulphide</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>mg L(^{-1})</td>
<td>Dissolved manganese (oxidation state ‘3)</td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>mg</td>
<td>Manganese (oxidation state ‘4)</td>
</tr>
<tr>
<td>NaCl</td>
<td>mg L(^{-1})</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>TA_meq/L</td>
<td>meq L(^{-1})</td>
<td>Alkalinity milliequivalents</td>
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</table>
TATemp °C  Temperature at total alkalinity analysis
TitrantVol ml  Titrant volume
TAPh pH  Total alkalinity; titrant analysis pH
TA$_{mg}$CaCO$_3$ mg L$^{-1}$ Total alkalinity as calcium carbonate

**Nutrients**

<table>
<thead>
<tr>
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<td>Ammonium cation (atomic mass = 18)</td>
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<tr>
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<td>mg L$^{-1}$</td>
<td>Ammoniacal nitrogen (atomic mass = 14)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>mg L$^{-1}$</td>
<td>Nitrate anion (atomic mass = 62)</td>
</tr>
<tr>
<td>NO$_3^-$ -N</td>
<td>mg L$^{-1}$</td>
<td>Nitrate as nitrogen (atomic mass = 14)</td>
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<td>NO$_2^-$</td>
<td>mg L$^{-1}$</td>
<td>Nitrite anion (atomic mass = 46)</td>
</tr>
<tr>
<td>NO$_2^-$ -N</td>
<td>mg L$^{-1}$</td>
<td>Nitrite as nitrogen (atomic mass = 14)</td>
</tr>
<tr>
<td>N$_r$</td>
<td>n/a</td>
<td>Reactive nitrogenous compound</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>mg L$^{-1}$</td>
<td>Sulphate</td>
</tr>
<tr>
<td>TON</td>
<td>mg L$^{-1}$</td>
<td>Total organic nitrogen</td>
</tr>
<tr>
<td>TRP</td>
<td>mg L$^{-1}$</td>
<td>Total reactive phosphorus</td>
</tr>
<tr>
<td>TOC</td>
<td>mg L$^{-1}$</td>
<td>Total organic carbon</td>
</tr>
</tbody>
</table>

**Physical Characteristics**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>units</th>
<th>Parameter Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baro</td>
<td>kPa</td>
<td>Barometric pressure</td>
</tr>
<tr>
<td>DO</td>
<td>mg L$^{-1}$</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>DO sat</td>
<td>%</td>
<td>Dissolved oxygen; percentage saturation</td>
</tr>
<tr>
<td>EC</td>
<td>μS cm$^{-1}$</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>Eh</td>
<td>μS cm$^{-1}$</td>
<td>Electrical conductivity (hydrogen electrode)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>n/a</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>N$_2$</td>
<td>n/a</td>
<td>Nitrogen Gas</td>
</tr>
<tr>
<td>ORP</td>
<td>mV</td>
<td>Oxidation-reduction potential</td>
</tr>
<tr>
<td>pH</td>
<td>pH</td>
<td>The acidity or basicity of an aqueous solution</td>
</tr>
<tr>
<td>SPC</td>
<td>μS cm$^{-1}$</td>
<td>Specific conductivity; EC temperature corrected</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Parameter Name</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>SpActual</td>
<td>Actual conductivity</td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
<td></td>
</tr>
<tr>
<td>Temp</td>
<td>Temperature</td>
<td></td>
</tr>
</tbody>
</table>

**QMap, Geological, and GIS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Parameter Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cong</td>
<td>Conglomerate</td>
</tr>
<tr>
<td>Coq</td>
<td>Coquina</td>
</tr>
<tr>
<td>Grv</td>
<td>Gravel</td>
</tr>
<tr>
<td>GrW</td>
<td>Greywacke</td>
</tr>
<tr>
<td>LST</td>
<td>Limestone</td>
</tr>
<tr>
<td>MST</td>
<td>Mudstone</td>
</tr>
<tr>
<td>SST</td>
<td>Sandstone</td>
</tr>
<tr>
<td>KEY_NAME</td>
<td>Combines stratigraphic age, stratigraphic name, and lithological information</td>
</tr>
<tr>
<td>MAIN_ROCK</td>
<td>Mainrocks QMap class derived from the most commonly encountered rocks in an particular area (scale 1:250,00)</td>
</tr>
<tr>
<td>QMap</td>
<td>Geological map series of N.Z.</td>
</tr>
<tr>
<td>SIM_NAME</td>
<td>Combines stratigraphic age and depositional environment</td>
</tr>
<tr>
<td>SUBROCK</td>
<td>subrocks QMap A class derived from subordinate rock types found with main rock types (scale 1:250,00)</td>
</tr>
<tr>
<td>SUBROCK_Simple</td>
<td>Sub rocks simplified and condensed</td>
</tr>
</tbody>
</table>

**Statistical**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Parameter Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANNOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>Cmp</td>
<td>Principal component derived by PCA</td>
</tr>
<tr>
<td>HCA</td>
<td>Hierarchal cluster analysis</td>
</tr>
<tr>
<td>IDF</td>
<td>Inverse-DF function used to normalise data</td>
</tr>
<tr>
<td>KMO</td>
<td>Kaiser-Meyer-Olkin measure of adequacy</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal component analysis</td>
</tr>
</tbody>
</table>
SPSS  
Statistics software from IBM

**General**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Parameter Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AirTemp</td>
<td>Ambient temperature at time of sampling</td>
</tr>
<tr>
<td>ATP</td>
<td>ATP adenosine triphosphate</td>
</tr>
<tr>
<td>CBE</td>
<td>Charge Balance Equation</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer Numerical Control</td>
</tr>
<tr>
<td>CPT</td>
<td>Cone Penetration test</td>
</tr>
<tr>
<td>DEA</td>
<td>Denitrifying enzyme activity</td>
</tr>
<tr>
<td>DEM</td>
<td>Digital Elevation model</td>
</tr>
<tr>
<td>DL</td>
<td>Detection limit</td>
</tr>
<tr>
<td>DNRA</td>
<td>Dissimilatory nitrate reduction to ammonia</td>
</tr>
<tr>
<td>DRASTIC</td>
<td>Drastic</td>
</tr>
<tr>
<td>FSL</td>
<td>FSL fundamental soil layers</td>
</tr>
<tr>
<td>GIS</td>
<td>Geographic information systems</td>
</tr>
<tr>
<td>GNS</td>
<td>New Zealand Crown Research Institute; formerly Institute of Geological and Nuclear Sciences</td>
</tr>
<tr>
<td>GPS</td>
<td>Global positioning system</td>
</tr>
<tr>
<td>PPK</td>
<td>Post Processing Kinematic GPS</td>
</tr>
<tr>
<td>GV</td>
<td>Guideline value</td>
</tr>
<tr>
<td>ha</td>
<td>Hectares</td>
</tr>
<tr>
<td>HRC</td>
<td>Horizons Regional Council (HRC)</td>
</tr>
<tr>
<td>KML</td>
<td>File extension registered with Google Earth software</td>
</tr>
<tr>
<td>LCDB</td>
<td>Land Cover Database version 4.1.</td>
</tr>
<tr>
<td>LRIS</td>
<td>Land Resource Information Systems Portal</td>
</tr>
<tr>
<td>MAV</td>
<td>Maximum allowable value</td>
</tr>
<tr>
<td>MP</td>
<td>Multi-purpose</td>
</tr>
<tr>
<td>NIWA</td>
<td>The National Institute of Water and Atmospheric Research Ltd.</td>
</tr>
</tbody>
</table>
| NOF          | National Objectives Framework which defines upper and }
lower limits for water quality parameters including nitrates

OC    Organic carbon
OM    Organic matter
OSH   Occupational Safety and Health
PET   Polyethylene terephthalate (thermoplastic polymer resin containers)
Redox Oxidation-reduction reaction
smarTROLL Handheld multi-parameter water quality instrument
Soln solution
SOM   Soil organic matter
Tararua GWMZ Tararua Groundwater Management Zone
TEAP Terminal electron acceptor process
Tg    $1 \times 10^6$ tonne
TVZ   Taupo Volcanic Zone
WHO   World Health Organization