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

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Peter Grant McGowan

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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.

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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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Major Inorganic Constituents

Abbreviation	units	Parameter Name
Ca^{2+}	mg L^{-1}	Dissolved calcium
Cl^{-}	mg L^{-1}	Dissolved chlorine
DIC	mg L^{-1}	Dissolved inorganic carbon
DOC	mg L^{-1}	Dissolved organic carbon
HCO_3^{-}	mg L^{-1}	Dissolved bicarbonate
K^{+}	mg L^{-1}	Dissolved potassium
Mg^{2+}	mg L^{-1}	Dissolved magnesium
Na^{+}	mg L^{-1}	Dissolved sodium
SiO_2	mg L^{-1}	Dissolved silica

Minor Inorganic Constituents

Abbreviation	units	Parameter Name
As	mg L^{-1}	Dissolved arsenic
B	mg L^{-1}	Dissolved boron
Br^{-}	mg L^{-1}	Dissolved bromide
Cd	mg L^{-1}	Dissolved cadmium
CH_4	mg L^{-1}	Dissolved methane (gas)
CO_2	mg L^{-1}	Dissolved carbon dioxide (gas)
F^{-}	mg L^{-1}	Dissolved fluoride
Fe(II)	mg L^{-1}	Dissolved Iron; ferrous (oxidation state $^{+}$2)
Fe(III)	mg	Iron; ferric (oxidation state $^{+}$3)
HS^{-}	mg L^{-3}	Dissolved bisulphide
H_2S	mg L^{-1}	Dissolved hydrogen sulphide
Mn(II)	mg L^{-1}	Dissolved manganese (oxidation state $^{+}$3)
Mn(IV)	mg	Manganese (oxidation state $^{+}$4)
NaCl	mg L^{-1}	Sodium chloride
TA_meq/L	meq L^{-1}	Alkalinity milliequivalents

TATemp	°C	Temperature at total alkalinity analysis
TitrantVol	ml	Titrant volume
TApH	pH	Total alkalinity; titrant analysis pH
TA_mgCaCO$_3$	mg L^{-1}	Total alkalinity as calcium carbonate

Nutrients

Abbreviation	units	Parameter Name
NH_4^+	mg L^{-1}	Ammonium cation (atomic mass = 18)
NH_4^+ -N	mg L^{-1}	Ammoniacal nitrogen (atomic mass = 14)
NO_3^-	mg L^{-1}	Nitrate anion (atomic mass = 62)
NO_3^- -N	mg L^{-1}	Nitrate as nitrogen (atomic mass = 14)
NO_2^-	mg L^{-1}	Nitrite anion (atomic mass = 46)
NO_2^- -N	mg L^{-1}	Nitrite as nitrogen (atomic mass = 14)
N_r	n/a	Reactive nitrogenous compound
SO_4^{2-}	mg L^{-1}	Sulphate
TON	mg L^{-1}	Total organic nitrogen
TRP	mg L^{-1}	Total reactive phosphorus
TOC	mg L^{-1}	Total organic carbon

Physical Characteristics

Abbreviation	units	Parameter Name
Baro	kPa	Barometric pressure
DO	mg L^{-1}	Dissolved oxygen
DOsat	%	Dissolved oxygen; percentage saturation
EC	µS cm^{-1}	Electrical conductivity
Eh	µS cm^{-1}	Electrical conductivity (hydrogen electrode)
O_2	n/a	Oxygen gas
N_2	n/a	Nitrogen Gas
ORP	mV	Oxidation-reduction potential
pH	pH	The acidity or basicity of an aqueous solution
SPC	µS cm^{-1}	Specific conductivity; EC temperature corrected

SpActual	$\mu S\ cm^{-1}$	Actual conductivity
TDS	ppm	Total dissolved solids
Temp	°C	Temperature

QMap, Geological, and GIS

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

Statistical

Abbreviation	Parameter Name
ANNOVA	Analysis of variance
Cmp	Principal component derived by PCA
HCA	Hierarchal cluster analysis
IDF	Inverse-DF function used to normalise data
KMO	Kaiser-Meyer-Olkin measure of adequacy
PCA	Principal component analysis

SPSS	Statistics software from IBM

General

Abbreviation	Parameter Name
AirTemp	Ambient temperature at time of sampling
ATP	ATP adenosine triphosphate
CBE	Charge Balance Equation
CNC	Computer Numerical Control
CPT	Cone Penetration test
DEA	Denitrifying enzyme activity
DEM	Digital Elevation model
DL	Detection limit
DNRA	Dissimilatory nitrate reduction to ammonia
DRASTIC	Drastic
FSL	FSL fundamental soil layers
GIS	Geographic information systems
GNS	New Zealand Crown Research Institute; formerly Institute of Geological and Nuclear Sciences
GPS	Global positioning system
PPK	Post Processing Kinematic GPS
GV	Guideline value
ha	Hectares
HRC	Horizons Regional Council (HRC)
KML	File extension registered with Google Earth software
LCDB	Land Cover Database version 4.1.
LRIS	Land Resource Information Systems Portal
MAV	Maximum allowable value
MP	Multi-purpose
NIWA	The National Institute of Water and Atmospheric Research Ltd.
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 x 10^6 tonne
TVZ	Taupo Volcanic Zone
WHO	World Health Organization