Long-term trend analysis of groundwater quality at Te Waikoropupū springs – Tākaka

M Moreau

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EXECUTIVE SUMMARY

Tasman District Council commissioned GNS Science to: (1) characterise natural variability (short- and long-term) and trend patterns of water chemistry at the Te Waikoropupū main spring; and (2) undertake statistical analysis of nitrate-nitrogen concentrations from duplicate samples collected in the context of changing sampling location, analytical method and laboratories. This report also provides guidance on how to deal with changes in analytical methods, laboratory and detection limits in the context of limit setting and future water quality monitoring.

Groundwater analyses were compiled for Te Waikoropupū spring systems for the 1970–2021 time period. The bulk of data consisted of (1) quarterly long-term monitoring water samples of the main spring as part of the National Groundwater Monitoring Programme (1990–current) and (2) monthly to currently bi-monthly monitoring water samples undertaken by the Friends of Golden Bay (2016–current); and was complemented via historic analyses collected during site investigation, including duplicate samples. Data was cleansed and checked, then processed for statistical trend testing (Mann-Kendall, Kruskal-Wallis tests, Sen's slope estimator). Cleansed and processed data are provided as an attachment to this report.

Groundwater at the main spring contains more total dissolved solids (median field conductivity of 700 µS/m over the 2016–2021 period) than most New Zealand groundwaters. Calcium, chloride, magnesium and sodium concentrations are also higher than national medians concentrations. Nutrient concentrations were below most New Zealand groundwaters and reported threshold for land-use-impacted waters (2.5 mg/L for nitrate-nitrogen; Morgenstern and Daughney 2012). Statistically perceptible trends were observed for three parameters over the 2011–2021 (short-term) and 1970–2021 (long-term) time periods: (1) decreasing dissolved reactive phosphorus concentrations (<0.001 mg/L per year, both period) and (2) increasing field dissolved oxygen (0.05 mg/L per year, long-term only) nitrate-nitrogen concentrations (0.006–0.019 mg/L per year, short- and long-term, respectively). The non-parametric Wilcoxon test was used to assess differences in analyses from split samples collected between 2016 and 2020. Neither the comparison of two methods and laboratories (n = 13) or sampling location (n = 6) exhibited statistically significant differences in median concentrations. In contrast, the test demonstrated that, within the same laboratory, nitrate-nitrogen concentrations measured using the cadmium reduction method were significantly different from those measured by ion chromatography (n = 15, p-value <0.005 at the 95% confidence level). A significant difference was also observed for samples analysed by ion chromatography at two separate laboratories (n = 9, p-value = 0.009 at the 95% confidence level).

Recommendations from this report are:

- Further investigations of long-term trend changes observed at the main spring, which would include documentation of land use and farming practice in the valley and contribution from karst uplands, as well as rainfall, to elucidate the cause of changing trends.
- Appropriate documentation of analytical results is important to build confidence in monitoring data and, should analytical methods or laboratory change, split sampling for a period allowing for sufficient sample size (n >10) for statistical testing is recommended.
- Karstic systems can include high-volume flow paths and high-yielding springs such as Te Waikoropupū, in which small increases in chemical concentration can translate to a large increase in chemical mass load at the receiving environments. These systems are quite unique in terms of flow process and hydraulic properties and therefore should be studied case by case in the context of limit setting. This should also include studies on attributability of contaminants regarding allogenic and /or anthropogenic sources.

- Groundwater quality monitoring at the spring, due to the karstic nature of its source aquifer, could include collection of both low- (e.g. quarterly) and high-frequency (e.g. storm) event-based groundwater quality sampling (provided samples can be obtained from the spring sources), avoiding localised runoff and flow monitoring. An alternative would be to consider a series of storm event-based grab sampling, avoiding localised runoff.

1.0 INTRODUCTION

Tasman District Council (TDC) has been developing a water management plan for the Tākaka catchment, which includes the karst groundwater system linked to the nationally recognised, iconic and wāhi tapu (sacred place) Te Waikoropupū springs. A Water Conservation Order application was filed by the Ngāti Tama ki Te Waipounamu Trust and Andrew Yuill to protect the groundwater system that feeds the springs and associated water bodies, which is a first in New Zealand. Water conservation orders currently exist for 13 rivers and two lakes in the country (Ministry for the Environment [2021]). Hearings on this application were conducted in 2018 by a Special Tribunal appointed by the Minister for the Environment. The Special Tribunal's recommendations were released in March 2020 and received numerous submissions. At the time of writing of this report, response to these submissions was being handled by an Environment Court enquiry process.

As part of the hearing, long-term groundwater quality data were presented, in particular, water samples collected at Te Waikoropupū springs (main spring and adjacent springs), Fish Creek and Fish Creek springs by TDC or other parties. These samples were analysed by multiple laboratories and different parties over the years. The received submissions highlighted contention on certain chemical parameters, their variability and what suitable limit on these parameters should be set. The final limits set will have significant impacts for the whole Tākaka valley and for TDC, who is responsible for the management of these outcomes.

There is a need to provide a clear understanding to both the TDC and community for any differences in results of the various parameters and also its significance in terms of derived short-, medium- and long-term variations. Such understanding will (1) add confidence to the significance of any trend evaluation undertaken, (2) provide a basis for comparisons of testing data from other sites and catchments in the Tasman region and (3) be potentially useful to other regions in New Zealand.

1.1 Scope

To provide authoritative information on the state and trend of water quality from the springs in the context of the Special Tribunal's recommendation, and to inform its long-term groundwater resources protection strategy, TDC commissioned GNS Science (GNS) to:

- Provide context information around laboratory results using literature review and inputs from chemists from several laboratories (e.g. Hill Laboratories). This information will specifically cover analytical measurement methods and modifications, accuracy and resolution, detection limit, uncertainty of measurement and appropriate method of reporting results.
- Compile all available groundwater quality data from Te Waikoropupū Springs, Fish Creek and Fish Creek springs; undertake and document data-quality checks. Cleaned and checked datasets are provided as an attachment to this report.
- Undertake state and trend analysis for time-series data using settings (e.g. time period, use of seasonal test, etc.) agreed on with TDC to characterise natural variability (short- and long-term) and review trend patterns.
- Provide guidance on how to deal with changes in analytical methods, laboratory and detection limits in the context of limit setting and future monitoring. This is to be informed by statistical analysis of paired nitrate-nitrogen concentrations from split samples collected in the context of changing sampling location, analytical method and laboratory.

1.2 Hydrogeological Setting

The Tākaka River catchment (928 km^2) includes sub-catchments of the Waingaro, Anatoki and Te Waikoropupū rivers (Figure 1.1). The Tākaka River catchment is dominated by a westerly weather system, with decreasing annual precipitation with catchment location: Anatoki (5000 mm/yr), Waingaro (3200 mm/yr) and Upper Tākaka (2700 mm/yr). Within each sub-catchment, rainfall increases with ground elevations (Stewart and Thomas 2008).

The north–south-oriented Tākaka valley is a 9-km-wide and 26-km-long depression (Figure 1.1). Most of the valley floor consists of Quaternary sand and gravel deposits overlying Tertiary sediments, which includes (in chronostratigraphical order) the Miocene Tarakohe Formation, the Oligocene Tākaka Limestone and the Eocene Brunner Coal Measures. The Tertiary sediments lie unconformably over the Ordovician Arthur Marble, which extends to the coast and is possibly intruded in the mid-valley by a diorite (Stewart and Thomas 2008).

The Quaternary sand and gravel deposits form the Tākaka Valley Unconfined Aquifer Gravel which is of local importance as a water source. The Tarakohe Formation consists of mudstone and acts as an aquiclude. The Tākaka limestone consists of limestone and acts as an aquifer. The Brunner Coal Measures (formerly known as Motupipi Coal Measures) comprises alternating sandstone, siltstone, carbonaceous mudstone and coal seams and acts as an aquiclude (Leask 1993; Stewart and Thomas 2008). The Arthur Marble extends to the sea and also outcrops east and west of the lower valley and in the upper reaches of the Waitui Stream. This is a main aquifer source in the valley and is referred to as the Aquifer Marble Aquifer (Figure 1.2).

Te Waikoropupū Springs consists of two main areas (Figure 1.3): the main springs, with about eight major deeper vents (4–5 below the water line); and the Dancing Sands springs, with multiple shallower (down to 2.7 m depth) vents. The springs discharge to Te Waikoropupū River, a tributary of the Tākaka River. Two small springs occur upgradient from the springs, c. 240 m southwest of the springs, and discharge into Fish Creek, a tributary of the springs' outflow (Michaelis 1974). The springs issue at an elevation of 14–17 m above sea level, have New Zealand's largest spring discharge (mean flow from the main spring is 10,000 L/s; Thomas and Harvey 2013) and are among the clearest waters in the world (Davies-Colley and Smith 1995).

Groundwater recharge of the main spring was quantified, using an isotope mass balance, as mainly occurring through the karstic upland (74%), with other contributions from the upper Tākaka River (18%), valley rainfall (8%) and a small contribution from seawater (0.5%); the later varying with flow and coming from the deeper aquifer. In contrast, the upper Tākaka River was found to contribute half of the Fish Creek springs groundwater, complemented in similar quantities by valley rainfall and karst uplands. Using chemical signature, the proposed conceptual model suggested that Fish Creek has a composition close to a shallow system, whereas the main spring is more representative of a deeper groundwater system. Age-tracer concentrations measured in groundwater indicated a mean residence time of 8 years at the main spring (Stewart and Thomas 2008).

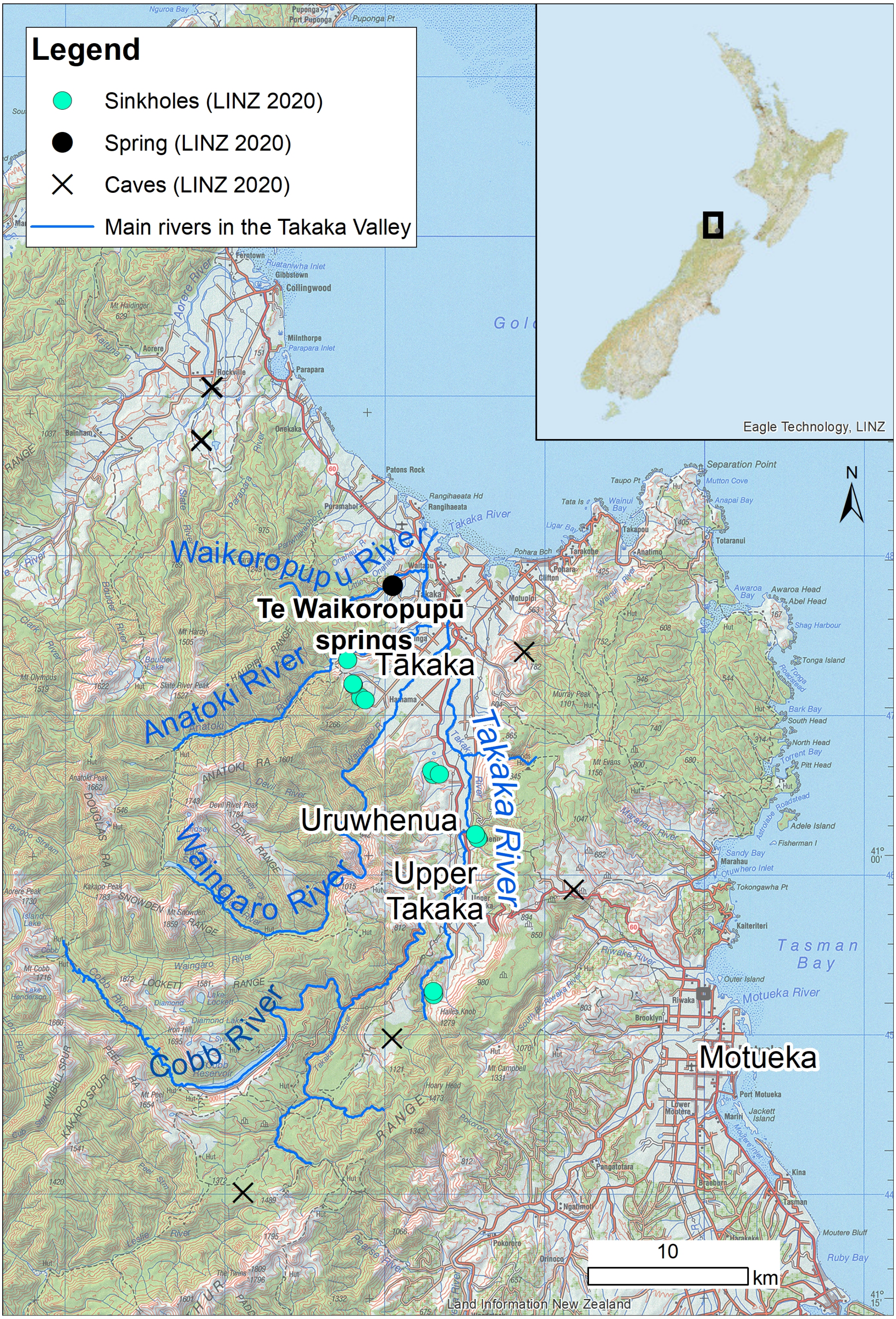

Figure 1.1 Map of the Tākaka valley showing the location of Te Waikoropupū springs and karstic features. The locations shown on the map for caves and sinkholes were sourced from the 1:50,000 scale topographic map (LINZ 2021a, 2021b). However, it is acknowledged that, at the local scale, multiple unrecorded caves and sinkholes are located in the catchment (Thomas 2021).

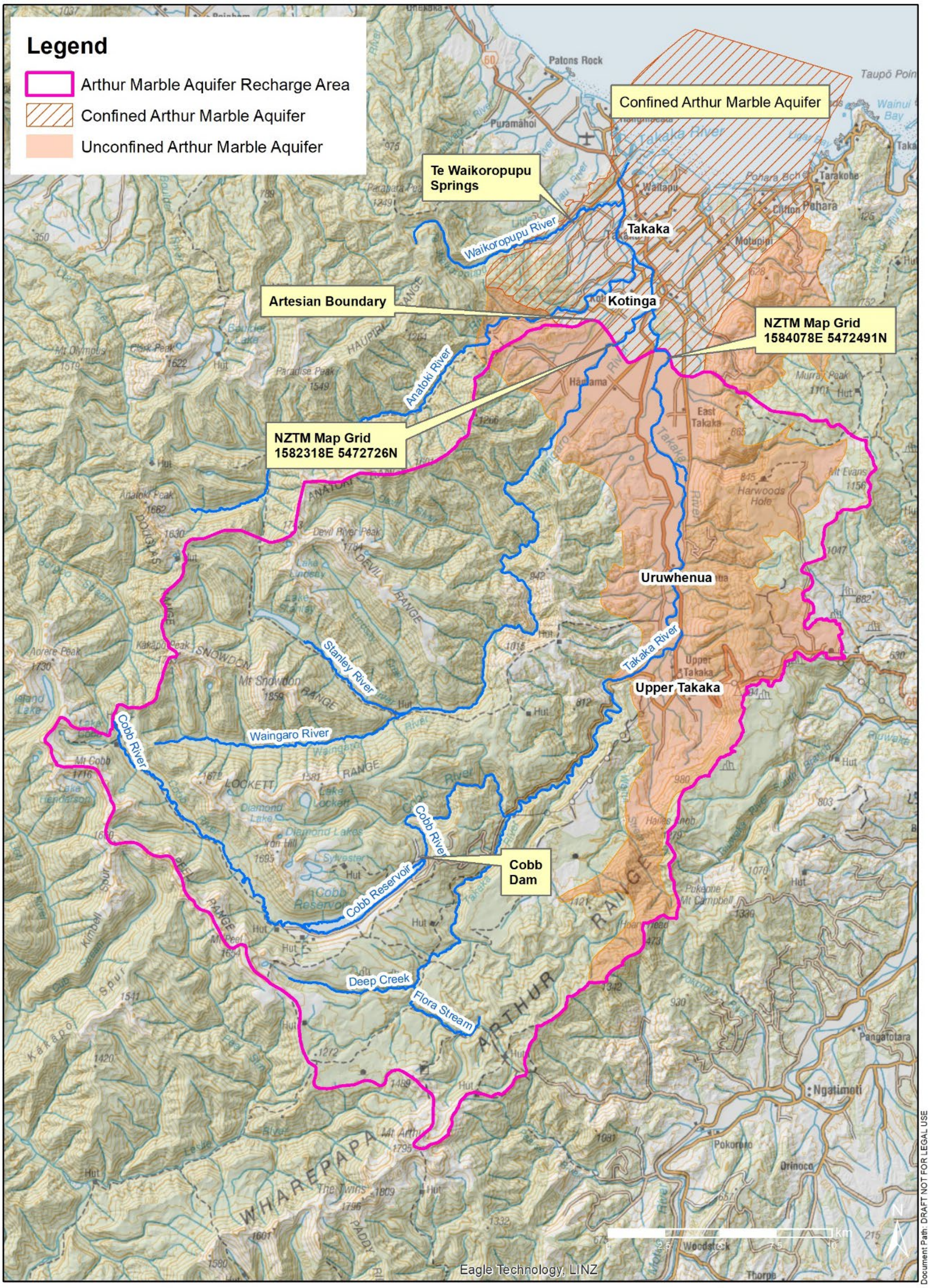

Figure 1.2 Tākaka River Basin, showing the Arthur Marble Aquifer recharge area derived from geological and surface water catchment boundaries. The figure also displays the confined and unconfined areas mapped for the Arthur Marble Aquifer (Thomas 2021).

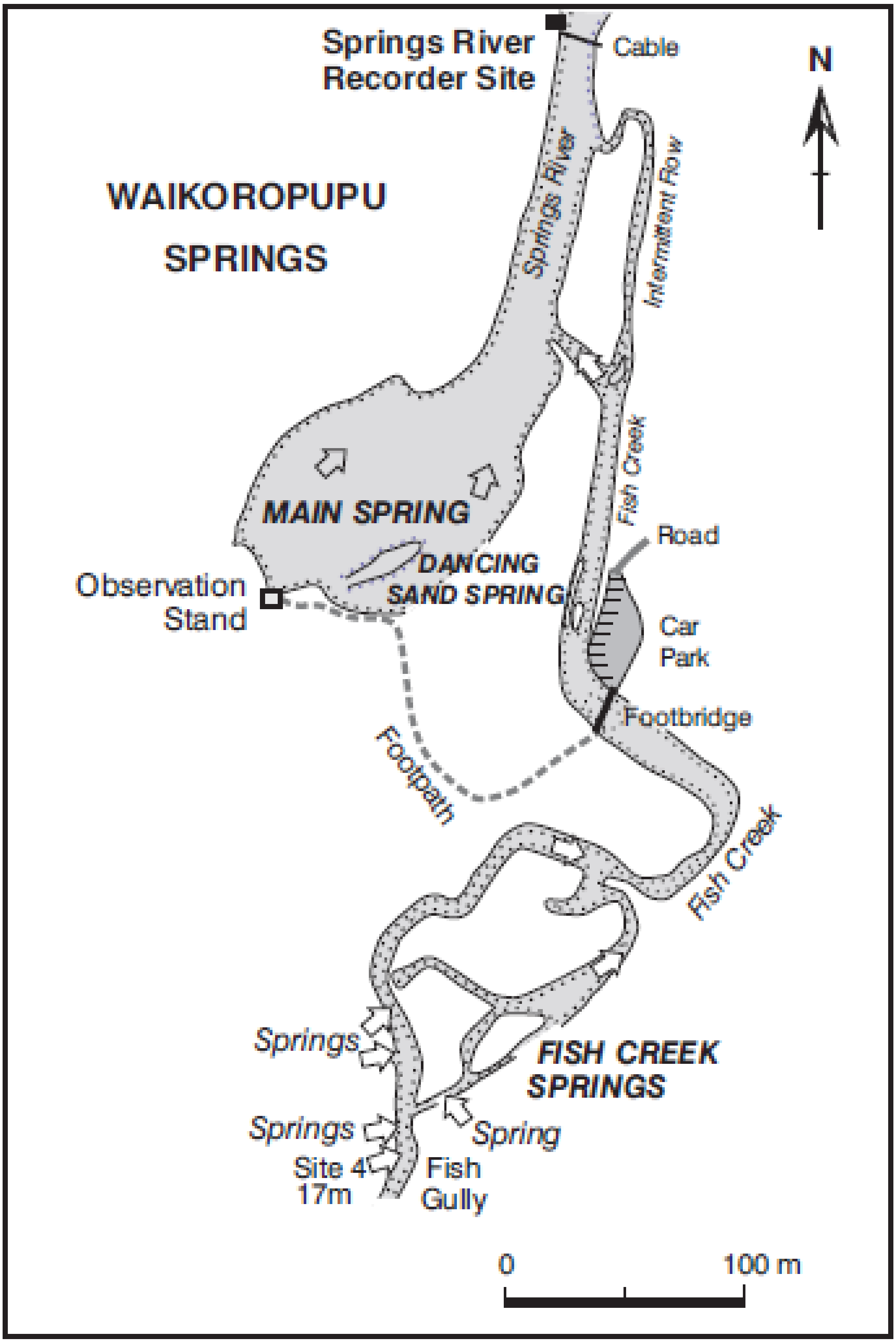

Figure 1.3 Schematic map showing the sampling point locations of the Te Waikoropupū Springs complex (modified from Stewart and Thomas 2008).

2.0 LABORATORY MEASUREMENTS ON GROUNDWATER SAMPLES

Reported laboratory test results include sample name; collection date; sample conditions upon reception at the laboratory (usually reported as a comment), where applicable; whether the sample was laboratory- or field-filtered; the analyte measured; measurement value; unit of measurement; detection limit; and associated uncertainty of measurement (upon request). The following sections detail how this context information is derived and captured.

2.1 Chain of Custody

Samples arriving at the laboratory are accompanied by a completed Chain of Custody form that enables sample traceability from the field to the laboratory. This form unequivocally identifies each sample bottle; outlines the test requested; and records the sample arrival condition and date, which informs on the sample integrity. For time-sensitive analyte (e.g. bacteria counts, radon), sample arrival time is also recorded (Milne 2019).

2.2 Analytical Method

For each analyte, multiple analytical methods are available to measure the relevant chemical concentrations in water samples. Analytical methods are recorded in Standards such as the *Standard Methods for the Examination of Water and Wastewater*, a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). Alternative Standards in use in New Zealand include, but are not limited to, the American Society for Testing and Materials (ASTM International c2021), the EPA Standards (EHS Online 2021) and the ISO Standards (ISO [2021]). Each Standard is peer-reviewed, updated and used routinely for environmental monitoring worldwide. For instance, the *Standard Methods*, which was first published in 1905, is a regularly reviewed, up-to-date (currently 23rd edition), comprehensive reference covering all aspects of water and wastewater analysis techniques (Baird et al. 2017).

Methods listed in these Standards are linked with the analytical techniques used (e.g. ion chromatography) and may be separated by targeted concentration range, water type (e.g. wastewater) and equipment. For example, in the *Standard Methods*, eight methods are listed for the determination of nitrate-nitrogen, within the range of concentrations measured at Te Waikoropupū main springs (0.12 mg/L to 0.92 mg/L). These methods are based on ultraviolet light techniques (APHA 4500-$NO3^-$ B; APHA 4500-$NO3^-$ E; APHA 4500-$NO3^-$ F; APHA 4500-$NO3^-$ H; APHA 4500-$NO3^-$ I), ion chromatography (APHA 4110B and APHA 4110C) and electrophoresis (APHA 4140B) (Baird et al. 2017).

Analytical methods are selected by laboratories from any of the existing Standards, considering the sample type (e.g. geothermal, groundwater, etc.), expected concentration range, health and safety, and operational aspects (e.g. equipment available, running costs) (Baird et al. 2017; Heron 2021; Sanderson 2021). Laboratories may modify a standard method to reduce a matrix effect that prevents obtaining a measurement, for instance, doubling the volume of a reagent to suit the range of concentrations expected in the batch of samples to be analysed. The National Environmental Monitoring Standard (NEMS) for Discrete Water Quality identifies specific methods for groundwater quality as ‘best-practice’ to achieve the highest-quality coding for various analytes in an effort to encourage consistent use and review of environmental data sourced from multiple organisations (Milne 2019; Heron 2021). However, provided that additional measurements are provided with appropriate context information, these may be used in conjunction with data collected using the specific methods outlined in the NEMS.

To ensure that analytical services are performed by a suitably qualified organisation, an accreditation process is in place in New Zealand that involves an independent assessment for a specific method from a published standard, for which the laboratory applies to annually. This accreditation is delivered by the International Accreditation New Zealand (IANZ), which is an autonomous Crown entity established by the Testing Laboratory Registration Act 1972. The accreditation process will consider any methods published from a Standard and allow for method modifications, provided that the certificate states the reference standard method with the suffix '(modified)' for transparency (Heron 2021; Sanderson 2021). Clear identification of any modification to the methods on the laboratory report is also a requirement of the National Environmental Monitoring Standard (NEMS) for Discrete Water Quality (Milne 2019).

Test methods may change over time, for example, through automation of a test, new method development in response to the discontinuation of reagents, technological advances or laboratory contracts. Changes in methods are likely to result in step changes, especially if a change in the chemistry of the test is involved, i.e. switching between methods. It is therefore good practice to store the test method information alongside the test results and only consider altering the basic chemistry of the test for a compelling reason, for instance, a much cheaper test providing similar or lower uncertainty (Milne 2019).

Because of these step changes, the NEMS recommends long-term monitoring programmes to retain the same laboratory, test method and associated instruments to avoid 'step' changes that can arise when a change is made to any one of these. However, if a change in test method occurs, efforts should be made to obtain duplicate analyses using both the old and new test methods for a short but sufficient time period to allow for the determination of a conversion factor to align the old method to the new method, if deemed applicable. This conversion factor will need to be applied by the monitoring programme manager, since laboratories can only report results for samples on an 'as received' basis. As an indicative period, the NEMS suggests aligning the sampling frequency to that of the monitoring programme using a period-enabling sufficient data point for statistical analysis (n >10). For example, monthly parallel testing over a 12-month period for a programme based on monthly sampling (Milne 2019). The overlap period should take into consideration the minimum point requirements for the statistical tests to be used. Note that there is no time threshold to define long-term monitoring; however, the minimum time period recommended to report on groundwater quality state varies between two and six years (European Commission 2009). Groundwater quality state and trends have been reported over periods of five-year, 10-year and longer time periods (Daughney and Randall 2009; Moreau and Daughney 2015).

2.3 Detection Limit

The method detection limit (MDL) for a laboratory test, also known as the limit of detection (or LOD), is statistically determined as the minimum concentration that the laboratory can be confident is above zero for a set confidence level. For instance, the EPA standard recommends the use of a 99% confidence for MDL calculations. It is determined from repeated analyses on separate occasions of a sample containing the analyte at levels 2–10 times the expected detection limit and considers all of the analytical operations on a sample (sub-sampling, extractions, digestions, dilutions, reagents, instrument parameters, etc.) (Ministry for the Environment 2011).

2.4 Uncertainty of Measurement

All laboratory measurements are accompanied by an uncertainty factor, which encapsulates a range of uncertainty sources (e.g. uncertainty in the chemistry involved, the reagent quality, the instrument, etc.). In addition, routine repeated measurements – performed on a set of standards – allows quantification of uncertainty of measurement (UoM) using a statistical method (Milne 2019). UoMs are typically calculated regularly, as per laboratory standard operating procedure, by independently measuring a set of standards several times. There are multiple ways to calculate this value. At the New Zealand Geothermal Analytical Laboratory (NZGAL), the UoM for the concentration range between standards is then extrapolated using a statistical formula to avoid impractical repeated testing at each level (Sanderson 2021):

$$uncertainty\ of\ measurement\ (\%) = \frac{2 \times standard\ deviation}{average\ measured\ value}$$

It follows that UoM will change with time and the range of concentrations for a given method performed on the same equipment (Table 2.1, Figure 2.1). UoM may be reduced through standard procedure and steps, for instance, using specific areas to conduct some analyses. These steps are part of laboratory quality assurance / quality control procedures. Table 2.1 and Figure 2.1 illustrate the variability of UoM for two methods and multiple concentration ranges. In this example, for a concentration of 0.4 mg/L (Sample ID 3), UoM varies from 0.01 mg/L (regular test) to 0.02 mg/L (low-level test), suggesting that the regular test is the most suited for the analysis, which is consistent with this concentration being outside the low-level test range (i.e. in this example, 0.003 to 0.1 mg/L).

Table 2.1 Uncertainty of measurement for nitrate-nitrogen concentration measured by ion chromatography (APHA4110B) at NZGAL in 2019.

Test	Lower Detection Limit	Concentration Range (mg/L)	Uncertainty of Measurement (%)	Sample ID	Example Concentration (mg/L)	Example Uncertainty (mg/L)
Nitrate-nitrogen (low level)	0.003	0.003–0.1	15.7	1	0.004	0.001
		0.003–0.1	15.7	2	0.040	0.006
		>0.1	3.9	3	0.40	0.02
Nitrate-nitrogen (regular)	0.01	<0.1	10.9	2	0.04	0.004
		0.1–0.5	1.5	3	0.40	0.01
		0.5–5	0.3	4	4.0	0.01
		>5	0.3	5	40	0.1

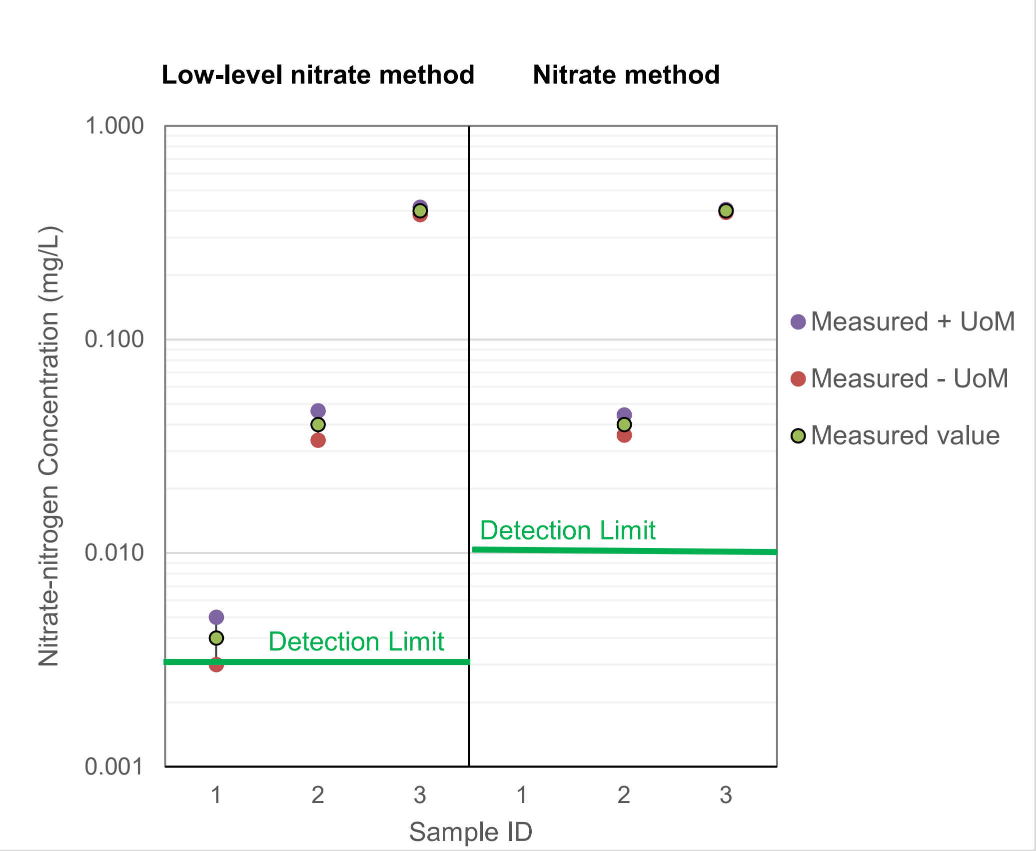

Figure 2.1 Visual representation of detection limit and uncertainty of measurement from the Table 2.1 examples.

3.0 STATE AND TRENDS FOR SELECTED PARAMETERS AT TE WAIKOROPUPŪ MAIN SPRING

3.1 Data Collection

Groundwater quality data was collected by GNS and TDC for the following sites (Figure 3.1):

- Te Waikoropupū main spring at the viewing platform. This site is associated with a long-term time-series dataset consisting of:
    - a combination of site investigations (Michaelis 1974; Stewart and Downes 1982; Mueller 1992; Miles 1999; Stewart and Thomas 2008)
    - recent (2019–2020) split samples (Thomas 2021)
    - recent (2016–2018) samples by the Friends of Golden Bay (FOGB), and
    - long-term monitoring (1991 to present) as part of the National Groundwater Monitoring Programme (NGMP) (GGW Database 2005–present).
- Dancing Sands springs. This site and its available dataset comprises sporadic site investigations (Michaelis 1974; Cawthron 1999).
- Fish Creek at the TDC sampling point. This site is associated with a dataset that includes:
    - site investigations (Michaelis 1974; Stewart and Downes 1982; Mueller 1992; Cawthron 1999) and
    - recent (2019–2020) duplicate samples (TDC 2021).

Site investigations covered a range of purposes: ecological spring study (major ion chemistry, Michaelis 1974), hydrological spring study (major ion chemistry and isotopes; Stewart and Downes 1982), a geohydrological study of the Tākaka valley (major ions, Mueller 1992) and a comparison of chemistry between Te Waikoropupū vents (Cawthron 1999). Duplicate samples were collected for comparative purposes (Thomas 2021) while sampling for state and trend monitoring (regular major ion chemistry and dissolved metal, occasional tracer elements and age tracers [GGW Database 2005–; TDC 2021]). The sampling objectives for all collected data are consistent with long-term state and trends characterisation, and therefore the assembled data is deemed suitable for this report's purpose.

Samples from Te Waikoropupū main spring site have been collected by TDC staff at the viewing platform on a quarterly basis, as part of the NGMP, since 1991. It was one of the first NGMP sites and, as such, is one of the longest groundwater quality time series in New Zealand (Figure 3.2). The NGMP programme is collaboratively operated between all regions and GNS. Samples are collected quarterly at all sites and analysed for more than 17 parameters at the GNS laboratory facility. These parameters include field temperature; field conductivity; and concentrations of dissolved calcium, sodium, magnesium, manganese, potassium, iron, chloride, fluoride, bromide, nitrate-nitrogen, ammonia-nitrogen, dissolved reactive phosphorus, sulphate and silicon. Dissolved reactive phosphorus sampling and analyses were initially undertaken annually, and then quarterly since 2015, as, in this case, the site of a spring. All NGMP samples have been analysed for a consistent analytical suite at NZGAL since June 1994 and made available via publicly accessible Geothermal and Groundwater public datasets since 2011 (https://ggw.gns.cri.nz/ggwdata).

As the NGMP dataset has been evolving with time and in consultation with TDC, early site investigation data were added with consideration for long-term data curation and public access. FOGB water quality dataset is an independent dataset. Only partial information from the FOGB dataset was included in this work, focusing on the main spring and duplicate samples. As an example, short-term water quality data at the Fish Creek FOGB sampling point (Figure 3.1) is omitted for this study, as trend analysis of the creek was out of scope.

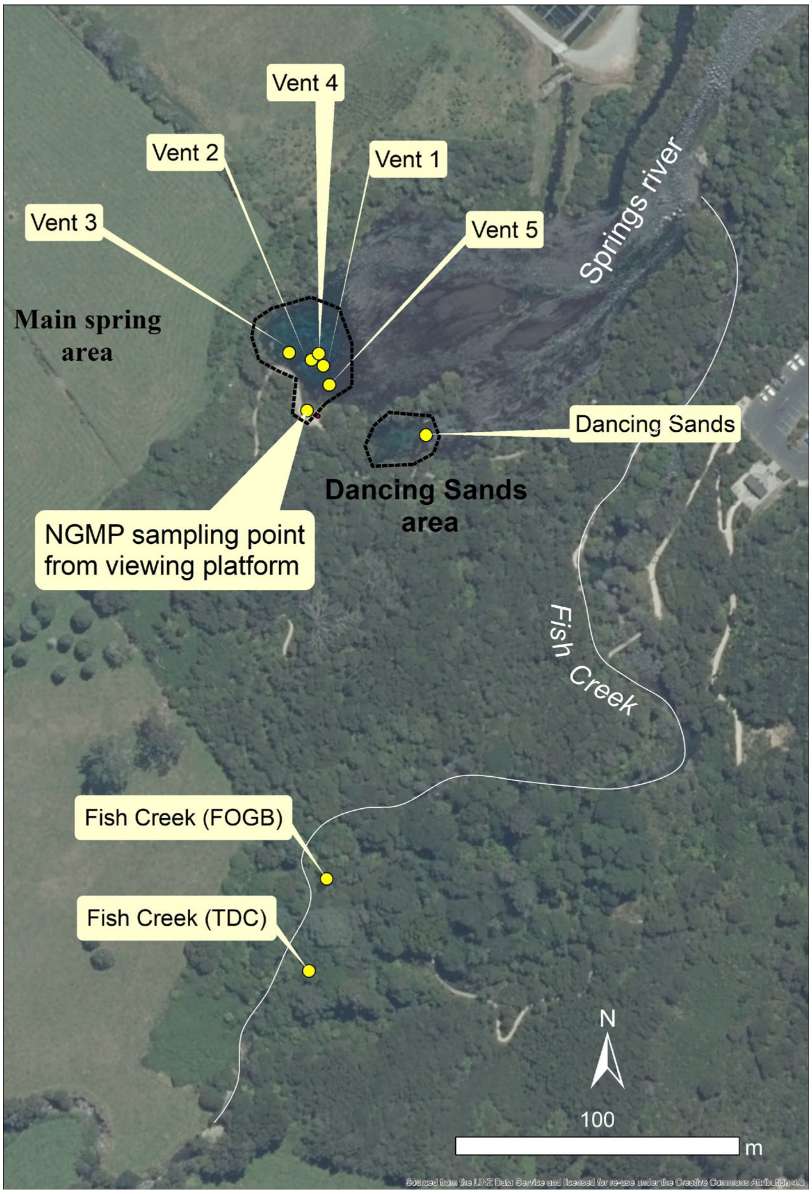

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Figure 3.1 Schematic map showing the sampling point locations of the Te Waikoropupū Springs complex.

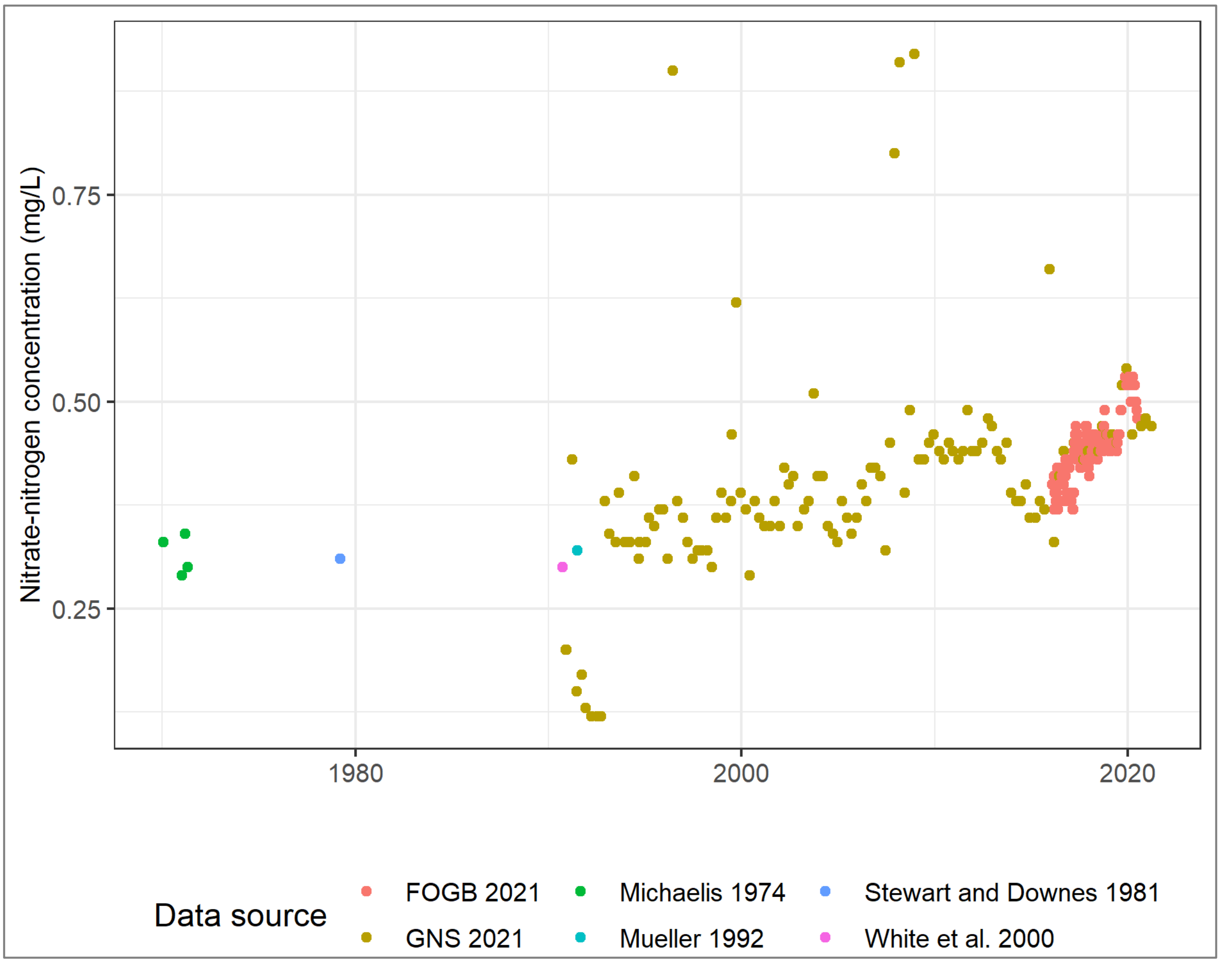

Figure 3.2 Nitrate-nitrogen time series at Te Waikoropupū main spring (1970–2021).

3.2 Data Processing

3.2.1 Data Cleaning

Analytical results from the NGMP dataset were combined with analytical results from the TDC database. The aggregated dataset was edited with the following steps:

1. A subset of the dataset was created that included the following parameters[1]: field dissolved oxygen; field pH; field conductivity; and concentrations of dissolved calcium, sodium, magnesium, potassium, chloride, nitrate-nitrogen, ammonia-nitrogen, dissolved reactive phosphorus and sulphate.
2. Site and parameter names were mapped and subsequently edited to be consistent throughout the dataset. Where applicable, analytical results were converted to a single unit or parameter form (i.e. ammonium-nitrogen converted to ammonia-nitrogen).
3. Groundwater quality was checked for inconsistencies and data capture error or partial capture (e.g. measured values negative, data gaps or reported as zeroes).
4. Nitrate time series were visually checked for inconsistency. Where outliers were visually identified, including lower and higher values in the 1990s, paper records were checked. However, no change in the dataset was actioned following the checking of early 1990s paper records.

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[1] After consultation with Tasman District Council.

5. Changes in NGMP analytical method, laboratory and organisation prior to June 1994 were reconstructed as part of this work, using the paper records from the programme held at GNS. This period includes the split of the Department of Scientific and Industrial Research (DSIR) into multiple Crown Research Institutes, including GNS, between 1991 and September 1992, where samples were processed at the DSIR water laboratory located in Christchurch, although the analytical method is recorded as ‘unknown’. Analyses undertaken at GNS were attributed to NZGAL from December 1992. Mapping of analytical methods used at NZGAL post-1994 has been published (Moreau and Daughney 2021). These changes have not yet been actioned to the GGW Database, as this is beyond the scope of the work.
6. Data sourced from FOGB water quality sampling consisted of field conductivity, nitrate-nitrogen and dissolved reactive phosphorus concentrations only. Samples were collected by FOGB according to the 2006 sampling protocol for State of Environment monitoring (Daughney et al. 2006; Thomas 2021).
7. Replicated analyses were removed for trend analysis purposes to avoid bias in statistics calculation. Practically, this meant that, on days where samples were collected concurrently by TDC and FOGB, GNS analyses were kept for consistency over the time period of the full record.

The final cleaned dataset consists of 1610 analytical results for 12 consistent parameters for samples collected at 11 sites, including 25 duplicate analyses.

3.2.2 Statistical Tests Selection and Implementation

The Mann-Kendall test, seasonally adjusted where relevant, was used for trend detection of temporal trends in groundwater quality. The Mann-Kendall test has a long history of use in water quality studies in general (Helsel and Hirsch 2002; Helsel et al. 2020) and has been applied in previous investigations of groundwater quality in New Zealand (Daughney and Randall 2009; Moreau and Daughney 2015). Seasonality was tested using the Kruskall-Wallis test, an equally widely used statistical test for environmental data analysis (Helsel and Hirsch 2002). Trend magnitudes are estimated using Sen’s slope estimator, which robustly handles typical groundwater quality data, i.e. non-normally distributed time series containing missing and censored values (Snelder and Fraser 2021).

Trend analysis was implemented using two methods:

- the Excel-spreadsheet format NGMP Calculator (Calculator; Daughney 2007, 2010), which has been used repeatedly in the past for reporting state and trend in groundwater quality (e.g. Daughney and Randall 2009; Moreau et al. 2016); and
- the R software (version 3.6.2) using the LWP-Trends (version 2101) and NADA (version 1.6-1.1) libraries (Lee 2020; Snelder and Fraser 2021). The latter method reflects recent advances in handling of censored data (Helsel 2012) that supersede methods used by the NGMP Calculator (Table 3.1). The NADA library implements the statistical methods to handle censored values. It is used here to calculate medians and median absolute deviations for time series with left-censored values. The LWP-Trends library was used to compute all statistical tests on censored and uncensored time series that have been processed with NADA methods; however, it does not output either medians or median absolute deviations, which were computed using the dplyr library (version 1.0.4, Wickham et al. 2021). This library also provides different trend descriptors (Snelder and Fraser 2021), described in the next section.

Table 3.1 Comparison of handling of censored values between the NGMP Calculator and the LWP-Trends and NADA R libraries (modified from Moreau 2018).

Statistics Type	LWP-Trends (Version 1804)	NADA	NGMP Calculator
Descriptive	Not applicable	Below 80% censoring, imputation using the robust regression on order statistics	Below 80% censoring, imputation using lognormal regression (Helsel and Cohn 1988)
Sen's slope estimator (includes seasonal)	Removal	Not applicable	Substitution to half the detection limit
Mann-Kendall (includes seasonal)	Left- and right-censored values are treated as two distinct ties statistical groups. Test statistics calculations are adjusted when censoring levels are multiple.	Not applicable	Substitution to half the detection limit
Kruskall-Wallis	Censored values and values less than the highest non-detect (<) are assigned the same low value and treated as ties (i.e. repeated values, which have the same rank). If the censored values are >, then all non-detects and values higher than the lowest non-detect (>) are assigned the same high value and are treated as ties.	Not applicable	Substitution to half the detection limit

To calculate meaningful state and trend metrics, minimum data point requirements were set as follows:

- Descriptive statistics (indicative of state): where more than half of the measurements are recorded below the detection limit (i.e. above a detection limit or censoring level of 50%), medians and trend metrics are reported as 'non-determined'. For censoring levels between 25% and 50% percentiles, data is insufficient to derive these values with confidence, and these values will be reported as 'non-determined'.
- Kruskall-Wallis test (includes seasonal, used for all time periods): the number of seasons considered for the analysis is four (Autumn, Winter, Spring and Summer). The annual time period commences on 1 March of the first year (start of Autumn). To enable seasonality state and trend assessments, all seasons must have at least one observation, and individual seasons require at least two data points.
- Mann-Kendall test and Sen's slope estimator (includes seasonal, used for the two trend assessment time periods): the time series must contain at least 10 data points, the maximum censored values must be smaller than the maximum observed values and, for each time series, at least five unique observations must be required.

In this report, three time periods were used: a 6-year period defined state (2015–2021); and two periods, 10-year (2011–2021) and full record (1970–2021), defined 'medium-term' and 'long-term' trends. Three datasets were processed: (1) NGMP data (which includes site investigations), (2) FOGB data and (3) a combination of the combined NGMP and FOGB datasets.

3.2.3 Reported Statistics

State and trend statistics are reported using the following metrics, in accordance with previous State of the Environment and national reporting (Daughney and Randall 2009; Moreau and Daughney 2015):

- Median and Median Absolute Deviation (MAD): the median is a measure of central tendency. It is a more robust measure than mean values because it is not affected by outliers. The MAD gives an indication of the data spread around the median; it is likewise more robust than the standard deviation, particularly to long distribution tails (Helsel and Hirsch 2002). In this report, outliers are defined as being more than four times the MAD. Values from two to four may be used, being more conservative with a higher number (Daughney 2010; Leys et al. 2013).
- Percentiles (5th, 25th, 50th, 75th, 95th): these also inform the data spread around the median. The median is the 50th percentile (Helsel and Hirsch 2002).
- Trend magnitudes: the rate of change in each parameter. In this report, the trend magnitudes are based on Sen’s slope estimator, which is commonly used for environmental reporting (Helsel and Hirsch 2002). Trend magnitude defined by Sen’s slope and its associated two-tail p-value. The Calculator also provide linear regression trend magnitude.
- Percentage annual change in slope. The annual change is calculated by dividing Sen’s slope by the median. In this instance, the median is calculated over the same time period as the slope and is subject to the same minimum data requirement.
- Statistical test p-values: in this report, several statistical tests were conducted to assess either the statistical significance of a trend, seasonality or distribution difference. For each test, a hypothesis is formulated and test statistics are calculated. An acceptable error rate is arbitrarily set to reject or accept the hypothesis, based on a data-calculated probability value (p-value). For this report, the significance level was set using a symmetric confidence interval and qualified in terms of uncertainty. Detailed information about the use of hypothesis tests in general and the tests used in this report can be found in Helsel and Hirsch (2002).
- Trend type or trend direction. Trend-type descriptor is only available for data processed using the NGMP Calculator and corresponds to the traditional trend descriptor, based on the sign of Sen’s slope (positive slopes are increasing trends), provided the trend test p-value is found below an arbitrarily defined confidence level (here set as 95% confidence). Possible values are: ‘increasing’, ‘decreasing’, ‘no trends’ or ‘not determined’. Trend direction is only available for data processed using the LWP-Trends library. This method was recently developed and applied to river quality state and trend assessments (Larned et al. 2016; McBride 2019) to replace the use of arbitrary confidence level compared to the trend test p-value to define trend type. In this method, a symmetric confidence interval around the trend is calculated. If this interval contains the zero value, the trend is described as ‘uncertain’. If this interval does not contain the zero value, this interval is ‘established with confidence’ and assigned either a ‘decreasing’ or ‘increasing’ descriptor.
- Lower and upper confidence interval bounds for Sen’s slope; this information is only available for data processed using the LWP-Trends library.

3.3 Results and Discussion

Although three datasets were processed for three time-periods, the body of the report focuses on description of current state using the combined dataset and the 6-year period (2015–2021); and trends calculated using the NGMP Calculator for the combined dataset for two periods, 10-year (2011–2021) and full record (1970–2021), defined medium-term and long-term trends. The comparison of trend calculation methods will be discussed for the nitrate-nitrogen time series. Comments are made with regards to consistency between the water quality datasets, but data itself is not shown; instead, it is provided in its entirety in a data output file (see Section 3.3.1).

3.3.1 Data Output

Cleaned and processed data are compiled in a digital data file accompanying the report (GNS CR2021-06 Data Output, *.xls* format) in the following worksheets:

- ‘Site_information’: contains a site list with an overview of the data available.
- ‘Clean_data’: contains groundwater quality data.
- ‘State’: contains groundwater quality state metrics per parameter, calculated over the 2015–2021 time period at the main spring.
- ‘Trends’: contains groundwater quality trend metrics, calculated over the 1970–2021 and 2011–2021 time periods at the main spring.

3.3.2 State

Field parameter values at Te Waikoropupū main spring were typical of oxidised New Zealand groundwaters for pH and dissolved oxygen, with median values of 7.6 (n = 19) and 6.2 mg/L (n = 19), respectively (Table 3.2). In contrast, median field conductivity was 700 µS/cm (n = 158), which is significantly above the reported national medians (160–235 µS/cm, Table 3.2) but lower than the highest medians (1000 µS/cm) that are found in the Gisborne district, where groundwaters are ‘evolved’ due to very slow movement and therefore increased total dissolved solids content via rock-interaction. At Te Waikoropupū main spring, high conductivities have been correlated with high flows / water levels. The current model suggests that high flow induces a small contribution from seawater via a Venturi effect (Stewart and Thomas 2018). This is somewhat demonstrated by the large variability of this parameter where the MAD (23 µS/cm) is about half of the interquartile range (50 mg/L), illustrated on the six-year time-series plot (Figure 3.4).

Major ion concentrations, which account for most of the total dissolved solids in groundwater, were also found at higher median values than reported nationally; for instance, the median calcium concentration was 63 mg/L compared to a reported national median of 14.6 mg/L (Table 3.2). The carbonate nature of the Arthur Marble Aquifer and the Tākaka Limestone are a likely source for calcium, carbonates and, to a lesser extent, magnesium for groundwater. Sodium and chloride sources include seawater but may also originate from rock interaction. All major ions exhibited some degree of natural variability expressed by up to 6 mg/L as MADs (Figure 3.3).

Nitrogen is mostly present in the form of nitrate-nitrogen, which is most common in oxidised groundwaters. Median nitrate-nitrogen was 0.44 mg/L, and ammonia-nitrogen consistently measured below the detection limit of 0.003 mg/L (Table 3.2, Figure 3.4). Nitrogen species may occur naturally from nitrogen-rich bedrock, natural soil leaching and sub-aqueous nitrification of organic nitrogen in the aquifer (Musgrove et al. 2016); however, an elevated concentration of nitrogen is also a possible indicator of land-use impact on groundwater quality (e.g. from sewage and fertiliser). Based on multivariate statistics, Daughney and Reeves (2005) established nitrate-nitrogen threshold values of 1.6 and 3.5 mg/L, respectively, for “probable” and “almost certain” land-use impact on New Zealand groundwaters. A separate study, combining groundwater chemistry and mean residence time, defined an intermediate threshold value of 2.5 mg/L of nitrate-nitrogen as an indication of land-use intensity (Morgenstern and Daughney 2012). Nitrate-nitrogen concentrations measured at the main springs are consistently measured well below these three thresholds.

Phosphorus can be naturally derived from rock interaction, decomposition of plant and animal tissue or originate from organic waste. It is also a land-use impact indicator, as fertilisers, manure and composted material contain phosphorus. Dissolved reactive phosphorus concentrations at the main spring remain low, with a range from <0.004 to 0.008 mg/L, which is lower than the national median (Table 3.2).

To assess the state over the period (2015–2021), concurrent water quality data with monthly (FOGB) and quarterly (NGMP) sampling period was utilised. Although the higher frequency captures more variability, visual examination of the time series suggests that the quarterly pattern is captured by the less frequent NGMP sampling (Figure 3.4). The non-parametric Mann-Whitney U test was used to assess the similarities of the nitrate-nitrogen concentrations between the two datasets. Median nitrate-nitrogen concentrations in the NGMP and FOGB groups were 0.44 mg/L and 0.43 mg/L, respectively, over the February 2016 to April 2019 period, and the distributions in the two groups did not differ significantly (n_1 = 13, n_2 = 145, p-value = 0.26 two-tailed). The observation that the spring natural variability is adequately captured by the less-frequent monitoring is consistent with a separate study, which compared water quality datasets collected by TDC and FOGB between February 2016 and February 2018 with discrete water quality measurements collected by FOGB and visual clarity measurements collected by NIWA between mid-October and mid-January 2018 (Gall and Milne 2018).

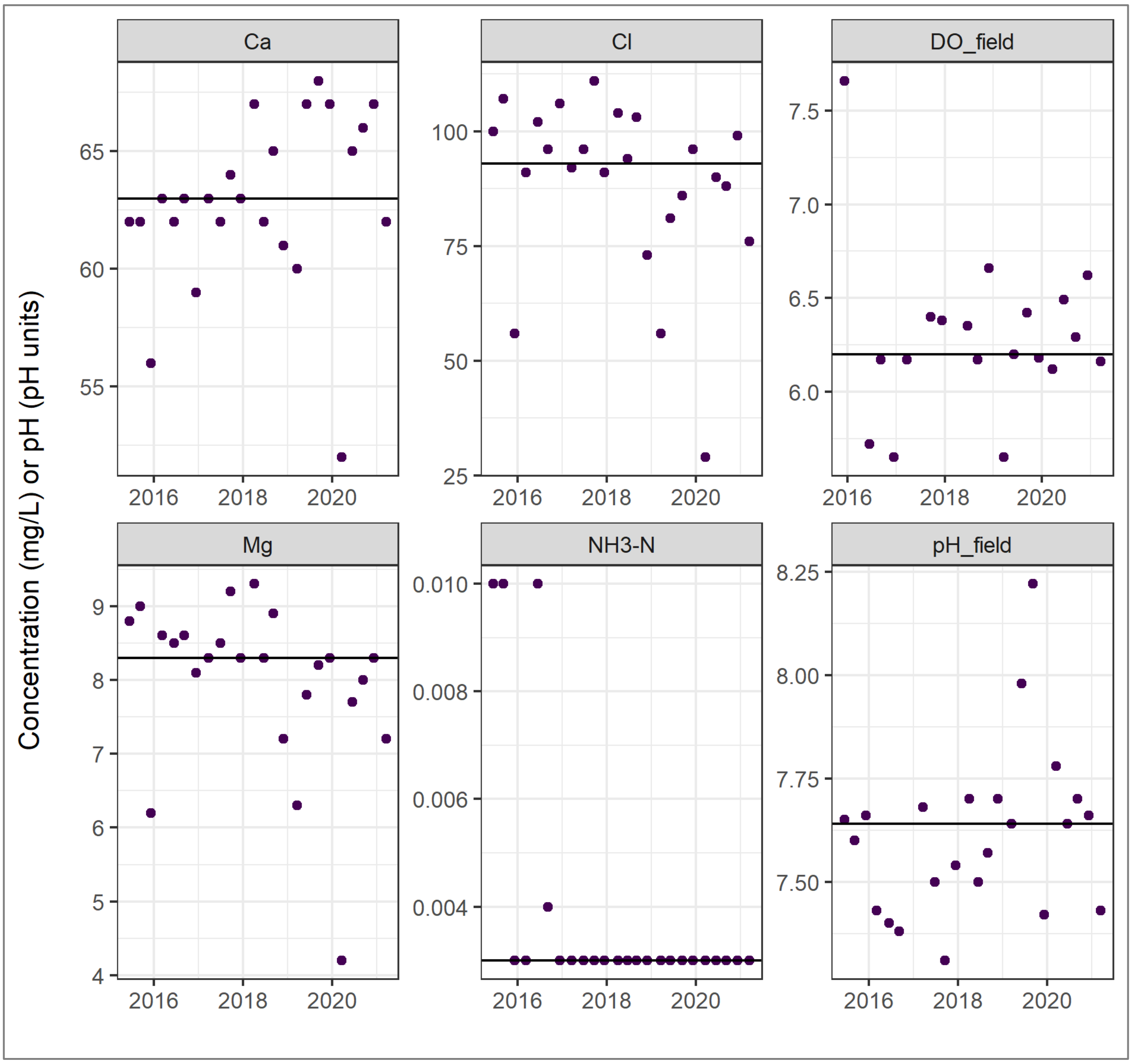

Figure 3.3 Time series for calcium (Ca), chloride (Cl), field, dissolved oxygen (DO_field), magnesium (Mg), sodium (Na), ammonia-nitrogen (NH3-N) and pH (pH_field) concentrations monitored at Te Waikoropupū springs for the period 2015–2021. The coloured line illustrates the median value calculated using the NGMP dataset.

Table 3.2 Summary state statistics for field conductivity (EC), pH, dissolved oxygen (DO), calcium (Ca), chloride (Cl), magnesium (Mg), sodium (Na), dissolved reactive phosphorus (DRP), ammonia-nitrogen (NH3-N) and nitrate-nitrogen (NO3-N) concentrations monitored at Te Waikoropupū springs for the period 2015–2021 using the NGMP Calculator. Previously reported national and global statistics for relevant settings are also provided for comparison (with the following references shown as superscripts: [1] Moreau et al. 2016; [2] Daughney and Randall 2009; [3] Daughney and Reeves 2005; [4] Larned et al. 2016). NA = not available, ND = not determined.

			Field Parameters			**Major Ions**				**Nutrients**		
			DO (mg/L)	**pH (mg/L)**	**EC (µS/cm)**	**Ca (mg/L)**	**Cl (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**DRP (mg/L)**	**NH3-N (mg/L)**	**NO3-N (mg/L)**
Te Waikoropupū main spring (2015–2021)		n	18	22	161	23	21	21	22	130	20	181
		% Censored	0	0	0	0	0	0	0	0	100	0
		Minimum	5.7	7.3	587	56.0	73.0	7.2	38.0	<0.004	<0.003	0.38
		5th percentile	5.7	7.4	624	59.1	76.0	7.2	45.2	0.004	<0.003	0.41
		25th percentile	6.2	7.4	670	62.0	90.0	8.1	53.8	0.005	<0.003	0.44
		Median	6.2	7.6	700	63	96	8.3	58.5	0.005	<0.003	0.46
		75th percentile	6.4	7.7	720	65.5	102	8.6	61.8	0.006	<0.003	0.47
		95th percentile	6.5	7.8	743	67.0	107	9.2	64.0	0.007	<0.003	0.52
		Maximum	6.7	8.0	779	68.0	111	9.3	65.0	0.008	<0.003	0.54
		MAD	0.18	0.08	23	2.00	6.00	0.30	4.00	0.001	ND	0.02
NZ groundwaters	2004–2013 [1]	Median	NA	NA	235	NA	NA	NA	NA	0.020	<0.01	0.55
	1995–2008 [2]	Median	NA	6.7	204	14.6	14	4.5	14	0.010	0.01	1.7
	1995–2008 [2]	95th percentile	NA	14.4	807	731	112.4	19.7	95.6	0.240	0.24	11
NZ oxidised groundwaters [3]	Cluster 1A-1	Median	NA	NA	NA	15.5	16.9	7.1	15.6	0.000	0.01	1.51
	Cluster 1A-2	Median	NA	NA	NA	13.1	24.7	7.8	20.8	0.020	0.01	4.68
	Cluster 1B-1	Median	NA	NA	NA	18.7	3.1	2.7	5.6	0.000	0.00	0.62
	Cluster 1B-2	Median	NA	NA	NA	6.4	7.3	2.3	8.4	0.020	0.02	0.73
NZ rivers (2009–2013) [4]	Natural land cover	Average	NA	NA	NA	NA	NA	NA	NA	0.0092	0.0064	0.08
	Exotic forest land cover	Average	NA	NA	NA	NA	NA	NA	NA	0.0301	0.0145	0.29
	Pastoral land cover	Average	NA	NA	NA	NA	NA	NA	NA	0.0225	0.0295	0.83

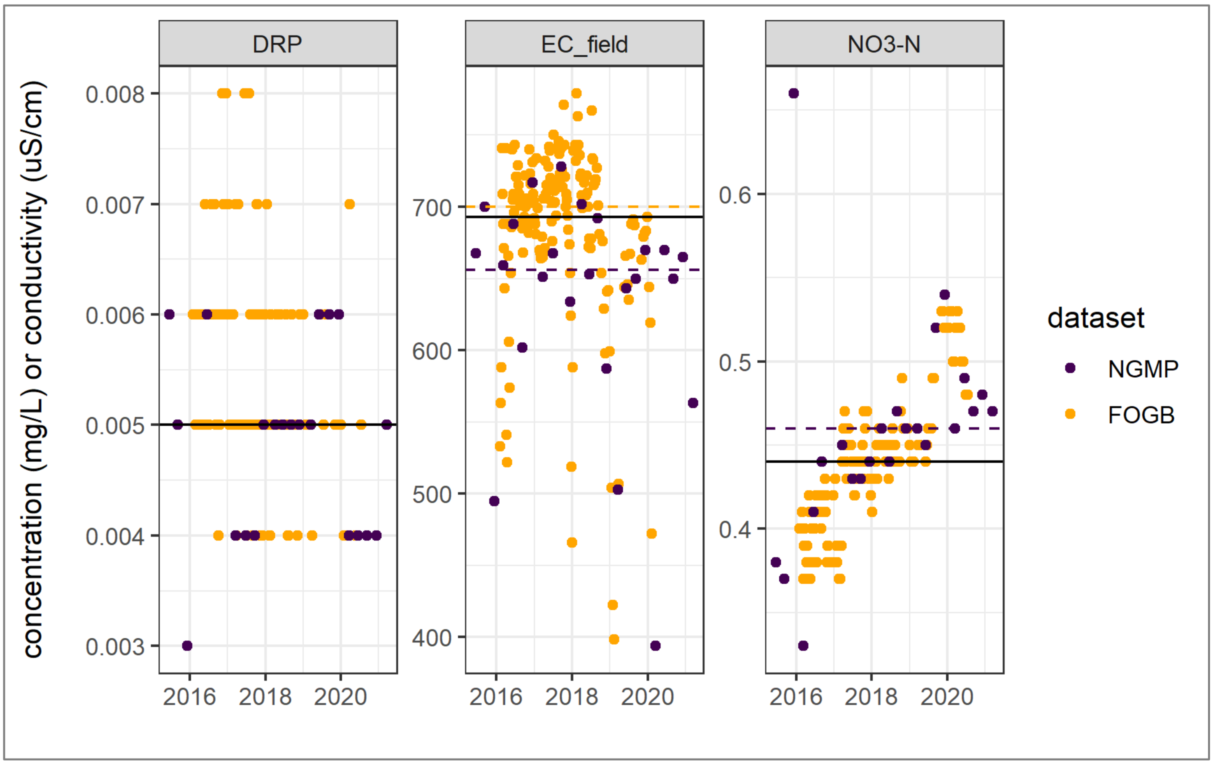

Figure 3.4 Time series for field conductivity (EC_field), dissolved reactive phosphorus (DRP) and nitrate-nitrogen (NO3-N) concentrations monitored at Te Waikoropupū springs for the period 2015–2021. The coloured lines illustrate the median value calculated using the NGMP Calculator for the three datasets: NGMP, FOGB and the combined dataset. Note that the DRP detection limit over the considered time series changed from 0.002 to 0.004 in 2018.

Table 3.3 Comparison of state statistics (2015–2021) for field conductivity (EC_field), dissolved reactive phosphorus (DRP) and nitrate-nitrogen (NO3-N) obtained from the NGMP, FOGB and combined datasets using the NGMP Calculator.

	Combined			**FOGB**			**NGMP**		
	EC_field	**DRP**	**NO3-N**	**EC_field**	**DRP**	**NO3-N**	**EC_field**	**DRP**	**NO3-N**
n*	158	164	181	142	147	166	19	20	20
Minimum	587	<0.004	0.37	619	<0.004	0.37	503	<0.004	0.38
5th Percentile	623	0.004	0.38	644	0.004	0.38	557	0.003	0.41
25th Percentile	671	0.005	0.41	681	0.005	0.41	639	0.004	0.44
Median	700	0.005	0.44	705	0.005	0.44	659	0.005	0.46
75th Percentile	721	0.006	0.46	722	0.006	0.45	690	0.005	0.47
95th Percentile	743	0.007	0.50	743	0.007	0.50	718	0.006	0.52
Maximum	779	0.008	0.52	779	0.008	0.52	728	0.006	0.54
Mean	694	0.005	0.44	702	0.005	0.43	651	0.005	0.46
MAD	23.0	0.001	0.02	21.0	0.001	0.02	29.0	0.001	0.02
Standard Deviation	38.1	0.001	0.04	31.3	0.001	0.04	55.7	0.001	0.04

* Note that processing through the calculator entails removal of outliers.

3.3.3 Trends

In this section, trend magnitudes (Sen's slope) are reported without consideration for the p-value, consistent with recent changes in reporting (McBride 2019). However, to account for the natural variability for a parameter at a given site, trends were classed as:

- 'perceptible', if the change in concentration (calculated over the time period) fell within four times the MAD, which is the criterion commonly used to detect extreme outliers (Daughney 2007); or
- 'imperceptible', if the change in concentration fell outside the 4×MAD range.

This classification is somewhat indicative of the confidence in the ability to detect the trend, over the natural range of variability in measured concentrations, measured through the MAD (Moreau and Daughney 2021).

Field dissolved oxygen increased consistently throughout both time periods, with only one perceptible increase at a rate of 0.05 mg/L over the 1970–2021 period. Both field pH and conductivity exhibited imperceptible trend reversal between the short- and long-term period (Figure 3.5, Table 3.4).

All trend magnitudes calculated for the major ions were imperceptible, and corresponding time series exhibited large natural variability (Table 3.4).

Dissolved reactive phosphorus exhibited consistent, statistically significant, slow decreases (magnitude below -0.001 mg/L per year) for both time periods. However, it is worthwhile to note that, over the full record, the detection limit that affects up to 7% of the data improved with time due to technological advances by a factor of 10 (currently 0.004 mg/L). Both decreases were classed as imperceptible.

The increasing rate for nitrate-nitrogen concentration was higher for the 2011–2021 time period (0.019 mg/L per year) compared to 0.006 mg/L per year for the 1970–2021 period (Table 3.4). Both trend magnitudes were classed as perceptible. However, graphical examination of the nitrate-nitrogen time series highlights that the assumption of a monotonous trend is not verified for the Mann-Kendall trend test, as nitrate-nitrogen concentrations were decreasing between late 2011 and early 2016. This decrease was followed by a trend reversal from March 2016 onward (Figure 3.5; Figure 3.6), and the nitrate-nitrogen time series are therefore exhibiting alternating increases and decreases. It was not possible to assess trends for ammonia-nitrogen due to the high censoring level (most measurements were below the detection limit).

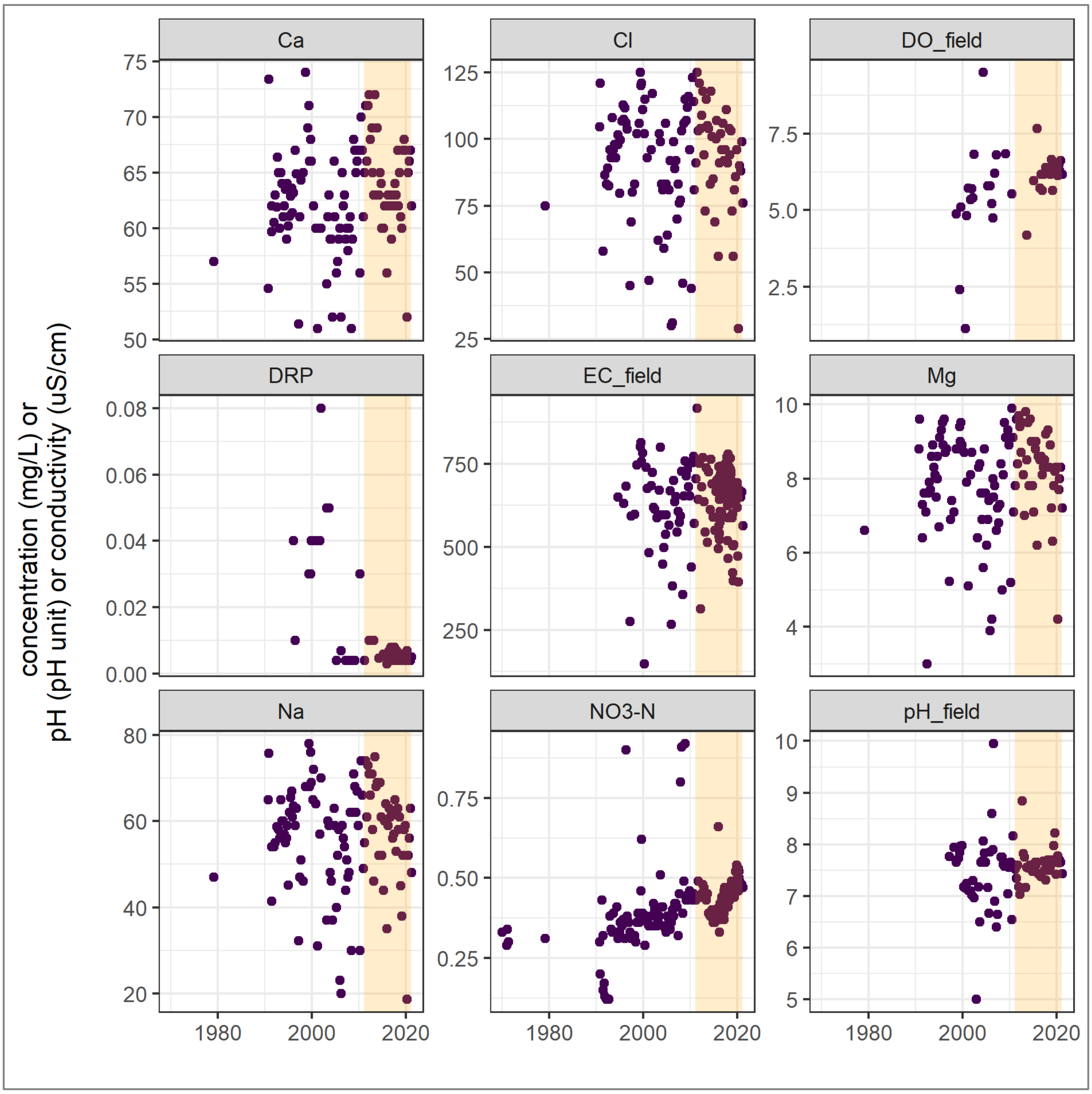

Figure 3.5 Time series for calcium (Ca), chloride (Cl), dissolved reactive phosphorus (DRP), dissolved oxygen (DO_field), field conductivity (EC_field), magnesium (Mg), sodium (Na), nitrate-nitrogen (NO3-N) and pH (pH_field) monitored at Te Waikoropupū springs for the full record (1970–2021). Ammonia-nitrogen (NH3-N) is not shown, as trend assessment was not possible due to high censoring. The orange box indicates the 2011–2021 time period.

The nitrate-nitrogen long-term dataset exhibits infrequent but re-occurring outliers (Figure 3.6). Outliers are observations whose values are quite different than others in the dataset; they should not be discarded prior to describing the data. Outliers can have one of three causes (Helsel and Hirsch 2002):

1. A measurement or recording error.
2. An observation from a population not similar to that of most of the data, such as an unusual concentration caused by a large flood event rather than by normal levels of precipitation.
3. A rare event from a single population that is quite skewed.

Analytical records were published for site investigation data (Michaelis 1974; Stewart and Downes 1982; Mueller 1992; Miles 1999; Stewart and Thomas 2008), including analytical methods. For the early NGMP data (1990–1994), it not possible to be conclusive on the integrity of the outliers corresponding to low nitrate-nitrogen concentrations (<0.25 mg/L) due to the absence of both field and laboratory records. Since 1994, the laboratory and analytical method remained consistent and were archived, which increases confidence in trend detection. For the 2005 to present period, paper and digital records corresponding to the sporadic high concentration outliers shown in Figure 3.6 do not indicate any error in data capture or any anomalies associated with the analyses. It is therefore possible that they are hinting at a process that is not well represented at the quarterly frequency. From 1994, the changes in laboratories and methods are uncorrelated to high concentration outliers, which gives confidence that these are correct measurements (Figure 3.6).

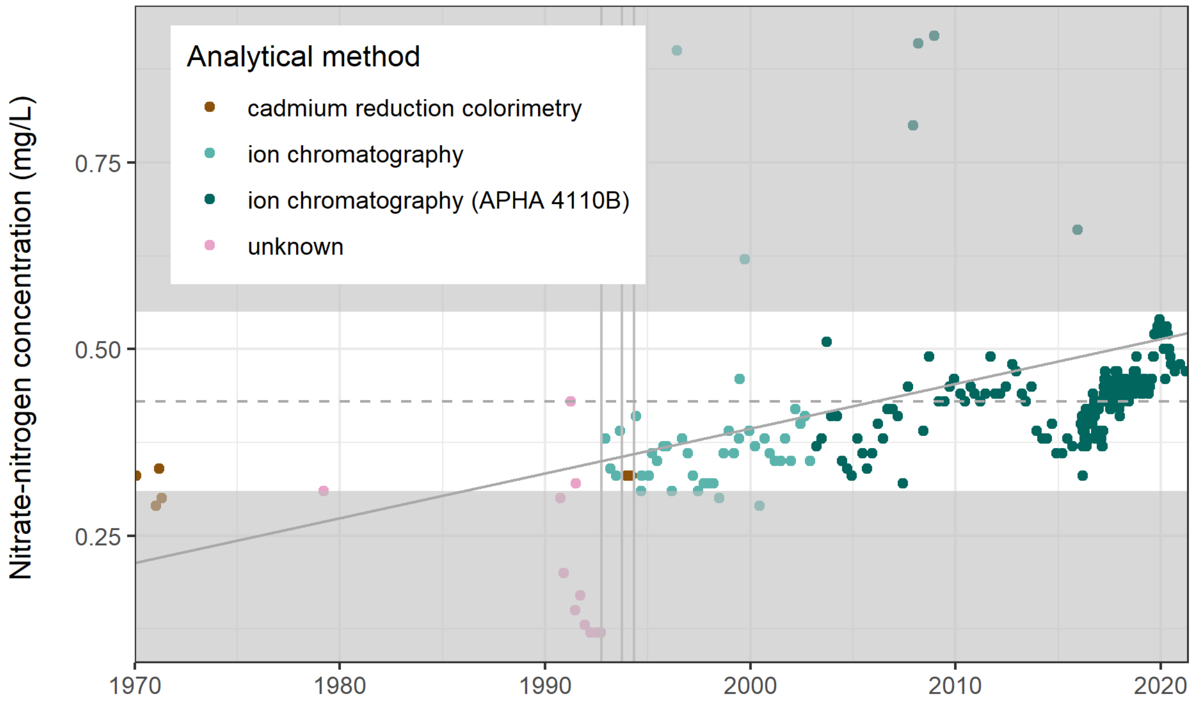

Figure 3.6 Nitrate-nitrogen concentration at Te Waikoropupū main spring for the 1970–2021 period (combined dataset). The full line indicates the trend, the dashed line indicates the median concentration and the white box indicates the natural variability defined by 4 MADs on either sides of the median; data points falling outside of this box are outliers. The vertical line indicates change in laboratories.

Table 3.4 Trend statistics for field conductivity (EC_field), pH, dissolved oxygen (DO_field), calcium (Ca), chloride (Cl), magnesium (Mg), sodium (Na), dissolved reactive phosphorus (DRP), ammonia-nitrogen (NH3-N) and nitrate-nitrogen (NO3-N) monitored at Te Waikoropupū springs using the NGMP Calculator. ND not determined. Perceptible trends are shown in bold.

Parameter	Period	n	% censored	Median	Trend Type	Trend Magnitude (units/year) by Sen's Estimator	Trend Magnitude (units/year) by Linear Regression	Mann-Kendall p-value	Seasonality?	Kruskal-Wallis p-value
DO_field (mg/L)	2011–2021	19	0.0	6.18	No	0.070	0.077	0.10	No	0.262
	1970–2021	36	0.0	6.16	Increasing	**0.049**	0.045	0.003	No	0.802
EC_field (µS/cm)	2016–2021	172	0.0	700	Decreasing	-5.06	-3.67	0.044	No	0.217
	1970–2021	218	0.0	693	No	0.142	0.753	0.888	No	0.054
pH_field (pH unit)	2011–2021	35	0.0	7.57	No	0.018	0.018	0.212	No	0.702
	1970–2021	74	0.0	7.6	No	-0.001	0.003	0.759	No	0.925
Ca (mg/L)	2011–2021	39	0.0	64	No	-0.268	-0.405	0.150	No	0.741
	1970–2021	114	0.0	63	No	0.059	0.061	0.146	Yes	0.040
Cl (mg/L)	2011–2021	37	0.0	99	Decreasing	-2.53	-2.21	0.004	Yes	0.042
	1970–2021	107	0.0	98	No	-0.087	-0.065	0.594	Yes	0.011
Mg (mg/L)	2011–2021	39	0.0	8.4	Decreasing	-0.167	-0.131	0.008	No	0.260
	1970–2021	106	0.0	8.3	No	0.006	0.009	0.526	No	0.075
Na (mg/L)	2011–2021	39	0.0	60	Decreasing	-1.749	-1.519	0.001	No	0.200
	1970–2021	110	0.0	59	No	0.000	0.007	1.00	Yes	0.013
DRP (mg/L)	2011–2021	165	4.2	0.005	Decreasing	<0.001	<0.001	<0.001	No	0.512
	1970–2021	172	7.0	0.005	Decreasing	<0.001	<0.001	0.023	No	0.966
NH3-N (mg/L)	2011–2021	22	100	<0.003	ND	ND	ND	ND	ND	ND
	1970–2021	76	96.1	0.004	ND	ND	ND	ND	ND	ND
NO3-N (mg/L)	2011–2021	197	0.0	0.44	Increasing	**0.019**	0.011	<0.001	No	0.078
	1970–2021	278	0.0	0.43	Increasing	**0.006**	0.004	<0.001	No	0.377

For the 2016–2021 and 1970–2021 time periods, trend statistics calculated using the NGMP Calculator and the LWP-trends R library are in good agreement (Table 3.5). For instance, for the 2016–2021 period, trend magnitudes were 0.021 and 0.023 using the Calculator or R, respectively. However, there were less consistencies for the 2011–2021 period, as mentioned above; during this period there is a violation of the monotony assumption, which is a requirement for the Mann-Kendall trend test. In addition, the LWP-trends R library does not exclude outliers for trend analysis, which will impact on trend determination. It is therefore possible that the trend reversal, combined with the exclusion of outliers, contributed to the inconsistencies in trend statistics calculated for the 2011–2021 period..

Table 3.5 Trend statistics for nitrate-nitrogen concentrations (mg/L) for varying time periods using the NGMP Calculator and the R LWP-Trends (LWP). NA = not available.

		1970–2021		**2011–2021**		**2015–2021**	
		Calculator	**LWP**	**Calculator**	**LWP**	**Calculator**	**LWP**
Season	Observations	278	298	197	205	181	189
	Kruskal-Wallis p-value	0.377	0.826	0.078	0.738	0.011	0.810
	Seasonality?	No	No	No	No	Yes	No
Trend	n outliers	20	NA	8	NA	8	NA
	Mann-Kendall p-value	<0.0005	<0.0005	<0.0005	0.005	<0.0005	<0.0005
	Intercept	NA	0.315	NA	0.406	NA	0.384
	Lower confidence interval	NA	0.004	NA	0.002	NA	0.018
	Upper confidence interval	NA	0.006	NA	0.013	NA	0.028
	Trend direction	NA	Increasing	NA	Increasing	NA	Increasing
	Trend type	Increasing	NA	Increasing	NA	Increasing	NA
	Trend magnitude (units/year) by Sen's estimator	0.006	0.005	0.019	0.007	0.021	0.023
	Trend magnitude (units/year) by linear regression	0.004	NA	0.011	NA	0.024	NA
	Median	0.43	0.43	0.44	0.44	0.44	0.44
	Percentage annual change	1.4	1.2	4.3	1.6	4.8	5.2

4.0 ASSESSMENT OF THE IMPACT OF OPERATIONAL CHANGES ON GROUNDWATER QUALITY DATA

In the following sections, differences between matched-paired datasets were evaluated using the Wilcoxon signed-rank test, a non-parametric alternative to the t-test for comparing two means. This test is particularly recommended in situations where the data are not normally distributed (Helsel et al. 2020), with an underlying assumption that the paired data are approximately symmetrical. Although the three paired datasets distributions were wide, mainly due to the small sample size, this assumption was verified in all cases (Appendix 1, Figure A1.1). Box plots were also generated to visualise the distribution of paired nitrate-nitrogen concentrations for each dataset (Appendix 1, Figure A1.2).

4.1 Change in Sampling Points at Te Waikoropupū Main Spring

The Wilcoxon signed-rank test on matched-paired samples was used to assess the impact of changing sampling points on groundwater quality analyses from six split samples collected between March 2016 and June 2018 from the viewing platform at Te Waikoropupū main spring (Table 4.1). All samples were collected following the national sampling protocol (Daughney et al. 2006), consistent with the NEMS guidance (Milne et al. 2019), and were analysed by NZGAL using ion chromatography (APAHA 4110 B).

The main spring area comprises eight major vents (Section 1.2; Michaelis 1974), of which five are located along the viewing platform. This paired dataset combines samples collected by TDC staff as part of NGMP and samples collected by FOGB consistently a couple of metres apart on the viewing platform (Thomas 2021).

The statistical test indicates that there is no significant difference (p-value = 0.58) in nitrate-nitrogen concentration medians from each data subset. The effect size (0.35) is moderate for this dataset, meaning that the difference between measurements is non-trivial, regardless of the paired sign test results. This result is consistent with historical concurrent sampling for multiple vents undertaken in 1999, which highlighted consistent chemistry between vents (Table 4.2).

Table 4.1 Nitrate-nitrogen (NO3-N) paired analyses from duplicated samples (2016–2018), analysed by ion chromatography (method APHA 4110B) at the NZGAL laboratory.

Site	Collection Date	NO3-N (mg/L) TDC	NO3-N (mg/L) FOGB
Te Waikoropupū main spring	9/03/2016	0.33	0.37
Te Waikoropupū main spring	15/06/2016	0.41	0.41
Te Waikoropupū main spring	7/09/2016	0.44	0.41
Te Waikoropupū main spring	13/12/2016	0.38	0.38
Te Waikoropupū main spring	19/09/2017	0.43	0.44
Te Waikoropupū main spring	19/06/2018	0.44	0.45

Table 4.2 Groundwater sample analyses for selected parameters analysis for samples collected on 30/06/1999 at multiple Te Waikoropupū springs vents (Miles 1999). Analytical methods: (1) field-meter (APHA 4500H.B), (2) field-meter, (3) field-meter (APHA 2510B), (4) Colorimetry (Solórzano 1969), (5) Calculation (APHA 4500-Co2D), (6) Atomic Spectrometry (APHA 311B/3114B, C), (7) Ion chromatography (APHA 4110B).

Parameter	Method	Dancing Sands	Main Spring Vent 1	Main Spring Vent 2	Main Spring Vent 3	Main Spring Vent 4
Field pH (pH unit)	1	8.07	7.97	7.98	8.03	8.02
Field temperature (°C)	2	11.6	12.3	12.3	12.2	12.2
Field conductivity (µS/cm)	3	612	813	814	750	816
Ammonia-nitrogen (mg/L)	4	0.02	0.019	0.006	0.008	0.011
Bicarbonate (mg/L)	5	200	220	220	220	230
Calcium (mg/L)	6	58	66	66	64	67
Chloride (mg/L)	7	67	120	120	100	120
Magnesium (mg/L)	6	6.5	9	9.2	8.4	9.2
Nitrate-nitrogen (mg/L)	7	0.46	0.46	0.46	0.47	0.46
Sodium (mg/L)	6	47	68	70	63	70

4.2 Change in Analytical Methods or Laboratory

In this section, two analytical methods are compared, either within the same laboratory or between laboratories. As outlined in Section 2, the selection of analytical methods is performed by laboratories with consideration on sample type, expected concentration range and operational aspects. For the same laboratory, the decision criteria may change with time, for instance, following an instrument or facility upgrade.

The cadmium reduction flow injection method (APHA 4500-NO3 I), or cadmium reduction for short, is an indirect measure of nitrate-nitrogen concentration of nitrate-nitrogen. The sample is first passed through a copperised cadmium column, which leads to the reduction of nitrate-nitrogen to nitrite-nitrogen. Secondly, a reagent is added to the sample, which transforms the nitrite-nitrogen into total oxidised nitrogen, releasing a magenta-coloured, water-soluble dye. Total oxidised nitrogen (TON) is determined using colorimetry, the intensity of the colour being proportional to the TON concentration. A measurement of the nitrite concentration alone is also performed using the same apparatus but removing the copperised cadmium column. The nitrate-nitrogen concentration (NO3-N) is then calculated using the formula:

$$NO3\text{-}N = TON - NO2\text{-}N$$

This method is particularly recommended for low nitrate-nitrogen level samples (<0.1 mg/L) (Baird et al. 2017). The recommended NEMS detection limit for this method is 0.002 mg/L. Hill Laboraties, at which samples collected by TDC as part of the State of the Environment monitoring are analysed, was accredited for this method in 1988 (Hill Laboratories c2021), with a current detection limit of 0.001 mg/L.

The ion chromatography method (APHA 4110 B) is a direct measure of concentration by which a water sample is injected into a stream of eluent and passed through a series of ion exchangers. The anions (negative ions) are separated on the basis of their interaction with a resin. As an ion-extracting liquid, the eluent runs through the column and the absorbed ions begin separating from the column. The ionic concentration is proportional to the ion retention times (Baird et al. 2017). The recommended NEMS detection limit for this method is 0.01 mg/L, which is about an order of magnitude higher than the aforementioned method. This is because this method is more tolerant to high chloride concentration. High nitrate-nitrogen concentrations (>10 mg/L) occur at some sites from the NGMP. The NZGAL laboratory, at which NGMP samples are analysed, has two tests for nitrate-nitrogen: one with a detection limit of 0.01 mg/L (used for samples with an expected concentration above 0.1 mg/L) and, since 2019, a low-level test with a lower detection limit of 0.003 mg/L (used for an expected concentration of up to 0.1 mg/L). The NZGAL laboratory was accredited for this test in 2001 (GNS Science [2021]). Hills Laboratories was accredited for the modified version of this method in 1988 (Hill Laboratories c2021), with a current detection limit of 0.05 mg/L.

4.2.1 Change in Method within a Laboratory

The Wilcoxon signed-rank test on matched-paired samples was used to assess the impact of changing analytical methods on groundwater quality analyses from 15 split samples collected between September 2019 and December 2020 at Te Waikoropupū main spring and Fish Creek (TDC) by TDC staff (Table 4.3). All samples were collected by TDC staff following the national sampling protocol (Daughney et al. 2006) consistent with the NEMS guidance (Milne et al. 2019) and were analysed by Hills Laboratories using either cadmium reduction or ion chromatography.

The statistical test indicates that median nitrate-nitrogen concentrations measured using cadmium reduction are significantly different (in this case higher) from the nitrate-nitrogen concentrations measured by ion chromatography (p-value = 0.0045). The effect size (0.74) is large, which means that the difference between measurements is significant, regardless of the paired sign test results.

Table 4.3 Nitrate-nitrogen (NO3-N) concentrations for paired analyses from duplicated samples analysed at Hill Laboratories (2014–2020). 1: Calculation from APHA 4500-NO3 I and APHA 4500-NO3 I. 2: APHA 4110B.

Site	Collection Date	NO3-N (mg/L) by Cadmium Reduction [1]	NO3-N (mg/L) by Ion Chromatography [2]
Te Waikoropupū main spring	2018-09-04	0.47	0.4
Fish Creek (TDC)	2018-11-27	0.39	0.4
Te Waikoropupū main spring	2018-11-27	0.38	0.44
Te Waikoropupū main spring	2019-03-06	0.44	0.4
Te Waikoropupū main spring	2019-03-19	0.42	0.41
Fish Creek (TDC)	2019-06-06	0.43	0.33
Te Waikoropupū main spring	2019-06-06	0.47	0.36
Te Waikoropupū main spring	2019-06-19	0.44	0.4
Fish Creek (TDC)	2019-09-10	0.46	0.387
Te Waikoropupū main spring	2019-09-10	0.47	0.384
Te Waikoropupū main spring	2019-12-10	0.5	0.45
Te Waikoropupū main spring	2020-03-18	0.49	0.44
Te Waikoropupū main spring	2020-06-15	0.46	0.41
Fish Creek (TDC)	2020-12-07	0.472	0.399
Te Waikoropupū main spring	2020-12-07	0.496	0.425

4.2.2 Different Methods, Different Laboratories

The Wilcoxon signed-rank test on matched-paired samples was used to assess the impact of changing analytical methods on groundwater quality analyses from 13 samples collected between March 2014 and December 2020 at Well GW802 and Te Waikoropupū main spring (Table 4.4). All samples were collected by TDC staff following the national sampling protocol (Daughney et al. 2006). This protocol is consistent with the Discrete Water Quality Sampling National Environmental Standard (Milne et al. 2019).

One sample set was dispatched to Hill Laboratories in Hamilton, as selected by TDC, and nitrate-nitrogen concentrations were determined using cadmium reduction. The second set of samples were routed to the NZGAL facility, as part of NGMP monitoring, and nitrate-nitrogen concentration was determined by ion chromatography.

The statistical test indicates that there is no statistically significant difference (p-value = 0.81) in nitrate-nitrogen concentration medians measured at the two laboratories using different methods. The effect size (0.087) is small, which means that the difference between measurements is trivial, regardless of the paired sign test results.

Table 4.4 Nitrate-nitrogen (NO3-N) concentrations for paired analyses from split samples collected to investigate differences in analytical laboratory and methods.

		Hill Laboratories	NZGAL Laboratory
Site	**Collection Date**	**NO3-N [1] (mg/L)**	**NO3-N [2] (mg/L)**
Well GW802	24/03/2014	1.04	1
Te Waikoropupū main spring	27/03/2014	0.46	0.38
Te Waikoropupū main spring	13/12/2017	0.52	0.44
Te Waikoropupū main spring	5/04/2018	0.51	0.46
Te Waikoropupū main spring	4/09/2018	0.47	0.47
Te Waikoropupū main spring	27/11/2018	0.38	0.46
Te Waikoropupū main spring	19/03/2019	0.42	0.46
Te Waikoropupū main spring	6/06/2019	0.47	0.45
Te Waikoropupū main spring	10/09/2019	0.47	0.52
Te Waikoropupū main spring	10/12/2019	0.5	0.54
Te Waikoropupū main spring	18/03/2020	0.49	0.46
Te Waikoropupū main spring	15/06/2020	0.46	0.49
Te Waikoropupū main spring	7/12/2020	0.496	0.48

[1] Hill Laboratories method: calculation from APHA 4500-NO3 I and APHA 4500-NO3 I.

[2] NZGAL laboratory method: APHA 4110B.

4.2.3 Same Method, Different Laboratories

The Wilcoxon signed-rank test on matched-paired samples was used to assess the impact of using different laboratories using the same method on groundwater quality analyses from nine samples collected between September 2018 and December 2020 at Te Waikoropupū main spring (Table 4.5). All samples were collected by TDC staff following the national sampling protocol (Daughney et al. 2006). This protocol is consistent with the Discrete Water Quality Sampling National Environmental Standard (Milne et al. 2019).

One sample set was dispatched to Hill Laboratories in Hamilton, and the second set of samples were routed to the NZGAL facility, as part of NGMP monitoring. Both sample sets were analysed for nitrate-nitrogen using ion chromatography.

The statistical test indicates that there is a significant difference (p-value = 0.009) in nitrate-nitrogen concentration medians measured at the two laboratories using different methods. The effect size (0.89) is large, which means that the difference between measurements is consistent and significant, regardless of the paired-sign test results. In this example, Hill Laboratories exhibits consistent lower nitrate-nitrogen concentrations.

Table 4.5 Nitrate-nitrogen (NO3-N) concentrations for paired analyses from split samples collected to investigate differences in analytical laboratories, both using ion chromatography (APHA 4110B).

		Hill Laboratories	**NZGAL Laboratory**
Site	**Collection Date**	**NO3-N (mg/L)**	**NO3-N (mg/L)**
Te Waikoropupū main spring	4/09/2018	0.40	0.47
Te Waikoropupū main spring	27/11/2018	0.44	0.46
Te Waikoropupū main spring	19/03/2019	0.41	0.46
Te Waikoropupū main spring	6/06/2019	0.36	0.45
Te Waikoropupū main spring	10/09/2019	0.384	0.52
Te Waikoropupū main spring	10/12/2019	0.45	0.54
Te Waikoropupū main spring	18/03/2020	0.44	0.46
Te Waikoropupū main spring	15/06/2020	0.41	0.49
Te Waikoropupū main spring	7/12/2020	0.425	0.48

5.0 RECOMMENDATIONS

Recommendations from this report are:

- In terms of both state and trend metric, the Mann-Whitney test conducted on the monthly and quarterly data did not exhibit significant differences. General guidance on monitoring karstic systems (Quinlan 1990; Minnesota Pollution Control Agency 2005) supports the collection of both low- (e.g. quarterly) and high-frequency, event-based groundwater quality and flow monitoring. Recent overseas studies (e.g. Qin et al. 2020; Zhang et al. 2020), supported by high-frequency monitoring through in-situ continuous sensors and coupled with modelling, have demonstrated that nitrate-nitrogen and chloride concentrations were locally affected by throughflow flushing and show randomness behaviour and that sinkholes were important transport and export pathways of nitrogen in karst catchments. Given the estimated high (74%) proportion of the karstic uplands to the spring flow (Stewart and Thomas 2008), conducting event-based high-frequency investigation is recommended for this aquifer system to complement long-term monitoring for a range of parameters.
- Long-term nitrate-nitrogen concentrations at the main spring have increased steadily since 1970 (perceptible trend magnitudes); however, the time series included unexplained sporadic high concentrations, as well as a sustained decrease between 2011 and 2016, shortly followed by a rise in nitrate-nitrogen concentrations. The outliers were checked and attributed to genuine observations. To elucidate this trend pattern, it is recommended to investigate potential activity changes over time in the recharge area, e.g. upland karst and valley land-use changes, farm practices (e.g. irrigation) and/or nitrogen-inputs changes (e.g. linked to policy changes), as well as potential changes in rainfall/recharge and storm patterns. A range of methods are available for this (e.g. imagery-based techniques, use of isotopes for source tracking, modelling). These studies should be informed by results of event-based data collection.
- This report provided clarification on reporting analytical results and how to deal with changes in analytical methods, laboratory and detection limits (Section 2). In the particular example of time series at the main spring, the effect of these changes on the dataset quality was assessed via statistical analysis of split samples and also through tracking changes on the long-term dataset. The test results and the examination of collected data through historical changes was not found to be impactful. It is recommended to continue capturing context information to enable testing of the effect of such changes on long-term record around analytical results, including accuracy and suitability of laboratory testing methods. When changes occur, if practical, the collection of split samples for statistical testing is recommended. It is also important to continue checking and, if warranted, capturing outliers, as these values may reflect real processes.

Karst aquifer systems, such as the Arthur Marble and the Takaka Limestone aquifers, comprise features such as caves, conduits, sinkholes and springs and exhibit high hydraulic properties of heterogeneity and anisotropy (Kalhor 2019 and references therein). In addition, karst systems only account for a small proportion of New Zealand groundwater systems (White 2001). Karstic systems can include high-volume flow paths and high-yielding springs such as Te Waikoropupū, in which small increases in contaminant concentration can translate to a large increase in contaminant mass load at the receiving environments. It is therefore recommended that the hydrogeology and hydrochemistry of these systems be assessed case by case in the context of limit setting. This assessment should also include studies on attributability of contaminants regarding allogenic and/or anthropogenic sources. The availability and continuation of consistent, well-documented, long-term monitoring groundwater quality and flow data will support these studies.

6.0 CONCLUSION

Long-term monitoring data at the Te Waikoropupū main spring complex were compiled, cleaned and processed for statistical trend analysis by GNS Science to characterise natural variability (short- and long-term) and review trend patterns. In addition, TDC commissioned GNS Science to undertake statistical analysis of paired nitrate-nitrogen concentration from split samples collected in the context of changing sampling location, analytical method and laboratories to provide guidance on how to deal with changes in analytical methods, laboratory and detection limits in the context of limit setting and future monitoring.

Groundwater at the main spring contains more total dissolved solids than most New Zealand groundwaters (e.g. median field conductivity of 700 μS/m over the 2015–2021 period). Nutrient concentrations were below most New Zealand groundwaters and the reported threshold for land-use-impacted groundwater. For example, nitrate-nitrogen concentrations over the 2015–2021 period ranged from 0.38 to 0.54 mg/L, which is below published land-use-impact thresholds (c. 3 mg/L; Daughney and Reeves 2005; Morgenstern and Daughney 2012). In terms of rates of change for the selected parameters, perceptible trends were observed for three parameters over the considered time periods: decreases for dissolved reactive phosphorus concentrations (2011–2021 and 1970–2021 periods) and field dissolved oxygen (1970–2021) and increasing nitrate-nitrogen concentrations (2011–2021 and 1970–2021). Even though small trends have been observed in some chemical parameters, measured concentrations remain below national thresholds to defined land-use-impacted groundwaters.

The non-parametric Wilcoxon test was used to assess difference in analyses from split samples collected between 2016 and 2020. Neither the comparison of two methods and laboratories (n = 13) or the sampling location (n = 6) exhibited statistically significant differences in median concentrations. In contrast, the test demonstrated that, within the same laboratory, nitrate-nitrogen concentrations measured using the cadmium reduction method were significantly different from those measured by ion chromatography (n = 15, p-value <0.005 at the 95% confidence level). A statistical difference was also observed for samples analysed by ion chromatography at two separate laboratories (n = 9, p-value = 0.009 at the 95% confidence level).

The following recommendations are provided to inform limit setting and future monitoring at the main spring and guidance with regard to changes in analytical methods, laboratory and detection limits in the context of long-term monitoring:

- Groundwater quality monitoring at the spring, due to the karstic nature of its source aquifer, should include collection of both low- (e.g. quarterly) and high-frequency, event-based groundwater quality and flow monitoring data for a range of parameters.
- Further investigations of long-term trend changes observed at the main spring, which would include documentation of land use and farming practice in the valley and contributing upland karst and rainfall, including storm events, over time to elucidate the cause of changing trends.
- Appropriate documentation of analytical results is important to build confidence in monitoring data and, should analytical methods or laboratory change, split sampling for a period allowing for sufficient sample size (n >10) for statistical testing is recommended.

Karst aquifer systems are unique in terms of flow process, hydraulic properties, karstic dissolution and connectivity and therefore should be studied case by case in the context of limit setting, including studies on the attributability of sources both allogenic and anthropogenic for the various chemical parameters.

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APPENDICES

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APPENDIX 1 MATCHED-PAIRED DATASET DISTRIBUTION

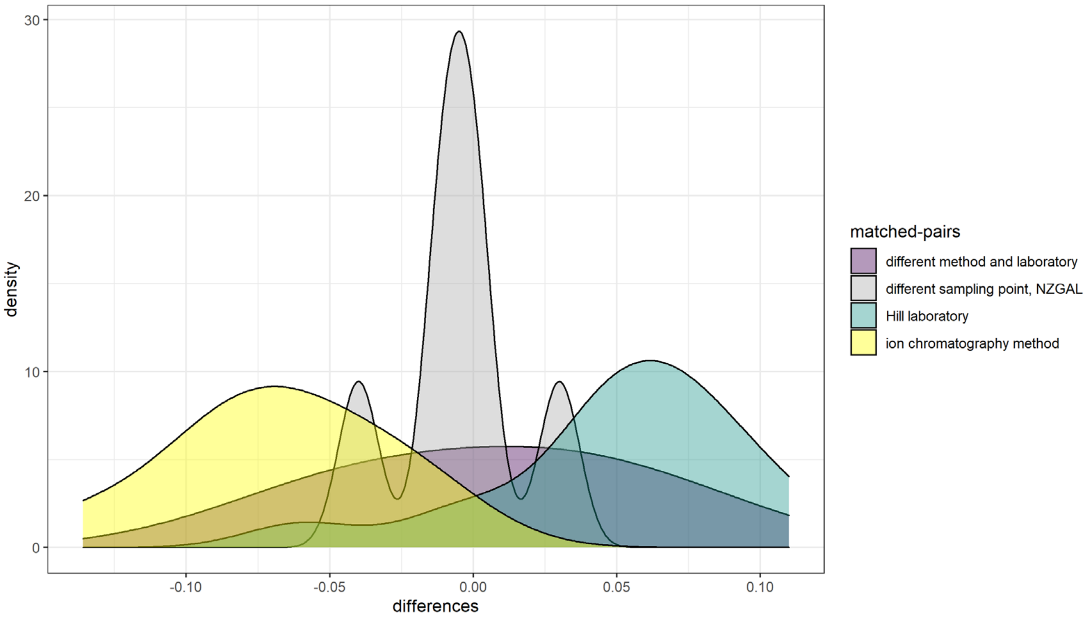

Figure A1.1 Density plot for paired nitrate-nitrogen concentrations.

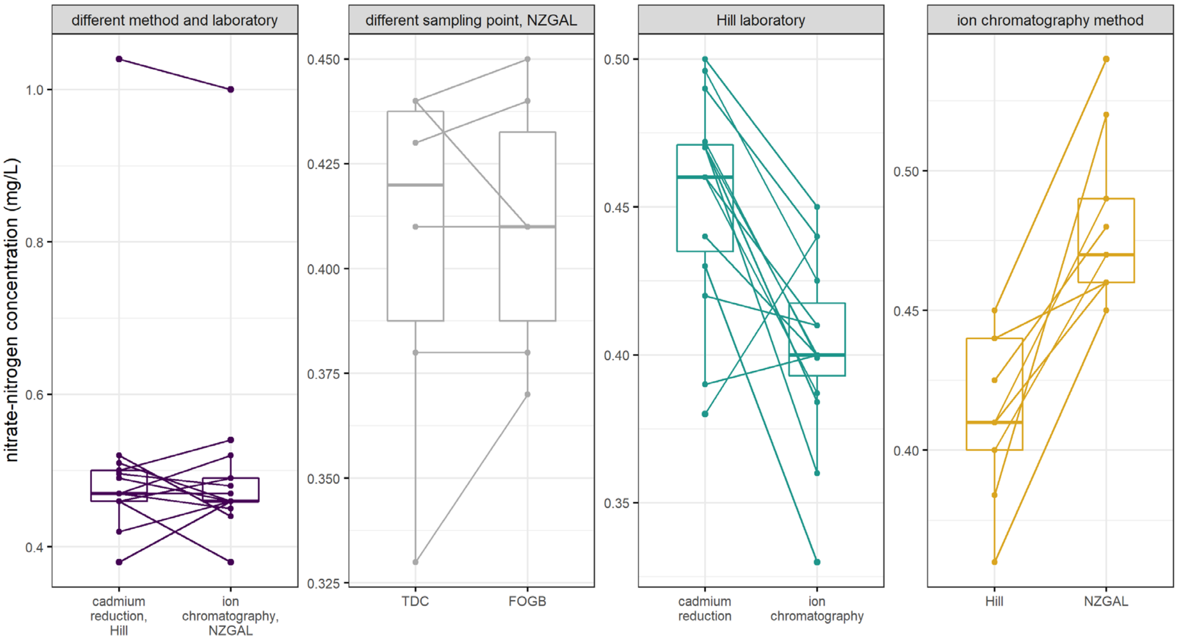

Figure A1.2 Paired boxplots for nitrate-nitrogen concentrations in split samples.

www.gns.cri.nz

Principal Location

1 Fairway Drive, Avalon
Lower Hutt 5010
PO Box 30368
Lower Hutt 5040
New Zealand
T +64-4-570 1444
F +64-4-570 4600

Other Locations

Dunedin Research Centre
764 Cumberland Street
Private Bag 1930
Dunedin 9054
New Zealand
T +64-3-477 4050
F +64-3-477 5232

Wairakei Research Centre
114 Karetoto Road
Private Bag 2000
Taupo 3352
New Zealand
T +64-7-374 8211
F +64-7-374 8199

National Isotope Centre
30 Gracefield Road
PO Box 30368
Lower Hutt 5040
New Zealand
T +64-4-570 1444
F +64-4-570 4657