

# REPORT NO. 4036

# SOURCES AND DRIVERS OF NITROGEN INPUTS TO THE TĀKAKA CATCHMENT

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# SOURCES AND DRIVERS OF NITROGEN INPUTS TO THE TĀKAKA CATCHMENT

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Prepared for Tasman District Council

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# **EXECUTIVE SUMMARY**

Concentrations of nitrate-nitrogen (nitrate-N) have increased over the last 50 years in the Main Spring at Te Waikoropupū Springs. Despite a long history of scientific studies of Te Waikoropupū, there is limited understanding of the sources and transformations of nitrogen within Te Waikoropupū and the wider Tākaka Catchment. During the recent (2021-2022) Environment Court hearing relating to the water conservation order application, a range of analyses were conducted in response to queries from the court. In this report we update, review and summarise the available information and data analyses to provide an overview of nitrogen sources, transformations and drivers of nitrogen dynamics within the Tākaka Catchment. This work aligns with Tasman District Council's resolution to develop an action plan to address the long-term increase in the concentrations of nitrate-N that has been observed at Te Waikoropupū and is relevant to, but separate from, the Environment Court's recommendation for an independent review of Tasman District Council's catchment monitoring programme.

The main sources of flow (and hence nitrogen) to the Arthur Marble Aquifer (AMA) and Te Waikoropupū are rainfall in the areas where water can drain directly into the marble; flow loss from the upper Tākaka River, parts of the Waingaro River and creeks draining into the upper Tākaka Valley; infiltration of rainwater falling on the Tākaka Valley floor; and a small input from seawater.

An assessment of contributions from all these sources needs to consider all types of dissolved and particulate nitrogen compounds that are involved. The majority of nitrogen coming from the upper catchments (upper Tākaka and upper Waingaro) is in the form of dissolved organic nitrogen (DON), while nitrate-N is likely the predominant type of nitrogen sourced from the Tākaka Valley floor.

We consider that export / leaching of nitrogen compounds is the primary source of the nitrogen load to the AMA, with different rates of nitrogen export expected from different land-use types. The highest rate of export will be from intensively farmed areas within the valley floor, indicating that this area of the catchment contributes a disproportionately large component of the overall nitrogen load to the aquifer. Geological sources of nitrogen, wastewater, explosives used in quarrying, and seawater are all expected to make a small contribution to the overall nitrogen load to the aquifer.

Previous efforts at determining the relative importance of nitrogen sources have provided contrasting indications of the significance of nitrogen inputs from the karst upland parts of the Tākaka Catchment. The key driver of these differences appears to be the variable conceptualisations of the AMA. Stewart and Thomas (2008) conceptualise the aquifer as having two different flow systems: one a deep system primarily recharged from the karst uplands and including the seawater contribution, and the other a shallower system with much younger water that is primarily recharged by the upper Tākaka River and valley rainfall. This conceptualisation assumes that any mixing of the waters from the two flow systems occurs

only shortly before the water emerges at Te Waikoropupū Springs. Other modelling of the aquifer (e.g. Williams 2023) conceptualises the aquifer as conduits of fast-flowing younger water within a marble matrix of fissures and pores through which older water moves more slowly. Some exchange of water is considered to occur between these features throughout the aquifer.

As the Stewart and Thomas model assumes that the majority of the flow to the Main Spring is sourced from the karst uplands and there is no mixing of sources until shortly before the water emerges at Te Waikoropupū Springs, it follows that a substantial proportion of the nitrogen load at the springs must also be from the karst uplands. In contrast, the Williams model allows for more mixing among the different water sources and indicates that a small volume of valley floor water with high nitrogen concentrations is responsible for much of the nitrogen load from the Main Spring.

Alternative modelling approaches using sub-catchment areas and likely rates of nitrogen export in each area (Weir and Fenemor 2017; Nitrate leaching JWS; Mead–Hickey JWS) tended to support the conclusions of the Williams modelling that 85–90% of the nitrogen load at the springs is sourced from farming, while the input from the karst uplands makes up the remainder, although Weir and Fenemor (2017) and the Nitrate leaching JWS focused solely on nitrate-N and did not incorporate organic nitrogen in their calculations. The Environment Court decision found that the proportions of nitrate-N load to Te Waikoropupū Springs coming from the valley floor were likely to be around 75% of the total load and within the range of 70–85%. They considered that approximately 20% of the total load comes from the karst uplands, including from gorse and broom, with the remaining approximately 5% coming from the upper Tākaka River and wastewater sources.

To our knowledge, there are no data on total nitrogen (TN) or organic nitrogen concentrations in any of the eastern (Spittals Spring, Ironstone Creek, Gorge Creek) or western (Kill Devil Creek, Sam Creek, Craigieburn Creek, Stony Creek) catchment tributaries. Therefore, we recommend that monthly sampling of nitrate-N and TN, along with other key water quality parameters (dissolved reactive phosphorus [DRP], total phosphorus [TP], specific conductivity, dissolved organic carbon [DOC]) at these sites should be considered in the independent review of catchment monitoring. We also recommend that monthly sampling of nitrate-N and TN, along with other key water quality parameters (DRP, TP, specific conductivity, DOC) should be considered for the Harwoods and Lindsays Bridge monitoring sites on the Tākaka River and the Hanging Rock monitoring site on the Waingaro River. Collection of data on the concentration of particulate organic nitrogen at these sites should also be considered in the independent review of catchment monitoring. Regular monthly monitoring over an extended period will enable the effects of climatic variation on nitrogen inputs to be better quantified.

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# GLOSSARY

AMA	Arthur Marble Aquifer
Ammoniacal nitrogen	Nitrogen associated with the ammonia (NH <sub>4</sub> ) form
_	of inorganic nitrogen
Aquifer	A body of permeable rock that can contain or
	transmit groundwater
Concentration	The amount of a substance that is found in a
	certain amount of liquid
DO	Dissolved oxygen – concentration of oxygen
	dissolved in water
	Dissolved organic carbon – the carbon component
DOC	of organic substances that are dissolved in water
	and will pass through a very fine (0.45 $\mu$ m) filter
DOM	Dissolved organic matter – organic substances that
	are dissolved in water and will pass through a very
	fine (0.45 μm) filter
DON	Dissolved organic nitrogen – measure of total
	nitrogen that will pass through a very fine (0.45 $\mu$ m)
	filter
DRP	Dissolved reactive phosphorus
ENSO	El Niño–Southern Oscillation
Epikarst	The upper part of a karst system where water is
	stored before it percolates to underlying aquifers
Export of nutrients	Rate of movement or leaching of nutrients from a
	particular area, normally in conjunction with
	drainage or surface water flow. Measured as
	kg/ha/y
Flow	The volume of water moving over a period of time.
	Measured as cubic metres/second (m <sup>3</sup> /s) or
	litres/second (L/s). 1 $m^3/s = 1,000 L/s$
FOGB	Friends of Golden Bay
JWS	Joint witness statement
Karst	A type of landscape where the dissolving of the
	bedrock has created sinkholes, sinking streams,
	caves, springs and other characteristic features.
	Karst is associated with soluble rock types such as
	limestone, marble and gypsum
Load	The mass of a substance moving over a period of
	time – calculated as the concentration of the
	substance multiplied by flow
Model	A physical and / or mathematical and / or
	conceptual representation of a system of ideas,
	events or processes

Nitrate-N	Nitrate-nitrogen – nitrogen associated with the				
	nitrate (NO <sub>3</sub> ) form of inorganic nitrogen				
Nitrite-N	Nitrite-nitrogen – nitrogen associated with the nitrite				
	(NO <sub>2</sub> ) form of inorganic nitrogen				
NZGAL	New Zealand Geothermal Analytical Laboratory				
Organic nitrogen	Nitrogen associated with organic molecules such				
	as amino acids, proteins and humic substances				
Particulate organic matter	Organic substances that are carried in water but				
	will not pass through a very fine (0.45 $\mu$ m) filter				
Recharge	The downward movement of water from the				
	unsaturated zone of soil or rock into the				
	groundwater saturated zone				
SOI	Southern Oscillation Index				
TDC	Tasman District Council				
TN	Total nitrogen – the sum of nitrate-N, nitrite-N,				
	organic nitrogen and ammoniacal nitrogen				
ТР	Total phosphorus				
Water conservation order	A legal instrument within the Resource				
	Management Act 1991 that is used to recognise				
	nationally outstanding characteristics of a				
	waterbody				

## 1. INTRODUCTION

Concentrations of nitrate-nitrogen (nitrate-N) have increased over the last 50 years in the Main Spring at Te Waikoropupū Springs (Young et al. 2017; Moreau 2021). This increase was one of the concerns that led to the application for a water conservation order for Te Waikoropupū. A considerable number of studies have been conducted on Te Waikoropupū over many years and have provided useful information on the age and likely sources of the water. However, there is limited understanding of the sources and transformations of nitrogen within Te Waikoropupū and the wider Tākaka Catchment. During the recent (2021-22) Environment Court hearing relating to the water conservation order application, a range of analyses were conducted in response to gueries from the court. The information and analyses included the relative importance of potential nitrogen sources (including atmospheric deposition, native forest, mountain tussock, gorse and intensive dairy farming), transformations of organic nitrogen to nitrate-N within the aquifer / catchment, and consideration of the potential role of long-term climatic patterns driving rainfall and cumulative nitrogen inputs / leaching to the Arthur Marble Aquifer (AMA) upstream of Te Waikoropupū Springs. Some of the information on these topics is available within expert evidence presented to the court, while other information and analyses were prepared quickly during the hearing. Other relevant information on these topics is available in earlier reports and scientific publications based on sampling within the Tākaka Catchment.

In this report we update, review and summarise the available information and data analyses to provide an overview of information on nitrogen sources, transformations and drivers of nitrogen dynamics within the Tākaka Catchment. However, a review of data relating to the age of water emerging from Te Waikoropupū Springs, trends in rainfall and river flow over time at hydrological monitoring sites and detailed farm-scale Overseer<sup>1</sup> nitrate leachate modelling is beyond the scope of this report.

This work aligns with the Council's resolution to develop a National Policy Statement for Freshwater Management action plan to address the long-term increase in the concentrations of nitrate-N that has been observed in the springs. Information on the relative importance of likely sources of nitrogen to the Tākaka Catchment will be critical for the development of the action plan.

<sup>&</sup>lt;sup>1</sup> Overseer is online software that connects farmers to information enabling sustainable farms that protect the environment, including predicted nitrogen leaching. See <u>https://www.overseer.org.nz</u>

# 2. CATCHMENT DESCRIPTION AND HYDROLOGY

Te Waikoropupū and the wider Tākaka River Catchment are located in the eastern side of Golden Bay / Mohua, with the total catchment area measuring 712 km<sup>2</sup> (Figure 1). The area has a rugged topography: steep ranges to the east, south and southwest have narrow valleys that broaden out towards Tākaka. The high ridges to the south are at elevations of between 1,500 m and 1,650 m, and to the east on the Pikikiruna Range they reach just over 1,000 m (Thomas and Harvey 2013).

This area has a variable and complex geology. The key geological groups can be broadly categorised as schist, igneous intrusive rocks (granite and diorite), Arthur Marble, metamorphic rocks of various types (including quartzite and argillite), tertiary sediments (including Tarakohe Mudstone, Tākaka Limestone and Motupipi Coal Measures), and recent sands, gravels and coastal deposits (Thomas and Harvey 2013). Much of the Tākaka Valley floor is covered by alluvial gravels.

The area experiences a generally mild climate with average to high sunshine hours (Thomas and Harvey 2013). Rainfall is variable, with the rainfall gradient declining from west to east and towards the coast. Local weather is affected by elevation, which also affects temperature and rainfall. Orographic precipitation due to westerly and northerly winds can generate heavy rainfall in the western and northwestern ranges.

The freshwater springs at Te Waikoropupū are part of a larger system comprising much of the Tākaka River Catchment and are connected with surface waters up-valley from the Waingaro River, the underlying aquifer and coastal waters in Golden Bay / Mohua (Figure 1). The springs are a large karst resurgence consisting of the Main Spring, with mean discharge of 10,000 L/s, and a number of smaller springs known as Fish Creek Springs, with mean discharge of 3,300 L/s (Thomas and Harvey 2013). The Fish Creek Springs go dry during extended drought. The springs are Aotearoa New Zealand's largest and the spring water is among the clearest water in the world (Davies-Colley and Smith 1995; Gall 2018).

The springs issue from the Arthur Marble Aquifer (AMA), which has an unconfined part in the upper and middle part of the catchment and a confined part in the lower part of the catchment (Figure 1). This underlying aquifer is very large (total volume 3.4 km<sup>3</sup> and measuring at least 500 m thick in places). A mean water residence time within the aquifer of 8 years was calculated based on tritium and CFC-11 measurements (Stewart and Thomas 2008).



Figure 1. Map of the Tākaka Catchment showing Te Waikoropupū Springs and the Wharepapa Arthur Marble Aquifer (WAMA or AMA) and aquifer recharge area.

The AMA comprises dense crystalline carbonate rocks with a mix of pores, fissures and larger conduits where water is present. Most groundwater storage is expected to be in fissures (on a scale of millimetres) and interconnected pores (sub-millimetre scale), whereas most water movement is expected to be through conduits, which offer much less resistance to flow (Williams 2022, 2023).

Rain and higher river flows (and increases in discharge from the Cobb Power Station) cause a recharge pulse that passes through the groundwater system in the marble. This flow pulse increases pressure within the aquifer and pushes out (and mixes with) some of the water already in storage but does not itself resurge at the springs until some years later.

Recharge of the aquifer is through rainfall in the areas where the marble is exposed or close to the surface and water can drain directly into the marble, from flow loss from the upper Tākaka River and parts of the Waingaro River and creeks draining into the upper Tākaka Valley, from infiltration of rainwater falling on the Tākaka Valley floor, and from a small seawater input (0.5%; Stewart and Thomas 2008) (Figure 1). An important feature to note is that the chloride concentration (and age) of the water discharging from the Main Spring increases with flow. The increase in water age with flow observed by Stewart and Thomas (2008) contradicted the assumption of Stewart and Downes (1981), who erroneously considered that there would be dilution of older aquifer water when inputs (and discharge from the springs) increase.

Because chloride (and water age) increase linearly with spring flow, Stewart and Thomas (2008) considered that there must be contributions from two (and only two) water types, one with high chloride concentration (i.e. containing seawater) and one with very low chloride concentration. Stewart and Thomas (2008) conceptualise the aquifer as two different flow systems with different predominant recharge sources for this reason. One system contains deeply penetrating old water (mean age 10.2 y) and a water volume of 3 km<sup>3</sup>, recharged from the karst uplands and including the seawater contribution. The other system, at shallow levels below the valley floor, has much younger water (mean age 1.2 y) and a water volume of 0.4 km<sup>3</sup>, recharged by the upper Tākaka River and valley rainfall. In the Stewart and Thomas (2008) conceptualisation, inputs to the aquifer from the Waingaro River are incorporated within the upland karst category. These two flow systems contribute in different average proportions to the Main Spring (76% deep, 24% shallow), Fish Creek Springs (20% deep, 80% shallow) and offshore springs (14% deep, 86% shallow) (Stewart 2022). The very different behaviours of the two flow systems, despite being in the same aquifer, are attributed by Stewart (2022) to the presence of a diorite intrusion below the surface of the lower Tākaka Valley, which diverts the deep system flow towards Te Waikoropupu Springs and allows much of the shallow system flow to pass over the intrusion and escape via offshore springs.

There is general agreement about the mix of waters contributing to flow in the Main Spring and that the Fish Creek Springs water is dominated by inputs from more recent sources. However, there are significant differences between the water balance models recently calculated for the AMA (Table 1). For example, Williams (2023) calculated that valley rainfall makes up about 10% of Main Spring flow, whereas Stewart (2022) calculated that valley rainfall makes up only 6% of Main Spring flow, with associated differences in the contribution from the Tākaka River balancing up the total flow. Similarly, the calculations in Williams (2023) indicate that the contribution of the karst uplands and Waingaro River to flows at the Fish Creek Springs is three times higher than that calculated by Stewart (2022). These differences in calculated flow inputs contribute in part to variations in calculations of the importance of different nitrogen sources (see Sections 7.1 and 7.2).

Courses	Inputs (L/s)		Main Spring outputs (L/s)		Fish Creek Springs outputs (L/s)		Remainder to sea (L/s)	
Source	PW	MS	PW	MS	PW	MS	PW	MS
Karst uplands E & W	8,598	0.000	6,887	7,624	1,056	649	660	926
Waingaro River	1,500	9,200	750		891		-141	
Tākaka River	8,350	8,350	1,253	1,741	1,190	1,735	5,908	4,875
Tākaka Valley rainfall	2,034	2,200	1,007	635	361	916	666	649
TOTAL	20,482	19,750	9,897	10,000	3,498	3,300	7,093	6,450

Table 1. A comparison of water balance estimates for water moving through the Arthur Marble Aquifer from Williams (2023) (PW) and Stewart (2022) (MS).

## 3. SUMMARY OF EXISTING NITROGEN DATA

#### 3.1. Te Waikoropupū sites

Nitrogen concentrations in oxygenated groundwater are typically dominated by the nitrate-nitrogen form of nitrogen (nitrate-N, NO<sub>3</sub>-N). Ammoniacal nitrogen (ammoniacal-N, NH<sub>4</sub>-N) concentrations have been measured sporadically in Te Waikoropupū Main Spring and are typically below or close to the laboratory detection limit (around 0.002 mg/L). We are aware of four samples from the Main Spring where both total nitrogen (TN) and nitrate-N have been analysed together. Nitrate-N constituted close to all of the nitrogen in these samples, meaning that there are negligible concentrations of ammoniacal-N or organic nitrogen in water emerging from the Main Spring.

### Box 1: Nitrogen comes in various forms in aquatic systems

In aquatic systems, nitrogen occurs in various inorganic forms: dissolved nitrogen gas (N<sub>2</sub>), ammoniacal nitrogen (ammoniacal-N, NH<sub>4</sub>-N), nitrite-nitrogen (nitrite-N, NO<sub>2</sub>-N) and nitrate-nitrogen (nitrate-N, NO<sub>3</sub>-N). It is also found in a wide range of dissolved organic compounds such as amino acids, proteins and humic substances, and collectively referred to as dissolved organic nitrogen (DON). Particulate organic material found in aquatic systems, such as algae, aquatic plants, tree leaves, wood and the bodies of aquatic and terrestrial organisms, also contains nitrogen.

Dissolved nitrogen gas is largely biologically inert and does not directly affect aquatic organisms, although some bacteria and cyanobacteria are able to transform (fix) nitrogen gas into biologically active forms of nitrogen.

Dissolved inorganic nitrogen is the combination of ammoniacal-N, nitrite-N and nitrate-N. Total nitrogen is the sum of dissolved inorganic nitrogen, and DON and particulate organic nitrogen. It does not include the dissolved nitrogen gas component. See Appendix 2 for details on how each form of nitrogen is measured in a laboratory.

Nitrogen is transformed from one form to another as part of the global nitrogen cycle. Key processes by which nitrogen are transformed include: nitrogen fixation (nitrogen gas is transformed into nitrate-N and nitrite-N), assimilation (plants absorb nitrate-N or ammoniacal-N and transform it into organic compounds), ammonification (conversion of organic nitrogen into ammoniacal-N), nitrification (conversion of ammoniacal-N to nitrate-N), denitrification (conversion of nitrate-N to nitrogen gas). Bacteria play a major role in many of these processes.

Nitrate-N concentrations have been measured in the Main Spring at Te Waikoropupū since 1970 (Figure 2). Concentrations of nitrate-N at the Main Spring have risen over the duration of the sampling record, from an average of 0.31 mg/L in the 1970s through to an average of 0.44 mg/L for the decade up to 2023. There was an increase in nitrate-N concentrations from 2006 to 2012, followed by a decrease from 2013 to 2016. Nitrate-N concentrations then increased from 2016 to 2021, followed by little change from 2021 to November 2023 (Figure 2).

It is worth noting that the particularly low nitrate concentrations (< 0.2 mg/L) recorded from seven samples in the early 1990s appear to have been an artefact of changes in the analytical method used by different laboratories and should be considered outliers in the dataset (Young et al. 2017). The six anomalous values indicating nitrate-N concentrations greater than 0.6 mg/L may also be outliers. There is no indication of a correlation between these spikes and spring flows or any other parameter.



Figure 2. Changes in nitrate-nitrogen concentration at Te Waikoropupū Main Spring over the full record (1971–2023). Data source: Tasman District Council and Friends of Golden Bay.

The load of nitrate-N (i.e. concentration  $\times$  flow) from the Main Spring varies with both flow and nitrate-N concentration, and has ranged from 187 kg/day up to 548 kg/day, with a median load of 372 kg/day (136 t N/y) over the period from 1999 to 2023 (Figure 3).



Figure 3. Changes in nitrate-nitrogen load (and flow) at Te Waikoropupū Main Spring from 1999 to 2023. Data source: Tasman District Council. Loads associated with the six anomalous samples with high nitrate-N concentration (> 0.6 mg/L) are not shown.

The sampling record for Fish Creek Springs (TDC monitoring site) is much shorter than for the Main Spring. Quarterly sampling at one of the Fish Creek Springs since late 2014 has found that nitrate-N concentrations range from 0.39 mg/L to 0.66 mg/L (Figure 4). The load of nitrate-N from the Fish Creek Springs has ranged from 32 kg/day up to 315 kg/day, with a median load of 129 kg/day (47 t N/y) over the period from 2014 to 2023 (Figure 5). There was also one anomalous recording, of 1.44 mg/L on 9 September 2015 (not shown on Figure 4 or Figure 5), but this is considered to be an outlier.



Figure 4. Changes in nitrate-nitrogen concentration at Fish Creek Springs. Data source: Tasman District Council. A sample on 9 September 2015 with a reported nitrate-N concentration of 1.44 mg/L was omitted.



Figure 5. Changes in nitrate-nitrogen load at Fish Creek Springs. Data source: Tasman District Council. The load calculated from a sample on 9 September 2015 with a reported nitrate-N concentration of 1.44 mg/L was omitted.

#### Box 2: Effects of different analytical methods and laboratories

Two main methods have been adopted over time for nitrate-N analysis: cadium reduction and ion chromatography. Most of the samples from the Main Spring have been analysed using the ion chromatography method (APHA 4110 B) at the New Zealand Geothermal Analytical Laboratory (NZGAL) run by GNS Science. Other samples have been analysed at Hills Laboratories using the ion chromatography method or the cadmium reduction method (APHA 4500 NO3).

Moreau (2021) compared the results of paired / tripled nitrate-N samples analysed using different methods and laboratories. She found a significant difference in the nitrate results between the Hills ion chromatography method and the other two approaches (NZGAL ion chromatography and Hills cadmium reduction). There was no significant difference in results between the latter two approaches.

In an updated analysis of similar paired / tripled samples, we found the same result, with the Hills ion chromatography method producing results that were on average 0.048 mg/L lower than the Hills cadmium reduction method (n = 50, p < 0.00001, 95th percentile difference 0.039–0.057 mg/L). There was no evidence for a significant difference between the Hills cadmium reduction method and the NZGAL ion chromatography method (p = 0.84).

Given these differences, where there are changes in analytical approaches used throughout the sampling record or multiple samples analysed using different methods, we have presented only results that are expected to be most consistent over time (i.e. NZGAL ion chromatography and Hills cadmium reduction).

#### 3.2. Other sites influencing Te Waikoropupū

Data on the concentration of various forms of nitrogen are also available for a range of other sites throughout the Tākaka Catchment (Figure 6).



Figure 6. Monitoring sites in the Tākaka Catchment.

#### 3.2.1. Tākaka at Harwoods

Concentrations of nitrate-N are typically very low at the Tākaka at Harwoods monitoring site (< 0.006 mg/L), but concentrations of TN range between 0.05 mg/L and 0.10 mg/L (median 0.06 mg/L, n = 57) (Figure 7). There was no evidence for a relationship between flow and either nitrate-N or TN at this site ( $R^2 < 0.1$ ; p > 0.05). Nitrate-N is generally less than 10% of the TN observed at this site, suggesting that other forms of nitrogen such as dissolved organic nitrogen (DON) must make up most of the nitrogen in the water at this site. This river monitoring data is consistent with the literature on nitrogen export from undeveloped forested areas (McGroddy et al. 2008). The water at the Harwoods site often has a tannin-stained appearance and dissolved organic carbon concentrations are relatively high (around 2 mg/L; Young et al. 2000), supporting the suggestion that dissolved organic material is probably the main component of the dissolved nitrogen at this site.



Figure 7. Concentrations of nitrate-nitrogen (NO<sub>3</sub>-N) and total nitrogen (TN) at the Tākaka at Harwoods monitoring site. Data source: Tasman District Council.

#### 3.2.2. Tākaka at Lindsays Bridge

Monitoring at Lindsays Bridge commenced shortly after monitoring at the Tākaka at Harwoods site ceased (2016), therefore the sampling was not concurrent. It is useful to compare the results between these sites, but the difference in the sampling time period needs to be kept in mind.

Concentrations of nitrate-N at the Tākaka at Lindsays Bridge monitoring site are generally about 10 times higher than those upstream at the Harwoods site (median 0.06 mg/L, n = 28), while TN concentrations range from 0.06 mg/L to 0.27 mg/L (median 0.12 mg/L) (Figure 8). There were statistically significant relationships between flow and nitrate-N ( $R^2 = 0.31$ , p = 0.002) and TN ( $R^2 = 0.43$ , p = 0.0002), respectively, at this site. Nitrate-N is typically just under half of the TN concentration (median 46%) at Lindsays Bridge. The increase in TN and nitrate-N between the Harwoods and Lindsays Bridge monitoring sites is likely due to inputs of nitrate-N through the reach between the monitoring sites. The difference between the median TN and median nitrate-N at each site (which can be interpreted as the DON concentration at that site) is comparable between sites (approximately 0.065 mg/L), indicating that there is limited processing of the organic N as the river water flows downstream over the short reach and / or that additional inflow loads of DON are comparable to the removal rate.



Figure 8. Concentrations of nitrate-nitrogen (NO<sub>3</sub>-N) and total nitrogen (TN) in the Tākaka at Lindsays Bridge monitoring site. Data source: Tasman District Council.

#### 3.2.3. Waingaro at Hanging Rock

Concentrations of nitrate-N at the Waingaro at Hanging Rock monitoring site are relatively low (median 0.01 mg/L, n = 15), while TN concentrations are similar to those measured at the Tākaka at Harwoods site (median 0.05 mg/L) (Figure 9). There was no evidence for a relationship between flow and either nitrate-N or TN at this site ( $R^2 < 0.1$ , p > 0.05). Nitrate-N typically makes up less than 30% of the TN (median 28%) at the site.



Figure 9. Concentrations of nitrate-nitrogen (NO<sub>3</sub>-N) and total nitrogen (TN) in the Waingaro River at Hanging Rock monitoring site. Data source: Tasman District Council.

#### 3.2.4. Other sites

Tasman District Council has also undertaken sporadic sampling at several other sites that may contribute water to the Arthur Marble Aquifer or be influenced by the aquifer (Figure 6). Higher-altitude sites (e.g. the upper parts of Rameka Creek) have low concentrations of nitrate-N, whereas spring-fed sites in the valley floor (Spring Brook and East Tākaka Spring) or closer to it (Spittals Spring) have higher nitrate-N concentrations (Figure 10). The particularly high nitrate-N concentrations at East Tākaka Spring probably reflects the contribution of water to this spring from the Tākaka Limestone Aquifer (Thomas 2022). To our knowledge, no data on TN concentrations are available for these sites.



Figure 10. Nitrate-nitrogen (NO<sub>3</sub>-N) concentrations at other sites that influence (or are influenced by) the Arthur Marble Aquifer.

McArthur (2022) reports results from monitoring carried out by Friends of Golden Bay at a range of sites (Table 2). Their results for the sites presented above are generally consistent with the TDC information.

Site	Period	Frequency and no. of samples ( <i>n</i> )	Median nitrate-nitrogen (mg/L)
Ironstone Creek	Nov 2016–Mar 2022	Occasionally; $n = 9$	0.030 (0.007–0.09)
Gorge Creek	Nov 2016–Mar 2022	Occasionally; $n = 9$	0.06 (0.041–0.18)
Rameka Creek at 'C'	Nov 2018–Mar 2022	Occasionally; $n = 6$	0.0105 (0.005–0.018)
Rameka Creek at Ford	Nov 2016–Mar 2022	Occasionally; $n = 9$	0.53 (0.1–0.65)
Rameka Creek tributary	Nov 2016–Mar 2022	Occasionally; $n = 6$	0.93 (0.87–1.0)
Waingaro at Hanging Rock	Sep 2018–Feb 2022	Monthly; $n = 39$	0.008
Tākaka at Harwoods	Sep 2018–Feb 2022	Monthly; $n = 39$	0.004
Fish Creek at Boundary	Feb 2016–Feb 2022	Fortnightly; $n = 224$	0.075

Table 2. Tākaka River catchment monitoring results from Friends of Golden Bay. Data source: modified from McArthur (2022).

# 4. TRANSFORMATIONS OF NITROGEN IN THE CATCHMENT AND AQUIFER

As described above, the majority of the nitrogen present at the Tākaka at Harwoods and Waingaro at Hanging Rock monitoring sites is in the form of dissolved organic nitrogen (DON). There will also be some particulate organic material containing nitrogen. This organic nitrogen will be slowly oxidised / decomposed to form nitrate-N. Based on the monitoring data from Te Waikoropupū Springs (i.e. the lack of organic nitrogen in the outflow), this oxidation process occurs within the Arthur Marble Aquifer to completion before the groundwater reaches the springs.

As highlighted by Young (2022), it possible to estimate the amount of organic matter that enters the aquifer and is decomposed using the known reduction in dissolved oxygen (DO) concentration that occurs in water during its prolonged passage through the fully wetted part of the aquifer away from interaction with the atmosphere (from around 10.5 mg/L down to 6.0 mg/L). From this, it is possible to estimate the level of nitrogen inputs to the water that may be due to breakdown of this organic matter within the wetted part of the aquifer. To calculate how much of the nitrate-N in the springs originates from organic nitrogen, we first calculate the total organic matter breakdown using the reduction in dissolved oxygen in the aquifer, which is expressed as the amount of carbon broken down per litre. Using estimates of the relationship between organic carbon and organic nitrogen concentrations in the surface water, we can then determine the concentration of nitrate-N.

Knowing that the water in the aquifer loses about 4.5 mg/L (i.e. 10.5 mg/L - 6.0 mg/L) of DO as it passes through it, and knowing that the stoichiometric relationship between DO uptake and carbon breakdown is 12/32, this means that  $12/32 \times 4.5 = 1.7 \text{ mg/L}$  of carbon is broken down as the water passes through the aquifer.

Assuming that a typical proportion of nitrogen is associated with the dissolved and particulate organic matter entering the aquifer, it is possible to estimate the amount of nitrogen released during the breakdown of this organic matter. The organic matter entering the aquifer will include a wide variety of forms, from dissolved proteins, amino acids, urea and dissolved humic material through to particulate material such as algae, leaves and wood. Therefore, its chemical composition is somewhat uncertain. Dissolved organic carbon (DOC) concentrations in rivers tend to be considerably higher than particulate organic matter concentrations (Young and Huryn 1997), and DOC concentrations recorded in the Tākaka River at Drummond Flat and Harwoods (both upstream of Lindsays Bridge) are around 2.0 mg/L (Young et al. 2000). Ratios of DOC to DON in river water are typically in the range of 5:1 to 30:1 (Yates et al. 2019).

As pointed out by Mead (2022), data from the Tākaka at Lindsays Bridge monitoring site can be used to estimate the ratio of DOC to DON in the Tākaka River. The

median concentration of DOC at Lindsays Bridge is 1.8 mg/L and the difference between the median TN concentration and nitrate-N concentration (which can be interpreted as the DON concentration at that site) is 0.064 mg/L, giving a DOC:DON ratio of 28:1.

So, knowing there is an average of one nitrogen atom for every 28 carbon atoms in the organic matter and knowing the stoichiometric relationship between nitrogen and carbon (14/12), this would correspond to  $1.7/28 \times 14/12 = 0.071$  mg/L of nitrogen released to the water as it passes through the aquifer. This is only a little higher than the estimated median DON concentration at this site (0.064 mg/L).

This calculation infers that the release of nitrogen during decomposition of dissolved and particulate organic matter within the fully wetted part of the aquifer is likely to be around 0.07 mg/L, which represents about 16% of the median nitrate-N concentration observed at the Main Spring over the last decade (0.44 mg/L), a modest but notable contribution. This result again emphasises the importance of considering concentrations of TN in all potential sources, not just nitrate-N. It is worth noting that these calculations do not include transformations of dissolved and particulate organic matter into nitrate-N that might be occurring in any aerated parts of the aquifer or the intermittently wetted epikarst.

Decomposition of organic matter within the aquifer relies on oxygen being available. If the aquifer became anoxic, the decomposition of organic matter would be reduced, potentially adversely affecting the health of the aquifer and the clarity of water emerging at Te Waikoropupū Springs. Hence, it is important to monitor DO concentrations at the springs and place a limit on DO in the water conservation order.

# 5. SOURCES OF NITROGEN

## 5.1. Leaching associated with land cover and land use

Leaching of nitrogen below the root zone can occur if the amount of nitrogen in the soil is more than plants and microbes can take up. Leaching is affected by the amount of nitrogen in the soil, the types of nitrogen compounds present, the amount of water moving down through the soil profile, and the soil type and structure. Climate, geology, land use and vegetation types have an influence on all of these factors (Rissman et al. 2024), leading to large differences in rates of nitrogen leaching. Rates of leaching are high in areas with excessive amounts of inorganic nitrogen in the soil (particularly nitrate-N), areas with intensive agriculture where stock leave concentrated patches of urine, areas with high soil moisture levels, and areas with sandy soils that have low water retention rates. Studies of nitrogen leaching have estimated leaching rates for a wide range of land-use types. See Section 7.4 for more details.

## 5.2. Atmospheric deposition

An important part of the nitrogen cycle is the atmospheric deposition of nitrate-N and ammoniacal-N. Increases in anthropogenic emissions of nitrogen compounds to the atmosphere via fossil fuel combustion and intensive farming have driven a global increase in atmospheric nitrogen (atmospheric-N) deposition (Holland et al. 1999). Despite Aotearoa New Zealand's atmosphere being considered relatively clean as a result of the country's location surrounded by ocean, average atmospheric-N deposition in the North Island has been calculated at 6.4 kg N·ha<sup>-1</sup>·y<sup>-1</sup>, while the South Island receives on average 2.35 kg N·ha<sup>-1</sup>·y<sup>-1</sup> (Verburg et al. 2016), both higher than rates expected in the absence of anthropogenic effects (1.5 kg N·ha<sup>-1</sup>·y<sup>-1</sup>; Parfitt et al. 2008). Highest deposition rates are expected in areas with the highest rainfall (Parfitt et al. 2008). An atmospheric deposition rate of 2.35 kg N·ha<sup>-1</sup>·y<sup>-1</sup> equates to 167 t N/y for the 712 km<sup>2</sup> Te Waikoropupū Springs catchment.

The levels of nitrogen export resulting from atmospheric-N deposition will depend on the level of nitrogen saturation of the ecosystem where the deposition occurs. In areas where the system is saturated, much of the atmospheric-N deposited will be exported as inorganic or organic nitrogen. In areas where there is a deficit of nitrogen, the majority of the atmospheric-N deposited will be taken up and recycled within the system.

#### 5.3. Geological sources of nitrogen

In some situations, geological sources of nitrogen (i.e. nitrogen sourced from the dissolution of rock) can constitute a significant component of the nitrogen budget of a catchment. For example, Holloway and Dahlgren (1999) found that geological sources of nitrogen represented 30–50% of the soil nitrogen pool in a Californian catchment. Nitrogen released from bedrock contributed to an excess of available nitrogen relative to biotic demands, leading to nitrate leaching and elevated concentrations of nitrate in stream water. Similarly, Dixon et al. (2012) found that marble contained a mean abundance of 4,300 mg N /kg, quartz schist 1,600 mg N/kg, biotite schist 4,300 mg N/kg, and garnet mica schist 4,500 mg N/kg. They considered that geological nitrogen may represent a large and reactive pool with the potential for considerable impact on the geochemical system. Williard et al. (2005) also concluded that bedrock geology is an important factor to consider when assessing forest nitrogen dynamics at a broad landscape scale.

As discussed above, marble is an important component of the geology in the Tākaka Catchment and particularly the Arthur Marble Aquifer (AMA). Marble is relatively soluble in water. Calcium concentrations in Te Waikoropupū Springs water are very high (64 mg/L; Michaelis 1976), and at least an order of magnitude higher than concentrations typically seen in surface waters in Aotearoa New Zealand (Close and Davies-Colley 1990). Assuming that 60 mg/L of the calcium concentration from Te Waikoropupū Springs is due to dissolution of marble (the remaining 4 mg/L being typical of background surface water concentrations) and given the average discharge from the springs of 10 m<sup>3</sup>/s, we calculate that around 19,000 t of calcium is discharged from the Main Spring every year (60 mg/L × 10,000 L/s × 86,400 s/day × 365 days/y). Marble is predominantly calcium carbonate, so based on the molecular weight of this compound, we can assume that calcium represents about 40% of the total mass of marble. So, 19,000 t of calcium is roughly equivalent to about 47,000 t of marble dissolving within the aquifer and being discharged at the springs each year. This dissolution of marble is what has formed, and continues to form, the characteristic features of the karst landscape in the Tākaka Catchment (distinctively shaped rock, sink holes, caves, springs, etc.).

Based on an average concentration at the Main Spring over the last decade of 0.44 mg N/L, the total load of nitrogen being discharged from the Main Spring is around 138 t per year (0.44 mg N/L × 10,000 L/s × 86,400 s/day × 365 days/y). The contribution of geological nitrogen to this load will depend on the concentrations of nitrogen within the marble that is dissolved. If nitrogen concentrations are as high as those reported by Dixon et al. (2012), then the total nitrogen load (and more) could be attributable solely to geological sources (4,300 mg N/kg × 47,000 t N/y = 202 t N/y). However, if nitrogen levels in the marble are considerably lower than this, then geological sources may be minor.

Young and Hay (2017) reported the results of a study of the nitrogen level of rock types within the Tākaka Valley to help determine the likely contribution of geological nitrogen to the nitrogen load from Te Waikoropupū Springs. Analyses of the nitrogen content from 15 rock samples (nine marble, two limestone, two mudstone, two coal measures) from throughout the Tākaka Valley were conducted at the GNS laboratory. The sites where the rock samples were collected are shown in Figure 11. The percentage of nitrogen in the samples ranged from 0.003% to 0.05% (30–500 mg N/kg) (Figure 12). The values are considerably lower than the concentrations reported by Dixon et al. (2012).



Figure 11. Locations of rock sampling sites in the Tākaka Valley for determining nitrogen content of the rock. Source: Young and Hay (2017).

Based on the average nitrogen concentration in marble (66 mg N/kg) determined from these analyses, the nitrogen load associated with dissolution of 47,000 t of marble per year would be 3 t N/y. This represents about 2% of the measured nitrogen load discharged from the Main Spring.

We note that the nitrogen content of mudstone and coal measures is substantially higher than that of marble (Figure 12). These geology types are less common than marble in the catchment / aquifer, and importantly, the rate of dissolution of mudstone and coal measures is expected to be much lower than that for marble. Therefore, mudstone and coal measures are not likely to make a significant contribution to the nitrogen load from Te Waikoropupū Springs.





#### 5.4. Wastewater

Wastewater discharges can potentially contribute nitrogen to downstream groundwater and other waterways. The importance of wastewater discharges depends on the volume of waste discharged and any treatment that occurs. Within the AMA recharge area, 247 residential and business points are assumed to have septic tank systems (TDC 2022). In addition, 13 properties are connected to the Upper Tākaka wastewater network, which discharges to a wetland in the Tākaka Valley. Using local information and various assumptions, TDC (2022) estimated that the wastewater contribution to nitrogen loading of the aquifer is around 1.2 t N/y. Using an alternative approach and assuming an average of 2.6 people per property and a load

of 10 g N/person/day (Potts and Ellwood 2000) gives an estimated load of 2.5 t N/y. Either way, these calculations indicate that wastewater will contribute less than 2% of the nitrogen load reaching Te Waikoropupū Springs.

## 5.5. Quarrying / explosives

Explosives used in quarrying operations are typically composed of ammonium nitrate  $(NH_4NO_3)$ . Undetonated explosives and blast residue containing nitrogen compounds can result in leaching of nitrate and ammonia. In an intensive study of contaminants associated with blasting agents in a rock quarry, Bailey et al. (2013) found that there was approximately 5% nitrogen loss from blasting explosives.

Quarrying activities occur in two locations within the AMA recharge area, but limited information is available on the amount of explosives used at these quarries. We anticipate that the contribution of nitrogen from explosives is small relative to the overall catchment nitrogen load. However, it is difficult to confirm this given the lack of data.

## 5.6. Seawater

As mentioned in Section 2, a small proportion of the flow at Te Waikoropupū Springs is sourced from seawater. Concentrations of nitrate-N vary in seawater and have been observed at levels up to 0.028 mg N/L in Tasman Bay / Te Tai-o-Aorere (Mackenzie 2004). Assuming that seawater makes up 0.5% of the 10 m<sup>3</sup>/s mean flow at the Main Spring and 0.1% of the 3.3 m<sup>3</sup>/s mean flow at the Fish Creek Springs (Stewart 2022), this corresponds to around 53 L/s of seawater contributing to flows at Te Waikoropupū Springs. If the nitrate-N concentration of the seawater was consistently 0.028 mg N/L, this would correspond to an annual nitrogen load of around 0.047 t N/y. This is less than 0.05% of the nitrogen load discharged from the Main Spring and therefore an insignificant source of nitrogen.

# 6. CLIMATIC DRIVERS OF NITROGEN INPUTS

As discussed in Section 3, the nitrate concentration in Te Waikoropupū Springs shows a generally increasing long-term trend that differs between time windows, alternating between increasing and decreasing concentrations over various periods (Figures 2 and 13). The Southern Oscillation Index (SOI; see Box 3) data for the last 50 years shows no overall increasing or decreasing trends but indicates three strong and persistent La Niña periods since 1998 (Figure 13). Notably, there is concordance between the strong and persistent La Niña events being associated with high nitrate concentrations in the springs and El Niño periods being associated with reduced nitrate concentrations (see numbered events in Figure 13 for persistent La Niña periods).

Three major La Niña and adjacent El Niño periods occurred over the monitoring period since 1990, with differing durations and intensity of the SOI. The periods of the recent persistent La Niña events ranged from 9 to 12 months in the period from July 1998 to February 2023, with El Niño events ranging from 2 to 12 months in the period from May 1997 to November 2023 (Table 3). Some La Niña / El Niño events transition abruptly (e.g. Events 1 and 3; Figure 13, Table 3), while others show a more gradual transition with periodic SOI fluctuations (e.g. Event 2). The nitrate concentrations in the springs consistently reduced by 8.7–13.5% for these three events when comparing the La Niña concentrations with the El Niño concentrations (Table 3, pooled comparison 13% reduction; *t*-test,  $\alpha = 0.05$ , n = 21, p = 0.01; Figure A1-3).



- Figure 13. Southern Oscillation Index (SOI) monthly average data (black points, 3-month moving average values) and Te Waikoropupū Springs nitrate-nitrogen (nitrate-N) concentration (red points) for the period June 1991 to December 2023. Dashed horizontal lines indicate lower and upper bounds for La Niña and El Niño phases of the SOI. Smoothing lines through the SOI (red) and the nitrate-N concentration (black) use a boxcar algorithm to compute a moving average of the data. Linear regression and equation are shown for nitrate-N concentration data. Bold numbers indicate La Niña events where comparative analyses are undertaken (see Table 3).
- Table 3. Summary of Southern Oscillation Index (SOI) event periods and average nitrate-nitrogen (NO<sub>3</sub>-N) concentrations for La Niña and El Niño phases. See Figure 13 for SOI event timing.

Event	Phase	Dates	Period (months)	SOI	NO₃-N (mg/L)	%NO₃
1	La Niña	Jul 1998–Apr 1999	9	11.5	0.37	
I	El Niño	May 1997–May 1998	12	-18	0.32	-13.5
2	La Niña	Jun 2010–Jun 2011	12	17.7	0.44	
2	El Niño	Jan 2016–Apr 2016	3	-14.5	0.39	-11.4
0	La Niña	Apr 2022–Feb 2023	10	14.8	0.46	
5	El Niño	Sept 2023–Nov 2023	2	-10.3	0.42	-8.7

#### Box 3: Southern Oscillation Index (SOI)

#### What is the SOI?

The Southern Oscillation Index (SOI) is an indicator that measures the El Niño– Southern Oscillation (ENSO), the movement of warm equatorial water across the Pacific Ocean and the atmospheric response. The SOI is calculated from the difference between the standardised surface air pressures at Tahiti and Darwin, Australia, and represents the strength of the tropical trade winds. This difference is represented by a positive or negative SOI. One or more consecutive 3-month-rolling average SOI is categorised as the La Niña (positive) or El Niño (negative) phase.

#### Why is the SOI important?

ENSO affects Aotearoa New Zealand's weather through changes in air pressure, sea temperature and wind direction. ENSO has three phases: neutral, El Niño and La Niña. It influences rainfall, temperature and wind patterns globally. In Aotearoa New Zealand, an El Niño phase in summer can bring increased westerly winds, more rain in the west and dryness in the east; in winter, it can lead to more frequent, cooler southerly winds. During a La Niña phase we may experience more northeasterly winds, wetter conditions in the north and east, and higher sea levels. We may also experience warmer-than-average air and sea temperatures. ENSO is one of several climate oscillations that affect our weather (other oscillations include, but are not limited to, the Interdecadal Pacific Oscillation [20–30-year duration] and the Southern Annular Mode [several weeks' duration, but changes phases quickly and unpredictably]). ENSO occurs every 2–7 years and typically lasts 6–18 months, with La Niña events generally persisting for longer periods than El Niño.

The SOI and sea surface temperatures can be used to compare the intensity of La Niña events.

#### Data source

Monthly values for the SOI for the period 1990 to December 2023 were obtained from the Australian Bureau of Meteorology, and we used the Troup convention, whereby index values are multiplied by 10. The SOI typically ranges from -30 to +30 and is quasi-periodic, with a period of 3–7 years. El Niño conditions are defined as an SOI < 8 over  $\geq$  3 months, while La Niña conditions are defined as an SOI > 8. We used a 3-month rolling average of the monthly SOI values to reduce variability in the SOI data.

Appendix 1 summarises the methodology and a provides a plot or the SOI index and La Niña and El Niño phases for the last 50-years.

#### Links

Stats New Zealand: <u>https://www.stats.govt.nz/indicators/el-nino-southern-oscillation</u> National Institute of Water and Atmospheric Research (NIWA): <u>https://niwa.co.nz/climate/information-and-resources/elnino</u> Bureau of Meteorology (BOM), Australia: http://www.bom.gov.au/climate/enso/soi The daily flow from Te Waikoropupū Springs shows a slightly increasing trend based on a linear relationship for the period from January 2000 to December 2023, with some periodic variability around the average flow of approximately 10 m<sup>3</sup>/s (Figure 14). A concordance of flow with the SOI is apparent with minimal lag, with slightly higher flows during the La Niña period and reduced flows during associated El Niño periods (Table 4).



Figure 14. Southern Oscillation Index (SOI) monthly average data (black points, 3-month moving average values) and Te Waikoropupū Springs daily flow (red points) for the period June 1991 to December 2023. Dashed horizontal lines indicate lower and upper bounds for La Niña and El Niño phases of the SOI. Smoothing lines through the SOI (red) and the flow (black) use a boxcar algorithm to compute a moving average of the data. Linear regression and equation are shown for flow data. Bold numbers indicate La Niña events where comparative analyses are undertaken (see Tables 3 and 4).

Table 4.Summary of SOI event periods, average Te Waikoropupū flows and nitrate-N loads for La<br/>Niña and El Niño phases. See Figure 13 for SOI event locations.

Event	Phase	Dates	Period (months)	Flow (m³/s)	NO₃-N load (t/y)	%NO₃	% Flow
2	La Niña	Jun 2010–Jun 2011	12	10.5	148		
Z	El Niño	Jan 2016–Apr 2016	3	10.0	129	-12.7	-4.8
3	La Niña	Apr 2022–Feb 2023	10	10.5	161		
	El Niño	Sept 2023–Nov 2023	2	9.7	126	-21.6	-7.6

The nitrate mass load discharged from the springs shows an overall increasing trend in the period from 2000 to December 2023, and alternated between increasing and decreasing trends. The maximum daily loads showed concordance with La Niña, and reduced loads occurred during El Niño (Figure 15). Comparison of data from two paired La Niña and El Niño phases showed lower flows (4.8% and 7.6%), along with associated lower nitrate loads (12.7% and 21.6%) for the El Niño phases (Table 4). The pooled nitrate load reduction for these two events was 16%, which was statistically significant based on the 14 measurement occasions (*t*-test = 4.132, *p* = 0.002; Figure A1-3).



Figure 15. Southern Oscillation Index (SOI) monthly average data (black points, 3-month moving average values) and Te Waikoropupū Springs nitrate (NO<sub>3</sub>) load (red points) for the period June 1991 to December 2023. Dashed horizontal lines indicate lower and upper bounds for La Niña and El Niño phases of the SOI. Smoothing lines through the SOI (red) and the nitrate-nitrogen (nitrate-N) load (black) use a boxcar algorithm to compute a moving average of the data. Linear regression and equation are shown for nitrate-N load data. Bold numbers indicate La Niña events where comparative analyses are undertaken (see Tables 3 and 4).

The results of these analyses of nitrate concentrations and mass load discharges from Te Waikoropupū Springs support the prediction that the strength and direction of water quality trends are associated with El Niño–Southern Oscillation (ENSO) variation. Elevated concentrations and loads occurred during La Niña periods, and reductions during El Niño periods. These changes were up to 14% for concentration and 22% for load, occurring over time periods of 1–5 years associated with the abruptness of the ENSO transition.

This potentially abrupt change in concentrations and loads has implications for trend monitoring to detect changes in water quality associated with land use and catchment management activities. The climate-related factors associated with the SOI include rainfall, wind (strength and direction), sunshine, temperature, and associated soil / land-use components affecting nitrogen loading, leaching and microbial process. This complex mix of components is likely to be site- or region-specific and will also depend on the duration of an ENSO period for factors such as soil moisture deficit and the antecedent weather period. The combined effects of a wide range of both climate and catchment factors are likely to confound efforts to establish definitive relationships with drivers of nitrogen loading to the springs.

The higher frequency of monitoring since 2016 has improved the quality of the data and facilitated a better understanding of the relationship between the SOI and the nitrate concentrations. Earlier nitrate monitoring had been conducted quarterly, and the frequency of data collection was insufficient to robustly detect changes in concentration linked to either short-term climate drivers (e.g. rainfall, seasonal variations) or more long-term indicators (e.g. SOI). The monthly monitoring of nitrate provides data that are better suited for comparison with climate indicators (such as the monthly SOI; Figure 14) and for undertaking statistical comparisons of La Niña and El Niño periods. Collection of future long-term monitoring data will make it easier to analyse relationships with both specific and multiple climate drivers and to develop diagnostic and predictive models to improve monitoring of management actions and reduce nitrogen loads to the springs.

This preliminary analysis indicates a high degree of concordance between the nitrate concentrations and loads in Te Waikoropupū Springs and the SOI. Multiple La Niña events are associated with elevated nitrate concentrations, with a progressive decreasing trend in concentration as the El Niño condition develops. While the data are limited for the number of successive periods, the general concordance for these events shows minimal time lag for the nitrate concentration with the SOI transition. This suggests that the nitrate concentrations in the springs are strongly influenced by surface processes (e.g. soil leaching, microbial activity, stock loading) and shallow flow paths linked to the springs. An alternative suggestion for this apparent direct concordance is that the time lag between several of these SOI transitions has coincidentally been about 10 years, which is the same as the mean residence time of the deep component water contributing to the springs, as shown by tritium measurements (Stewart and Thomas 2008). Therefore, a period with elevated nitrate concentrations observed at the springs may be the result of a La Niña event that occurred a decade earlier rather than a current La Niña event, and thus does not infer an influence of shallow flow paths and surface processes.

Relationships between the SOI and river flow and water quality have been identified from long-term monitoring programmes in Aotearoa New Zealand rivers (Scarsbrook et al. 2003; Snelder et al. 2022a, 2022b). Those authors' results indicated that climate variability makes a significant contribution to water quantity and quality trends, even at timescales longer than ENSO cycles, with SOI relationships differing between regions and the water quality variable. Snelder et al. (2022a, 2022b) have developed models quantifying the contribution of individual sites and aggregated trends at river sites for monthly monitoring for a range of water quality measures. Notably, Snelder et al. (2022a) provide an example plot for SOI and TN concentration in the Hurunui River

(their figure 3 for State Highway 1), which shows an elevated increasing TN concentration in the La Niña period prior to 2014, followed by a rapid decline and minimum in the 2016 El Niño period. This shows a close similarity to the SOI / nitrate concentration pattern observed in Te Waikoropupū Springs for that period (Figure 13), suggesting that similar climate-related drivers and processes may have been operating at both locations over this SOI event. The Hurunui River is a large, braided river receiving alpine snowmelt and lake outflow to major tributaries, with sheep and beef farming (54%), forestry (4%) and dairy / dairy support (5%) in the catchment, which will affect surface and sub-surface contaminant discharges. This contrasts with the Te Waikoropupū aquifer, where most of the flow is derived from the Arthur Marble Aquifer and has a long average residence time. However, the similarity of the SOI-related response may indicate that generalised river-derived models may be used to provide better predictions of water quality trends in Te Waikoropupū Springs.

# 7. REVIEW OF PREVIOUS EFFORTS EXAMINING NITROGEN SOURCES

## 7.1. Stewart (2022) modelling

Stewart (2022) adapted and updated the hydrological sources model that was initially reported in Stewart and Thomas (2008). The model used  $\delta^{18}$ O isotopes and chloride as tracers to calculate flow contributions from three different sources: 1) karst uplands (including Waingaro and Anatoki Valleys, and karst areas on the eastern and western flanks of the valley); 2) Tākaka River – infiltration / flow of river water into the AMA through the upper and central Tākaka Valley; and 3) valley rainfall in the floor of the upper and central Tākaka Valley. This model uses the conceptualisation of the aquifer described in Section 2, where there are two different flow systems with different predominant recharge sources: one deep system containing old water, largely recharged from the karst uplands and including the seawater contribution; and a shallower system with younger water, dominated by recharge from the upper Tākaka River and valley rainfall. The use of the chloride tracer for deep water is somewhat confusing because the deep system water is also referred to as 'Upland Karst' water. However, the chloride in the deep system water does not originate from the karst, but is from the seawater component of the deep water.

The nitrate source modelling conducted by Stewart (2022) was based on the flow contribution model described above. It focused on nitrate concentrations only and used the average of nitrate-N concentrations measured at the Tākaka at Lindsays Bridge and Tākaka at Kotinga<sup>2</sup> monitoring sites as the Tākaka River input nitrate-N concentration (0.15 mg/L). Known nitrate-N concentrations of Main Spring (0.44 mg/L) and Fish Creek Springs (0.44 mg/L) were also used as inputs to the model. The model predicted estimates of nitrate-N concentrations for karst upland water (0.45 mg/L) and Tākaka Valley floor water (0.98 mg/L). Stewart (2022) notes that the model is constrained – i.e. no other solutions will fit all the other  $\delta^{18}$ O isotope, chloride and flow data.

The model also examined changes in nitrate-N concentration over time in the different sources. There was an increase in nitrate-N in all sources, including karst uplands (from 0.36 mg/L pre-1991 to 0.46 mg/L for 2012–21). The increase in Tākaka River nitrate-N concentration (0.07 mg/L to 0.15 mg/L) and Tākaka Valley floor nitrate-N concentration (0.33 mg/L to 0.98 mg/L) over the same period were even more marked (Stewart 2022).

The Stewart (2022) model prediction of nitrate-N concentrations in water sourced from the karst uplands was high given the nitrate-N concentrations that have been

<sup>&</sup>lt;sup>2</sup> The Tākaka at Kotinga monitoring site is on the Tākaka River at the Kotinga Bridge downstream of the Waingaro River confluence and upstream of the Anatoki River confluence.

measured in rivers draining the less modified parts of the Tākaka Catchment. Stewart (2022) noted that evidence to support the considerable background nitrate-N concentration of karst uplands included: 1) elevated nitrate concentrations in other springs from marble in the Tākaka area (e.g. Spittals Spring, Riuwaka Resurgence), 2) similar background-level measurements in pristine karst systems elsewhere in the world from the scientific literature, 3) evidence of nitrate being produced by nitrification of organic nitrogen in karst channels in the literature, and 4) the likelihood of some geological nitrogen being sourced from the Arthur Marble itself.

In a summary of his modelling results, Stewart (2022) noted, 'In terms of nitrate loads, 80% of the Main Spring load came from karst uplands recharge in 2017 while 14% came from Valley Rainfall recharge, so that a smaller increase in the Karst Upland recharge concentration will make a bigger increase in the load to the Main Spring than a bigger change in the Valley Rainfall recharge concentration.'

## 7.2. Williams (2022, 2023) modelling

The Williams modelling of the contribution of water and nitrate-N sources to the aquifer and springs was initially reported in Williams (2022) and subsequently revised as Williams (2023). Water sources included in the modelling were the upper Tākaka River, Lower Waingaro River, karst upland east and west flanks of the catchment, and the middle Tākaka Valley floor. The model used  $\delta^{18}$ O isotope and nitrate-N concentrations as tracers. Williams (2022) initially assumed nitrate was a conservative tracer, with no transformations occurring in the aquifer, but in the subsequent paper (Williams 2023) an allowance of 16% nitrification for all sources was applied iteratively to make the model balance.

The model focused on nitrate-N concentrations only and used the median nitrate-N concentration for Tākaka at Lindsays Bridge monitoring site as the Tākaka River input (0.054 mg/L), nitrate-N from Ironstone and Gorge Creeks to estimate upland karst input (0.1 mg/L), and nitrate-N from Waingaro at Hanging Rock as input for the Waingaro River (0.01 mg/L).

Williams (2023) noted that his discharge component values for the Main Spring broadly confirmed earlier estimates by Stewart and Thomas (2008). However, his model shows the proportion of water contributing to flow in Fish Creek Springs to be rather different from those estimated previously (see Table 1 comparing results from Williams [2023] and Stewart [2022]).

The nitrate source model produced an estimate of Tākaka Valley floor nitrate-N of 4.05 mg/L. Williams (2023) noted that while his model is unconstrained in the sense that some of the input areas and values could be estimated differently according to the criteria used, the model inputs and outputs still needed to balance, measured

values were used as inputs for some variables, and some results could be verified against independent evidence.

In summary, Williams (2023) noted:

The 49 km<sup>2</sup> of agricultural land across floodplains and terraces in the middle Tākaka valley upstream of the artesian boundary is the most critical area from the point-of-view of water quality management because it is part of the unconfined aquifer and an area of relatively intensive farming. Although only 10% of discharge at Te Waikoropupū is derived from that source, it introduces most of the nitrate-N in the groundwater (and could be associated with other agricultural chemicals).

### 7.3. Weir and Fenemor (2017) modelling

Weir and Fenemor (2017) conducted another modelling study examining flows and nitrogen sources in the Tākaka Catchment. The focus of this modelling was on comparing the effects of different irrigation scenarios on flows and nitrate-N concentrations at Te Waikoropupū Springs. The modelling was based on known areas with different land-use types, used estimated infiltration and nitrate-N leaching rates for each land-use type, and summarised the results up to a catchment scale. The modelling focused on nitrate-N alone and assumed that zero nitrate-N was coming from the upper, less modified parts of the catchment.

In terms of nitrate-N leaching rates, the authors used 106 kg  $N \cdot ha^{-1} \cdot y^{-1}$  for intensive farming, 68 kg  $N \cdot ha^{-1} \cdot y^{-1}$  for dryland pasture, 2.5 kg  $N \cdot ha^{-1} \cdot y^{-1}$  for native grassland / scrub, and 0.65 kg  $N \cdot ha^{-1} \cdot y^{-1}$  for forestry (presumably meaning plantation forest).

Various additional irrigation scenarios, and the effects at various monitoring sites, were modelled. For example, if the full Tākaka Valley floor was irrigated, the modelled nitrate-N concentrations were predicted to increase from a current concentration of approximately 0.42 mg/L to approximately 0.54 mg/L.

In his summary of the modelling, Fenemor (2022) noted, 'current development, mainly farming in that part of the valley floor of the Tākaka Valley recharging the AMA, contributes most of the nitrate-nitrogen in the Te Waikoropupū Springs flow'. However, he also noted that the results of the model:

take no account of temporal variability of nitrogen inputs, nor any attenuation (such as nitrification, denitrification, biological and chemical degradation) within the Arthur Marble Aquifer karst, nor any historical sources of nitrogen, nor the time lag averaging 8 years for rainfall and river flows to reach the springs. If the upland-sourced nitrate is more significant, then the contribution from valley floor land uses will be lower than modelled, perhaps significantly lower.

## 7.4. Nitrate leaching joint witness statement (June 2022)

During the Te Waikoropupū water conservation order hearing, the Environment Court requested that some of the expert witnesses (Mirka Langford, Dr Don Mead, Alison Dewes and Dr Jacqueline Rowarth) prepare a joint witness statement (JWS) relating to nitrate leaching in the Tākaka Catchment. The discussions were solely focused on nitrate-N, so there was no consideration of other forms of nitrogen.

The group usefully prepared a table showing the range of nitrate-N leaching rates and nitrate-N loads that would be expected from different land uses within the Tākaka Catchment (Table 5).

In summary, the nitrate-N leaching JWS concluded that nitrate-N loads from the 'National Park Land and exotic forest amounts to 1.73% as compared to Dairy at 54.6% and with the remaining high productive grassland at 34.7%. The total load attributed to pastoral farming systems amounts to 89.3% of the load.'

#### Nitrate-nitrogen (nitrate-N) leaching rates and nitrate-N loads for different land uses. Table 5. Source: nitrate-N leaching JWS (June 2022).

Nitrate-N loss T/yrnitrate-N T/yrloss nitrate-N lossSq KmHectaresIndicative Likely ValueRange		Area	Nitrate-N L	Nitrate-N Leaching. kg/ha/yr		Est range of	% Total
Image						nitrate-N loss	nitrate-N
Sq KmHectaresIndicative Likely ValueRangeTotal Area of Catchment AMARA71471396.3Treed area exotic forest and bush.618618140.0810.01 - 324.9450.618 - 1851.73High Producing Grassland (LCDB)65.565506550655.76 - 105.528.2Dairy farming Irrigated 2018-19. (sits within High Producing Grassland as8.6857.99465-123480.6455.76 - 105.528.2					loss T/yr	T/yr	loss
Likely ValueLikely ValueLikely ValueTotal Area of Catchment AMARA71471396.3Treed area exotic forest and bush.618618140.0810.01 - 324.9450.618 - 1851.73High Producing Grassland (LCDB)65.56550655065-123480.6455.76 - 105.528.2Dairy farming Irrigated 2018-19. (sits within High Producing Grassland as8.6857.99465-123480.6455.76 - 105.528.2		Sq Km Hec	tares Indicative	e Range			
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Total Area of Catchment       714       71396.3       1396.3         AMARA       Treed area exotic forest and bush.       618       61814       0.081       0.01 - 32       4.945       0.618 - 185       1.73         High Producing Grassland (LCDB)       65.5       6550       6550       1.73       1.73         Dairy farming Irrigated 2018-19. (sits within High Producing Grassland as       8.6       857.9       94       65-1234       80.64       55.76 - 105.5       28.2	Total Area of Catabrant	744 740	Value				
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Integration and bush.       618       61814       0.08*       0.01 - 3*       4.945       0.618 - 185       1.73         High Producing Grassland (LCDB)       65.5       6550       6550       65-1234       80.64       55.76 - 105.5       28.2         Dairy farming Irrigated 2018-19. (sits within High Producing Grassland as       857.9       94       65-1234       80.64       55.76 - 105.5       28.2	Tread area evotic forest	010 010	0.001	0.01.02	4.045	0.010.105	4 70
High Producing Grassland       65.5       6550       6550         LCDB)       Dairy farming Irrigated       8.6       857.9       94       65-123 <sup>4</sup> 80.64       55.76 - 105.5       28.2         2018-19. (sits within High Producing Grassland as       as       94       65-123 <sup>4</sup> 80.64       55.76 - 105.5       28.2	and bush	618 618	0.08	0.01 -3*	4.945	0.618 -185	1.73
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Producing Grassland as	2018-19. (sits within High						
	Producing Grassland as						
mapped by Mirka)	mapped by Mirka)						
Dairy         Farming         non         15.7         1573.9         48         45-60         75.5         70.8 - 94.4         26.4	Dairy Farming non	15.7 157	3.9 48	45-60	75.5	70.8 -94.4	26.4
irrigated (dryland)	irrigated (dryland)						
Subtotal Dairy Farming 156.14 54.6	Subtotal Dairy Farming				156.14		54.6
Contribution	Contribution						
Irrigated with Effluent 3.3 326.2	Irrigated with Effluent	3.3 326	.2				
(note that this is part of the	(note that this is part of the						
average dairy so NA)	average dairy so NA)						
Non irrigated (extra water) 1.6 163	Non irrigated (extra water)	1.6 163					
but effluent irrigation only.	but effluent irrigation only.						
Dairy Support Blocks & 39.73 3973 25 19-37 99.3 75.48 -147 34.7	Dairy Support Blocks &	39.73 397	3 25	19-37	99.3	75.48 -147	34.7
Drystock	Drystock						
Horticulture – Negligible	Horticulture – Negligible						
Gorse and Broom         5.7         570.8         45 <sup>5</sup> 30 -60         25.6         17.1 – 34.2         8.95	Gorse and Broom	5.7 570	.8 455	30 -60	25.6	17.1 – 34.2	8.95
Anything over 5 kg N 40 Ha 170 <sup>7</sup> 120 -270 6.8 4.8 - 10.8	Anything over 5 kg N	40	Ha 170 <sup>7</sup>	120 -270	6.8	4.8 – 10.8	
leached per ha. Note TBC	leached per ha. Note			TBC			
Intensive winter forage	Intensive winter forage						
cropping grazed in situ	cropping grazed in situ						
over winter months. <sup>6</sup>	over winter months.6						
TOTAL 285.98 100	TOTAL				285.98		100

<sup>&</sup>lt;sup>1</sup> Based on the calculation of 1440 exotic plantation at 3 kg Nitrate leached/ha yielding 4320kg, and 60,374 ha of bush at 0.01 kg nitrate leached/ha yields total of 4923.7 kg N or an average leaching of treed area of 0.079 kg Nitrate/ha. <sup>2</sup> From Overseer default

<sup>&</sup>lt;sup>4</sup> Source from Farm envt plans 2018-2019. 11 farms data source.

 <sup>&</sup>lt;sup>4</sup> Source from Farm envt plans 2018-2019. Thatms usual source.
 <sup>5</sup> Note: There is limited published data on this
 <sup>6</sup> We have not included point source discharges such as septic tanks, silage pits and the Upper Takaka Sewage Plant. This may accumulate to over 5t Nitrate (DM estimates up to 8t nitrate-N).
 <sup>7</sup> 2019 Farm Environment Plans was 38 Ha of the AMARA was intensively winter forage cropped and grazed with cows in situ – range of crops from Fodder Beet – Kale – Swedes.

## 7.5. Modelling and geohydrology joint witness statement (June 2022)

During the Te Waikoropupū water conservation order hearing, the Environment Court also requested that the modelling and geohydrology expert witnesses (Andrew Fenemor, Dr Paul Williams, Joseph Thomas, Julian Weir, Dr Mike Stewart, Kura Stafford, Margie Little, Dr Don Mead) prepare a JWS on the likely volumes of groundwater (and associated nitrogen loads) reaching Te Waikoropupū Springs from each of the generic land-use types.

The modelling and geohydrology JWS noted that two types of models were made available to the court. One type is designed to assess the effects of different land covers on discharge at the springs (e.g. Weir and Fenemor [2017] modelling), and the other type is designed to track water flows and nitrate movement from input to output sites under average conditions (e.g. Stewart [2022], Stewart and Thomas [2008] and Williams [2022] models).

The experts agreed that in the absence of complete datasets describing all components of the hydrological system, all modelling methods have a relatively large degree of uncertainty, particularly when hydraulic models and nitrogen loss models are combined.

The experts noted that the models were focused on nitrate-N and not total nitrogen (TN). Similarly, they noted that the nitrate-N leaching estimates provided in the nitrate-N leaching JWS do not account for nitrification of organic N that occurs after the nitrogen leaves the root zone, nor any nitrogen loads originating from organic matter in the karst. However, it is not known how significant these contributions might be – there were differing views among the experts. There was general agreement (JWS, p. 15) that denitrification is likely rare and having a negligible effect in the aquifer, but nitrification of organic N will be occurring and contributing to nitrate-N concentrations at Te Waikoropupū Springs.

The experts noted the substantial difference in findings from the Stewart (2022) and Williams (2022) modelling. The Stewart model indicates that nitrate-N from nitrification in karst uplands recharge provides 80% of the nitrate-N in the Main Spring, while agricultural nitrate in valley rainfall recharge provides 62% of the nitrate in Fish Creek Springs (Stewart 2022, table 7). In contrast, the Williams model indicates that activities in the central valley provide 86% of the nitrate load at Te Waikoropupū Springs. Dr Williams acknowledged that while the karst uplands are a significant contributor of nitrate-N (about 13%), he considers that the 'addition of nitrate from nitrification while theoretically possible is not so far demonstrated by any field evidence / measurements in the AMA' (JWS, p. 24).

Dr Stewart gave more weight to the predictions of the Stewart (2022) modelling as he believed that it provides a good explanation for all of the observations and is strongly

supported by the literature on pristine to mildly impacted karst systems. His concerns with the Williams (2022) model related to nitrate being considered as a conservative tracer, when nitrification is likely occurring.<sup>3</sup> He also considered that the Williams model is mathematically underdetermined and predictions from it are not unique (the number of unknowns is greater than the number of equations). In contrast, the Stewart nitrate model has two unknowns constrained by two equations based on nitrogen at Main Spring and Fish Creek Springs. Only the nitrate concentration of Tākaka River is estimated. Therefore, Dr Stewart said he believed that the predictions from the Stewart model are unique.

Dr Williams gave more weight to the predictions of the Williams (2022) modelling as he considered that it is conceptually in line with international understanding of how karst aquifers in crystalline carbonate rocks operate. He considered that the conceptualisation within the Stewart (2022) modelling is incorrect and that it is not appropriate to separate shallow from deep systems, which permits no mixing until just before the springs. He considered that this is unobserved in karst systems and so results based on that premise must be untenable and are unsupported by field observations from samples collected from the AMA. He considered the Stewart modelling to be misleading, because 'fast flow in conduits passes right through slow flow in fissures and water exchange occurs between the two, with slow flow in fissures (containing relatively old water) being misconceived as deep flow' (Modelling and geohydrology JWS, p. 28). He also considered the Stewart modelling to be based on a 'misunderstanding of the influence of the geology as well as of the karst groundwater dynamics' (Modelling and geohydrology JWS, p. 28). This concern relates to possible diorite intrusion, considered by Stewart to separate the deep and shallow groundwater systems, which according to Dr Williams 'does not allow the "shallow system" to pass over it, because the Motupipi syncline with coal measures to 350 m below sea level diverts groundwater towards Te Waikoropupū before it even reaches the site of the possible intrusion' (Modelling and geohydrology JWS, p. 28).

The experts generally agreed that there will be increased leaching of nitrate as nitrogen builds up in the soil as a result of farming. Therefore, much of the increase in concentration of nitrate-N at Te Waikoropupū Springs is associated with farming in the Tākaka Valley. However, the Stewart (2022) modelling also indicated an increase in nitrogen loading from the karst landscape over time, although much smaller than that from the valley floor. Dr Stewart noted that possible explanations for an increase from the karst area could relate to human-induced disturbance within the karst area and / or be related to climate-induced changes to nitrogen inputs / losses.

<sup>&</sup>lt;sup>3</sup> Williams (2022) assumed that nitrate was a conservative tracer, but Williams (2023) included an allowance of 16% nitrification for all sources to make the model balance.

## 7.6. Mead–Hickey joint witness statement (July 2022)

During the Te Waikoropupū water conservation order appeal hearing, the Environment Court also requested that Dr Chris Hickey and Dr Don Mead prepare a JWS on the importance of looking at TN and not just nitrate-N for calculation of nitrogen loads in the Tākaka Catchment.

The experts considered McGroddy et al. (2008) as an important paper demonstrating that the majority of nitrogen exported from undeveloped forested catchments is in the form of dissolved organic nitrogen (DON), with often minimal nitrate-N. Both experts agreed that an indicative TN export coefficient for the 'treed area' of the catchment should be around 0.3 kg N·ha<sup>-1</sup>·y<sup>-1</sup>, giving 18 t N/y of export from that land use. Based on mean flows and median TN concentrations, the experts calculated that nitrogen load from the Tākaka River to the AMA would be about 13 t N/y.

The experts conducted some useful mass balance calculations to derive their conclusion that 85–90% of the nitrogen load at the springs is sourced from farming, while the input from the karst uplands is the remaining 10–15%. However, the experts noted several weaknesses in their calculations, including that median flows and median concentrations were used to calculate loads in the Tākaka and Waingaro Rivers, particulate-N components were not included, and the nitrate loss rates from the farming area were largely sourced from Overseer and so are subject to considerable error.

## 7.7. Te Waikoropupū Springs water conservation order Environment Court findings (July 2023)

The decision from the Environment Court on the Te Waikoropupū water conservation order hearing (Environment Court 2023) included a lengthy analysis relating to the court's findings as to nitrogen in the Tākaka River Catchment. The analysis aimed to summarise the process followed by the court to understand where nitrate-N and other forms of nitrogen come from, reasons why nitrogen levels have increased and how they change as they pass through the groundwater system, and what that means for nitrate-N reaching Te Waikoropupū Springs. The court pulled together the range of information it had received in evidence and conducted further calculations where it felt they were needed.

Based on the evidence received, the Environment Court recognised the importance of considering all types of nitrogen compounds, not just nitrate-N, and that nitrification of organic nitrogen is likely to occur within the aquifer. The court considered that while rainfall is a major driver of leaching, peak rainfall intensities and increased general 'wetness' of the soils result in increased leaching compared to when the soils contain less water.

The court sought guidance on nitrate-N leaching rates for different land uses in the catchment and found that, other than for treed areas, it was satisfied that the information presented in the nitrate leaching JWS (see Section 7.4) represented the best available information. For the treed area of the upper catchment, the court accepted the advice in the Hickey–Mead JWS (see Section 7.6) that the leaching rate should have been 0.3 kg N·ha<sup>-1</sup>·y<sup>-1</sup>, giving 18 t N/y of export from that land use. The court also noted the nitrate leaching experts estimate that gorse and broom in the catchment could leach an indicative additional quantity of 26 t N/y as nitrate-N, within a likely range of 17–34 t N/y. In addition, the court recognised that the majority of the monitoring data are based on dissolved nitrogen and that an additional 20% could be attributed to a particulate component.

Based on the above, and assuming TN is converted to nitrate-N within the aquifer, the court estimated the mean nitrate-N load reaching Te Waikoropupū Springs from the karst uplands to be 48 t N/y, with an estimated likely upper limit from this source as 76 t N/y. The court noted that this was at odds with the load predictions from the Stewart (2022) modelling (up to 130 t N/y), which it concluded does not reflect observations in the catchment by a significant margin.

Using the nitrate-N leaching rate information for the farming area in the valley floor, the court adopted a likely minimum load of 200 t N/y, an indicative load of 220–250 t N/y and a worst-case load of 350 t N/y from farming activities in the valley floor.

The court accepted the advice from the Hickey–Mead JWS that the nitrogen load from the Tākaka River would be around 13 t N/y and a contribution from wastewater in the order of 4 t N/y.

Overall, the court found no evidence to support the proposition that nitrate-N leaching from the upland karst had increased over the last three decades, other than as a result of climatic conditions from time to time. The court recognised that deficit irrigation as currently practised in the aquifer recharge area is unlikely to cause significant, if any, increased nitrate-N loss at the time of, or immediately following, irrigation. However, it considered that the increased nitrogen held in the soil in whatever form increases the overall quantity of nitrogen potentially available to be flushed out during heavy rainfall.

The court noted that the irrigated area in the Tākaka Catchment increased from less than 150 ha in 2003 to more than 500 ha in 2005, more than 800 ha in 2010, more than 950 ha in 2012 and more than 1,000 ha in 2016.

Based on all the evidence, the court found that the proportions of nitrate-N load to Te Waikoropupū Springs coming from the valley floor were likely to be around 75% of the total load and within the range of 70–85%. The court considered that approximately 20% of the total load comes from the karst uplands, including from gorse and broom,

with the remaining approximately 5% coming from upper Tākaka River and wastewater sources.

The Environment Court also concluded that increases in nitrate-N concentrations and loads reaching Te Waikoropupū Springs have resulted from the increased use of irrigation and, to an extent, increased cow numbers from 2005 onwards.

## 8. SUMMARY

There is strong evidence to indicate that nitrate-nitrogen (nitrate-N) concentrations have increased over the last 50 years at the Te Waikoropupū Main Spring, from an average of 0.31 mg/L in the 1970s through to an average of 0.44 mg/L for the decade up to 2023. In conjunction with this overall long-term increase in concentrations, there have been shorter-term periods of increases and decreases in nitrate-N concentration that appear to coincide with climatic patterns represented by the Southern Oscillation Index (SOI). Higher concentrations and loads of nitrate-N occur during prolonged periods of La Niña conditions, and lower nitrate-N concentrations and loads occur during El Niño conditions.

The Arthur Marble Aquifer (AMA) and Te Waikoropupū Springs are recharged through: 1) rainfall in the areas where water can drain directly into the marble, 2) flow loss from the upper Tākaka River and parts of the Waingaro River and creeks draining into the upper Tākaka Valley, 3) infiltration of rainwater falling on the Tākaka Valley floor, and 4) input from seawater (a small proportion). Nitrogen will also enter the aquifer via these sources.

An assessment of contributions from all these sources needs to consider all types of dissolved and particulate nitrogen compounds that are involved. The majority of nitrogen coming from the upper catchments (upper Tākaka and upper Waingaro) is in the form of dissolved organic nitrogen, and this is transformed into nitrate-N as the water moves through the AMA. Nitrate-N is likely the predominant type of nitrogen sourced from the Tākaka Valley floor. This nitrate-N arises from nitrification of other nitrogen-containing compounds (e.g. urea, ammonia) within the soil – sourced initially from fertilisers, animal wastes and nitrogen fixed by legumes. Atmospheric deposition of nitrate-N is expected to occur throughout the catchment at a rate of 2–6 kg N·ha<sup>-1</sup>·y<sup>-1</sup>, with highest rates expected in the high-rainfall parts of the catchment.

We consider that export / leaching of nitrogen compounds is the primary source of the nitrogen load to the AMA, with different rates of nitrogen export expected from different land-use types. The highest rate of export will be from intensively farmed areas within the valley floor, meaning that this area of the catchment contributes a disproportionately large component of the overall nitrogen load to the AMA compared to other areas with different land uses. Geological sources, wastewater, explosives used in quarrying and seawater are all expected to make a small contribution to the overall nitrogen load to the AMA – collectively probably less than 5% of the overall load.

Previous efforts to determine the relative importance of nitrogen sources have provided contrasting indications of the importance of nitrogen inputs from the karst upland parts of the Tākaka Catchment. The key driver of these differences appears to be the different conceptualisations of the AMA. Stewart and Thomas (2008) conceptualise the aquifer as having two different flow systems: one deep system, primarily recharged from the karst uplands and including the seawater contribution; and a shallower system with much younger water that is primarily recharged by the upper Tākaka River and valley rainfall. This conceptualisation assumes that any mixing of the waters from the two flow systems occurs only shortly before the water emerges at Te Waikoropupū Springs. Other modelling of the aquifer (i.e. Williams 2023) conceptualises the aquifer as a mix of conduits carrying fast-flowing younger water within a marble matrix of fissures and pores through which older water moves more slowly. Some exchange of water is considered to occur between these features throughout the aquifer.

As the Stewart (2022) model assumes that the majority of the flow to the Main Spring is sourced from the karst uplands with little mixing before the waters emerge at the springs, it follows that a substantial proportion of the nitrogen load at the springs must also be from the karst uplands. In contrast, the Williams (2023) model allows for more mixing among the different water sources and indicates that a small volume of valley floor water with high nitrogen concentration is responsible for much of the nitrogen load discharged from the Main Spring.

Alternative modelling using sub-catchment areas and likely rates of nitrogen export in each (Weir and Fenemor 2017; Nitrate leaching JWS; Mead–Hickey JWS) tend to support the conclusions of the Williams (2023) modelling that 85–90% of the nitrogen load at Te Waikoropupū Springs is sourced from farming, while the input from the karst uplands is the remaining 10–15%. The Environment Court report relating to the water conservation order application (Environment Court 2023) found that the proportions of nitrate-N load to the springs coming from the valley floor were likely to be around 75% of the total load and within the range of 70–85%. The court considered that approximately 20% of the total load comes from the karst uplands, including from gorse and broom, with the remaining approximately 5% coming from the upper Tākaka River and wastewater sources.

The nitrate concentration in Te Waikoropupū Springs shows a generally increasing long-term trend, alternating between increasing and decreasing concentration trends over various periods. There is concordance between the strong and persistent La Niña events (measured by the SOI) being associated with high nitrate concentrations in the springs and El Niño periods being associated with reduced nitrate concentrations. The general concordance for these events shows minimal time lag for the nitrate concentration with the SOI transition, suggesting that both the nitrate concentrations and mass loads in the springs are strongly influenced by surface processes (e.g. soil leaching, microbial activity, stock loading) and shallow flow paths linked to the springs.

This potentially abrupt change in concentrations and loads has implications for trend monitoring used to detect changes in water quality associated with land-use and catchment management activities. The combined effects of a wide range of both climate and catchment factors are likely to confound efforts to establish definitive relationships with drivers of nitrogen loading to the springs and to extend the monitoring period required to detect statistically significant reductions in the water quality of the springs.

## 8.1. Knowledge gaps and considerations for future monitoring

To our knowledge, there are no data on total nitrogen (TN) or organic nitrogen concentrations in any of the eastern (Spittals Spring, Ironstone Creek, Gorge Creek) or western (Kill Devil Creek, Sam Creek, Craigieburn Creek, Stony Creek) tributaries, which are significant gaps in information. We recommend that monthly sampling of nitrate-N and TN, along with other key water quality parameters (dissolved reactive phosphorus, total phosphorus, specific conductivity, dissolved organic carbon) at these sites should be considered in the independent review of catchment monitoring. This will enable a better understanding of the concentrations of all forms of nitrogen in these tributaries. These tributaries arguably also represent likely inputs to the aquifer from the karst uplands, which otherwise have been calculated only by differences in the various models used to determine the nitrogen contributions of various potential sources.

There are no data on the concentration of particulate organic nitrogen in any of the main sources. Based on data from other catchments, it is likely that particulate organic nitrogen is less important than dissolved organic nitrogen under most flow conditions, but it would be good to confirm this.

The datasets for the Tākaka at Harwoods and Tākaka at Lindsays Bridge monitoring sites are valuable for providing information on the nitrogen load from the upper Tākaka River. However, the sampling periods at these two sites do not coincide, making it difficult to robustly comment on changes in water quality between them. The Harwoods record covers 15 years from 2000 to 2015, but is based only on quarterly data. The Lindsays Bridge record is also based on quarterly data, but dates from December 2016. The existing data at Lindsays Bridge show a significant positive relationship between flow and nitrate-N and TN concentrations, something that was not observed in the Harwoods data. In our opinion, it would be good to monitor both the Harwoods and Lindsays Bridge monitoring sites concurrently on a monthly basis. With a longer dataset and more frequent samples, it will be possible to calculate a more accurate nitrogen load using relationships between flow and nitrogen concentrations. In our opinion, it is important that both nitrate-N and TN continue to be measured at these sites, along with other key water quality parameters.

Data from the Waingaro at Hanging Rock monitoring site on the Waingaro River are very limited, with only quarterly data available over the period March 2001 to

November 2004 (and one sample in February 2016). The independent review of catchment monitoring should consider monthly monitoring at this site for both nitrate-N and TN, along with other key water quality parameters.

Relationships between the SOI and river flow and water quality have been identified from long-term monitoring programmes in Aotearoa New Zealand rivers. Further analysis of the various climate factors (including rainfall patterns, temperature, wind strength / direction, sunshine, soil moisture, river and spring flows) associated with La Niña and El Niño periods should be undertaken in the Golden Bay / Mohua region and monitoring data from Te Waikoropupū Springs. This analysis should be targeted to establishing SOI-related responses and implementing river-derived deterministic models that can be used to provide better predictions of water quality trends in the springs.

# 9. APPENDICES

# Appendix 1. Southern Oscillation Index (SOI) analysis methods

## A1.1 Methods for SOI analysis

Monthly values for the Southern Oscillation Index (SOI) for the period January 1990 to December 2023 were obtained from the Australian Bureau of Meteorology (BOM),<sup>4</sup> and we used the Troup convention, whereby index values are multiplied by 10. The SOI typically ranges from -30 to +30 and has a quasi-periodic oscillation period of 3–7 years. El Niño conditions are defined as an SOI < 8 over  $\geq$  3 months, and La Niña conditions are defined as an SOI > 8.

Figure A1-1 shows the SOI for the past 50 years, from 1974 to 2024. No linear trend is evident over this period. The La Niña or El Niño events may occur for relatively short periods, with the majority of the time spent in the intermediate condition, often trending to more persistent ENSO periods. The labels indicate periods of  $\geq$  3 months of La Niña events for comparative analysis with adjacent El Niño periods.



Figure A1-1. Southern Oscillation Index (SOI) monthly average monitoring data for the last 50 years, from 1974 to 2024. Blue shading indicates the La Niña condition and pink shading the El Niño condition, with the unshaded area showing intermediate conditions. Boxed event numbers indicate La Niña periods for data analysis (see Box 3 for a description of SOI). Source: Bureau of Meteorology (BOM), Australia.<sup>4</sup>

The time series data for Te Waikoropupū nitrate-nitrogen (nitrate-N) concentration and nitrate-N load are shown in Figure A1-2, highlighting the La Niña and El Niño events used for statistical analysis. Each of these events was chosen from the monthly SOI

<sup>&</sup>lt;sup>4</sup> <u>http://www.bom.gov.au/climate/enso/soi</u>

data where there were  $\geq$  3 months of exceedance of the SOI classification condition (i.e. ±8 SOI) based on the 3-month moving average values, the event was located near the maximum of the period, and monitoring data for nitrate concentrations were available. There are additional SOI periods that could potentially satisfy these criteria based on the exceedance of the SOI classification condition (see Figure A1-1); however, the generally quarterly nitrate concentration monitoring prior to January 2016 (when monthly monitoring was implemented) limits the resolution of SOI relationships with the periodicity of the springs nitrate concentrations and load. The increasing nitrate concentration and load baseline trend (Figures 14 and 16) limit the utility of the statistical comparison of the pooled La Niña and El Niño period data for the three events. In addition, the El Niño condition for 2023/24 may not yet have fully developed (Figure A1-1).



Figure A1-2. (A) Te Waikoropupū Springs time series for nitrate-nitrogen (nitrate-N) concentration since 1990. (B) Nitrate-N concentration since 1998 (on same scale as nitrate-N load plot). (C) Nitrate-N load discharged since 1998. Points labelled for La Niña (\*) and El Niño (Δ) correspond to comparative periods for concentration (Table 3) and load (Table 4) comparisons.

#### A1.1.1 Smoothing

The smoothing macro uses a boxcar algorithm to compute a moving average of data points to generate a curve. An average of 100 data points was used to generate the smoothed curve for the SOI and monitoring data.

The smoothed curve is intended to provide a visual indication of the location of La Niña and El Niño peaks, durations and trends in the SOI, and potentially associated monitoring variables. The smoothed curve is not intended as an analytical fit to any of the parameters and no deterministic equation is generated for the curve.

#### A1.2 Additional results for SOI analysis

The data distribution for the nitrate-N concentration and nitrate-N load for the selected La Niña and El Niño combined peak periods (Figure A1-2) is shown in Figure A1-3, with results for each of the three event periods summarised in Tables 3 and 4. The mean nitrate-N concentration difference was 13% and the nitrate-N load difference was 16%, with these differences likely attributed to the slight reduction (6%) in flow from the springs between La Niña and El Niño periods.



Figure A1-3. Combined data for Te Waikoropupū Springs nitrate-N concentration (A) and nitrate-N load discharged (B) for selected La Niña and El Niño periods (see Figure A1-2) for statistical analysis. Box plots show median values, with the interquartile range for box and range of data indicated by whiskers.

# Appendix 2. Hill labs technical note regarding analysis of different types of nitrogen compounds





## NITROGEN SPECIES

Nitrogen is present in water samples in a variety of different forms including;

- Total Nitrogen
- Organic Nitrogen
- TKN (Total Kjeldahl Nitrogen)
- NH4N (Total ammoniacal nitrogen)
- NOxN (Total oxidised nitrogen)
- NO3N (Nitrate nitrogen)
- NO2N (Nitrite nitrogen)

#### **Total Nitrogen**

Total nitrogen is measured by combusting the sample in an oxygen atmosphere, then measuring the nitrogen dioxide produced. This gives the total elemental nitrogen present in the sample in both organic and inorganic forms, including cyanide. Combustion analysis requires specialised (and expensive) laboratory instrumentation which few laboratories are equipped with.

Total nitrogen can also be analysed using persulphate/UV or persulphate oxidative digestion followed by analysis of the nitrate-N formed. These methods are not suitable for samples with high organic loading (which will require dilution before digestion, raising the detection limit), or for some industrial organic nitrogen compounds.

Total nitrogen may be calculated (approximately) by adding TKN and NOxN. See comments for each of these tests. This is the default method currently used by Hill Labs. However, we recommend that for clean waters (low particulates) and saline waters, the TN by persulphate oxidative digestion method is used as the detection limit for this method is significantly lower than for the TN calculation method.

#### Organic Nitrogen

"Organically bound nitrogen in the trivalent state." It does not include all organic nitrogen compounds, but includes such natural materials as proteins and peptides, nucleic acids, urea, and many synthetic organic materials (eg quaternary ammonium compounds, nitrogen containing pesticides, polymers, etc).

Analytically, organic nitrogen and ammonium nitrogen are determined together as Total Kjeldahl Nitrogen (TKN), a term which reflects the method used rather than any specific chemical form of nitrogen.

The Organic Nitrogen is then calculated as Norg = TKN - NH4N

Protein concentration may be approximated from; Protein = Total Organic N x 6.25<sup>1</sup> = [TKN – NH4N] x 6.25

#### TKN (Total Kjeldahl Nitrogen)

This form of nitrogen is defined by the test method used (i.e. a 'Kjeldah' digestion) which determines nitrogen in the trivalent state. The method does not determine nitrogen present in azide, azine, azo, cyanide, hydrazone, nitroso, oxime, or

<sup>1</sup> United Nations Food and Agriculture Organization (FAO), FOOD AND NUTRITION PAPER 77, Chapter 2 (https://www.fao.org/3/Y5022E/y5022e03.htm).

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semicarbazone forms, nor as nitrate or nitrite, and also does not recover nitrogen from some industrial chemicals (eg refractory tertiary amines).

TKN can be considered to comprise

- Ammonium-N (NH4N)
- Protein N
- Non-protein N eg urea, DNA, benzalkonium salts

#### Dissolved Kjeldahl nitrogen (DKN)

DKN is TKN analysed on a sample which has been filtered through a 0.45µm membrane filter. DKN thus represents the soluble portion of TKN.

#### Ammonia/Ammonium-N (NH4N)

In solution total ammoniacal nitrogen may be present as either Ammonia ("Free ammonia", NH3) or Ammonium ion depending on the pH and temperature.

$$NH_3 + H^+ \Leftrightarrow NH_4^+$$

"Free" ammonia is toxic to aquatic organisms. Ammonia is a toxic gas which is very soluble in water.

At low pH (i.e. more H\*) the equilibrium is to the right and NH4\* predominates. Below a pH of about 6.5 over 99.9% of the ammonia is in this form (see Table). At higher pH the un-ionised or 'free' form of ammonia predominates.

Environmentally, the term ammonia refers to two chemical species, which are in equilibrium in water (NH3, un-ionized and NH4\*, ionized). These species are present in the environment from the metabolism of nitrogen species by humans, bacteria, etc. More rarely, they may come from a spill or leak or liquefied ammonia gas, which is often used in large refrigeration units (e.g. freezing works) or fertilizer production.

The toxicity (e.g. to fish, insects) to ammonia in water is primarily attributable to the un-ionized form (NH3), as opposed to the ionized form (NH4<sup>+</sup>). In general, more NH3 and greater toxicity exists at higher pH. However, limited data also indicate that less NH3 is needed at lower pH to produce its toxic effects.

High NH4N levels in water also stimulate the growth of aquatic plants and algae, sometimes leading to 'blooms' which may then die and produce anoxic conditions because of decomposition.

Tests for ammonia usually measure total ammonia (NH3 plus NH4<sup>+</sup>) and the results reported as "Total ammoniacal nitrogen (NH4N)".

NH4N results are reported to allow easy comparison of nitrogen budgets – all nitrogen species are reported as the nitrogen content only e.g. NH4N, NO2N, NO3N, TKN.

To determine the amount of un-ionised ammonia it is necessary to

a. determine the percentage of un-ionised ammonia at a given pH and temperature from tables such as those in ANZECC Guidelines for Fresh and Marine Water Quality, then

Convert the ammonium-N result from N to NH3 (multiply by the molecular weight of NH3/atomic weight of N = 17/14 = 1.21. This value can then be compared with reference tables eg that below – check source for latest version.

b. Trigger values as total ammonia-N (g.m<sup>3</sup>) at different pH (Temperature is not taken into consideration)

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pH	Freshwater Trigger Value (g.m <sup>-3</sup> as NH4-N)	Marine Trigger Value (g.m <sup>-3</sup> as NH4-N)	рH	Freshwater Trigger Value (g.m <sup>3</sup> as NH4-N)	Marine Trigger Value (g.m³ as NH4-N)
6.0	2.57	5.96	7.6	1.47	1.85
6.1	2.56	5.87	7.7	1.32	1.56
6.2	2.54	5.76	7.8	1.18	1.32
6.3	2.52	5.63	7.9	1.03	1.10
6.4	2.49	5.47	8.0	0.90	0.91
6.5	2.46	5.29	8.1	0.78	0.75
6.6	2.43	5.07	8.2	0.66	0.62
6.7	2.38	4.83	8.3	0.56	0.51
6.8	2.33	4.55	8.4	0.48	0.42
6.9	2.26	4.24	8.5	0.40	0.35
7.0	2.18	3.91	8.6	0.34	0.29
7.1	2.09	3.56	8.7	0.29	0.24
7.2	1.99	3.20	8.8	0.24	0.20
7.3	1.88	2.84	8.9	0.21	0.17
7.4	1.75	2.49	9.0	0.18	0.14
7.5	1.61	2.15			

#### [Adapted from ANZECC Freshwater Guidelines, 2000, Table 8.3.7]

#### NOxN (Total oxidised nitrogen)

Total oxidised nitrogen is the sum of nitrate-N plus nitrite-N

Note that the abbreviation TON can be used to mean both Total Oxidised Nitrogen and Total Organic Nitrogen, so use of this abbreviation is discouraged.

- NO2N = nitrite N
- NO3N = nitrate N

There are several different methods for measuring oxidised nitrogen species in the laboratory.

1. Measure NOxN and NO2N (cadmium reduction, colourimetry), then calculate NO3N from the difference between these.

NO3N = NOxN - NO2N

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This is our preferred method for environmental samples as it is the most robust method and gives the lowest detection limit.

- Ion chromatography [Useful if other anions (e.g. CI, SO4) are being analysed at the same time, though not if these are
  present in very high concentrations (e.g. seawater, trade wastes, leachates). Note that NO2N is not analysed by this
  method at Hill Labs, and the detection limit of NO3N is significantly higher than in the cadmium reduction and
  colourimetry method].
- Specific colorimetric tests [Useful if the matrix is well characterised. Doesn't give low DL, and each method has specific interferences. Often used with portable instruments]

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### **Calculated Nitrogen species**

A number of 'derived' values can be calculated from the preceding tests.

Dissolved Organic Nitrogen	DON	DKN - NH4N	
Total Dissolved Nitrogen	TDN	DKN + NOxN	
Total Inorganic Nitrogen	TIN	NOxN + NH4N	
Total Nitrogen	TN	TKN + NOxN	
Total Organic Nitrogen	TON	TKN - NH4N	

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## **10. ACKNOWLEDGEMENTS**

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