# Nitrate source evaluation of surface water and groundwater in the Franklin area using a dual stable isotope approach

KM Rogers LE Buckthought

GNS Science Report 2022/02 February 2022

#### DISCLAIMER

The Institute of Geological and Nuclear Sciences Limited (GNS Science) and its funders give no warranties of any kind concerning the accuracy, completeness, timeliness or fitness for purpose of the contents of this report. GNS Science accepts no responsibility for any actions taken based on, or reliance placed on the contents of this report and GNS Science and its funders exclude to the full extent permitted by law liability for any loss, damage or expense, direct or indirect, and however caused, whether through negligence or otherwise, resulting from any person's or organisation's use of, or reliance on, the contents of this report.

#### BIBLIOGRAPHIC REFERENCE

Rogers KM, Buckthought LE. 2022. Nitrate source evaluation of surface water and groundwater in the Franklin area using a dual stable isotope approach. Lower Hutt (NZ): GNS Science. 30 p. (GNS Science report; 2022/02). doi:10.21420/NBSK-MT83.

KM Rogers, GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand

LE Buckthought, Auckland Council, Private Bag 92300, Victoria Street West, Auckland 1142, New Zealand

ABST	RACT						
KEYV	VORDS	S					
1.0	INTRODUCTION						
	1.1	Report Objectives	2				
2.0	BAC	KGROUND	4				
	2.1 2.2 2.3 2.4	Franklin Land-Use and Hydrological History Franklin Nitrate Issues Nitrates Dual Isotope Nitrate Approach	4 4 5 9				
3.0	ANA	LYTICAL METHODS	12				
	3.1 3.2	Nitrate Concentrations Nitrate Isotopes	12 12				
4.0	RES	ULTS	13				
	4.1 4.2	Nitrate Concentrations Nitrate Isotopes 4.2.1 Water Samples 4.2.2 Leachate Samples	13 14 15 17				
5.0	DISC	USSION	19				
	5.1	Summary and Classification of Franklin Samples	19				
6.0	CON	CLUSIONS	21				
7.0	ACK	NOWLEDGMENTS	23				
8.0	REFE	ERENCES	23				

#### CONTENTS

# FIGURES

Figure 1.1	Location of sampling sites in this study	2
Figure 2.1	Dual nitrate isotope biplot highlighting the mechanism of nitrate formation and transformat water	ion in 7
Figure 2.2	Dual nitrate isotope results of groundwater and surface water from 1000 sites across New Zealand	10
Figure 4.1	Nitrate biplot of $\delta^{15}$ N and $\delta^{18}$ O in the collected Dataset 1 and Dataset 2 water samples fro Franklin area	m the
Figure 4.2	Nitrate biplot of $\delta^{15}$ N and $\delta^{18}$ O from Dataset 1 water samples	16
Figure 4.3	Nitrate biplot of $\delta^{15}$ N and $\delta^{18}$ O from Dataset 2 vadose zone leachate samples	17
Figure 4.4	Nitrate biplot of $\delta^{15}$ N and $\delta^{18}$ O from Dataset 2 vadose zone leachate samples identified by month of sampling	y 18

# TABLES

Table 2.1	Description of indicator biplot zone classifications	11
Table 4.1	Nitrate isotopes and concentrations of the Franklin samples	13
Table 5.1	Classification of source and fate of Franklin area samples based on their nitrate isotopes and	
	concentrations	19

# APPENDICES

APPENDIX 1	FRANKLIN AREA DATASET 1	29
APPENDIX 2	ROOTZONE REALITY PROJECT DATASET 2	

#### ABSTRACT

GNS Science was contracted by Auckland Council to interpret the nitrate (NO3-N) concentrations and nitrate isotope signatures of 36 water samples collected in 2014 and 2015 in the Franklin area, Auckland, to identify possible sources and transport environmental processes in the context of elevated nitrate concentration in groundwater.

The sample set consists of eight surface water and four groundwater samples collected in 2014 to investigate elevated nitrate concentration in the Franklin area and 24 vadose zone leachate samples from a farm in Franklin collected to understand the impact of fertiliser application on soil leachate in 2015. Analysis for nitrate concentration and isotopes was undertaken and reported as analytical results at the time of sampling, and this interpretive report is based on these results.

Using a dual nitrate isotope approach, the findings include:

- The key contaminant source was identified as synthetic fertilisers rather than farming effluent due to their isotopic signature falling into the fertiliser and Mixed soil nitrogen (Soil N) and fertiliser zones.
- The samples had NO3-N concentrations ranging from 0.002 to 69.6 mg/L and nitrate isotope values from -6.7 to 9.2 % for  $\delta^{15}$ N and -2.0 to 10.0 % for  $\delta^{18}$ O.
- Surface water samples with high NO3-N concentrations (>5 mg/L) indicate contamination from recent fertiliser application, as the nitrate concentrations are above expected background levels (of <1 mg/L).</li>
- Groundwater samples with higher NO3-N concentrations (>5 mg/L) indicate fertiliser breakthrough into the aquifer and/or subsurface transport of leached nutrients from soils.
- Groundwater with lower nitrate concentrations (<3 mg/L), suggesting denitrification (based on isotopes) or lower contamination levels and sufficient assimilation within the ecosystem to assimilate any excess nutrients. There is only one site (LB02, a 47-m-deep bore from Fielding Road) where NO3-N concentrations are very low, with low dissolved oxygen and higher NH4-N levels, suggesting that it has probably reset to natural background levels due to denitrification.
- δ<sup>15</sup>N and δ<sup>18</sup>O values reflect the nitrate source and its subsequent fate. Key processes
   observed in these samples involve mineralisation and transformation of nitrogen sources
   through to the denitrification zone. If further fertiliser pulses or applications occur,
   the cycle can reset, and nitrate isotopes reflect the new input. Only when the removal
   process rate from denitrification or ecosystem uptake exceeds the additive rate will
   nitrates decline through ecosystem assimilation or denitrification.

This information will contribute to an ongoing research strategy by Auckland Council to improve understanding of the dynamics and interactions of groundwater and surface water nitrate in the Franklin area. The findings will help inform future management strategies that aim to reduce these nitrate concentrations over time in order to meet the requirements of the National Policy Statement for Freshwater Management 2020.

#### **KEYWORDS**

Nitrate, nutrient, Franklin, stable isotopes, source, groundwater, surface water

This page left intentionally blank.

#### 1.0 INTRODUCTION

Nitrate has been an issue in Auckland Council's Franklin area groundwater for decades (White et al. 2019). This study, commissioned by Auckland Council, uses GNS Science's Stable Isotope Laboratory to interpret nitrate isotopes in two sets of historical water samples collected by Auckland Council. These samples were analysed for a range of water chemistry, including nitrate stable isotopes ( $\delta^{15}N$  and  $\delta^{18}O$ ), nitrate nitrogen (NO3-N) and ammonia nitrogen (NH4-N) concentrations close to the time of collection (see Appendices 1 and 2).

**Dataset 1:** A set of samples was collected in 2014 to determine the usefulness of stable isotope ratios to identify/distinguish sources of nitrate in surface and groundwater in the Franklin area. Eight surface water and four groundwater samples were collected in 2014 across several catchments in the Franklin area and analysed for  $\delta^{15}$ N and  $\delta^{18}$ O to see if a clear 'isotopic source signature' could be identified (Figure 1.1).

**Dataset 2:** In 2015, a joint project called the 'Rootzone Reality Project' was undertaken between Plant and Food, the Sustainable Farming Fund, Horticulture New Zealand, councils and growers to assess leaching of nitrogen (Norris et al. 2017). A range of horticultural sites around New Zealand were chosen, and a leaching trial was set up under different cropping regimes. Leaching is notoriously hard to measure in horticultural systems, as lysimeters are difficult to install in working farms (Norris et al. 2017). Soil suction cups also do not measure drainage volume, so it was not possible to get an accurate measure of drainage/leaching flux. However, the Plant and Food team developed 'fluxmeters' that could capture soil leachate and were buried 2 m underground (so cropping could continue, leaving the fluxmeters undisturbed).

The Franklin area Rootzone Reality project used a farming site near Pukekohe on Patumahoe clay loam soil (Norris et al. 2017), which was planted with potatoes in June 2015 and harvested in November 2015. A dozen fluxmeters collected drainage water in 14 L storage vessels that were routinely emptied over a period of four months during 2015. A total of 318 kg N/ha was applied as fertiliser during the trial.

- Application 1 of approximately 1000 kg/ha of Green Fertiliser and 300 kg/ha of ammonium sulphate was applied in June 2015 during planting, and
- Application 2, with 500 kg/ha of Calcium Ammonium Nitrate (CAN) was applied over two applications: 300 kg/ha on 5/8/2015 (the day after the August fluxmeter samples were taken) and 200 kg/ha on 8/9/2015.

Twelve fluxmeters were sampled each month and archived in the freezer for testing. However, samples from only six of the fluxmeters were submitted for isotope testing each month from the same fluxmeters due to budget constraints. There were frequent and often heavy rainfall periods over the late autumn to early spring period (April to November), and modelled soil water content remained high during this period (Norris et al. 2017). Flooding occurred at the site during August and September (affecting samples collected on 6/8/2015 and 8/9/2015), which may have affected drainage estimates and diluted the NO3-N concentrations. October and November were drier, and there were higher NO3-N concentrations. The 'Rootzone Reality' project samples were analysed for NO3-N concentration and nitrate isotopes in 2016 at GNS Science.



Figure 1.1 Location of sampling sites in this study. Franklin area samples from Dataset 1 are represented by the prefix LB (12 sites). The Rootzone Reality Project site (Dataset 2, one site) is indicated by the circle to the left of Pukekohe. Sample locations and reported results are listed in Table 4.1 and Appendices 1 and 2.

## 1.1 Report Objectives

This report undertakes a review and interpretation of historical groundwater nitrate isotope data collected in 2014 and 2015 for the Franklin area and reported to Auckland Council as raw laboratory results by GNS Science in 2014 and 2016. The review includes:

- compilation and interpretation of two available nitrate isotope datasets from the Franklin area, and
- a report on findings.

To support the work, the following datasets have been provided by Auckland Council:

- Nitrate isotopes of the Franklin area (Dataset 1, Appendix 1), collected in May 2014. The full report consists of physical chemistry and nitrate isotope (δ<sup>15</sup>N and δ<sup>18</sup>O) results from the following 12 surface water and groundwater sites: Rifle Range Road (surface water), Fielding Road bore, BP Bombay bore, Patumahoe Spring, Hickey Spring, Whangamaire Stream (upper and lower catchment), Ngakoroa Stream (upper and lower catchment) and Hingaia Stream (upper, middle and lower catchment).
- Nitrate isotopes from the 'Rootzone Reality' project (Dataset 2, Appendix 2) sampled from leaching trial fluxmeters from July to October 2015. Twelve leachate samples were collected as part of the Rootzone Reality project each month between August, September, October and November 2015, and samples for six of the sites (i.e. a total of 24 samples) were analysed; see above.

# 2.0 BACKGROUND

# 2.1 Franklin Land-Use and Hydrological History

The Franklin area in Auckland has a long history of cultivation and livestock farming over the last 100 years (Meijer et al. 2016). Vegetable production (onions, potatoes) is a key economic activity in Pukekohe, and, accordingly, intensive horticulture requires high levels and frequent applications of nitrogenous fertilisers to sustain high-quality agricultural production. When fertiliser input exceeds plant assimilative capacity, these excess nutrients are transported into surface water run-off and are susceptible to leaching through the soil into groundwater.

The Franklin area covers an area of 43,224 ha in size and is characterised by a frost-free climate with rich volcanic soils, suitable for pastural farming and horticulture. Local shallow aquifers were historically formed by several volcanic centres that produced lava flows in the Manukau lowlands (Auckland Regional Council 1991), and the geology comprises mainly sand and basaltic volcanic rocks (Meijer et al. 2016 and references therein). It is in groundwater from these shallow (10–50 m) volcanic aquifers that the elevated nitrate concentrations are observed. Beneath these shallow aquifers lies the Kaawa Formation, which is a deeper confined aquifer characterised by a porous shell bed, sand deposits and weakly cemented sandstone. The Pukekohe volcanic aquifer is hydraulically connected to the underlying Kaawa aquifer, with a vertical hydraulic gradient from the volcanic to the sedimentary aquifer (Viljevac et al. 2002).

Several major surface water catchments drain from Pukekohe Hill north towards the Manukau Harbour. These include, but are not necessarily limited to, the Waitangi (19.5 km<sup>2</sup>), Mauku (38 km<sup>2</sup>), Whangamaire (23 km<sup>2</sup>), Whāngapōuri (51 km<sup>2</sup>), Oira (18.5 km<sup>2</sup>), Ngakoroa (38 km<sup>2</sup>) and Hingaia (57 km<sup>2</sup>) catchments (Viljevac et al. 2002). All streams gain water from the Pukekohe volcanic aquifers, except for the Hingaia and Ngakoroa streams that gain water from the Bombay and Drury volcanic aquifers, respectively.

Groundwater recharge into the unconfined aquifers is almost exclusively from drainage of rainfall and irrigation water (Burden 1982) due to the shallow water table and relatively high porosity of the Franklin soils (Auckland Regional Council 1991). These volcanic aquifers are highly susceptible to periods of drought and heavy rainfall, which affects the mobility of surface applied nutrients, potentially resulting in nutrient 'hot spots' and 'pulses' as excess surface nutrients may be remobilised in an intensive slug, rather than continuous leaching over time.

## 2.2 Franklin Nitrate Issues

Elevated nitrate concentrations in Franklin surface waters and groundwaters have been identified as early as 1959 and are described in previous reports (Meijer et al. 2016). Long term State of the Environment (SOE) data shows that concentrations of nitrate-N in shallow volcanic groundwater and surface water are consistently elevated in parts of the Franklin area (Meijer et al. 2016; Ingley and Groom 2021).

Annual median NO3-N concentrations in SOE monitored rivers in Franklin range from below 0.5 to above 13 mg/L (Ingley and Groom 2021). Some of these rivers exceed or are approaching the national bottom line for nitrate toxicity (2.4 mg/L) as defined in the National Policy Statement for Freshwater Management 2020 (Ministry for the Environment 2020).

Annual median concentrations of NO3-N across eight SOE and four national groundwater sites in the Franklin area range from below 0.01 mg/L in the deep Kaawa and Waitemata aquifers to up to 26 mg/L in the shallow volcanic aquifers (Foster and Johnson 2021). Some of these sites far exceed the drinking water maximum acceptable value of 11.3 mg/L (Ministry of Health 2018).

In general, high concentrations of nitrate in Franklin's shallow volcanic aquifers and groundwater-fed streams have been linked to soil quality and intensive horticulture in the region (Williams et al. 2000), as horticultural land use is suggested to have the highest surplus nitrogen (kg/ha). Crush et al. (1997) report that onion and potato farming hold the highest risk for potentially leachable nitrogen, particularly for crops planted in the winter months when soil temperatures are low, and therefore plant growth and nutrient uptake are reduced, with the excess nitrogen leached away by higher seasonal rainfalls.

In order to sustain high productivity, vegetable growers have used upwards of 400–500 kg N/ha of fertiliser applied to crops, while dairy pastures are estimated to receive between 65 and 95 kg N/ha through April to October (Francis 2003). Around 14% of the Franklin reporting area is suggested to be used for arable farming or short-term crops and is located directly above the South Auckland volcanic aquifer recharge zone, while up to 72% of the reporting area is under pastoral land. Native bush and urban dwellings both represent 4% and 8% of the area, respectively (Meijer et al. 2016). Apart from farming and horticulture, other potential nutrient sources include urban wastewater discharges and leakages from reticulated water infrastructure, natural background-level nitrogen from native bush or forestry and natural organic soil nitrogen (Soil N) from greenspaces or urban backyards.

A recent study has shown that Mean Residence Time (MRT) of groundwater in the Bombay and Pukekohe aquifer system ranged from 16 to 99 years (van der Raaij 2015). NO3-N concentrations showed an inverse relationship with groundwater MRT, primarily due to land-use change and intensification in recent times. There is limited information about groundwater and surface water connectivity and the dispersal of nitrates across these aquifers. Moreover, the source and fate of these nitrates is unknown. At the time of writing this report, another groundwater age study led by GNS Science and commissioned by Auckland Council is underway that includes groundwater samples collected in 2021.

Surface water quality may also fluctuate due to land run-off and leachate transportation through the vadose zone. Baseflow ratios suggest that the Whangamaire Stream was predominantly fed by groundwater (80%) and that the Hingaia tributary, Hingaia lower and Whāngapōuri Stream sites also had significant groundwater contributions (45–49%). The Maketū, Mauku, Ngakoroa and Waitangi downstream sites had a moderate groundwater contribution (27–45%), while baseflow for the Hingaia upper and Oira Stream sites had relatively low groundwater connectivity (12–14%). Baseflow data is not available for the Mauku downstream, Puhitahi and Whangamarie downstream sites (White et al. 2019).

## 2.3 Nitrates

Nitrate can pose a human health hazard in drinking water and lead to accelerated eutrophication (causing hypoxia and algal blooms) of surface waterways – the two most prevalent water quality problems globally (United Nations 2014; OECD 2017). Approximately 40% of long-term groundwater monitoring sites in New Zealand historically show above-baseline concentrations (Daughney and Wall 2007; Moreau et al. 2016).

NO3-N concentration characterises the level of nitrate contamination in a water body and is a primary indicator of water quality (Ballantine and Davies-Colley 2014). New Zealand's drinking water standards are set at a maximum acceptable value of 50 mg/L for total nitrate (Ministry of Health 2018), which corresponds to 11.3 mg/L NO3-N, in line with World Health Organization guidelines (WHO 2016, 2017). Current regulations maintain that, if community-supplied drinking water NO3-N reaches half of the permissible level (5.65 mg/L), additional monitoring must be undertaken given potential links to cancer and other health issues, such as methemoglobinemia (blue baby syndrome), which can cause depletion of oxygen in blood supply.

In the last 10 years,  $\delta^{15}N$  and  $\delta^{18}O$  values and NO3-N concentrations from a range of freshwater investigations across New Zealand have been reported, providing evidence of local freshwater contamination issues and ecosystem assimilation processes (e.g. Stewart et al. 2011; Parfitt et al. 2012; Clague et al. 2015; Wells et al. 2016; Morgenstern et al. 2019; Martindale et al. 2019; Stewart and Aitcheson-Earl 2020). Nitrate isotopes ( $\delta^{15}N$  and  $\delta^{18}O$ ) have been used as environmental indicators to tease out more complex nitrogen contributions (Wassenaar 1995; Kendall 1998; Silva et al. 2000; Widory et al. 2004; Xue et al. 2009; Jung et al. 2020) and identify which processes (nitrification, anammox, mineralisation and denitrification) dominate systems.

Sources of nitrate in the environment can have a wide range of  $\delta^{15}N$  and  $\delta^{18}O$  values (Figure 2.1). Using a dual nitrate isotope approach, it is possible to identify different sources based on their isotopic composition. There may also be overlap of the isotopic signals from different nitrate sources. When this occurs, it is important to understand the composition of nitrate sources, contamination level, age of contamination and flow paths from the source to sampling site.

Various environmental and biological processes affect the isotopic composition of nitrate. These processes can be classified by their isotopic signature and plotted on a biplot of  $\delta^{15}$ N versus  $\delta^{18}$ O. In New Zealand, contributions from atmospheric nitrates (found in rainfall or dust deposition and formed via lightning or volatilisation of ammonia or other anthropogenic sources) are considered to be negligible compared to other sources (Nichols et al. 2018). Most nitrates come from either fertilisers or animal waste such as urine (ammonia or urea) or manure. Soil nitrate, considered to be a relatively low-level contribution, acts as a sink to assimilate excess nitrogen from other sources, mitigating and removing nitrate.



Figure 2.1 Dual nitrate isotope biplot (nitrogen  $\delta^{15}N$  and oxygen  $\delta^{18}O$ ) highlighting the mechanism of nitrate formation and transformation in water (Kendall 1998).

The various mechanisms of nitrate formation and transformation are described as follows:

**Nitrification** is the biological oxidation of organic nitrogen, ammonia or ammonium (from urea) to nitrite, followed by further oxidation to nitrate by either ammonia-oxidising bacteria (AOB) or ammonia-oxidising archaea (AOA) (Watson et al. 1981). Nitrosomonas is frequently the most common genus associated with AOB (Equation 2.1), followed by further AOA oxidation (Equation 2.2). In this second step, *Nitrobacter* is the most frequently identified genus, but others include *Nitrosococcus* and *Nitrosospira*. Different heterotrophic bacteria or fungi can also carry out nitrification. There is generally low fractionation of <sup>15</sup>N during ammonification, meaning that the ammonium (NH4) formed retains some of the isotopic signature of the organic nitrogen (Kendall 1998). Most soils have  $\delta^{15}$ N values in the range of +2 to +8 ‰ (Kendall 1998).

$$Organic-N \rightarrow NH4 + \rightarrow NH3 \rightarrow NO2 + 3H + 2e$$
- Equation 2.1

$$NO2 - + H2O \rightarrow NO3 - + 2H + + 2e$$
- Equation 2.2

**Anammox** (anaerobic ammonium oxidation) is an important microbial process that converts nitrite and ammonium ions directly into nitrogen gas and water rather than via oxidative steps (Winkler et al. 2012). Frequently seen in wastewater treatment, ammonium undergoes partial nitrification to nitrite by AOB (Equation 2.3), then the remaining ammonium and nitrite is directly converted using the anammox process to nitrogen gas (Equation 2.4).

 $2NH4- + 302 \rightarrow 2NO2- + 4H+ + 2H$ Equation 2.3  $NH4+ + NO2- \rightarrow N2 + 2H2O$ Equation 2.4

**Mineralisation** results in the production of NH4 from organic Soil N (Equation 2.5). During mineralisation, soil microbes depolymerise organic matter that is rich in carbon and nitrogen (Fujii et al. 2020). The decomposition process results in monomers that are then mineralised

into inorganic compounds such as ammonium or assimilated by the microbes for their biosynthetic needs. Nitrogen mineralisation depends on the carbon to nitrogen (C:N) ratio of the organic matter. In general, if the C:N ratio is higher than 30:1, then there may be insufficient nitrogen available for mineralisation and the decomposing microbes will absorb the nitrogen for their own biosynthesis. When the C:N ratio is less than 25:1, nitrogen mineralisation results in a loss of ammonium to the environment. Under favourable conditions, ammonium is further converted by micro-organisms to inorganic nitrate.

$$N(org) \rightarrow NH4 + \rightarrow NO3$$

**Denitrification** is a multi-step NO3-N removal process via microbes that consume and assimilate diffuse NO3-N sources, followed by the stepwise reduction of the NO3-N to N<sub>2</sub> gas in the presence of carbon as an electron donor (Kendall and Aravena 2000; Equation 2.6). This fractionation process enriches the <sup>15</sup>N of the water sample through preferential consumption (removal) and uptake of the biologically (more) available <sup>14</sup>N by bacteria. This step is twofold, where both the residual nitrate-<sup>15</sup>N increases and the NO3-N concentration decreases. As denitrification progresses through several intermediary steps to the end-product (N<sub>2</sub> gas), isotope fractionation may be refreshed (reset back to original values) or interrupted through new contaminant pulses in the environment. Mobilisation (or remobilisation) of surface contaminants from irrigation or precipitation causes further contaminant infiltration into the vadose or phreatic zones, mixing with residual contaminants that may be more or less denitrified. In this instance, transportation and anammox processes will also influence the fractionation processes.

$$NO3 \rightarrow NO2 \rightarrow NO(g) \rightarrow N2O(g) \rightarrow N2(g)$$
 Equation 2.6

Previous studies have shown that groundwater samples with elevated iron and ammonia-N concentrations are generally reducing (higher redox potential) and likely to encourage microbial denitrification and loss of NO3-N (Snow 2018). They also found that surface water samples with elevated nitrate contents also tended to have elevated chloride, sulphate, iron and ammonia-N. Moreover, the lighter <sup>16</sup>O isotope is also preferentially removed by bacteria during denitrification, enriching residual nitrates in <sup>18</sup>O as denitrification progresses, although temperature, dilution and mixing with rainfall (new water) and groundwater (old water) have also been shown to affect these contributions (Jung et al. 2020).

**Volatilisation** occurs when ammonia gas released from urea-based fertilisers or animal waste is hydrolysed to ammonia and lost from soils to the atmosphere (Equation 2.7). Residual soil ammonia is enriched in <sup>15</sup>N with the loss of the lighter <sup>14</sup>N fraction and, with nitrification, enriches the <sup>15</sup>N of resulting nitrate.

$$CO(NH2)2 + 2H2O \rightarrow 2NH4 + 2CO2 \rightarrow 2NH3 + 4H +$$
 Equation 2.7

Globally, there is a recognised range of typical  $\delta^{15}N$  values for different nitrogenous sources (Xue et al. 2009; Figure 1.1).

**Synthetic nitrate fertilisers** (manufactured via the Haber-Bosch method), urea fertiliser or ammonification of urine induces lower  $\delta^{15}$ N values in water, typically from -4 to +4 ‰ (Loo et al. 2017; Suchy et al. 2018; Figure 2.1). Dissolved inorganic nitrogen (DIN) supplied by fertilisers, manure or urban waste is transported into groundwater by contaminated surface water percolating through the root zone (source load) and sub-surface sediments (in the vadose and phreatic zones). Generally, coarse-grained, permeable sediments provide the fastest direct nitrate entry route into a receiving freshwater body, i.e. aquifer (delivered load), with minimal likelihood of retention or remediation processes such as microbial denitrification. Redox

processes convert root-zone DIN loss into nitrates under oxic conditions, while denitrification occurs under reducing conditions, changing the nitrate back to harmless nitrogen gas (Wilson et al. 2020).

**Organic soil nitrogen** covers a broad range of  $\delta^{15}$ N values from +4 to +10 ‰ (Kendall 1998; Figure 2.1). Freshwater with  $\delta^{15}$ N values greater than +10 ‰ are typically classed as undergoing denitrification when on a 1:1 linear relationship with  $\delta^{18}$ O, or as containing effluent when on a 2:1 linear relationship with  $\delta^{18}$ O (Figure 2.1).  $\delta^{18}$ O values were found to be more useful than  $\delta^{15}$ N values to separate atmospheric NO3 deposition from microbially produced soil NO3, as their  $\delta^{18}$ O values were significantly different (Wassenaar 1995).  $\delta^{18}$ O values produced by nitrification in freshwater range from -15 to +15 ‰, while atmospheric NO3 has a  $\delta^{18}$ O range from +15 to +70 ‰ (Granger and Wankel 2016). Previously, it was thought that the mechanism of nitrate formation during nitrification was oxidation of NH3 to NO2, which incorporated one oxygen from air and one oxygen from water, while subsequent oxidation of NO2 to NO3 incorporated an oxygen from water, providing a 1:1 denitrification trajectory on the nitrate biplot (Figure 2.1).

More recent work has shown that  $\delta^{18}O_{H2O}$  kinetic isotope effects are associated with denitrification, as well as the isotopic equilibrium of the oxygen atoms between NO2 and water, which has an inverse kinetic effect on NO2 to NO3. In freshwater systems, these nitrifiers can coexist with denitrifiers, revealing that nitrates can be replenished by co-existing NO2 oxidising bacteria and anammox processes during denitrification (Granger and Wankel 2016). This results in a lower denitrification trajectory, providing a 2:1 gradient, which integrates the replenishment of <sup>15</sup>N from anammox processes. Furthermore,  $\delta^{18}O_{NO3}$  values can be up to 5 ‰ higher if the  $\delta^{18}O_{H2O}$  value is isotopically enriched as a result of evaporation, which can occur in surface water, denitrification ponds and seasonal groundwater recharged from higher altitudes, or if the soil  $\delta^{18}O$  value is higher than atmospheric O<sub>2</sub> due to fractionation during soil bacterial respiration (Zhang et al. 2019). Other reactions may also induce higher fractionation in  $\delta^{18}O_{H2O}$  than the theoretical fractionation, such as low pH environments, water with a high redox potential or fractionation processes occurring during the initial nitrification process.

# 2.4 Dual Isotope Nitrate Approach

A study of New Zealand surface water and groundwater has been undertaken to establish classification boundaries based on the relationship between  $\delta^{15}N$ ,  $\delta^{18}O$  and nitrate concentration (Rogers et al. 2022; Figure 2.2). Characteristics of each class are provided in Table 2.1. Samples with low  $\delta^{15}N$  and  $\delta^{18}O$  values, and low nitrate concentrations (<1 mg/L), are classed as baseline results typical of background-level residual Soil N, while high nitrate concentrations (>5 mg/L) imply nitrogenous fertiliser or urine/urea (after conversion to nitrate) leaching into the water. In general, most samples tend to fall into the Mixed Soil N fertiliser region. It characterises background nitrogen levels (low NO3-N concentrations) found in untilled soils and soils that have low levels of land-use intensity, as well as acting as a transition zone for nitratecontaminated water (mixed fertilisers) to transition through to denitrification. Conversely, once entering the denitrification zone, additional nitrogenous input may cause the isotopic values to decrease again and return to the Mixed Soil N and Fertiliser (Mixed SF) zone, or even return to the Urine and Urea Fertiliser (UUF) zone. In this case, if further mixing or remobilisation of nutrients occurs, the nitrate concentration will usually also increase. If NO3-N concentrations are higher (>3-4 mg/L), then it is likely that there is a mixture of nitrogenous fertilisers or urine/urea and background Soil N.

Denitrification is considered to have occurred when  $\delta^{15}N$  values increase (>8 ‰), as the lighter  $^{14}N$  isotope is preferentially removed during nitrate attenuation, resulting in more positive  $\delta^{15}N$  values.



Figure 2.2 Dual nitrate isotope results (nitrogen  $\delta^{15}$ N and oxygen  $\delta^{18}$ O) of groundwater and surface water from 1000 sites across New Zealand. Nitrate concentration is represented by the bubble size and ranges from 0.01 mg/L to 76.6 mg/L.

Class	Name	Description
Baseline	Baseline	Low-concentration background nitrate with low $\delta^{15}$ N and $\delta^{18}$ O values.
Urine and Urea Fertilisers (UUF)	Urine and Urea Fertiliser	Breakthrough and mineralisation of urine, urea or inorganic ammonium fertilisers into groundwater and surface water. Higher NO3-N concentrations (>5 mg/L with low $\delta^{15}$ N and $\delta^{18}$ O values; <4 ‰ for both isotopes).
Fertiliser NO3	Nitrate Fertiliser	Nitrate-bearing fertilisers such as NH <sub>4</sub> NO <sub>3</sub> or Ca(NO <sub>3</sub> ) <sub>2</sub> that have low $\delta^{15}$ N and high $\delta^{18}$ O values.
Soil N	Soil N	Typical diffuse background-level nitrate matches soil organic $\delta^{15}$ N, sits on 1:1.5 'denitrification and mixing' line with moderate $\delta^{15}$ N values; NO3 concentration decreases with increasing $\delta^{15}$ N values.
Mixed Soil N and Fertilisers	Mixed SF	UUF and/or Fertiliser NO3 transition through the Soil N zone towards the denitrification zone. This interaction creates a Mixed SF transition zone. Higher concentration of nitrate may characterise fertiliser samples from Soil N samples. $\delta^{15}$ N and $\delta^{18}$ O values increase along the denitrification gradient. Some UUF / Fertiliser NO3 samples may be diluted with Soil N water.
Denitrification	Denitrified	Higher $\delta^{15}$ N and $\delta^{18}$ O values and decreasing NO3-N concentrations suggest that denitrification has occurred.
Effluent	Effluent	Breakthrough of effluent-derived nitrate: higher NO3-N concentration with higher $\delta^{15}$ N values.

 Table 2.1
 Description of indicator biplot zone classifications.

# 3.0 ANALYTICAL METHODS

#### 3.1 Nitrate Concentrations

Thirty-six surface and groundwater samples (12 samples from Dataset 1 and 24 samples from Dataset 2) were collected from sites around Franklin by Auckland Council staff and were submitted to Hills Laboratory in 2014 and 2015 for nitrate concentration assessment. On arrival, water samples were filtered through Whatman 0.45 µm acetate membrane filters and refrigerated for a few days until analysis. Water samples (250 mL) were analysed for NO3-N according to standard methods (APHA 2012) and other basic chemistry, including nitrite, and NH4-N concentrations were also supplied with Dataset 1.

## 3.2 Nitrate Isotopes

Stable isotope ratios <sup>15/14</sup>N and <sup>18/16</sup>O of dissolved nitrate in groundwaters and surface waters were measured at the Stable Isotope Laboratory at GNS Science in Lower Hutt. Isotopes are measured to understand the source and fate of nitrogen. The isotopic ratios are expressed as  $\delta$  values with respect to air for  $\delta^{15}$ N and Vienna Standard Mean Ocean Water (V-SMOW) for  $\delta^{18}$ O:

$$\delta^{b}E(\%_{0}) = [b/aR_{sample} - b/aR_{reference}]/b/aR_{reference}$$
Equation 3.1

where *a* and *b* are the lighter and heavier mass numbers of element *E*, and  $R_{sample}$  and  $R_{reference}$  is the heavy-to-light ratio of element *E* in sample and reference materials, respectively. This isotopic delta ( $\delta$ ) value is usually presented as per mil (‰), which is based on multiples of 1000.

The water samples were collected and filtered through GF/F filters (0.2 or 0.45 µm) into HDPE bottles and preserved by freezing or acidification to pH 2–3 by adding 1 mL 2.5 mM sulfanilic acid in 10% (degassed) HCl to remove nitrite to each 100 mL of sample. The isotope sample analysis process involves conversion of nitrate (NO<sub>3</sub><sup>-</sup>) to nitrite (NO<sub>2</sub><sup>-</sup>) using spongy cadmium, then to nitrous oxide (N<sub>2</sub>O) using sodium azide in an acetic acid buffer. The N<sub>2</sub>O is purged from the water sample and, after going through a series of chemical traps to remove H<sub>2</sub>O and CO<sub>2</sub>, N<sub>2</sub>O is cryogenically trapped with liquid nitrogen and subsequently passed through a gas chromatograph column and into an Isoprime isotope ratio mass spectrometer (IRMS) to determine its isotopic signature of nitrogen and oxygen ( $\partial^{15}N$  and  $\partial^{18}O$  values). The method is modified from McIlvin and Altabet (2005).

All results are reported with respect to AIR for  $\delta^{15}N$  and VSMOW for  $\delta^{18}O$  and normalised to international standards: USGS 34 ( $\delta^{15}N = -1.8 \%$  and  $\delta^{18}O = -27.9 \%$ ), IAEA-NO3 ( $\delta^{15}N = +4.7 \%$  and  $\delta^{18}O = +25.6 \%$ ), USGS 32 ( $\delta^{15}N = +180.0 \%$  and  $\delta^{18}O = +25.7 \%$ ) and USGS 35 ( $\delta^{15}N = +2.7 \%$  and  $\delta^{18}O = +57.5 \%$ ); and to our internal standard: KNO3-b ( $\delta^{15}N = +10.7 \%$  and  $\delta^{18}O = +11.7 \%$ ). The analytical precision for these measurements was ±0.3 % for both  $\delta^{15}N$  and  $\delta^{18}O$ , except for samples below 0.5 mg/L NO3-N, which may have lower precision. Only one sample (LB02) fell within this range, although precision was not compromised.

#### 4.0 RESULTS

#### 4.1 Nitrate Concentrations

NO3-N concentrations from Franklin groundwater and surface water (Dataset 1) ranged from below detection levels (0.002 mg/L) at the Fielding Road bore (LB02, Drury Volcanic) to 26 mg/L at Patumahoe Spring (LB04, Pukekohe Volcanic) (Table 4.1), which exceeds the maximum acceptable value. Patumahoe Spring and Hickey Spring (LB05) had elevated NO3-N concentrations, with the highest values (26 and 20 mg/L, respectively). It is likely that these springs feed the Whangamaire Stream (LB06), which has higher NO3-N concentrations, ranging between 11 and 17 mg/L, and signals the geographical dispersal of nitrates within the catchment. The other locations all had Franklin area NO3-N concentrations below 5 mg/L, apart from BP Bombay (LB03, Bombay Volcanic Aquifer), a groundwater bore with 11 mg/L NO3-N. Nitrite concentrations were measured but found to be negligible (<0.008 mg/L).

	Site No.	Site Name	Sample Type	Collection Date	δ <sup>15</sup> N (‰)	δ <sup>18</sup> Ο (‰)	NO <sub>3</sub> -N (mg/L)
	LB01	Rifle Range Rd	Surface water ponding	20/05/2014	7.3	4.4	1.4
	LB02	Fielding Rd	Groundwater – Drury Volcanic (shallow)	20/05/2014	6.5	7.2	0.002
	LB03	BP Bombay	Groundwater – Bombay Volcanic (shallow)	20/05/2014	5.0	5.6	11.0
	LB04	Patumahoe Spring	Groundwater – Pukekohe Volcanic	20/05/2014	3.5	3.7	26.0
	LB05	Hickey Spring (Seddon St)	Groundwater – Pukekohe Volcanic	20/05/2014	4.3	4.4	20.0
et 1	LB06	Whangamaire Upper (Ostrich Rd)	Stream	20/05/2014	6.5	5.7	17.0
Datase	LB07	Whangamaire Dwn (Charles Rd)	Stream	20/05/2014	6.3	6.0	11.0
	LB08	Ngakaroa Upper (Mill Rd)	Stream	20/05/2014	7.4	5.8	3.0
	LB09	Ngakaroa Dwn (Kern Rd)	Stream	20/05/2014	9.2	7.0	2.9
	LB10	Hingaia Upper (Ararimu Rd)	Stream	20/05/2014	5.4	5.4	4.7
	LB11	Hingaia Mid (Quarry Rd)	Stream	20/05/2014	6.0	6.0	3.5
	LB12	Hingaia Dwn (Flanagan Rd)	Stream	20/05/2014	5.5	5.4	2.9
N	NS2-1	North Site 2-1	Vadose Zone Leachate	9/07/2015	3.2	2.0	30.4
set ;	NS2-3	North Site 2-3	Vadose Zone Leachate	9/07/2015	2.5	1.1	41.2
Data	NS2-5	North Site 2-5	Vadose Zone Leachate	9/07/2015	3.2	0.6	13.3
	NS2-7	North Site 2-7	Vadose Zone Leachate	9/07/2015	3.5	1.1	29.9

 Table 4.1
 Nitrate isotopes and concentrations of the Franklin samples.

	Site No.	Site Name	Sample Type	Collection Date	δ <sup>15</sup> N (‰)	δ <sup>18</sup> Ο (‰)	NO <sub>3</sub> -N (mg/L)
	NS2-9	North Site 2-9	Vadose Zone Leachate	9/07/2015	2.0	2.0	30.0
	NS2-11	North Site 2-11	Vadose Zone Leachate	9/07/2015	3.1	2.0	21.8
	NS2-13	North Site 2-13	Vadose Zone Leachate	6/08/2015	1.6	1.0	24.0
	NS2-15	North Site 2-15	Vadose Zone Leachate	6/08/2015	3.5	-2.0	28.5
	NS2-17	North Site 2-17	Vadose Zone Leachate	6/08/2015	2.0	4.8	22.6
	NS2-19	North Site 2-19	Vadose Zone Leachate	6/08/2015	2.0	0.7	9.6
	NS2-21	North Site 2-21	Vadose Zone Leachate	6/08/2015	1.7	0.2	25.5
	NS2-23	North Site 2-23	Vadose Zone Leachate	6/08/2015	-1.4	3.7	36.4
2	NS2-25	North Site 2-25	Vadose Zone Leachate	8/09/2015	-6.7	2.6	43.7
set	NS2-27	North Site 2-27	Vadose Zone Leachate	8/09/2015	0.1	2.8	32.4
Data	NS2-29	North Site 2-29	Vadose Zone Leachate	8/09/2015	-2.7	3.4	21.3
-	NS2-31	North Site 2-31	Vadose Zone Leachate	8/09/2015	-2.1	10.0	12.7
	NS2-33	North Site 2-33	Vadose Zone Leachate	8/09/2015	-4.6	1.7	44.0
	NS2-35	North Site 2-35	Vadose Zone Leachate	8/09/2015	0.7	7.9	35.4
	NS2-37	North Site 2-37	Vadose Zone Leachate	1/10/2015	-6.3	2.1	37.0
	NS2-39	North Site 2-39	Vadose Zone Leachate	1/10/2015	0.3	5.6	39.1
	NS2-41	North Site 2-41	Vadose Zone Leachate	1/10/2015	-2.2	2.2	54.1
	NS2-43	North Site 2-43	Vadose Zone Leachate	1/10/2015	-2.1	8.9	48.2
	NS2-45	North Site 2-45	Vadose Zone Leachate	1/10/2015	-3.7	2.5	45.8
	NS2-47	North Site 2-47	Vadose Zone Leachate	1/10/2015	-2.0	5.7	69.6

Leachate samples (Dataset 2) were sampled over four months during winter and their NO3-N concentrations ranged from 9.6 to 69.6 mg/L. Mean monthly NO3-N concentrations were 27.8, 24.4, 31.6 and 49.0 mg/L for August to November, respectively, indicating near-constant NO3-N leaching during August and September due to higher rainfall (including flooding) and dilution of the nitrates. Concentrations increased during October and November when the local precipitation was lower. These nitrate levels are significantly above background levels, indicating ongoing and increased nitrate leaching into subsurface soils. Two fertiliser events are noted, one on planting in June 2015 and another in August 2015. It is likely that the second fertiliser event is overprinting the basal load from the first fertiliser event.

## 4.2 Nitrate Isotopes

Dual isotope analysis of nitrogen and oxygen ( $\delta^{15}N$  and  $\delta^{18}O$ ) of the Franklin water and leachate samples are plotted on a biplot to investigate the nitrate source and subsequent chemical transformation that occurs in soil and groundwater zones (Figure 4.1). Datasets 1 and 2 show three main trends. Groundwater and surface water samples (crimson colour circles) plot mainly in the Mixed SF zone, and leachate samples (blue/grey colour circles) plot in the Fertiliser NO3 mineralisation/nitrification UUF and Mixed SF zones with slightly more positive  $\delta^{15}N$  values.



Figure 4.1 Nitrate biplot of  $\delta^{15}$ N and  $\delta^{18}$ O in the collected Dataset 1 (crimson circles) and Dataset 2 (blue circles) water samples from the Franklin area. The size of the symbol is proportional to NO3-N concentration. Source classification is described in Table 2.1.

#### 4.2.1 Water Samples

Franklin Dataset 1 (crimson colour) shows a linear and increasing trend along the 1:1 denitrification line (Figures 4.1 and 4.2), with the stream samples tending to lie further along the denitrification line than the sub-surface (bore and spring) samples. The NO3-N concentrations generally decrease with increasing  $\delta^{15}N$  and  $\delta^{18}O$  values. Samples with the highest NO3-N concentrations (Patumahoe Spring LB04 and Hickey Spring LB05, represented by larger crimson bubbles) have the lowest  $\delta^{15}N$  and  $\delta^{18}O$  values, suggesting that these samples are the closest match for the isotopic signature of the source contaminant, which is most likely a leached fertiliser. The remaining Franklin stream samples (those with  $\delta^{15}N > 4.5 \%$ ) are likely to be fed by groundwater. The trend is defined by water samples with a similar contaminant source but that have undergone various amounts of denitrification, and their concentrations attenuated during this process approach lower NO3-N concentrations than expected from non-anthropogenic point sources such as background Soil N. The soil organic matter in contact with this water is acting as an effective sink for any excess fertilisers, and the remnant levels are currently manageable via environmental assimilation and attenuation.

Some groundwater sites (e.g. Patumahoe and Hickey spring) suggest that nitrogen breakthrough has occurred where nitrate has passed through the soil into the groundwater system but that in the stream samples (where NO3-N is less than 5 mg/L) either dilution from uncontaminated sources or denitrification has taken place. Minor deviations from the 1:1 denitrification gradient (such as for Rifle Range surface water, LB1) may suggest a contribution from another uncontaminated groundwater source input, which may cause the  $\delta^{18}$ O values to become more negative, or that natural background Soil N has a larger contribution to the  $\delta^{15}$ N value of this sample.

The isotopic signatures of the water samples suggest that the nitrates are primarily derived from fertilisers rather than animal effluent (which tends to denitrify on a 1:2 gradient), and therefore the main contaminant source is a urea/ammonia-based fertiliser.



Figure 4.2 Nitrate biplot of  $\delta^{15}$ N and  $\delta^{18}$ O from Dataset 1 water samples. The size of the symbol is proportional to NO3-N concentration. Source classification is described in Table 2.1. Crimson colour identifies stream samples; pink colour identifies spring or shallow bore samples.

#### 4.2.2 Leachate Samples

The Franklin Dataset 2 biplot indicates two main groups of samples corresponding to separate sampling events (Figures 4.3 and 4.4). Group 1 samples were sampled on 9/7/2015 and 6/8/2015, and Group 2 was sampled on 8/9/2015 and 1/10/2015, although a single sample (NS2-23) from the August survey lies within the Group 2 samples. The latter could be a genuine result, a faulty analysis or potentially a mislabelled sample that may have been exchanged with NS2-27.



Figure 4.3 Nitrate biplot of  $\delta^{15}$ N and  $\delta^{18}$ O from Dataset 2 vadose zone leachate samples. The size of the symbol is proportional to NO3 concentration. Source classification is described in Table 5.1 and labels (XX) represent sample numbers NS2-XX.

During the 'Rootzone Reality' project, two crop-scale fertilisation events occurred; an initial fertiliser application of Green Fertiliser and ammonium sulphate (Source 1) in June 2015 and further applications of CAN (Source 2) in August and September 2015.

The nitrate isotope fluxmeter results clearly show smaller nitrate concentrations in Group 1 samples (monthly mean of 27.8 and 24.4 mg/L NO3-N for July and August) associated with Application 1. A change in fertiliser type in August produced a different nitrate isotope cluster (Group 2) with increased monthly mean nitrate concentrations of 31.6 and 49.0 mg/L NO3-N for September and October 2015. Based on the nitrate zones from Figure 4.1, Group 1 samples clearly fall into a Mixed SF zone, typical of urea/ammonia-based fertilisers and natural 'composting N' fertiliser similar to a Soil N signature. Based on the fertilisers used in June, these values are entirely consistent with the mixed nature of the fertiliser source. Subsequent to the application of CAN, an ammonia-nitrate-based fertiliser, the isotopic signature is changed and the Group 2 samples lie in the NO3 fertiliser zone and overlap into the 'Urea/Ammonia fertiliser' zone, overprinting the original nitrate signature seen in Group 1 and generating a different signature for Group 2 samples taken in September and October. It is clear that the fertiliser contribution is larger in the Group 2 cluster than the Group 1 cluster, in part due to mineralisation of the fertilisers and the high amount (500 kg/ha CAN) applied compared to 300 kg/ha ammonium sulphate and 1000 kg/ha Green Fertiliser. There was also a higher initial rainfall (including flooding) during July and August, potentially diluting the fertiliser, and a strong assimilative uptake by the crops during this rapid growth time.



Figure 4.4 Nitrate biplot of  $\delta^{15}$ N and  $\delta^{18}$ O from Dataset 2 vadose zone leachate samples identified by month of sampling. The size of the symbol is proportional to NO3 concentration. Source classification is described in Table 5.1.

#### 5.0 DISCUSSION

#### 5.1 Summary and Classification of Franklin Samples

Based on the nitrate isotopic bubble biplots, it is possible to classify the source and fate of nitrate isotopes in the Franklin samples (Table 5.1). The groundwater and surface water samples are mostly a mix of background Soil-N-attenuated samples and mixed fertiliser / Soil N samples, with low levels of denitrification occurring. The leachate samples are all strongly nitrate-contaminated samples showing two distinctive isotope signatures based on the use of two distinct fertilisers during separate application events. Using the dual nitrate isotope approach, the isotopic signature of the Group 1 samples shifts to a new isotopic signature for the Group 2 samples. The nitrate isotope signature of the Group 1 samples clearly relates to the ammonium sulphate fertiliser (a urea/ammonia-based fertiliser) applied in early June 2015. Group 2 samples have an isotopic signature that reflects the CAN fertiliser (a nitrate-based fertiliser) applied in August and September 2015, as the initial fertiliser application is no longer dominant in the leachate samples.

	Site No.	Site Name	Collection Date	δ <sup>15</sup> N Value	δ <sup>18</sup> Ο Value	NO <sub>3</sub> -N (mg/L)	Classification (as per Figure 4.1 Biplot)		
	LB01	Rifle Range Rd	20/05/2014	7.3	4.4	1.4	Soil N		
	LB02	Fielding Rd	20/05/2014	6.5	7.2	0.002	Soil N		
	LB03	BP Bombay	20/05/2014	5.0	5.6	11.0	Soil N and Mixed fertiliser		
	LB04	Patumahoe Spring	20/05/2014	3.5	3.7	26.0	Soil N and Mixed fertiliser		
	LB05	Hickey Spring (Seddon St)	20/05/2014	4.3	4.4	20.0	Soil N and Mixed fertiliser		
	LB06	Whangamaire Upper (Ostrich Rd)	20/05/2014	6.5	5.7	17.0	Soil N and Mixed fertiliser		
Dataset 1	LB07	Whangamaire Dwn (Charles Rd)	20/05/2014	6.3	6.0	11.0	Soil N and Mixed fertiliser		
	LB08	Ngakaroa Upper (Mill Rd)	20/05/2014	7.4	5.8	3.0	Soil N		
	LB09	Ngakaroa Dwn (Kern Rd)	20/05/2014	9.2	7.0	2.9	Denitrified (slightly)		
	LB10	Hingaia Upper (Ararimu Rd)	20/05/2014	5.4	5.4	4.7	Soil N		
	LB11	Hingaia Mid (Quarry Rd)	20/05/2014	6.0	6.0	3.5	Soil N		
	LB12	Hingaia Dwn (Flanagan Rd)	20/05/2014	5.5	5.4	2.9	Soil N		
	NS2-1	North Site 2-1	9/07/2015	3.2	2.0	30.4	Fertiliser NO3- Source 1		
it 2	NS2-3	North Site 2-3	9/07/2015	2.5	1.1	41.2	Fertiliser NO3- Source 1		
Itase	NS2-5	North Site 2-5	9/07/2015	3.2	0.6	13.3	Fertiliser NO3- Source 1		
Da	NS2-7	North Site 2-7	9/07/2015	3.5	1.1	29.9	Fertiliser NO3- Source 1		
	NS2-9	North Site 2-9	9/07/2015	2.0	2.0	30.0	Fertiliser NO3- Source 1		

 Table 5.1
 Classification of source and fate of Franklin area samples based on their nitrate isotopes and concentrations.

	Site No.	Site Name	Collection Date	δ <sup>15</sup> N Value	δ <sup>18</sup> Ο Value	NO <sub>3</sub> -N (mg/L)	Classification (as per Figure 4.1 Biplot)	
	NS2-11	North Site 2-11	9/07/2015	3.1	2.0	21.8	Fertiliser NO3- Source 1	
	NS2-13	North Site 2-13	6/08/2015	1.6	1.0	24.0	Fertiliser NO3- Source 1	
	NS2-15	North Site 2-15	6/08/2015	3.5	-2.0	28.5	Fertiliser NO3- Source 1	
	NS2-17	North Site 2-17	6/08/2015	2.0	4.8	22.6	Fertiliser NO3- Source 1	
	NS2-19	North Site 2-19	6/08/2015	2.0	0.7	9.6	Fertiliser NO3- Source 1	
	NS2-21	North Site 2-21	6/08/2015	1.7	0.2	25.5	Fertiliser NO3- Source 1	
	NS2-23	North Site 2-23	6/08/2015	-1.4	3.7	36.4	Fertiliser NO3- Source 1	
	NS2-25	North Site 2-25	8/09/2015	-6.7	2.6	43.7	Fertiliser NO3- Source 2	
it 2	NS2-27	North Site 2-27	8/09/2015	0.1	2.8	32.4	Fertiliser NO3- Source 2	
tase	NS2-29	North Site 2-29	8/09/2015	-2.7	3.4	21.3	Fertiliser NO3- Source 2	
Da	NS2-31	North Site 2-31	8/09/2015	-2.1	10.0	12.7	Fertiliser NO3- Source 2	
	NS2-33	North Site 2-33	8/09/2015	-4.6	1.7	44.0	Fertiliser NO3- Source 2	
	NS2-35	North Site 2-35	8/09/2015	0.7	7.9	35.4	Fertiliser NO3- Source 2	
	NS2-37	North Site 2-37	1/10/2015	-6.3	2.1	37.0	Fertiliser NO3- Source 2	
	NS2-39	North Site 2-39	1/10/2015	0.3	5.6	39.1	Fertiliser NO3- Source 2	
	NS2-41	North Site 2-41	1/10/2015	-2.2	2.2	54.1	Fertiliser NO3- Source 2	
	NS2-43	North Site 2-43	1/10/2015	-2.1	8.9	48.2	Fertiliser NO3- Source 2	
	NS2-45	North Site 2-45	1/10/2015	-3.7	2.5	45.8	Fertiliser NO3- Source 2	
	NS2-47	North Site 2-47	1/10/2015	-2.0	5.7	69.6	Fertiliser NO3- Source 2	

There appears to be a relationship between the Franklin groundwater and surface water and the leachate samples' nitrate isotope signatures, with nitrate signatures for Group 1 leachate samples plotting on a similar denitrification trajectory as the Franklin waters. Given that the Rootzone Reality project is freshly applied fertiliser that had limited time to denitrify, it is likely that nitrogen isotopes will follow a 1:1 denitrification trajectory (Figure 4.1). If this were the case, the Group 1 leachate samples' nitrate isotopic signature would shift over time to a similar location as the water samples and circles would reduce in size (i.e. nitrate concentrations would reduce) with the onset of denitrification, resulting in a similar fingerprint.

If this were the case, it could be assumed that the nitrogen source of much of the water sampled in the Franklin area could be from green fertilisers and ammonium sulphate-based fertilisers, rather than nitrate-based fertilisers. The combination of plant nutrient nitrogen from green compost and ammonium sulphate provides a mixed, natural Soil N background signal combined with an ammonia (non-nitrate) fertiliser signal, resulting in slightly more positive  $\delta^{15}$ N values and lower  $\delta^{18}$ O values than nitrate-based fertilisers. Subsequently, it may also be of interest to investigate if there is also elevated S or Ca found in the water. Depending on the use of these fertilisers, specific trace elements may be present at elevated concentrations, providing yet another mechanism to estimate leaching and flow paths of nitrate into surface and sub-surface strata.

#### 6.0 CONCLUSIONS

High nitrate concentrations have been noted in surface water and groundwater around the Franklin area since as early as 1959. Nitrate isotopes were used to investigate the source or origin of these nitrates on water and leachate samples. A series of water samples collected from local springs, streams and ponds in the Franklin area confirms fertiliser contamination in surface water and groundwater overprinting natural background Soil N and lies in the Mixed Soil N and fertiliser zone. Sampled from springs, streams and ponds around the Franklin area have not undergone significant denitrification and reflect the isotopic composition of their contaminant source.

Fluxmeter drainage samples from a 'Rootzone Reality' study (Dataset 2) provides comparative evidence of nutrients leaching from green and synthetic fertilisers (ammonium sulphate and calcium ammonium nitrate) that were applied to crops. The preservation of the fertiliser isotope signals in the leachate samples suggests minimal denitrification over this short-term study.

In summary, the following conclusions can be made from the data:

- Using a dual nitrate isotope approach, the key contaminant source was identified as synthetic fertilisers rather than farming effluent due to their isotopic signature falling into the 'Fertiliser' and 'Mixed Soil N and Fertiliser' zones.
- Surface water with higher NO3-N concentrations (>5 mg/L) indicates contamination from recent fertiliser application, as the nitrate concentrations are above expected background levels.
- Groundwater with higher NO3-N concentrations (>5 mg/L) indicate fertiliser breakthrough into the aquifer and/or subsurface transport of leached nutrients from soils.
- Groundwater from the shallow volcanic aquifers with lower NO3-N concentrations (<3 mg/L) indicates denitrification (based on isotopes), lower contamination levels or sufficient assimilation within the ecosystem to assimilate any excess nutrients. There appears to be only one groundwater sample from Field Road (LB02) that has been sufficiently reset to natural background Soil N levels through denitrification.
- δ<sup>15</sup>N and δ<sup>18</sup>O values reflect the nitrate source and its subsequent fate. Key processes
   involve mineralisation of nitrogen sources and transformation into the mixed Soil N and
   fertiliser zones and through to the denitrification zone. If further fertiliser pulses or
   applications occur, the cycle can reset and nitrate isotopes reflect the new input,
   often resulting in a cyclic addition/removal system, as seen in the isotopic transitional
   change in the fluxmeter samples from fertiliser Application 1 (Group 1 samples) to fertiliser
   Application 2 (Group 2 samples). Only when the removal process rate exceeds the
   additive rate will nitrates decline through ecosystem assimilation or denitrification.

Stable nitrate isotope signatures combined with nitrate concentrations provide clear evidence of horticulture-induced contamination of these waters sampled in 2014 and 2015 from applied fertilisers, rather than animal effluent from farming, although future efforts should investigate nitrate isotope ratios of groundwaters located near dairy farms. Longer-term monitoring is recommended to understand the status of these waters with regards to their nitrate concentrations and isotopic signatures. With decreasing nitrogenous loads, the nitrate concentrations will subsequently decrease, and the isotopic values will shift into the 'denitrification' zone or towards a 'baseline' load in the Mixed Soil N and fertiliser zone.

Dual nitrate isotopes, combined with nitrate concentrations of surface water and groundwater, is a practical approach to improve our understanding of the origin and fate of nitrate in the Franklin area. The findings will inform future strategies around baseline nitrate monitoring, investigative surveillance and mitigation of this pervasive contaminant and will contribute to meeting the requirements of the National Policy Statement for Freshwater Management 2020 (Ministry for the Environment 2020).

#### 7.0 ACKNOWLEDGMENTS

Thanks to Coral Grant (Auckland Council), Paul White, Matt Coble and Magali Moreau (GNS Science) who provided useful feedback on the draft report.

#### 8.0 REFERENCES

- [APHA] American Public Health Association. 2012. 4500-NO<sub>3</sub><sup>-</sup> nitrogen (nitrate). In: *Standard methods for the examination of water and wastewater*. 22<sup>nd</sup> ed. Washington (DC): American Public Health Association.
- Auckland Regional Council. 1991. Pukekohe Plateau: groundwater resource report, water allocation and management plan, 1991. Auckland (NZ): Auckland Regional Council. 67 p. Technical Publication 109.
- Ballantine DJ, Davies-Colley RJ. 2014. Water quality trends in New Zealand rivers: 1989–2009. *Environmental Monitoring Assessment*. 186(3):1939–1950. doi:10.1007/s10661-013-3508-5.
- Burden RJ. 1982. Nitrate contamination of New Zealand aquifers: a review. *New Zealand Journal of Science*. 25(3):205–220.
- Clague JC, Stenger R, Clough TJ. 2015. Evaluation of the stable isotope signatures of nitrate to detect denitrification in a shallow groundwater system in New Zealand. *Agriculture, Ecosystems & Environment.* 202:188–197. doi:10.1016/j.agee.2015.01.011.
- Crush JR, Cathcart SN, Singleton P, Longhurst RD. 1997. Potential for nitrate leaching from different land uses in the Pukekohe area. *Proceedings of the New Zealand Grassland Association*. 59:55–58. doi:10.33584/jnzg.1997.59.2266.
- Daughney CJ, Wall M. 2007. Groundwater quality in New Zealand: state and trends 1995–2006. Lower Hutt (NZ): GNS Science. 65 p. Consultancy Report 2007/23. Prepared for the Ministry for the Environment.
- Foster C, Johnson K. 2021. Groundwater quality state and trends in Tāmaki Makaurau/Auckland 2010–2019. State of the Environment reporting. Revised October 2021. Auckland (NZ): Auckland Council, Research and Evaluation Unit (RIMU). Technical Report 2021/03-2.
- Francis GS, Trimmer LA, Tregurtha CS, Williams PH, Butler RC. 2003. Winter nitrate leaching losses from three land uses in the Pukekohe area of New Zealand. *New Zealand Journal of Agricultural Research*. 46(3):215–224. doi:10.1080/00288233.2003.9513548.
- Fujii K, Yamada T, Hayakawa C, Nakanishi A, Funakawa S. 2020. Decoupling of protein depolymerization and ammonification in nitrogen mineralization of acidic forest soils. *Applied Soil Ecology*. 153:103572. doi:10.1016/j.apsoil.2020.103572.
- Granger J, Wankel SD. 2016. Isotopic overprinting of nitrification on denitrification as a ubiquitous and unifying feature of environmental nitrogen cycling. *Proceedings of the National Academy of Sciences*. 113(42):E6391-E6400. doi:10.1073/pnas.1601383113.
- Ingley R, Groom J. 2021. River water quality in Tāmaki Makaurau/Auckland. 2019 annual reporting and national policy statement for freshwater management current state assessment. Auckland (NZ): Auckland Council, Research and Evaluation Unit. Technical report 2021/11.
- Jung H, Koh D-C, Kim YS, Jeen S-W, Lee J. 2020. Stable isotopes of water and nitrate for the identification of groundwater flowpaths: a review. *Water*. 12(1):138. doi:10.3390/w12010138.
- Kendall C. 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall C, McDonnell JJ, editors. *Isotope tracers in catchment hydrology*. Amsterdam (NL): Elsevier. p. 519–576.

- Kendall C, Aravena R. 2000. Nitrate isotopes in groundwater systems. In: Cook PG, Herczeg AL, editors. *Environmental tracers in subsurface hydrology*. Boston (MA): Springer. p. 261–297.
- Loo SE, Ryan MC, Zebarth BJ, Kuchta SH, Neilsen D, Mayer B. 2017. Use of δ<sup>15</sup>N and δ<sup>18</sup>O values for nitrate source identification under irrigated crops: a cautionary vadose zone tale. *Journal of Environmental Quality*. 46(3):528–536. doi:10.2134/jeq2016.08.0294.
- Martindale H, van der Raaij R, Daughney CJ, Morgenstern U, Singh R, Jha N, Hadfield J. 2019. Assessment of excess N2 for quantifying actual denitrification in New Zealand groundwater systems. *Journal of Hydrology (NZ)*. 58(1):1–17.
- McIlvin MR, Altabet MA. 2005. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Analytical Chemistry*. 77(17):5589–5595. doi:10.1021/ac050528s.
- Meijer K, Buckthought L, Curran-Cournane F, Martindale M, Prebble N, Long L. 2016. Elevated nitrate concentrations in Franklin surface and groundwater: a review. Auckland (NZ): Auckland Council. Technical report 2016/015.
- Ministry for the Environment. 2020. National Policy Statement for Freshwater Management 2020. Wellington (NZ): Ministry for the Environment; [accessed 2021 Oct 01]. <u>https://www.mfe.govt.nz/sites/default/files/media/Fresh%20water/national-policy-statement-for-freshwater-management-2020.pdf</u>
- Ministry of Health. 2018. Drinking-water Standards for New Zealand 2005 (Revised 2018). Wellington (NZ): Ministry of Health. 120 p.
- Moreau M, Riedi MA, Aurisch K. 2016. Update of national groundwater quality indicators: state and trends 2005–2014. Wairakei (NZ): GNS Science. 36 p. Consultancy Report 2015/107. Prepared for Ministry for the Environment.
- Morgenstern U, van der Raaij RW, Baisden WT, Stewart MK, Martindale H, Matthews A, Collins S. 2019. Ohau and Waikawa catchments of the Horowhenua Groundwater Management Zone: groundwater dynamics, source, and hydrochemical processes as inferred from the groundwater tracer data. Lower Hutt (NZ): GNS Science. 52 p. (GNS Science report; 2018/06).
- Nichols KL, Del Grosso SJ, Derner JD, Follett RF, Archibeque SL, Delgado JA, Paustian KH. 2018. Nitrous oxide and ammonia emissions from cattle excreta on shortgrass steppe. *Journal of Environmental Quality*. 47(3):419–426. doi:10.2134/jeq2017.12.0463.
- Norris M, Johnstone P, Green S, van der Klei G, van den Dijssel C, Thomas S, Wright P, Clark G.
  2017. The MPI SFF root zone reality project (401484) and the HortNZ northern fluxmeters project (HortNZ RI 1009) summary of year 1 and year 2 activity. [Auckland] (NZ): Plant & Food Research. 116 p. PFR SPTS no. 14210. Prepared for Foundation for Arable Research, Horticulture New Zealand, Environment Canterbury, Horizons Regional Council, Hawke's Bay Regional Council, Environment Waikato, Auckland Regional Council, Ravensdown Cooperative Ltd.
- [OECD] Organisation for Economic Cooperation and Development. 2017. OECD economic surveys: New Zealand 2017. Paris (FR): OECD Publishing. [accessed 2021 Oct 01]. <u>https://www.oecdilibrary.org/economics/oecd-economic-surveys-new-zealand-2017\_eco\_surveys-nzl-2017-en</u>
- Parfitt RL, Stevenson BA, Dymond JR, Schipper LA, Baisden WT, Ballantine DJ. 2012. Nitrogen inputs and outputs for New Zealand from 1990 to 2010 at national and regional scales. *New Zealand Journal of Agricultural Research*. 55(3):241–262. doi:10.1080/00288233.2012.676991.

- Rogers KM, van der Raaij R, Phillips A, Stewart MK. 2022. A national isotope survey to define New Zealand's nitrate contamination sources. *Journal of Hydrology* (in review).
- Silva SR, Kendall C, Wilkison DH, Ziegler AC, Chang CCY, Avanzino RJ. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *Journal of Hydrology*. 228(1–2):22–36. doi:10.1016/S0022-1694(99)00205-X.
- Snow D. 2018. Nitrate-N isotope results and interpretation. Lincoln (NE): University of Nebraska Water Science Laboratory. Prepared for Eastern Research Group Prime Contract #EP-W-15-006; [accessed 2021 Oct 01]. <u>https://www.epa.gov/sites/default/files/2018-10/documents/isotope\_study\_report\_erg\_csd-may\_june2018.pdf</u>
- Stewart MK, Aitchison-Earl PL. 2020. Irrigation return flow causing a nitrate hotspot and denitrification imprints in groundwater at Tinwald, New Zealand. *Hydrology and Earth System Sciences*. 24(7):3583–3601. doi:10.5194/hess-24-3583-2020.
- Stewart MK, Stevens G, Thomas JT, van der Raaij R, Trompetter V. 2011. Nitrate sources and residence times of groundwater in the Waimea Plains, Nelson. *Journal of Hydrology (NZ)*. 50(2):313–338.
- Suchy M, Wassenaar LI, Graham G, Zebarth B. 2018. High-frequency NO3– isotope (δ<sup>15</sup>N, δ<sup>18</sup>O) patterns in groundwater recharge reveal that short-term changes in land use and precipitation influence nitrate contamination trends. *Hydrology and Earth System Sciences*. 22(8):4267–4279. doi:10.5194/hess-22-4267-2018.
- United Nations. 2014. New York (NY): United Nations. International decade for action 'Water for Life' 2005–2015: Water quality; [updated 2014 Oct 23; accessed 2021 Oct 01]. https://www.un.org/waterforlifedecade/quality.shtml
- van der Raaij RW. 2015. Groundwater residence times and chemistry of the Pukekohe and Bombay basalt aquifers. Lower Hutt (NZ): GNS Science. 50 p. (GNS Science report; 2015/11).
- Viljevac Z, Murphy G, Smaill A, Crowcroft G, Bowden D. 2002. South Auckland groundwater, Kaawa aquifer recharge study and management of the volcanic and Kaawa aquifers. Auckland (NZ): Auckland Regional Council. 193 p. Technical Publication 133.
- Wassenaar LI. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of <sup>15</sup>N and <sup>18</sup>O in NO<sub>3</sub>-. *Applied Geochemistry*. 10(4):391–405. doi:10.1016/0883-2927(95)00013-A.
- Watson SW, Valois FW, Waterbury JB. 1981. The Family Nitrobacteraceae. In: Starr MP, Stolp H, Trüper HG, Balows A, Schlegel HG, editors. *The Prokaryotes: a handbook on habitats, isolation, and identification of bacteria*. Berlin (DE): Springer-Verlag. p. 1005–1022.
- Wells NS, Baisden WT, Horton T, Clough TJ. 2016. Spatial and temporal variations in nitrogen export from a New Zealand pastoral catchment revealed by stream water nitrate isotopic composition. *Water Resources Research*. 52(4):2840–2854. doi:10.1002/2015WR017642.
- White PA, Moreau M, Mourot F, White JT, Johnson K, Hill MP. 2019. Groundwater in the Franklin area. Wairakei (NZ): GNS Science. 105 p. Consultancy Report 2019/81. Prepared for Auckland Council, Waikato Regional Council.
- [WHO] World Health Organization. 2016. Nitrate and nitrite in drinking-water: background document for development of WHO guidelines for drinking-water quality. Geneva (CH): World Health Organization. 33 p.
- [WHO] World Health Organization. 2017. Guidelines for drinking-water quality. 4<sup>th</sup> ed., incorporating the 1<sup>st</sup> addendum. Geneva (CH): World Health Organization. 631 p.

- Widory D, Kloppmann W, Chery L, Bonnin J, Rochdi H, Guinamant J-L. 2004. Nitrate in groundwater: an isotopic multi-tracer approach. *Journal of Contaminant Hydrology*. 72(1–4):165–188. doi:10.1016/j.jconhyd.2003.10.010.
- Williams PH, Tregurtha CS, Francis GS. 2000. Strategies for reducing nitrate leaching from vegetable crops grown in Pukekohe. In: *Fertiliser research: unlocking the potential of New Zealand Agriculture: conference proceedings. New Zealand Fertiliser Manufacturers' Research Association 26<sup>th</sup> Technical Conference; 2000 Nov 14–15; Lincoln, New Zealand.
   [Auckland] (NZ): New Zealand Fertiliser Manufacturers' Research Association. p. 70–76.*
- Wilson SR, Close ME, Abraham P, Sarris TS, Banasiak L, Stenger R, Hadfield J. 2020. Achieving unbiased predictions of national-scale groundwater redox conditions via data oversampling and statistical learning. *Science of the Total Environment*. 705:135877. doi:10.1016/j.scitotenv.2019.135877.
- Winkler MKH, Yang J, Kleerebezem R, Plaza E, Trela J, Hultman B, van Loosdrecht MCM. 2012. Nitrate reduction by organotrophic Anammox bacteria in a nitritation/anammox granular sludge and a moving bed biofilm reactor. *Bioresource Technology*. 114:217–223. doi:10.1016/j.biortech.2012.03.070.
- Xue D, Botte J, De Baets B, Accoe F, Nestler A, Taylor P, Van Cleemput O, Berglund M, Boeckx P. 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. *Water Research*. 43(5):1159–1170. doi:10.1016/j.watres.2008.12.048.
- Zhang Y, Shi P, Song J, Li Q. 2019. Application of nitrogen and oxygen isotopes for source and fate identification of nitrate pollution in surface water: a review. *Applied Sciences*. 9(1):18. doi:10.3390/app9010018.

APPENDICES

This page left intentionally blank.

# APPENDIX 1 FRANKLIN AREA DATASET 1

Site No.	Order Sampled	Date	Time	Site Name	Туре	Easting (NZTM)	Northing (NZTM)	DO (%)	DO (ppm)	EC (mS/cm)	Temp (°C)	рН	Salinity (psu)	Total N (mg/L)	NH4-N (mg/L)	DON (mg/L)	NO3-N (mg/L)	NO2-N (mg/L)	pH (lab)	δ <sup>15</sup> N (‰)	δ <sup>18</sup> Ο (‰)
LB01	1	20/05/2014	9.30 am	Rifle Range Rd	Surface water	1766295	5880987	No measu Sample ta	urements ta aken from p	ken. onded water	next to bore	es, not bor	e water.	3.1	0.019	0.51	1.4	0.002	6.6	7.26	4.38
LB02	8	20/05/2014	2.10 pm	Fielding Rd bore	Groundwater	1774435	5890642	2.5	0.24	304.4	17.62	7.8	0.17	0.72	0.58	0.1	0.002	0.002	7.8	6.52	7.18
LB03	5	20/05/2014	10.55 am	BP Bombay	Groundwater	1775891	5881877	78.3	7.94	224.1	14.53	7.11	0.13	11	0.005	0.1	11	0.002	7.2	4.96	5.56
LB04	2	20/05/2014	9.40 am	Patumahoe Spring	Spring	1764114	5889239	84.8	8.52	300.5	15.11	6.19	0.18	29	0.005	0.1	26	0.002	6.5	3.5	3.69
LB05	7	20/05/2014	12.00 pm	Hickey Spring (Seddon St)	Spring	1768720	5882057	86.1	8.58	251.1	15.53	6.62	0.15	21	0.005	0.1	20	0.002	6.5	4.32	4.44
LB06	3	20/05/2014	9.55 am	Whangamaire Up (Orstrich Rd)	Stream	1763578	5884625	87.7	9.48	237.4	11.77	7.21	0.15	17	0.012	0.25	17	0.0078	7.4	6.51	5.7
LB07	4	20/05/2014	10.15 am	Whangamaire Dwn (Charles Rd)	Stream	1765440	5889202	55.8	5.98	229.6	12.24	7.13	0.15	11	0.008	0.2	11	0.0024	7.1	6.34	5.97
LB08	6	20/05/2014	11.15 am	Ngakoroa Up (Mill Rd)	Stream	1775164	5881624	90.9	9.83	132.6	11.82	7.34	0.08	3.3	0.017	0.24	3	0.0048	7.3	7.4	5.78
LB09	9	20/05/2014	12.50 pm	Ngakoroa Dwn (Kern Rd)	Stream	1773491	5886645	89.8	9.82	155.3	11.28	7.45	0.1	3.1	0.013	0.17	2.9	0.0034	7.5	9.16	6.99
LB10	10	20/05/2014	1.00 pm	Hingaia Up (Ararimu Rd)	Stream	1775380	5887586	96.4	10.35	165.5	12.14	7.72	0.1	4.9	0.023	0.23	4.7	0.0054	7.7	5.35	5.39
LB11	11	20/05/2014	1.25 pm	Hingaia Mid (Quarry Rd)	Stream	1774461	5889625	92.7	10.04	153.9	11.72	7.6	0.1	3.6	0.018	0.26	3.5	0.0068	7.6	6	5.97
LB12	12	20/05/2014	1.45 pm	Hingaia Dwn (Flanagan Rd)	Stream	1773119	5891376	108.4	11.44	185.4	12.66	8.61	0.12	3.4	0.016	0.24	2.9	0.0059	8	5.53	5.42

# APPENDIX 2 ROOTZONE REALITY PROJECT DATASET 2

SIL ID	External Site ID	Site ID	Replicate Number	Fluxmeter	Collection Date	NO3-N mg/L	δ¹⁵N (‰)	δ <sup>18</sup> Ο (‰)
N-1600001	NS2-1	North Site 2-1	1	1	9/07/2015	30.42	3.2	2.0
N-1600002	NS2-3	North Site 2-3	1	3	9/07/2015	41.17	2.5	1.1
N-1600003	NS2-5	North Site 2-5	2	1	9/07/2015	13.34	3.2	0.6
N-1600004	NS2-7	North Site 2-7	2	3	9/07/2015	29.92	3.5	1.1
N-1600005	NS2-9	North Site 2-9	3	1	9/07/2015	30.02	2.0	2.0
N-1600006	NS2-11	North Site 2-11	3	3	9/07/2015	21.77	3.1	2.0
N-1600007	NS2-13	North Site 2-13	1	1	6/08/2015	24	1.6	1.0
N-1600008	NS2-15	North Site 2-15	1	3	6/08/2015	28.53	3.5	-2.0
N-1600009	NS2-17	North Site 2-17	2	1	6/08/2015	22.59	2.0	4.8
N-1600010	NS2-19	North Site 2-19	2	3	6/08/2015	9.63	2.0	0.7
N-1600011	NS2-21	North Site 2-21	3	1	6/08/2015	25.46	1.7	0.2
N-1600012	NS2-23	North Site 2-23	3	3	6/08/2015	36.42	-1.4	3.7
N-1600013	NS2-25	North Site 2-25	1	1	8/09/2015	43.7	-6.7	2.6
N-1600014	NS2-27	North Site 2-27	1	3	8/09/2015	32.39	0.1	2.8
N-1600015	NS2-29	North Site 2-29	2	1	8/09/2015	21.33	-2.7	3.4
N-1600016	NS2-31	North Site 2-31	2	3	8/09/2015	12.67	-2.1	10.0
N-1600017	NS2-33	North Site 2-33	3	1	8/09/2015	44	-4.6	1.7
N-1600018	NS2-35	North Site 2-35	3	3	8/09/2015	35.38	0.7	7.9
N-1600019	NS2-37	North Site 2-37	1	1	1/10/2015	36.95	-6.3	2.1
N-1600020	NS2-39	North Site 2-39	1	3	1/10/2015	39.11	0.3	5.6
N-1600021	NS2-41	North Site 2-41	2	1	1/10/2015	54.08	-2.2	2.2
N-1600022	NS2-43	North Site 2-43	2	3	1/10/2015	48.19	-2.1	8.9
N-1600023	NS2-45	North Site 2-45	3	1	1/10/2015	45.82	-3.7	2.5
N-1600024	NS2-47	North Site 2-47	3	3	1/10/2015	69.6	-2.0	5.7