Nitrate transport and transformation processes in the Pukekohe–Bombay area

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ABSTRACT

High-intensity land use – mainly market gardening on the weathered basalts that form rich horticultural soils – has caused high nitrate concentrations in groundwater and streams discharging from the Pukekohe and Bombay volcanoes. These concentrations significantly exceed the national bottom line for nitrate toxicity in rivers from the National Policy Statement for Freshwater Management 2020 and maximum acceptable value for nitrate in drinking water in this area.

The main nitrate load in the Pukekohe–Bombay area, from market-gardening activity, infiltrates into large groundwater stores in the basalt formation. It discharges mainly through three large springs: the Patumāhoe and Hickey springs at Pukekohe, with a Mean Transit Time (MTT) of 17 years; and Hillview Spring at Bombay, with a MTT of 36 years.

Within the basalt formation, no electron donors (for example, from organic matter) are present to facilitate microbial denitrification reactions. Without denitrification in this groundwater system, the entire nitrate load into the basalt formation eventually returns to the surface with a lag time of 17 and 36 years at the abovementioned springs and high nitrate-N concentrations up to 25 mg/L. This causes high nitrate-N concentrations in the receiving streams near the springs: 9 mg/L in Hingaia Stream, 14 mg/L at Whangapouri Creek and 19 mg/L in Whangamaire Stream. Because of the long MTTs of nitrate load through the basalt formation, the results of potential source-mitigation actions will be significantly delayed.

For this study, several stream sites that had been comprehensively sampled during summer baseflow conditions were re-sampled during winter baseflow. This was done to improve understanding of the hydrologic system and its associated nitrate loads, including seasonal variability. Similar concentrations of radon in these streams between summer and winter indicate that increased flow contributions during winter baseflow are also maintained from a groundwater system, as opposed to shallow flow with MTTs of only days, and surface run-off, which would both have lower radon concentrations. Tritium data showed that all sampled streams contained younger water in winter compared to summer, indicating activation of shallower flow paths into the streams during the wet season. However, even at winter baseflow, the stream waters were still relatively old, with MTTs between 6 and 12.5 years.

In stream catchments where shallow flow paths were activated during winter and contributed to basalt-discharge-dominated flow, nitrate concentrations were lower compared to summer, likely due to dilution. Where the discharge from a large basalt spring also dominated the flow at winter baseflow, nitrate concentrations were similar between summer and winter. In catchments without basalt discharge, nitrate concentrations were higher during winter baseflow compared to summer baseflow where shallow flow paths were activated during winter. This applies particularly to the area with Pleistocene geology, resulting in nitrate from pastural farming (dairy and drystock) being flushed into the streams via near-surface and shallow groundwater flow paths.

While the passage of the high nitrate load through the basalt formation and the seasonal flushing of nitrate from the pastoral grazing land in the Pleistocene is reasonably well understood, little is known about nitrate sinks within this catchment. Nitrate loads significantly decreased along the course of most of the sampled streams. Some streams, mainly those in the Pleistocene formation, had near-zero nitrate concentrations despite pastural farming being the predominant land use in their catchments. This implies that there are significant nitrate sinks in these catchments. Better understanding of these nitrate sinks may enable enhancement of natural attenuation of existing high nitrate loads in these waterways.

Anoxic groundwater discharges from the volcanics/unconsolidated formations, the presence of excess nitrogen (the decay product of denitrification) in groundwater that has evolved to complete denitrification, and potential dilution of stream nitrate loads by anoxic groundwater discharges indicate that denitrification in groundwater systems occurs in these formations. Unfortunately, it was not possible to access significant anoxic discharges to quantify their contributions to the overall nitrate sink.

The largest nitrate sinks within the catchment were found within the surface waterways – in streams and ponds/wetlands. Nitrate stable isotopes, despite their science being somewhat ambiguous, indicate that the main process of nitrate removal from these waterways is through natural denitrification into nitrogen gases. This is likely to occur within the shallow layers of the sediments, with the nitrate transported into the sediments through hyporheic exchange. Denitrification, as opposed to uptake by aquatic plants, implies that the nitrate is being removed from the waterways permanently.

In smaller streams (Ngakoroa, Oira) and a pond (Puk5), 80–100% of the nitrate from land-use activities was found to have been removed. In two of the largest streams (Whangamaire and Whangapouri), nitrate-load reductions of c. 30% were observed between the sampled sites along the courses through the Pleistocene formations. It is likely that denitrification also occurs above and below these sampled stream sections, implying that total nitrate load reduction over the entire stream length is significantly higher. For example, in the top part of Whangamaire Stream, between Patumāhoe Spring and the first sampling site, nitrate concentrations had already been reduced by 30%, probably mainly within the pond/wetland at Patumāhoe Spring. Ponds/wetlands and stream beds appear to be efficient nitrate sinks in the Pukekohe–Bombay area.

In the Pleistocene formation, where land use is mostly pastural farming, nitrate is flushed out seasonally. This area discharges water and nitrate loads only via shallow flow paths, which are not active in summer. In Oira Creek, for example, nitrate had been completely removed from the water during the low summer flow. But even in winter, when discharges are active, it is likely that more than 80% of the nitrate is being removed from the water. This nitrate removal may partially occur within the stream bed but could also have significant contributions from within the soil and near the redox interface in this geologic formation.

KEYWORDS

Pukekohe volcano, Bombay volcano, basalt, groundwater, nitrate load, denitrification, water transit time, groundwater storage, nitrate stable isotopes, tritium, radon

1.0 INTRODUCTION

Since the 1970s, high-intensity land use that began in the 1950s – mainly market gardening on the weathered basalts that form rich horticultural soils – has caused high nitrate concentrations in groundwater and streams discharging from the Pukekohe and Bombay volcanoes (Crush et al. 1997; Auckland Regional Council 2010). Some of the groundwater concentrations exceed New Zealand's Drinking Water Standards maximum acceptable value of 11.3 mg/L NO_3-N (Taumata Arowai 2024). These groundwaters with their high nitrate loads discharge via springs into streams, which has a negative effect on the health of the streams. Observed concentrations for most of the streams in the Pukekohe–Bombay area significantly exceed the national bottom line for nitrate toxicity in rivers of 2.4 mg/L NO_3-N (annual median) set in the National Policy Statement for Freshwater Management (NPS-FM) 2020 (Ministry for the Environment 2020).

The development of improved nutrient-management tools to minimise the environmental impacts of land-use activities requires a more complete conceptual understanding of groundwater and flow, connection with surface water, nitrate pathways, potential risk of nitrate contamination of deeper aquifers, 'future nitrate loads to come' and connections within the aquifer system (Stenger et al. 2022).

In 2022, to inform nitrate-mitigation strategies for the Pukekohe vegetable-growing area[1], Auckland Council commissioned GNS Science to provide an understanding of the main processes of nitrate transport and transformation from land through groundwater to streams discharging into Manukau Harbour. This work was done under service agreements PIN CW9929 (project 900W4167) and CW137092 (project 900W4242). GNS Science's Endeavour programmes 'Te Whakaheke o Te Wai' and 'Future proofing groundwater systems' provided co-funding to interpret:

- age- and source-tracer data to provide an improved understanding of the groundwater flow dynamics in this system, and
- excess nitrogen and nitrate isotope data for assessing denitrification in groundwater and surface water.

GNS Science's Groundwater Strategic Science Investment Fund (SSIF) provided co-funding for development and application of excess-nitrogen gas-tracer techniques.

Phase 1 of this project used groundwater age- and source-tracer techniques to enable detailed understanding of groundwater flow processes, including conceptual groundwater flow, connection with surface water, nitrate pathways and 'future nitrate loads to come' (Morgenstern et al. 2023).

In addition to improving the understanding of nitrate transport processes through groundwater systems, Phase 2 of this project (this report) aims to investigate whether natural nitrate attenuation occurs in the groundwater systems in the Pukekohe–Bombay area by measuring excess nitrogen in groundwater discharges. Excess nitrogen ('excess N_2') is the main product of denitrification. It accumulates along the groundwater flow paths, providing a quantitative measure of nitrogen from denitrification (Burbery 2018). We also applied nitrate stable isotopes

1 The NPS-FM 2020 came into force in September 2020. It included provisions related to "specified vegetable growing areas". Pukekohe was one of the two specified vegetable-growing areas identified. In December 2023, the Court of Appeal quashed Clause 3.33 and Appendix 5 of the NPS-FM, removing the provisions relating to specified vegetable-growing areas.

in both phases of this project (Rogers 2022, 2024). Nitrate isotopes have limitations in providing quantitative measures of denitrification. However, these may provide the source of nitrate and a qualitative indication of denitrification in surface waters where the excess N_2 method cannot be applied.

Phase 2 of this project was proposed for 2023. However, sampling was delayed due to the disturbance of the hydrologic system caused by the Auckland Anniversary flooding on 27 January 2023. While we were able to complete part of the Phase 2 sampling in 2022, mainly from the large springs discharging the Pukekohe and Bombay basalt formations, the remaining sampling for Phase 2 was possible only at the end of 2023, when the hydrologic system returned to summer baseflow.

In the Phase 1 report (Morgenstern et al. 2023) for this project, we summarised the geology and hydrogeology and established the drainage patterns of the area. The report showed active subsurface drainage through large groundwater reservoirs occurring through the basalt lava of the Pukekohe and Bombay volcanoes and, to a lesser extent, through the unconsolidated volcanic materials.

Despite the long transit time through the basalt formations (18 years for the Patumāhoe and Hickey springs, 36 years for Hillview Spring), the water in these large discharges is oxic, suggesting an absence of denitrification in the basalt groundwater system. This agrees with the high nitrate concentrations observed in these springs (15–25 mg/L NO_3-N), which is caused by nitrate leaching from predominantly market-gardening activity in the basalt recharge areas. The high spring nitrate loads subsequently dominate nitrate concentrations in the receiving streams.

However, not all streams measured were found to carry high nitrate loads. Nitrate concentrations in some streams were very low (<0.02 mg/L NO_3-N), despite significant portions of their catchments being used for pastural (dairy and drystock) farming. Further, despite a high proportion of market-gardening coverage in the recharge area, in one stream nitrate concentrations decreased significantly downstream where anoxic groundwater appeared to discharge into the stream from unconsolidated volcanics. This suggests that, outside of the basalt formations, possibly related to the unconsolidated volcanic deposits, groundwater systems with active anaerobic denitrification are discharging low-nitrate water into streams in these areas.

In addition to providing a more complete understanding of discharges of nitrate loads into streams from weathered basalts used for market gardening, this Phase 2 report also provides a better understanding of nitrate load discharges from land dominated by pastoral grazing activities, which was not covered in the Phase 1 report. Pastural grazing activities include dairy, beef cattle and lifestyle blocks. Appendix 2 shows a detailed map of main farm types and Figures 5.7, 5.9 and 5.12 include an overview of the areas of vegetable production and dairy/grazing.

Pastural grazing is located mainly in the areas of Pleistocene deposits, which were found to allow very little active water circulation through deeper groundwater systems. Rainfall infiltration into these deposits therefore drains, mainly during the wet season, through shallow, fast-flow paths without sufficient storage reservoir to sustain significant stream baseflow during summer. As a result, the main nitrate loads from pastoral land were not captured during the summer baseflow sampling. These nitrate loads are flushed into the streams during the wet winter season when the shallow flow paths are active.

For this reason, Morgenstern et al. (2023) suggested [Recommendation 8.1(1)] that Auckland Council:

> *"Perform a similar study at winter baseflow conditions to quantify (i) baseflow and nitrate loads from the basalt aquifers during winter; and (ii) surface drainage from the Pleistocene deposits and unconsolidated volcanic deposits, as well as related nitrate loads into the streams and harbour (high dairy cover). Note that the nitrate flow pathways from the Pleistocene deposits and unconsolidated volcanic deposits are likely to be active only during the wet season."*

In response to this recommendation, Auckland Council sampled 13 stream sites on 8 August 2023, covering winter baseflow conditions. Sampling included previously sampled high-nitrate streams draining market-gardening-covered basalt formations, low-nitrate streams draining mainly pastoral-grazing-covered Pleistocene and unconsolidated volcanic deposits and a new stream not sampled previously draining pastoral grazing land. The streams were sampled for radon, tritium, water stable isotopes and hydrochemistry to provide information on groundwater recharge source, groundwater discharge into streams and water transit time.

In addition to radon, tritium and water stable isotopes, the streams, springs and seeps were sampled for nitrate stable isotopes during summer and winter baseflow in 2022 and 2023. The results are presented and discussed in Rogers (2024) in relation to general dual isotope trends and nitrate sources.

In this report, we present a detailed spatial analysis of the nitrate isotope composition of the spring, seep and stream waters to identify nitrate sinks on stream-catchment scales, including contrasting nitrate loads between summer and winter baseflow. Groundwater source and age tracers are interpreted to provide understanding of flow dynamics, also contrasting between summer and winter baseflow for streams. For the springs and seeps, excess-N_2 data is used to quantify denitrification in their respective groundwater systems. For the streams, the dual nitrate isotopes are used to differentiate between different nitrate sinks and microbial denitrification versus uptake.

2.0 SETTING

2.1 Hydrology and Hydrogeology

Previous investigations of the hydrology and the hydrogeology of the Pukekohe and Bombay area are summarised in detail in Morgenstern et al. (2023) and, together with the age-, isotope- and chemistry-tracer information, provide a detailed understanding of groundwater flow processes in this area.

Active subsurface drainage through large groundwater reservoirs only occurs through the basalt lava of the Pukekohe and Bombay volcanoes and, to a lesser extent, through the unconsolidated volcanic materials, including tuff and tephra. The active groundwater flow systems in the basalt lava have sufficient storage to maintain significant stream baseflow over the course of years.

Groundwaters in the aquifers underlying the Pleistocene deposits and in the deep basalt aquifers are all old, implying very little active circulation through these deeper systems. Rainfall infiltration into the Pleistocene deposits therefore drains, mainly during the wet season, through shallow, fast-flow paths, without a sufficient storage reservoir to sustain significant stream baseflow during the dry season.

Three main spring systems – Hickey, Hillview and Patumāhoe – drain the Pukekohe–Bombay basalt lava groundwater systems, feeding three main streams: Whangamaire Stream, Whangapouri Creek and Hingaia Stream. On the southwestern flanks of these volcanoes, the upper reaches of the Mauku and Ngakoroa streams also receive discharge from the basalt lava.

Whangamaire Stream and Whangapouri Creek drain the Pukekohe basalt lava at the northern perimeter of the plateau, where they receive most of their flow. Groundwater age, isotopes and hydrochemistry from these locations match those of the water in these streams, including high nitrate concentrations. There was no significant flow gain north of the basalt lava within the Pleistocene deposits, indicating absence or insignificance of deep groundwater flux to these streams. This implies that these areas drain only via shallow flow paths that are depleted during summer baseflow conditions.

Hingaia Stream receives water in its upper reaches partially from impermeable greywacke basement rock catchments and partially from the northeastern perimeter of the basalt lava. The mixing of essentially pristine water from the greywacke catchment with water recharged in areas of high nitrate-leaching activities results in medium nitrate concentrations (2.5–4.3 mg/L NO_3-N). At the northern perimeter of the volcano, where Hillview Spring discharges into Hingaia Stream, flow more than doubles, as does the nitrate concentration. Groundwater ages, isotopes and hydrochemistry in this area match those of the water discharging from Hillview Spring, including high nitrate concentrations.

In the upper reaches of Ngakoroa Stream, isotopes and nitrate concentrations indicate flow contribution from the southwestern, low-altitude flanks of the Bombay basalt lava. North of the basalt, the stream does not gain any significant flow. However, nitrate concentration decreases significantly, probably due to in-stream processes.

In summer baseflow conditions, Oira Creek has very low flow, discharging locally recharged, relatively old, groundwater with low nitrate concentrations. In a similar way, Waitangi Stream also discharges locally recharged groundwater with low nitrate concentrations.

Mauku Stream gains flow in its upper reaches from the Pukekohe basalt lava along its southwestern perimeter. Groundwater ages, isotopes and hydrochemistry in this basalt lava aquifer match those of the water in the upper reaches of the stream. From the northwestern flanks of the Pukekohe volcano, the stream receives significant amounts (approximately 60 L/s) of water from a groundwater system recharged at lower altitudes and likely to be anoxic. Stream flow more than doubles there, while nitrate concentrations become diluted, despite the land in this area being used for purposes associated with high nitrate leaching. This indicates that there is potential for significant nitrate attenuation in this groundwater system. Denitrification may also be possible in the shallow drainage system of the Pleistocene deposits, near the redox interface.

The introduction of high-intensity market gardening in the 1950s, associated with high nitrate leaching, has resulted in high nitrate loads into the transmissive basalt lava of the Pukekohe and Bombay volcanoes. These basalt lavas discharge oxic groundwater into streams, indicating an absence of organic matter and inorganic electron donors in the aquifer, which would be required for the facilitation of microbial reactions, including denitrification. Without denitrification, the nitrate load is expected to discharge from this basalt lava without any nitrate attenuation, with a lag time equal to the travel time (age) of the water through the aquifer.

On average, it takes 18 years for the nitrate load to travel through the Pukekohe basalt lava and 36 years for it to travel through the Bombay basalt lava. Assuming constant nitrate load for 65 years since the onset of industrial agriculture in c. 1955, groundwater discharges from the basalt have essentially adjusted to the high nitrate loads from intensive land use in the recharge areas. However, nitrate concentrations in the deeper groundwater are still increasing and adjusting to the high nitrate loads in the recharge areas. Due to the relatively long lag times noted above, the effects of reducing land-use nitrate loads will take decades to manifest in the baseflow spring discharges from the basalt in the Pukekohe–Bombay area.

2.2 Sampling

To improve understanding of water and nitrate load contributions from pathways that are active only during the wet winter season, Auckland Council gauged and re-sampled[2] 12 stream sites during winter baseflow conditions on 8 August 2023. One new stream (Te Hihi) was introduced to represent the discharge from Pleistocene deposits with predominant pastoral farming (dairy and drystock) catchment land use. In Figure 2.1, the stream sites sampled during winter baseflow are indicated by magenta labels. The streams (Table 2.1) were gauged near bridges. At these gauging sites, stream field parameters were also measured, and water samples were collected for tritium, stable-isotope (water and nitrate), radon and hydrochemistry analysis. To capture more detail about groundwater discharges into these streams, radon samples were also collected upstream and downstream from the gauging sites, as far as practical, but usually several tens of metres. The flow and field parameters, together with radon results, are listed in Table 2.1. Tracer analysis results from samples collected only at the gauging sites are listed in Table 4.1. The full suite of analysed parameters are available as Appendix 3.

Age and source tracers were sampled from 11 springs and seeps in 2022 and 2023 to characterise the groundwater flow system, and neon samples were taken to enable quantification of excess-N_2 from denitrification. Gas-tracer sampling (including excess-N_2) requires sampling at discrete springs with a reasonable flow. This enables pumping or siphoning water from below the surface to exclude contact of the water with air, which would compromise the gas-tracer signature.

2 Sampled during the previous summer on 2 February 2022.

The large springs (Patumāhoe, Hickey and Hillview), together with a small spring at Crisp Avenue and a spring at Pilgrim Road providing domestic supply were sampled during the first reconnaissance trip on 7 April 2022, by Uwe Morgenstern (GNS Science) and Kolt Johnson (Auckland Council). A second sampling campaign on 15 November 2023 targeted springs and seeps on the northwestern flanks of the Pukekohe volcano, where anoxic low-nitrate discharges were expected (Morgenstern et al. 2023, Section 8.2). Sampling was done by Uwe Morgenstern, Peter Gardner (GNS Science) and Laura Buckthought (Auckland Council). Photos of the spring and seep sampling sites, with sampling arrangements to capture seepage water without air contact for gas-tracer analysis, are shown in Appendix 1.

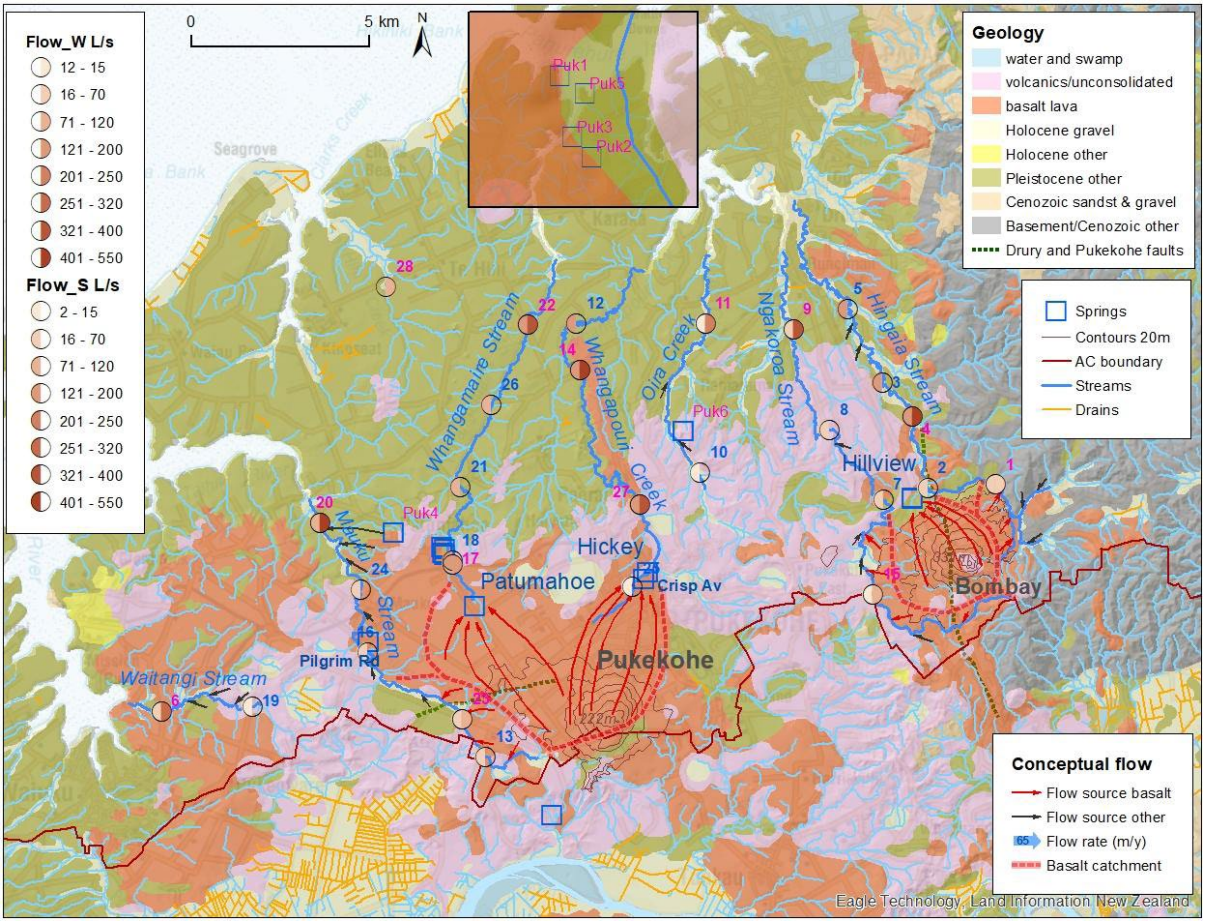


Figure 2.1 Sampling sites and stream flow in the Pukekohe–Bombay area. Previously sampled stream sites (blue labels) and conceptual flow are from Morgenstern et al. (2023). Winter sampling sites and a new site (28) are shown with magenta labels. Only 12 previously sampled stream sites were re-sampled in winter. Stream flow during summer baseflow (2 February 2022) is shown in the left half of the circles and during winter baseflow (8 August 2023) in the right half, at identical scales. The inset shows the cluster of springs and seeps near the upper Whangamaire Stream; site 18.

Hickey and Hillview springs are contained, as these are associated with municipal drinking-water supplies. Therefore, these could not be sampled directly at the springs. The springs were sampled at the first access point that allowed sampling, very likely prior to air contact. Patumāhoe Spring was sampled at a discrete outflow at the base of the road, next to the old, abandoned drinking-water well. The spring at Crisp Avenue is a small discharge from the bank of Whangapouri Creek opposite Hickey Spring. The spring at Pilgrim Road was sampled by lowering a Bennett pump in beside the domestic pump.

Table 2.1 Stream winter baseflow sampling site coordinates, field parameters and radon results. Radon samples were collected at the gauging sites (GS) at the road bridges, as well as upstream (US) and downstream (DS) from the bridges, as far as practical but usually several tens of metres. Flows were also gauged at some representative stream sites on the day of spring/seep sampling 15 November 2023. Data from previous sampling campaigns are included in grey for comparison.

Site No.	Site ID	NZTM Easting	NZTM Northing	Flow (L/s)			Electrical Conductivity (µS/cm)		Dissolved Oxygen (mg/L)		pH	Temperature (°C)	Radon (Bg/L)		±
				2/02/22	8/08/23	15/11/23	2/02/22	8/08/23	2/02/22	8/08/23	8/08/23	8/08/23	2/02/22	8/08/23	8/08/23
1	Hingaia at Cascades (US)	1778675	5884685	-	-	-	-	-	-	-	-	-	0.6	0.9	0.1
	Hingaia at Cascades (GS)	1775156	5881614	67	53	-	198	129	9.4	11.1	7.33	10.5	0.49	-	-
	Hingaia at Cascades (DS)	1778531	5884743	-	-	-	-	-	-	-	-	-	0.46	0.3	0.1
4	Hingaia at Maxted Rd (US)	1776260	5886530	-	-	-	-	-	-	-	-	-	0.19	0.6	0.1
	Hingaia at Maxted Rd (GS)	1776266	5886598	152	540	-	253	178	9.6	11.2	7.54	11.4	0.19	-	-
	Hingaia at Maxted Rd (DS)	1776200	5886637	-	-	-	-	-	-	-	-	-	0.12	0.7	0.1
23	Mauku at Fallows Bridge (US)	1763621	5878050	-	-	-	-	-	-	-	-	-	0.66	1.6	0.2
	Mauku at Fallows Bridge (GS)	1763614	5878117	26	100	-	285	261	7.9	9.7	6.95	12.7	0.46	1.6	0.2
	Mauku at Fallows Bridge (DS)	1763628	5878178	-	-	-	-	-	-	-	-	-	0.41	1.6	0.2
20	Mauku at Swede (Patullo Road) (US)	1759661	5883527	-	-	-	-	-	-	-	-	-	0.53	0.4	0.1
	Mauku at Swede (Patullo Road) (GS)	1759645	5883625	107	490	213	280	231	7.8	10.5	7.21	11.8	0.51	0.7	0.1
	Mauku at Swede (Patullo Road) (DS)	1759588	5883687	-	-	-	-	-	-	-	-	-	0.46	0.7	0.1
15	Ngakoroa at Mill Road (US)	1775181	5881562	-	-	-	211	-	-	-	-	-	0.58	0.9	0.1
	Ngakoroa at Mill Road (GS)	1775156	5881614	12	99	-	211	149	-	10.5	7.17	10.9	0.65	-	-
	Ngakoroa at Mill Road (DS)	1775159	5881666	-	-	-	209	-	-	-	-	-	0.24	0.4	0.1
9	Ngakoroa at Runciman Rd (US)	1772942	5888982	-	-	-	-	-	-	-	-	-	0.33	0.5	0.1
	Ngakoroa at Runciman Rd (GS)	1772926	5889050	41	392	-	245	185	4.5	9.8	7.04	10.6	0.35	-	-
	Ngakoroa at Runciman Rd (DS)	1772910	5889125	-	-	-	-	-	-	-	-	-	0.26	0.4	0.1
11	Oira at Swing Bridge (US)	1770429	5889133	-	-	-	-	-	-	-	-	-	0.6	0.7	0.1
	Oira at Swing Bridge (GS)	1770444	5889210	14	209	-	232	152	1.8	9.3	6.78	10.9	0.69	-	-
	Oira at Swing Bridge (DS)	1770482	5889315	-	-	-	-	-	-	-	-	-	1.04	0.5	0.1
6	Waitangi at SH Bridge (US)	1755227	5878339	-	-	-	-	-	-	-	-	-	0.34	0.7	0.1
	Waitangi at SH Bridge (GS)	1755188	5878322	46	299	-	211	188		11.9	7.46	12.7	0.49	0.7	0.1
	Waitangi at SH Bridge (DS)	1755108	5878322	-	-	-	206	-	-	-	-	-	0.21	0.4	0.1
22	Whangamaire at Fantail (US)	1765446	5889133	-	-	-	282	-	-	-	-	-	0.16	0.7	0.1
	Whangamaire at Fantail (GS)	1765472	5889178	128	350	176	282	246	9.6	11.8	7.36	11.9	0.21	0.6	0.1
	Whangamaire at Fantail (DS)	1765480	5889248	-	-	-	274	-	-	-	-	-	0.13	0.7	0.1
17	Whangamaire at Railway Culvert (US)	1763342	5882513	-	-	-	-	-	-	-	-	-	0.56	1.1	0.1
	Whangamaire at Railway Culvert (GS)	1763335	5882462	93	149	114	282	309	8.7	10.1	7.16	12.7	0.55	1.4	0.2
	Whangamaire at Railway Culvert (DS)	1763334	5882432	-	-	-	-	-	-	-	-	-	0.56	0.8	0.1

Site No.	Site ID	NZTM Easting	NZTM Northing	Flow (L/s)			Electrical Conductivity (µS/cm)		Dissolved Oxygen (mg/L)		pH	Temperature (°C)	Radon (Bg/L)		±
				2/02/22	8/08/23	15/11/23	2/02/22	8/08/23	2/02/22	8/08/23	8/08/23	8/08/23	2/02/22	8/08/23	8/08/23
14	Whangapouri at Glenbrook Rd Bridge (US)	1766942	5887819	-	-	-	-	-	-	-	-	-	0.73	0.5	0.1
	Whangapouri at Glenbrook Rd Bridge (GS)	1766935	5887913	178	465	368	282	239	7.6	10.8	7.41	12.7	0.78	0.4	0.1
	Whangapouri at Glenbrook Rd Bridge (DS)	1766890	5887956	-	-	-	-	-	-	-	-	-	0.84	0.7	0.1
27	Whangapouri at Paerata Falls (US)	1768668	5884097	-	-	-	-	-	-	-	-	-	4.41	5	0.4
	Whangapouri at Paerata Falls (GS)	1768620	5884142	168	357	339	287	247	8.5	9.1	6.88	13.4	4.36	5.8	0.4
	Whangapouri at Paerata Falls (DS)	1768558	5884246	-	-	-	-	-	-	-	-	-	5.04	5.6	0.4
28	Te Hihi at Linwood Rd (US)	1761506	5890194	-	-	-	-	-	-	-	-	-	-	1.5	0.2
	Te Hihi at Linwood Rd (GS)	1761488	5890250	-	114	-	-	210	-	8.8	6.97	12.5	-	1.4	0.2
	Te Hihi at Linwood Rd (DS)	1761468	5890298	-	-	-	-	-	-	-	-	-	-	1.2	0.1
24	43737 Mauku at Wrights Winter Gardens	1760776	5881756	48	-	151	-	-	-	-	-	-	-	-	-

For sampling anoxic groundwater discharges, many potential discharge sites, identified previously by Auckland Council staff (Morgenstern et al. 2023, Section 8.2), were found to be unsuitable for gas-tracer sampling. These are often ponds or urban drainage systems, with water having air contact prior to sampling access. In consultation with community groups and landowners, we identified several sites suitable for sampling:

- In the upper Whangamaire catchment, we sampled two springs: one in a reserve (Puk1); and one at a nearby lifestyle block, used as the domestic supply (Puk2). Puk1 was cleared of mud and debris the day prior to sampling to enable identification of seepage points. Puk2 was dammed at the outflow of the PVC pipe and flushed overnight prior to sampling, with the water siphoned from below the surface of the pooled water without air contact. For another seep on the lifestyle property, with brown staining indicating discharge of anoxic water, we were able to dam the seepage flow and let it flush overnight. This allowed sampling for gas tracers the next day (Puk3). We also sampled a pond on the property that collects seepage water from various small gulleys (Puk5). The pond was not sampled for gas tracers because of water contact with air.
- In the upper Mauku Stream catchment, we identified a seep into a small (duck) pond that discharged anoxic water, indicated by thick iron-hydroxide staining of the stream bed. We were able to intercept the groundwater seepage into the pond by digging a small hole, allowing for gas-tracer sampling excluding air contact. Sampling was difficult because of very low flow. At the only point where we could intercept the flow into the pond, the ground was unstable. We could only dig a 10-cm-deep hole without it collapsing. The hole provided a pathway for groundwater seepage and encouraged overflow into the pond. After letting things settle and the hole flush overnight, we were able to collect gas samples via a low-flow Bennett pump while maintaining overflow, which protected the sampled water from contact with air.
- In the Oira Creek catchment, we sampled a seepage emerging from under a log dump by damming the seepage flow overnight, allowing sampling for gas tracers the next day (Puk6). Oira Creek exhibits very low nitrate concentrations, despite large coverage by pastural farming (dairy and drystock) in the catchment, and therefore had a special focus in this survey. However, it was not possible to find other suitable discrete spring sampling sites.

Table 2.2 lists the coordinates, field parameters and redox-sensitive parameters.

Table 2.2 Spring and seep coordinates, field parameters and analysis results of redox-sensitive parameters. Estimated flow on 15 November 2023 – Puk2 and Puk5 measured; others only estimated to provide order of magnitude.

ID	Name/Remark	NZTM Easting	NZTM Northing	Estimated Flow (L/min)	Electrical Conductivity (µS/cm)	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	NH_4N (mg/L)	CH_4 (µmol/kg)	±
Puk1	Sacred puna (spring)	1763057	5882936	20	160	16.5	6.4	7.3	<0.005	0	0.2
Puk2	Domestic supply	1763136	5882735	30	256	16.8	6.5	8.3	<0.005	0	0
Puk3	Anoxic spring	1763088	5882785	0.3	275	17.7	6	3.35	<0.005	0	0
Puk4	Duck pond	1761691	5883347	-	362	15.7	6.1	0.3	0.151	26.4	1.3
Puk5	Collection pond (also collects road runoff)	1763120	5882892	23.5	169	-	7.5	11.4	0.008	Not sampled	
Puk6	Log dump	1769820	5886198	0.5	148	17	5.2	7.8	0.007	0.1	0.2
Hickey	Hickey Spring	1768730	5882046	-	295	16.1	-	9.59	0.005	0	0
Crisp Av	Crisp Ave Spring	1768830	5882229	-	291	16.1	-	8.91	0.005	0	0
Patum	Patumāhoe Spring	1763975	5881279	-	358	16.2	-	10.17	0.005	0	0
Hillview	Hillview Spring	1776264	5884330	-	290	16	-	9.88	0.005	0	0
Pilgrim Rd	Pilgrim Rd Spring	1760979	5880276	-	311	17.1	-	6.42	0.012	0	0

2.3 Stream Flow and Status of the Hydrologic System at Winter Sampling

As expected, most of the sites at winter sampling had significantly elevated flow compared to summer (Table 2.1; Figure 2.1). Only one site – the most upstream site at Hingaia Stream (1) – had similar flow during summer and winter sampling. This was likely to be due to the flashy flow response to rain from the basement catchment, which would cause high flow variability depending on the rain history of the previous days. The winter flow at Whangamaire Stream near Patumāhoe Spring (17) was only slightly elevated. This indicates that the spring system discharging the deeper basalt dominates the stream flow in that location. Downstream of the other two large springs, being Hillview at Hingaia Stream (4) and Hickey at Whangapouri Creek (27,14), flow in winter had significantly increased. This indicates that shallow flow contributions were active at that time.

These active flow contributions from the Pleistocene formations contrast with the situation during summer low-flow when these flow paths are dried up. Morgenstern et al. (2023) concluded that only shallow flow paths contribute to the drainage of the Pleistocene formation and that these are not active during summer baseflow. This is indicated in Figure 2.1 by similar stream flows at the various gauging sites along the streams in the Pleistocene formation. It can be seen in more detail in Figure 2.2, which shows the change in flow during summer (2 February 2022) for the five streams with more than two gauging sites. None of the streams in the Pleistocene formation with sufficient data (Whangapouri, Whangamaire, Ngakoroa) showed any significant flow gain in this formation (green symbols).

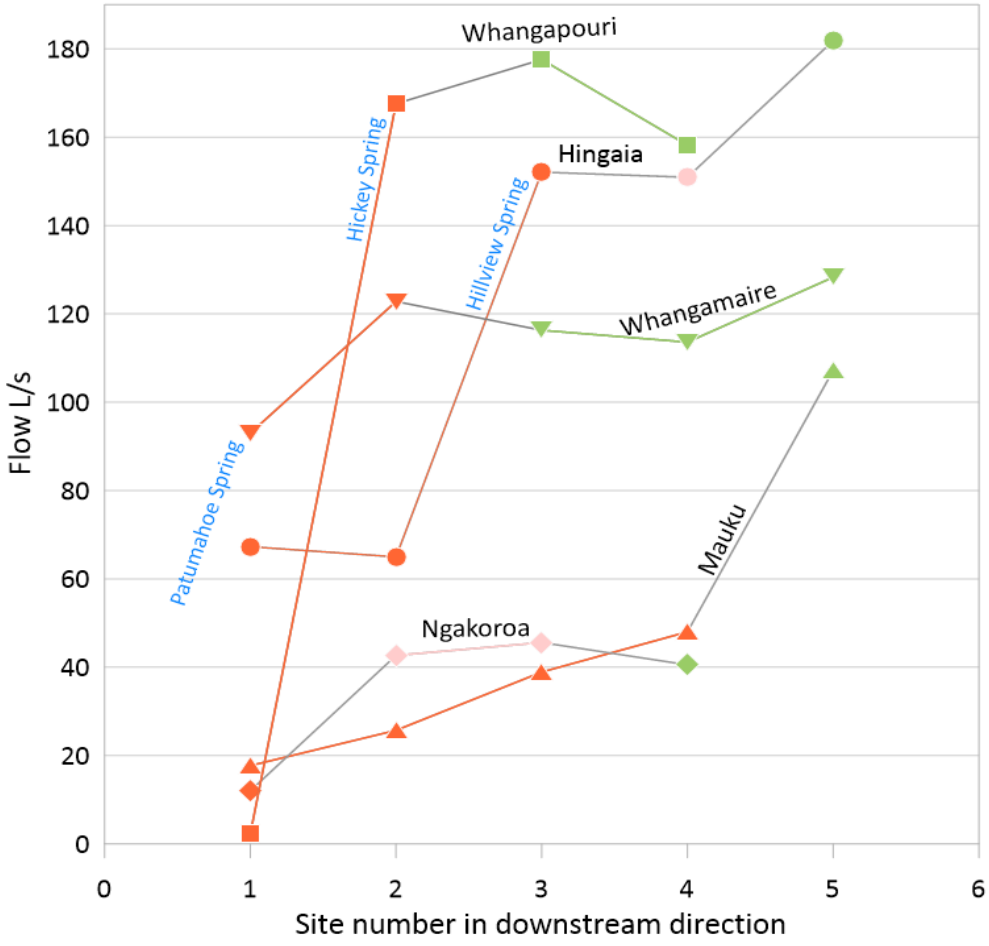


Figure 2.2 Stream flow along the five streams with more than two gauging sites. Colour coding of symbols is in accordance with the colours of geologic units in Figure 2.1. The position of the three large springs (Patumāhoe, Hickey, Hillview) is indicated in blue font in relation to gauging sites, showing the large flow increase due to these springs.

The quantity and quality of surface-water flows depend on the rainfall history in the catchment prior to sampling. Therefore, we assessed hydrographs and flow duration exceedance of gauged streams in this area. The first sampling campaign on 2 February 2022 was aimed at characterising the hydrologic system during low summer baseflow. However, because discharges into streams in the areas of Pleistocene deposits are inactive (not flowing) during summer low-baseflow, the streams draining most of the pastoral-grazing areas were not discharging nitrate loads at this time (Morgenstern et al. 2023). The nitrate loads from these areas were expected to be flushed out via the streams during winter when these streams are flowing. The second sampling campaign, on 8 August 2023 during winter baseflow, aimed to characterise these nitrate loads. The following figures show the hydrologic system at the time of summer and winter baseflow sampling.

- Figure 2.3 shows the hydrographs for two streams (Ngakoroa and Waitangi) with flow recorders in the Pukekohe–Bombay area. The red dots show the flow and time of stream sampling.
- Figure 2.4 shows the flow exceedance curves, with the red dots again indicating the flow at the time of stream sampling.

The samples from the two stream sampling campaigns are representative of average summer and winter flow conditions. The summer samples are about 90% and the winter samples are about 30% of flow exceedance, respectively. Note that there was an unusually wet period for about 1.5 years prior to the winter sampling campaign in 2023 (Figure 2.3).

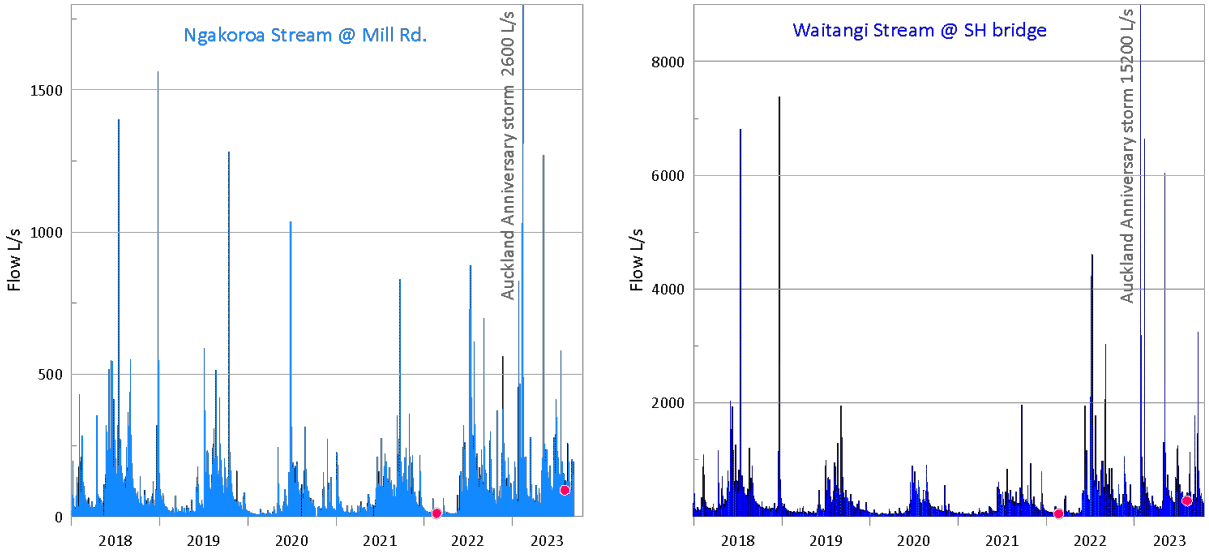


Figure 2.3 Hydrographs for two gauged streams in the Pukekohe–Bombay area for the period 2018–2024. Flow and time of sampling is shown by red dots at summer baseflow (2 February 2022) and winter baseflow (8 August 2023).

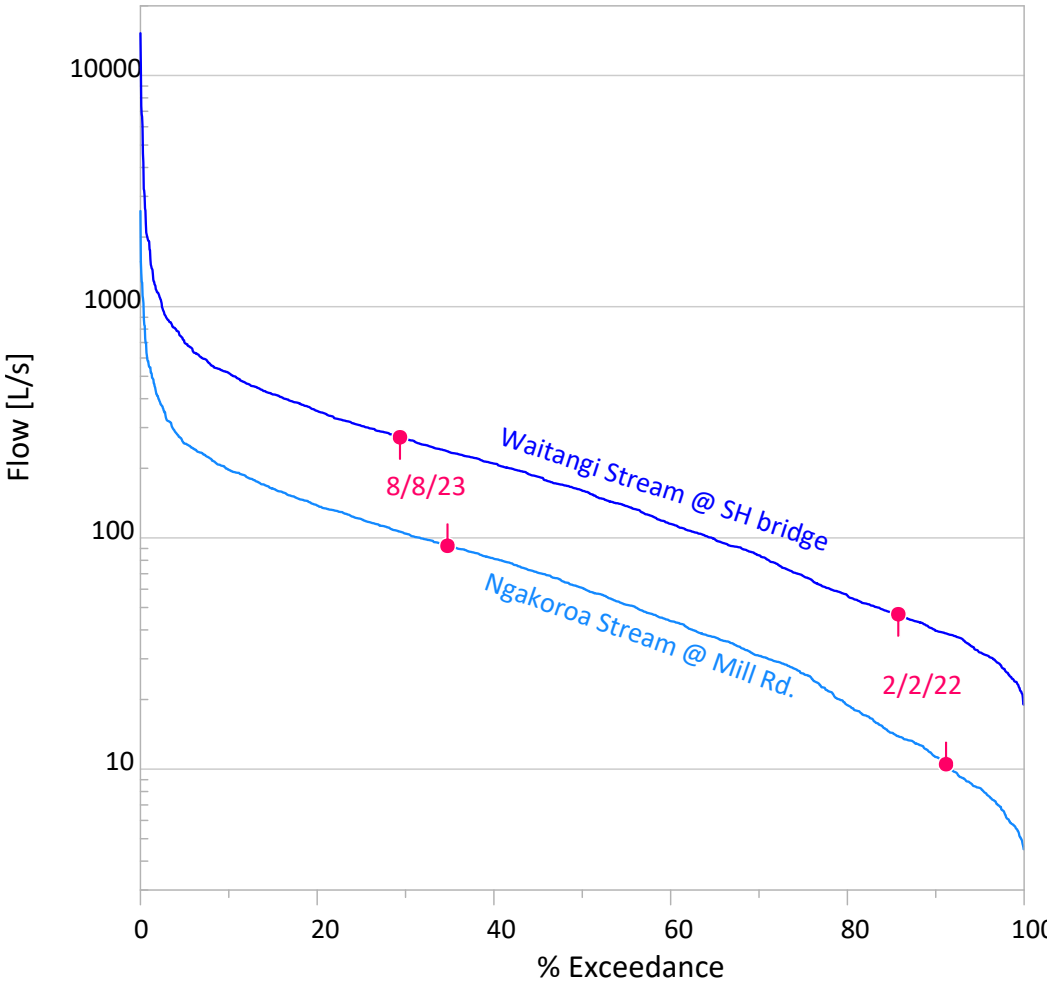


Figure 2.4 Flow-exceedance curves for the flow data from January 2018 to October 2023. Red dots indicate flow at sampling.

Some representative streams were also gauged on 15 November 2023 when springs and seeps were sampled. The results (Table 2.1) indicate that the eastern Mauku and Whangamaire stream catchments were at elevated flow compared to very low flow conditions in summer 2022 but still significantly below winter baseflow. However, the Whangapouri Creek catchment was at a flow comparable to winter baseflow. Oira Creek was not gauged on 15 November 2023 but had high flow similar to that of winter baseflow. Thus, the eastern part of the Pukekohe–Bombay area was wetter prior to sampling of the small springs and seeps compared to the western part of the area. The sample from seep Puk6 in the Oira Creek catchment is therefore representative of winter baseflow conditions, while samples Puk1–5 represent conditions closer to summer baseflow.

3.0 METHODS

Sampling and analytical methods, groundwater age interpretation and hydrochemistry data processing are described in detail in the methods section of Morgenstern et al. (2023). The analyses of nitrate isotopes are described in Rogers et al. (2023). In addition to the previously described analyses, including argon and dinitrogen (N_2), neon was also analysed to quantify denitrification in the groundwater system. Neon concentrations, together with argon, enable isolation of the two sources of N_2 in the groundwater: one being N_2 derived from the atmosphere and the second being N_2 from denitrification reactions (e.g. Martindale et al. 2019). The concentration of N_2 from denitrification reactions, in excess to N_2 derived from the atmosphere (excess-N_2), quantifies the amount of nitrogen from denitrification reactions along the entire flow path of the water.

3.1 Neon Analysis

Samples were collected and analysed using the methods described in Coble et al. (2024), except that gas chromatography analysis was performed using a 0.5 mL sample loop and 200 mL compression syringe of the type described in Martindale et al. (2018). All neon samples were collected in 500 mL Giggenbach bottles with approximately 30 mL headspace and viton o-ring seals (except for samples from the spring at Crisp Avenue, which had teflon seals). Analysis could only be performed four months after sample collection due to equipment issues. Therefore, a correction factor for neon leakage of the Giggenbach bottles was applied using an average neon leak rate of 1.63×10^{-6} mlSTP/kg/month, as determined by Coble et al. (2024).

For future denitrification studies, a more sensitive noble-gas mass spectrometer is currently under construction in the Water Dating Lab at GNS Science. This will allow for simple sampling using copper tubes instead of large glass bottles. This method also avoids air head space, which leads to more accurate analyses.

4.0 RESULTS

4.1 Streams

Tritium, mean transit time, stable-isotope and hydrochemistry results for the 13 stream sites sampled at winter baseflow are listed in Table 4.1. Measured concentrations are also available as Appendix 3. Hydrochemistry results were supplied by Auckland Council.

4.2 Springs

Table 4.2 lists age-tracer concentrations (tritium, SF_6, Halon-1301, chlorofluorocarbons [CFCs]), mean transit time, excess air and recharge temperature, radon concentrations, water and nitrate stable-isotope ratios and excess-nitrogen (as derived from argon and neon concentrations) for the 11 springs and seeps sampled in 2022 and 2023 (upper table). Measured concentrations are also available as Appendix 3. The lower part of the table includes additional hydrochemistry results as supplied by Auckland Council.

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Table 4.1 Tracer results for streams sampled at winter baseflow gauging sites. 'T Code' refers to the tritium lab code for reference, 'TR' is the measured tritium ratio, 'MTT' is the calculated mean transit time, 'DRP' is dissolved reactive phosphorous and 'TDS' is total dissolved solids. D^2H and $d^{18}O$ are the water stable-isotope ratios of hydrogen and oxygen. NO_3 $d^{15}N$ and NO_3 $d^{18}O$ are the nitrate stable-isotope ratios of nitrogen and oxygen (from Rogers [2022, 2024]). For comparison, the summer data are added in grey.

No.	Site ID	T Code	TR		±	MTT (Years)		d^2H ‰		$d^{18}O$ ‰		NO_3 $d^{15}N$ ‰		NO_3 $d^{18}O$ ‰		NO_3-N mg/L		NO_2-N (mg/L)	DRP (mg/L)	Total P (mg/L)	Mg (mg/L)	Ca (mg/L)	Total Alkaline (mg/L CaCO3)	TDS (mg/L)
		8/08/23	2/02/22	8/08/23		2/02/22	8/08/23	2/02/22	8/08/23	2/02/22	8/08/23	2/02/22	8/08/23	2/02/22	8/08/23	2/02/22	8/08/23							
1	Hingaia at Cascades	TA390	0.648	1.008	0.026	21	9.5	-29.3	-27.7	-5.15	-5.17	5.0	5.7	3.5	5.0	4.3	2.5	0.004	0.010	0.019	3.5	5.7	22.4	84
4	Hingaia at Maxted Rd	TA389	0.548	0.919	0.025	30	11	-29.3	-27.9	-5.28	-5.48	5.1	5.1	4.2	4.0	8.8	5.1	0.003	0.010	0.021	6.0	9.1	33.3	116
23	Mauku at Fallows Bridge	TA378	0.724	0.894	0.026	17	12	-26.5	-26.6	-4.85	-4.61	6.5	5.8	5.1	4.8	14.8	13.7	0.010	0.033	0.047	9.8	12.2	33.6	170
20	Mauku at Swede Patullo Road	TA379	0.686	1.049	0.028	19	8.5	-26.5	-26.0	-4.65	-4.34	11.4	6.8	8.8	5.6	4.5	7.8	0.005	0.005	0.019	7.6	11.0	33	150
15	Ngakoroa at Mill Road	TA386	0.908	1.191	0.027	11	6	-25.3	-27.0	-4.33	-4.90	7.6	7.9	4.7	5.1	2.9	4.1	0.005	0.002	0.011	4.8	6.8	24.6	97
9	Ngakoroa at Runciman Rd	TA387	0.77	1.061	0.027	15	8.5	-27.1	-26.3	-4.48	-4.87	15.2	8.4	10.5	6.3	0.7	3.9	0.006	0.008	0.030	5.6	9.6	28	120
11	Oira at Swing Bridge	TA388	0.576	1.047	0.027	28	8.5	-28.2	-26.1	-4.63	-5.00	13.1	9.6	11.0	6.1	0.0	0.6	0.004	0.011	0.033	3.6	6.2	26.7	99
6	Waitangi at SH Bridge	TA380	0.714	0.882	0.026	17	12	-25.6	-26.2	-4.78	-4.67	No result	7.8	No result	6.3	0.0	3.7	0.005	0.004	0.012	5.8	6.9	27.3	122
22	Whangamaire at Fantail	TA385	0.674	0.912	0.025	20	11.5	-26.4	-26.6	-4.81	-4.75	9.4	6.0	8.0	5.1	11.3	8.7	0.008	0.009	0.022	8.6	12.5	37.8	-
17	Whangamaire at Railway Culvert	TA382	0.77	0.901	0.025	15	12	-26.4	-26.2	-4.85	-4.49	7.3	5.0	6.0	4.4	18.8	18.2	0.004	0.008	0.010	13.3	13.9	38.2	-
14	Whangapouri at Glenbrook Rd Bridge	TA384	0.699	0.869	0.025	18	12.5	-27.1	-26.5	-4.97	-4.78	9.0	4.3	7.1	3.6	11.5	9.9	0.008	0.010	0.021	8.5	12.2	39.8	-
27	Whangapouri at Paerata Falls	TA383	0.758	0.922	0.026	15.5	11	-27.2	-26.7	-4.86	-5.08	4.8	4.2	4.3	4.1	13.9	11.3	0.014	0.006	0.017	9.3	12.4	36.8	-
28	Te Hihi at Linwood Rd	TA381	Not sampled	1.09	0.027	Not sampled	8	Not sampled	-25.8	Not sampled	-4.76	Not sampled	11.8	Not sampled	7.6	Not sampled	1.8	0.017	0.021	0.111	4.7	12.6	39	136

Table 4.2 Age, gas, stable-isotope and radon analysis results for springs and seeps (upper table); and hydrochemistry results as supplied by Auckland Council (lower table). 'T Code' is the tritium lab code for reference, 'TR' is the measured tritium ratio and 'MTT' is the calculated mean transit time. For tracer background information and units, refer to methods section. 'RT' is the recharge temperature as derived from argon and nitrogen concentrations. 'Rn' is the radon-222 concentration. D^2H and $d^{18}O$ are the water stable-isotope ratios of hydrogen and oxygen. NO_3 $d^{15}N$ and NO_3 $d^{18}O$ are the nitrate stable-isotope ratios of nitrogen and oxygen (from Rogers [2022, 2024]), with Puk4 having no result due to insufficient NO_3. Excess N_2 is excess nitrate as derived from argon and neon concentrations.

ID	T Code	Date	TR	±	SF_6 (pptv)	±	Halon (pptv)	±	CFC11 (pptv)	±	CFC12 (pptv)	±	CFC13 (pptv)	±	MTT (Years)	Excess Air [mL(STP)/kg]	±	RT (°C)	±	Rn (Bq/L)	±	d^2H	$d^{18}O$	NO_3 $d^{15}N$	NO_3 $d^{18}O$	Excess N_2 (mg/L)	±
Puk1	TA392	15/11/23	0.859	0.024	8.36	0.51	2.56	0.21	217	65	479	131	71	23	13	1.1	0.8	17	7.8	20	0.6	-27.6	-5.02	6.1	6.5	-0.1	0.3
Puk2	TA393	15/11/23	0.784	0.024	9	0.36	2.6	0.11	221	12	459	22	125	8	15	0.8	0.5	17	1.1	10	0.4	-27	-4.9	6.2	6.9	0.0	0.3
Puk3	TA394	15/11/23	0.826	0.022	7.37	0.24	2.33	0.1	178	10	393	26	61	5	13.5	2.1	0.4	17	1	31	0.9	-27.8	-4.96	8.2	10	0.2	0.2
Puk4	TA395	15/11/23	1.138	0.030	6.11	0.21	0.96	0.06	3	0	311	17	2	3	7	2.6	0.6	15	1.2	17	0.6	-28.9	-5.05	No result		0.7	0.2
Puk5	TA396	15/11/23	1.119	0.025	Not sampled										7.5	Not sampled				0.4	0.1	-23	-3.8	13.4	11.9	Not sampled	
Puk6	TA397	15/11/23	0.971	0.024	4.63	0.15	1.32	0.06	223	11	469	20	74	6	10	1	0.4	17	1	9.2	0.4	-29.1	-5.01	6.2	5.7	-0.2	0.4
Hickey	TA354	7/04/22	0.732	0.024	9.74	0.4	3.23	0.21	1123	142	804	57	85	7	18	0.9	0.6	17	1.6	25	1.6	-27.4	-4.99	4.5	4.6	-0.1	0.4
Crisp Av	TA352	7/04/22	0.707	0.024	9.91	0.41	3.14	0.21	836	106	850	62	85	7	18	0.2	0.6	17	1.6	27	1.6	-28.5	-5.04	5	4	-0.3	0.4
Patumāhoe	TA353	7/04/22	0.699	0.023	9.3	0.43	3.2	0.23	477	56	1645	127	95	9	17	1.1	0.7	17	1.9	13	1.9	-26.5	-4.93	4.7	4	-0.1	0.4
Hillview	TA355	7/04/22	0.473	0.021	8.76	0.4	2.98	0.21	290	25	738	57	83	8	36	0.8	0.6	19	1.8	21	1.8	-29	-5.42	5.2	4.3	0.2	0.4
Pilgrim Rd	TA356	7/04/22	0.656	0.022	5.5	0.28	2.4	0.16	260	22	618	46	67	6	21	2	0.7	16	1.7	9.6	1.7	-28.1	-5.01	5.9	5.9	0.6	0.5

ID	HCO_3 (mg/L 25°C)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Cl (mg/L)	NO_2N (mg/L)	NO_3N (mg/L)	Dissolved Reactive Phosphorous (mg/L)	SiO_2 (mg/L)	SO_4 (mg/L)
Puk1	32	3.9	5.2	0.93	19.9	16.5	0.0016	5	0.0019	28	2.9
Puk2	38	7	11	1.24	25	24	< 0.0010	11.5	0.0101	30	2.1
Puk3	34	7.3	10.6	1.48	30	34	0.0018	9.4	< 0.0010	29	3.8
Puk4	48	7.6	9.6	2.5	37	49	< 0.010	0.01	0.119	34	18.3
Puk5	44	5.6	6.1	0.76	20	23	0.018	0.73	< 0.0010	11.1	2.5
Puk6	3.4	1.19	4.2	0.24	19.4	28	0.0017	3.9	0.0107	14.1	2.7
Hickey	49	-	13.6	1.65	21	21	-	17.6	-	34	3.1
Crisp Av	50	-	13.8	1.65	22	22	-	17.5	-	35	2.5
Patumāhoe	41	-	17.5	1.77	25	26	-	25	-	33	2.8
Hillview	63	-	15.6	1.66	19.4	19.9	-	15.1	-	42	1.9
Pilgrim Rd	46	-	15.2	1.65	24	32	-	15.8	-	31	2.3

5.0 DISCUSSION

5.1 Spring Hydrology

All identified springs and seeps appeared to occur at the transition from a more hydraulically conductive formation to the less conductive Pleistocene deposits: Puk1–4 from basalt and Puk6 from volcanic unconsolidated material (Figure 2.1). The Pleistocene deposits were identified in Morgenstern et al. (2023) to have low hydraulic conductivity. Transition to this formation is likely to be the reason for these groundwater discharges. We were not able to identify discrete springs anywhere within the Pleistocene formation even after consulting with landowners and local communities. Discharges into streams appeared to be diffuse and not suitable for gas-tracer sampling, unless these could be intercepted by shallow drilling (e.g. push drill).

5.2 Agrochemicals

Morgenstern and Daughney (2012) showed that elevated concentrations of nitrate, magnesium and calcium in groundwater are associated with high intensity land use, as these are all ingredients found in agrochemicals. In the Pukekohe–Bombay area, elevated concentrations of nitrate, magnesium and calcium were observed mainly in streams discharging from the Pukekohe basalt formation (Table 4.1). This is consistent with the high-intensity market gardening in this area.

These elevated ion concentrations are also reflected in the elevated electric conductivity of the water (Table 2.1). While hydrochemistry was not measured before, electric conductivity measured in summer 2022 and winter 2023 allowed comparison between the summer and winter seasons. Winter electric conductivity was lower at all stream sampling sites except one. Lower electric conductivity in winter indicates the diluting effect of shallower flow-path water entering the streams. Electric conductivity was higher in winter only at the Whangamaire at Railway culvert (17). This was likely to be caused by a point-source discharge.

5.3 Radon

Radon-222 (^{222}Rn; half-life 3.8 days) is a radioactive decay product of uranium, which is ubiquitous in almost all rocks and soils. Radon is high in groundwater and low in surface water, where it is separated from its source, escapes into the atmosphere and decays. The contrast between high radon concentrations in groundwater and low concentrations in surface water allows for the identification of groundwater seepage into surface water as indicated by elevated radon concentrations in streams.

At the stream sampling sites with repeat sampling, we observed similar radon concentrations between summer and winter (Table 2.1; Figure 5.1), indicating that the increased flow during winter baseflow is also maintained from a deeper groundwater flow system. This is somewhat unexpected. The increased flow during winter is generally thought to originate from shallow flow and surface run-off, which is low in radon, in contrast to deeper groundwater with higher radon concentrations.

At most of the sites – Hingaia Stream (1, 4), Mauku Stream (20, 23), Ngakoroa Stream (15), Waitangi Stream (6), Whangamaire Stream (17, 22) and Whangapouri Stream (27) – the radon concentration in the stream water was even higher in winter compared to summer. This is likely the result of the larger volume of water in this period of higher rainfall maintaining its radon concentration further downstream.

The measured radon concentrations in the springs and seeps (Table 4.2; Figure 5.1) are generally consistent with those measured in groundwater of this area (Morgenstern et al. 2023).

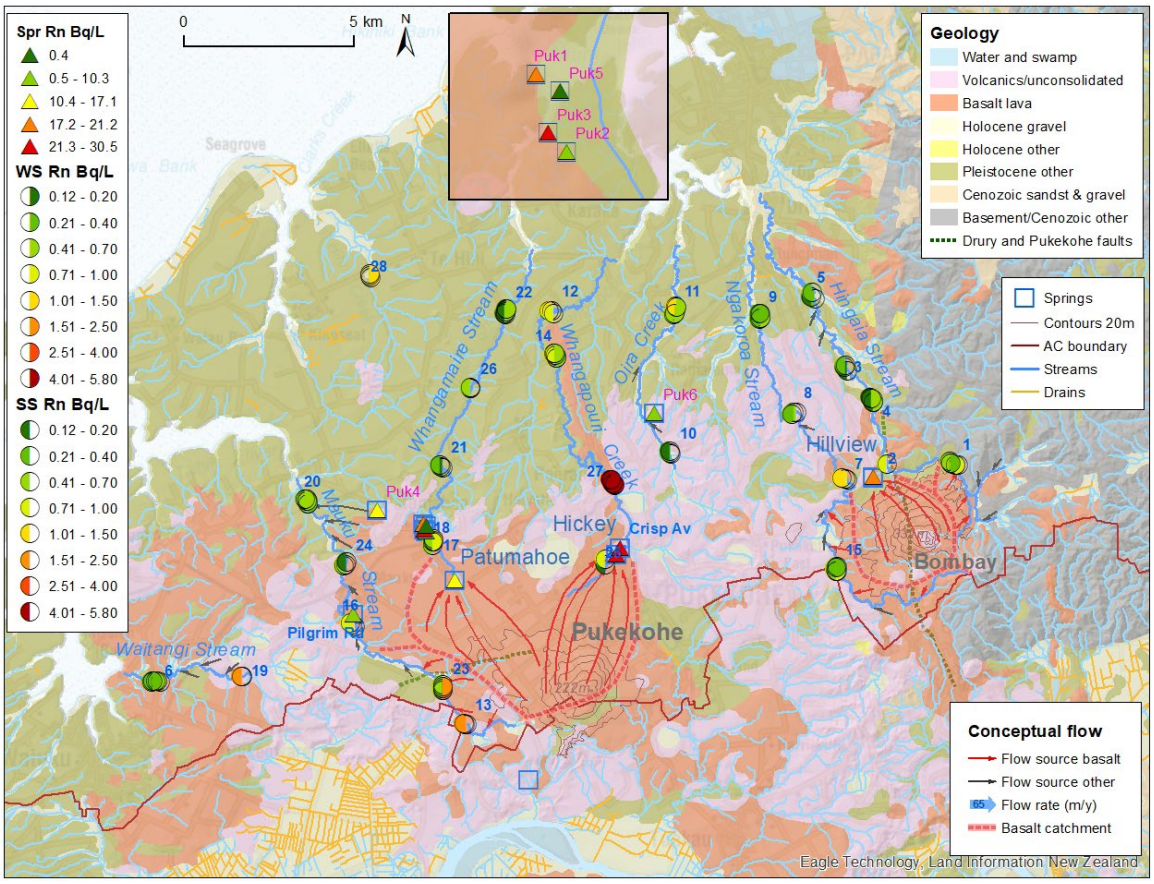


Figure 5.1 Map of Radon-222 concentrations in stream and spring/seep water. Stream results at winter baseflow are shown in the right half of circles, whereas summer results are shown in the left half. Abbreviations: Spr = spring, WS = winter stream, SS = summer stream. Note the different scales for stream and spring water. Conceptual flow is from Morgenstern et al. (2023). The inset shows the results for the cluster of springs and seeps near the upper Whangamaire Stream site 18.

5.4 Dissolved Oxygen

Dissolved oxygen in groundwater is consumed by oxidation of organic matter or other electron donors (e.g. pyrite). Reduction of oxygen is energetically the most favourable reaction that micro-organisms use, which means that other reduction reactions (e.g. denitrification) typically do not occur until most of the dissolved oxygen has been consumed (Morgenstern and Daughney 2012; Burbery 2018).

At all stream sites with repeat sampling, dissolved oxygen was higher during winter baseflow compared to summer baseflow (Table 2.1; Figure 5.2). The winter dissolved oxygen was near water-air equilibrium concentration (approximately 9–12 ppm). Radon concentrations generally indicate similar groundwater discharges during the elevated winter flows compared to summer flows (as opposed to surface run-off). Therefore, it is likely that most of the low dissolved oxygen concentrations observed in streams during summer were caused by in-stream bacterial processes that consume oxygen for the decomposition of organic matter at low-flow and warmer conditions. Where and when these processes result in nearly complete oxygen consumption, bacteria can switch from aerobic to anaerobic respiration. Microbial reduction of nitrate through the process of denitrification under such conditions can result in substantial nitrate removal from streams. Observed shifts in nitrate isotope ratios in the streams (Section 5.8) are consistent with instream anaerobic denitrification in the Pukekohe–Bombay area.

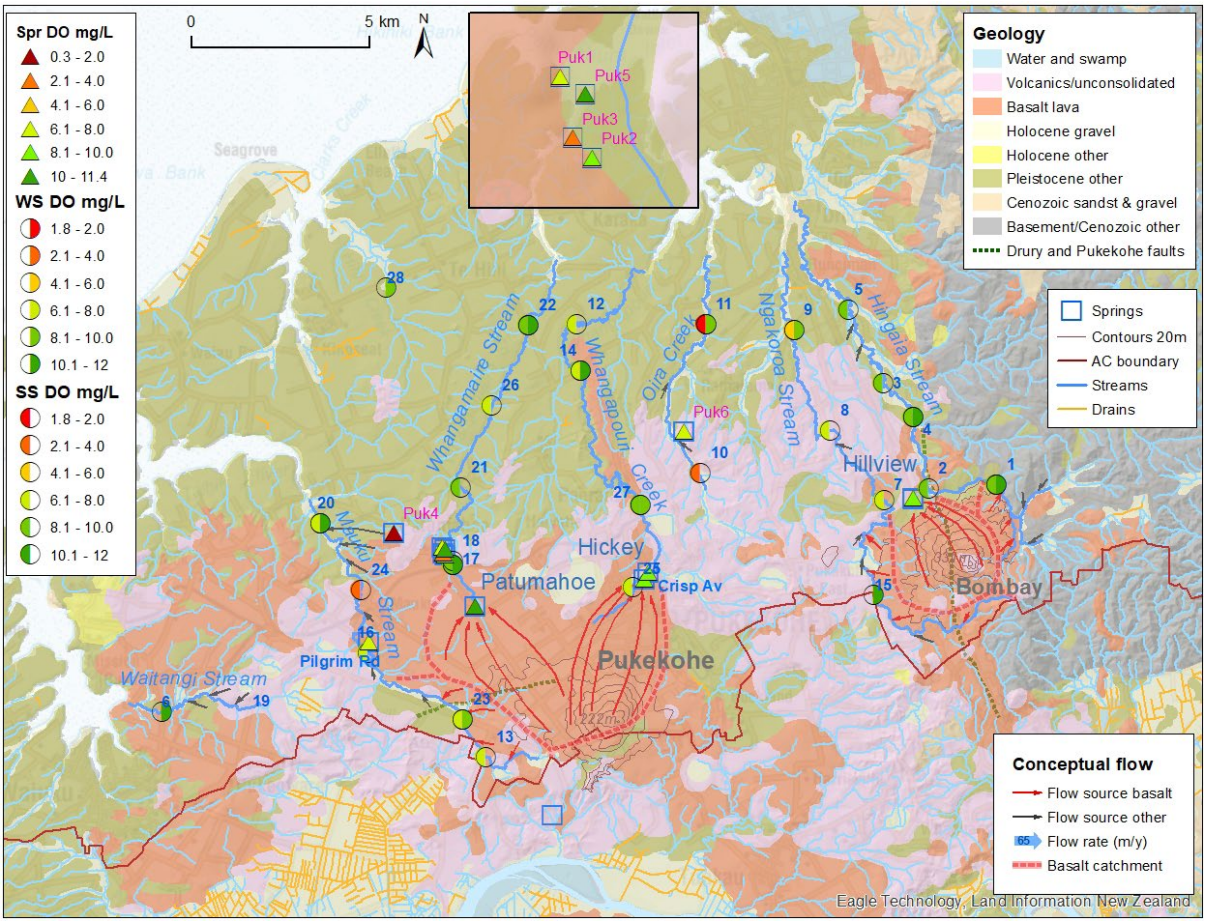


Figure 5.2 Map of dissolved oxygen (DO) in stream, spring and seep water. Stream results at winter baseflow are shown in the right half of circles, whereas summer results are shown in the left half. Abbreviations: Spr = spring, WS = winter stream, SS = summer stream. New Phase 2 spring/seep results are shown with magenta labels, with the insert showing the location of springs near Whangamaire Stream sampling site 18 with higher resolution. Conceptual flow is from Morgenstern et al. (2023).

All previously sampled springs that drain the basalt formation contained relatively high dissolved oxygen, indicating an absence of anaerobic processes, including microbial denitrification. Therefore, the Phase 2 sampling campaign focused on areas with potential for anoxic groundwater discharges [Morgenstern et al. 2023, Recommendation 8.1(1)]. While it was difficult to find discrete spring discharges that would enable sampling of water for gas-tracer analysis without air contact, with the help of the local communities, we managed to find a mix of springs and seeps to sample. These included anoxic groundwater discharges, as indicated by depletion of oxygen and by brown staining from iron hydroxide. The presence of dissolved iron in the water, which precipitates as iron hydroxide when in contact with air, indicates anaerobic processes beyond oxygen consumption, with potential for denitrification.

We found only two seeps – Puk3 and Puk4 – discharging highly anoxic water (Figure 5.2; Table 2.2). However, three of the sampled springs – Puk1, Puk2 and Puk6 – discharged water with significantly reduced dissolved oxygen. Despite the presence of oxygen in these waters, we also sampled them for excess-N_2, as they may partly originate from highly reducing environments with potential for denitrification in their groundwater systems. This is illustrated by the gas-tracer results of groundwater seep Puk3.

For Puk3, the tritium and SF_6 concentrations were in excellent agreement (Figure 5.3, refer to the methods section in Morgenstern et al. [2023]). However, the Halon-1301 and all CFC concentrations were about 20% too low. Halon-1301 and all CFCs are known to be consumed by bacteria in anaerobic environments. This depletion in Halon-1301 and CFCs indicates that about 20% of this seepage water originates from highly anoxic flow paths in which Halon-1301 and the CFCs have been consumed. This explains the brown staining downstream of the seep, despite 3.4 ppm (parts per million) of dissolved oxygen. At this seep, oxic and anoxic flow paths converged.

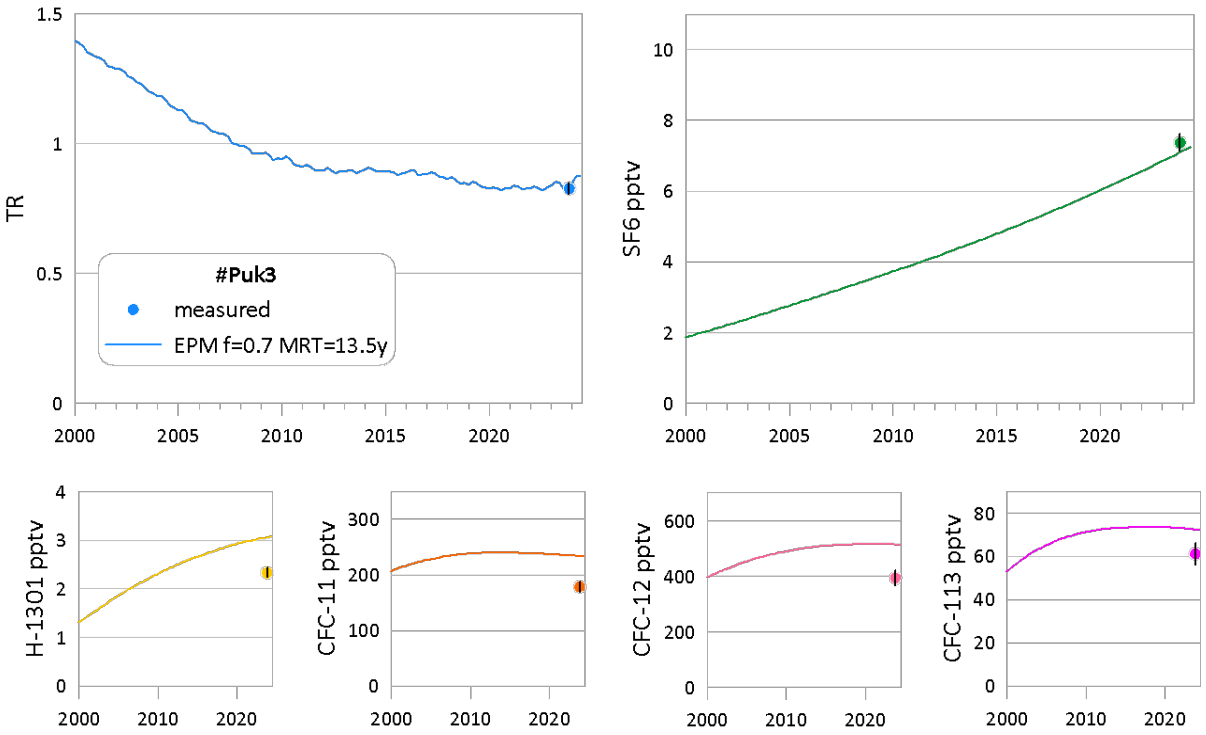


Figure 5.3 Age-tracer concentrations for anoxic seep Puk3. While tritium and SF_6 show excellent agreement for a mean transit time of 13.5 years, Halon-1301 and all CFCs are too low, indicating partial consumption.

In summary, the mix of springs and seeps sampled for excess-N_2 can be expected to provide a first quantification of groundwater denitrification in the Pukekohe–Bombay area from partly anoxic environments, compared to the oxic water discharging from basalt formations.

5.5 Water Isotopes

The water stable-isotope composition of samples collected in 2022 provided detailed information about recharge source and groundwater–stream connection in the Pukekohe–Bombay area (Morgenstern et al. 2023). Figure 5.4 shows this data in the $\delta^{18}O$ versus $\delta^{2}H$ plot alongside the new 2023 data (Tables 4.1 and 4.2). Results for streams sampled in winter 2023 are shown by cyan diamonds and results from summer 2022 are shown by blue circles. All spring and seep data are shown by yellow circles.

Compared to the summer data, less of the winter-stream data plot near the brown evaporation line, indicating less impact on the streams by evaporation during winter, as expected. The spring data plot closer to the black local meteoric water line, indicating that the recharge feeding these springs is from direct rain infiltration without significant exposure of the water to evaporation processes (for example in surface ponds, etc.) prior to infiltration.

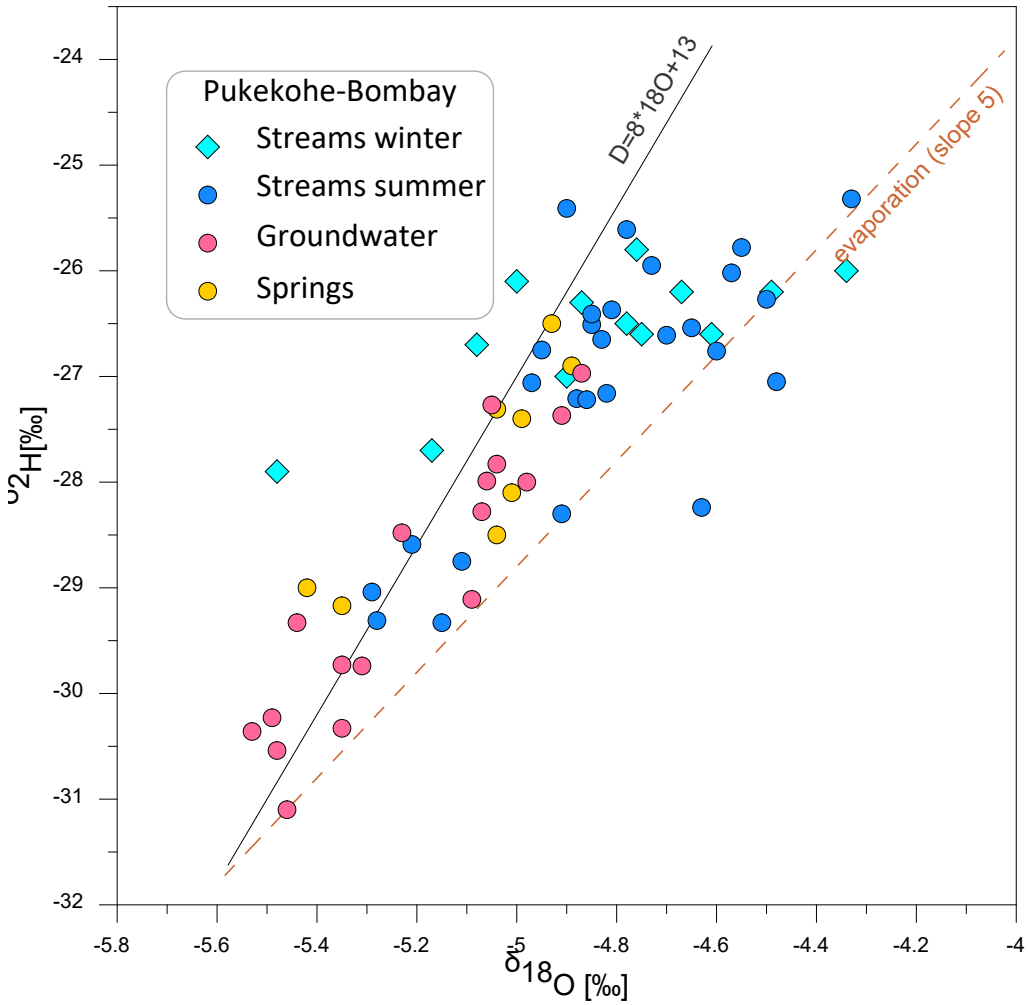


Figure 5.4 Plot of $\delta^{18}O$ versus $\delta^{2}H$ for surface water and groundwater in the Pukekohe–Bombay area.

Figure 5.5 shows the spatial distribution of $\delta^{18}O$ for springs, seeps and streams sampled in summer and winter, at identical scales. The winter data show a less consistent pattern. However, the figure generally confirms the consistent $\delta^{18}O$ spatial pattern found in summer flow conditions (Morgenstern et al. 2023), with Hingaia Stream – furthest inland from the west coast and at highest altitude – having the most negative isotope ratios.

Towards the west, in Ngakoroa Stream and Oira Creek, the water had more negative $\delta^{18}O$ ratios in winter than in summer. In the Whangamaire and Mauku streams, the water had less negative $\delta^{18}O$ ratios in winter than in summer. There is insufficient data available over time to determine the reason for this pattern.

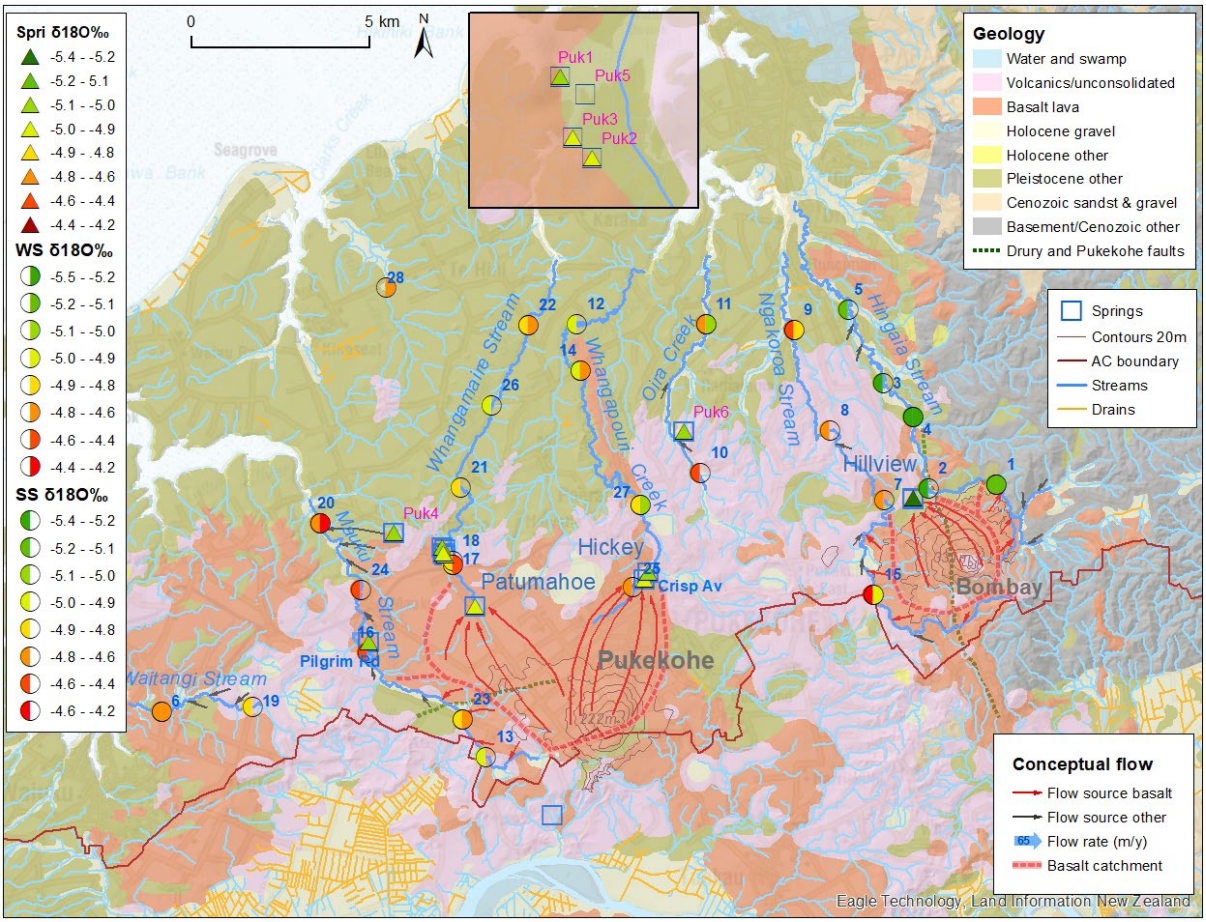


Figure 5.5 Spatial distribution of $\delta^{18}O$ of stream, spring and seep water. Stream results at winter baseflow are shown in the right half of circles, whereas summer results are shown in the left half. Abbreviations: Spr = spring, WS = winter stream, SS = summer stream. Conceptual flow is from Morgenstern et al. (2023). The inset shows the results for the cluster of springs and seeps near the upper Whangamaire Stream site 18.

The $\delta^{18}O$ ratios of the springs and seeps around Whangamaire and Mauku streams match those of the groundwater discharges from the basalt formation.

5.6 Mean Transit Time

The methodology of groundwater age interpretation is described in detail in Morgenstern et al. (2023). Age-tracer data and calculated MTTs are listed for streams in Table 4.1 and for springs and seeps in Table 4.2. All tritium concentrations were significantly lower than those of recent rain, indicating older water. In springs and seeps that could be sampled for gas tracers, older water was also confirmed by relatively low SF_6 concentrations.

All streams contained younger water during winter, indicating activation of shallower flow paths into the streams during the wet season. However, even at winter baseflow, the stream waters were still relatively old, with MTTs between 6 and 12.5 years. This implies that groundwater discharge dominated stream flow even at the higher flows observed during the winter sampling. The spatial distribution of MTTs is shown in Figure 5.6.

At Mauku Stream, during winter baseflow, the water in the upper reaches (23) was slightly older compared to the lower reaches (20). This indicates the dominance of old water discharges from the basalt formation in the upper reaches and contribution of younger water from activated shallower flow paths further down. In Whangamaire Stream and Whangapouri Creek, the MTT was similar upstream (17, 27) and downstream (22, 14). This indicates that

the flow along the entire stream is dominated by the large Patumāhoe and Hickey springs, respectively. At Hingaia Stream, the MTT was similar between the upstream (1) and downstream (4) sites. This indicates that the northeast of the Bombay basalt formation discharges water of a similar age to that of the Hillview Spring discharges, northwest of the Bombay basalt formation.

The water sampled from Oira Creek during winter was significantly younger than during summer (Table 4.1) and matched that of a spring discharge sampled during winter from the volcanic unconsolidated formation (Puk6). This suggests that, during winter baseflow, the elevated flow in Oira Creek is also sustained mainly from the volcanic unconsolidated formation, as opposed to discharges from the Pleistocene formation. The situation may be similar at Ngakoroa Stream.

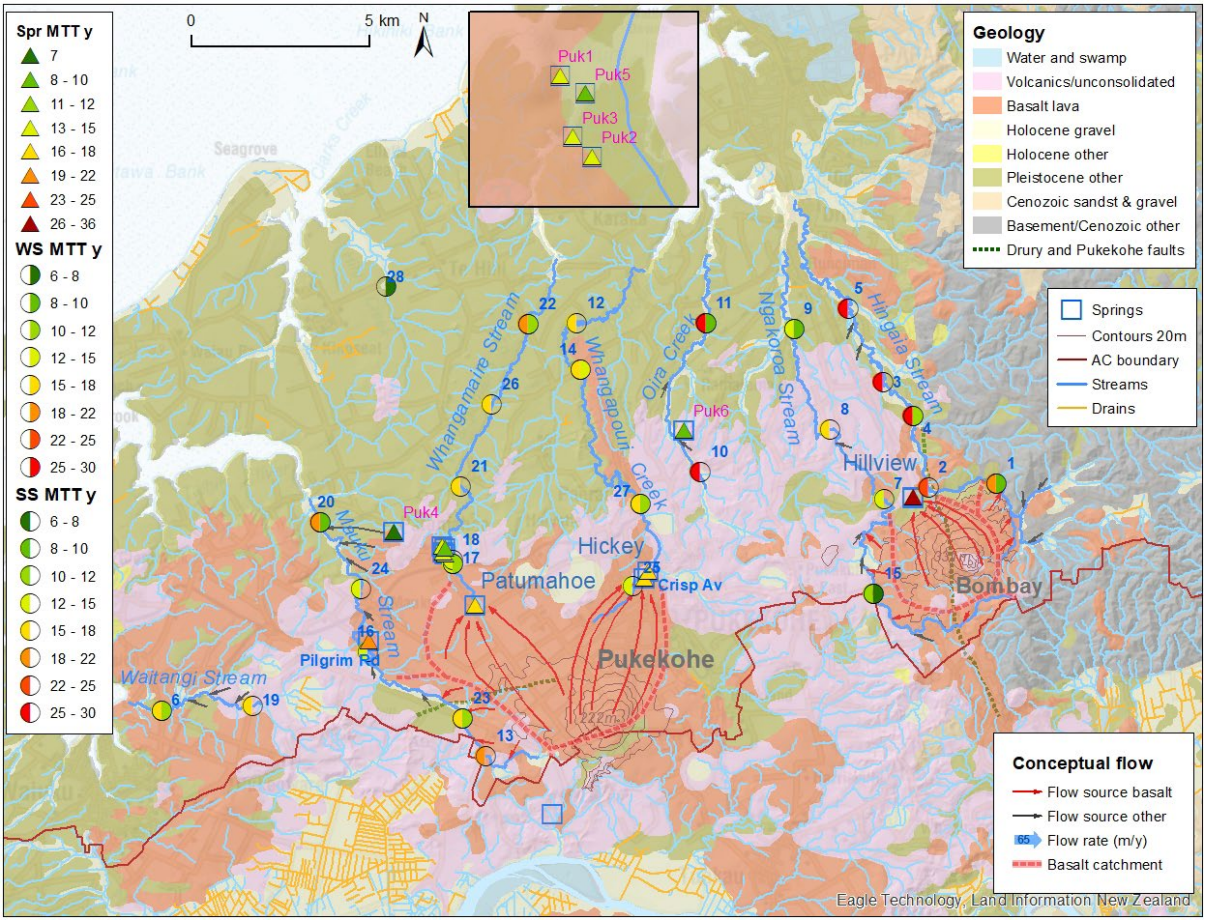


Figure 5.6 Spatial distribution of water mean transit times (MTT). Stream results at winter baseflow are shown in the right half of circles, whereas summer results are shown in the left half. Conceptual flow is from Morgenstern et al. (2023). Abbreviations: Spr = spring, WS = winter stream, SS = summer stream. The inset shows the results for the cluster of springs and seeps near the upper Whangamaire Stream site 18.

5.7 Nitrate Concentrations

Nitrate-N concentrations, as provided by Auckland Council, are listed in Table 4.1 for the winter stream sampling sites and in Table 4.2 for the springs and seeps sampled in 2022 and 2023. Their spatial distributions are shown in Figure 5.7. Several patterns can be broadly differentiated based on the baseflow samplings in summer (2022) and winter (2023).

Nitrate concentrations were lower during winter baseflow compared to summer baseflow at several sites, including Hingaia Steam sites 1 and 4, Whangapouri Creek sites 14 and 27 and Whangamaire Stream at site 22. This is likely to be caused by dilution at:

- Hingaia Stream – increased flows from the more pristine basement catchment (higher rainfall at higher elevation with forest/bush cover).
- Whangapouri Creek – flow contributions from the unconsolidated volcanic formation and Pleistocene deposits (nitrate concentrations are lower in discharges from land dominated by pastoral use compared to market gardening).
- The lower Whangamaire Stream – flow contributions from Pleistocene deposits (shallow pathways and lower land-use intensity than near the source).

Nitrate concentrations were similar between summer and winter baseflow at the upper Whangamaire Stream near Patumāhoe Spring. This indicates that Patumāhoe Spring also dominates water quality at this site during winter baseflow conditions.

Nitrate concentrations were higher during winter baseflow compared to summer baseflow at several sites, including Mauku Stream (20), Ngakoroa Stream (9 and 15), Oira Creek (11) and Waitangi Stream (6). All of these sites had relatively low nitrate concentrations during summer baseflow, when shallow nitrate flow paths are not active and only older, deeper groundwater discharges sustain stream flow. During these low-flow conditions, nitrogen uptake by plants in the stream and/or denitrification may diminish nitrate concentrations, indicated by nitrate concentrations as low as 0 mg/L. However, shallow flow paths are activated during winter, particularly in Pleistocene geology, as indicated by the large flow increase in Whangapouri Creek between sites 27 and 14. This suggests that nitrate from the overlying pastoral-grazing land use is being flushed into the streams via near-surface and shallow groundwater flow pathways.

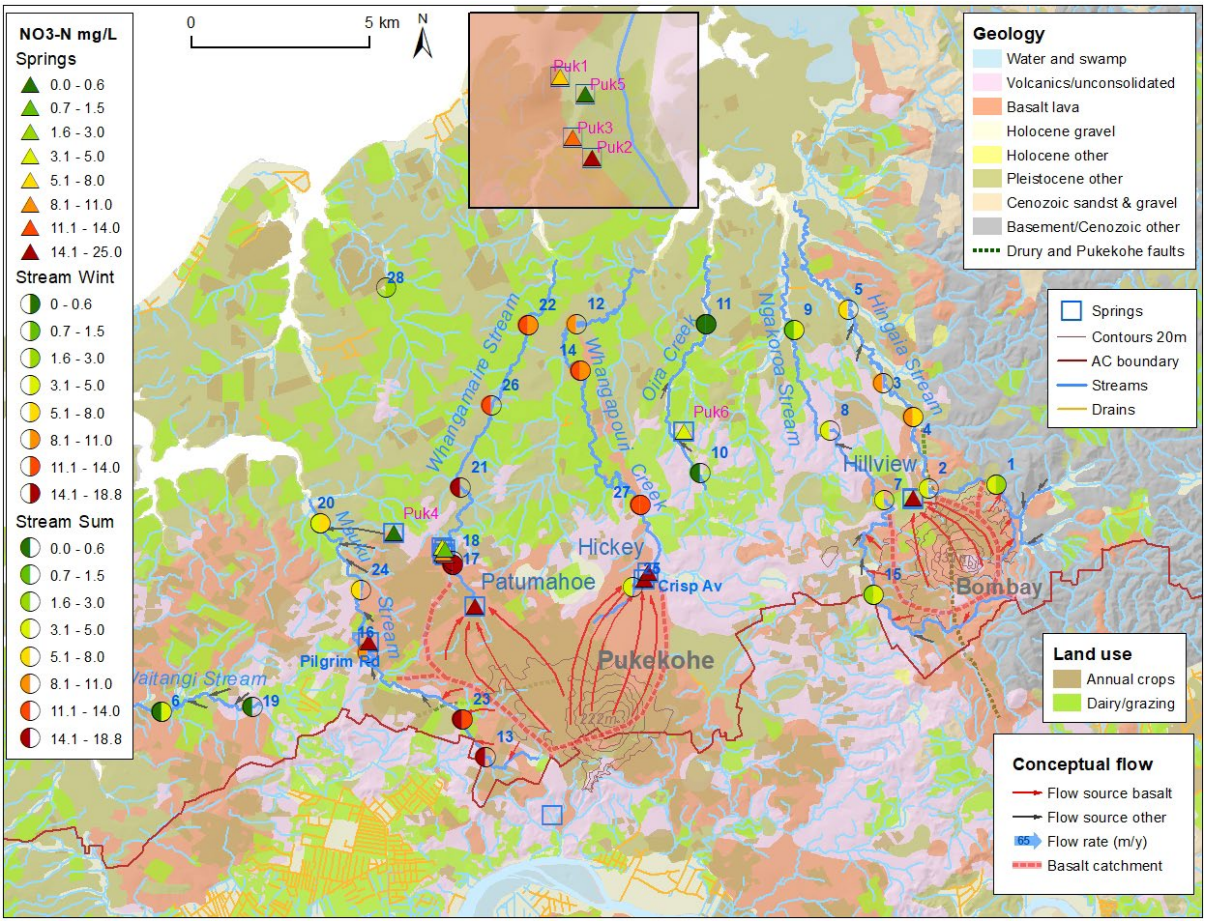


Figure 5.7 Spatial distribution of nitrate concentrations (NO_3-N). Stream results at winter baseflow are shown in the right half of circles, whereas summer results are shown in the left half. Conceptual flow is from Morgenstern et al. (2023). In addition to geology, market garden and dairy/grazing land uses are shown. Abbreviations: Spr = spring, WS = winter stream, SS = summer stream. The inset shows the results for the cluster of springs and seeps near the upper Whangamaire Stream site 18.

The water in Oira Creek also has very low nitrate concentrations (0.6 mg/L NO_3-N) at winter baseflow, despite its vastly increased flow (by a factor of 15). These low nitrate concentrations can be explained by nitrate uptake through in-stream processes. There is little doubt that groundwater discharges from the mostly pastoral land, active during winter, supply water with significantly higher nitrate concentrations into the stream. Spring Puk6 is such a discharge, with a relatively high nitrate concentration (3.9 mg/L NO_3-N). In-stream nitrate removal (denitrification and/or uptake) seems plausible because the stream environment appears to be such that the water has a relatively long residence time in the stream, with a relatively large riparian boundary (Figure A1.11). Instream nitrate removal in Oira Creek is also indicated by a large shift of the nitrate stable-isotope ratios downstream toward heavier isotopes (Section 5.8).

Similar in-stream denitrification processes may also occur in the nearby lower Ngakoroa Stream in a similar geologic setting. In summer, we observed a significant decrease in nitrate concentration in this stream's lower reach, as well as a large shift downstream toward heavier nitrate isotopes. All of these facts point toward significant in-stream nitrate removal in Oira Creek and Ngakoroa Stream.

Te Hihi Stream (28) also drains mainly pastoral land. It was only sampled in winter 2023 and found to contain water with relatively low nitrate concentration (1.8 mg/L NO_3-N). The reason for this may be similar in-stream processes to those described above. Other possibilities are that significant fractions of nitrate are removed through denitrification in the shallow drainage system near the redox boundary or that not much nitrate had accumulated in the soil when samples were taken, as the winter baseflow sampling occurred after a 1.5-year period of unusually high rainfall (Figure 2.3).

Seasonal variations in nitrate loads are smoothed out in the old water discharges from basalt formation due to the integrating effect of their large groundwater stores (Morgenstern et al. 2023). However, strong seasonal variations in nitrate loading are expected in discharges from the Pleistocene formations where the nitrate leached from pastoral farming is flushed out seasonally. This is demonstrated by Auckland Council stream water-quality monitoring results (RIMU 2024) from three streams in the Pukekohe–Bombay area, Waitangi, Whangamaire and Ngakoroa streams (Figure 5.8). The results from the two synoptic sampling campaigns in summer 2022 and winter 2023 in these streams are in good agreement with Auckland Council's long-term monitoring results.

Nitrate concentrations in samples taken at Waitangi Stream at Falls Bridge were highly variable, with usually very low concentrations in summer and high concentrations in winter. This shows that nitrate is flushed from the sub-surface only during the wet season, when shallow discharges are active. During summer, in the absence of significant rain infiltration, nitrate stays in the soil (where it might partially be recycled to pasture by plant uptake).

In contrast, in Whangamaire Stream at Woodhouse Road, nitrate concentrations were found to be always high. This is because the flow at that location is dominated by Patumāhoe Spring, which carries the smoothed nitrate loads from basalt soil market-gardening areas. Occasional spikes of lower nitrate at this stream monitoring site are caused by dilution from fresh rainfall pulses observed at these times.

In Ngakoroa Stream at Mill Road, nitrate concentrations were also found to be elevated most of the time due to the relatively constant flow contribution from the basalt formation covered by market gardening. The higher seasonal variability at this location is caused by shallow flow contributions to the stream from outside market garden areas (Morgenstern et al. 2023). Large spikes are likely to be caused by point sources (localised nitrate application). Note that, in the early 1990s, Ngakoroa Stream was still adjusting to previous land-use changes, with the summer baseflow showing the greatest impact. As the summer baseflow has an MTT of 11 years, the land-use change causing the increase in nitrate concentrations most likely occurred in the early 1980s.

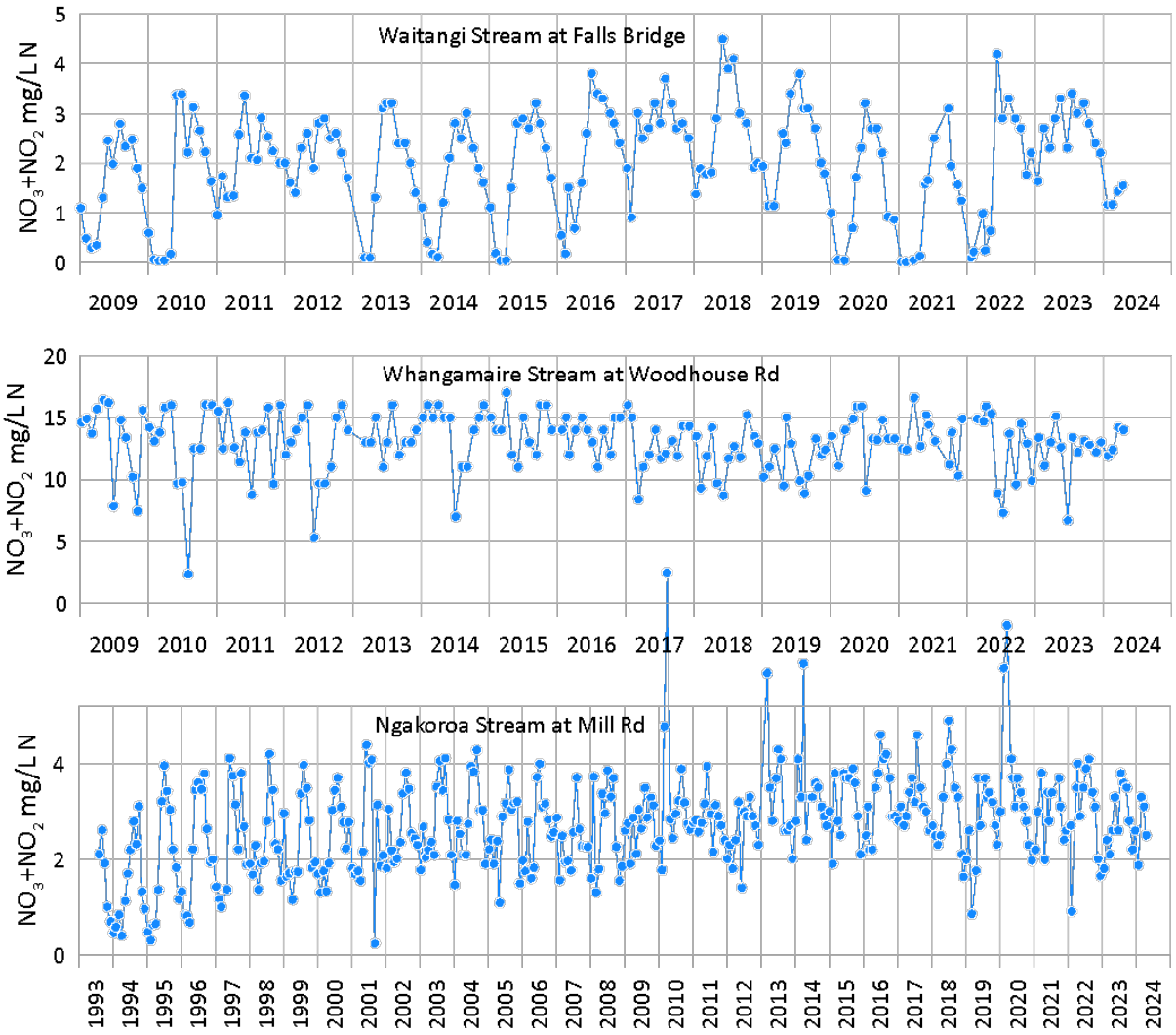


Figure 5.8 Auckland Council water-quality monitoring results for three streams in the Pukekohe–Bombay area (RIMU 2024). Shown is the sum of nitrogen as nitrate (NO_3) and nitrite (NO_2), as this is the most complete dataset. However, most of the nitrogen occurs as nitrate; NO_2 is usually negligible. Note the different time scale for Ngakoroa Stream.

The nitrate concentrations found in the springs and seeps (Puk1–6 in Figure 5.7) are consistent with nitrate concentrations of groundwater in the Pukekohe–Bombay area (Morgenstern et al. 2023). Samples Puk1–5 represent discharges from the basalt formation at the transition to Pleistocene deposits (Section 5.1), with Puk1–3 in the Whangamaire Stream and Puk4 in the Mauku Stream catchment.

Nitrate concentrations of Puk1–3 were lower than those of the groundwater discharging via the large Patumāhoe and Hickey springs further up. The flows of spring Puk1 and seep Puk3 are small, and these are likely to be discharges from the surrounding urban area. Seep Puk3 may be affected by denitrification in the groundwater – brown staining at the seep indicated anoxic conditions. Spring Puk2 had higher flow and higher nitrate concentration, more representative of the groundwaters of the market-gardening-covered basalt formations further up. Sample Puk5 was from a pond that collects seepage water from various small creeks. Its nitrate concentration was significantly lower than water sampled directly at springs and seeps. This is likely a result of denitrification processes in the pond providing an excellent environmental service by removing nitrate from the waterways. Note that the pond also collects road run-off (information provided by landowner), but we sampled it at baseflow when such flow paths were not active.

Seep Puk4 is located immediately below a market garden area on basalt but was found to have zero nitrate. One reason for the absence of nitrate is likely to be denitrification in the groundwater system. This seep is located at the boundary to the Pleistocene formation and the discharging water is highly anoxic, as indicated by the thick brown staining of the creek bed (Figure A1.9, right). Another possible cause for absence of nitrate may be low nitrate input. We could only dig a very shallow sampling hole without it collapsing (Figure A1.9, left). As a result, we may have captured mostly the shallow flow from within the gully, which is covered by bush.

Spring Puk6 discharges at the transition from volcanic unconsolidated to the Pleistocene formations. Relatively high dissolved oxygen (Figure 5.2) and nitrate (Figure 5.7) indicate that this water discharges from an oxic groundwater system.

5.8 Nitrate Isotopes

Various nitrate transformation processes are associated with nitrate isotope fractionation, which usually results in heavier isotopic compositions in the remaining nitrate pools compared to the transformation products, unless the reactions go to completion (Kendall 1998). Isotope separation is specific to processes, therefore observed differences in isotope enrichment between the two different isotopes of nitrogen and oxygen may make it possible to distinguish between various nitrate-transformation processes, for example, denitrification versus uptake by plants and algae. Nitrate isotope enrichment is easier to interpret in groundwater, where uptake is usually absent. However, in surface freshwater systems, a myriad of uptake processes are involved and there are potential point sources with highly variable isotope signatures.

It is important to understand the contribution of the various processes that remove nitrate from water. Some processes only remove nitrate temporarily (e.g. uptake by algae and macrophytes, with the organic nitrate potentially becoming re-mineralised under adverse conditions, for example, in winter). Other processes remove nitrate permanently (e.g. denitrification, with transformation of the nitrate into benign dinitrogen gas). Knowing which processes are active in an environment, and under which conditions, may enable enhancement of natural attenuation of high nitrate loads in these waterways.

In groundwater systems, nitrate isotope signatures make it possible to distinguish denitrification from dilution because the latter is not associated with isotope enrichment. Furthermore, the ability to measure the denitrification product excess-N_2 in groundwater offers a robust way of quantifying denitrification in groundwater systems (Section 5.9). In surface waterways, on the other hand, the presence of multiple nitrate processes, including dilution, denitrification, uptake and localised sources, can be too complex to allow attribution of observed isotope enrichments to individual processes. Other tracers may help to isolate these various processes.

Freshwaters have been considered to have undergone denitrification when $\delta^{18}O\text{-}NO_3$ increases linearly with $\delta^{15}N\text{-}NO_3$ at enrichment ratios of between approximately 1:2 and 1:1, corresponding to slopes in $\delta^{18}O\text{-}NO_3$ versus $\delta^{15}N\text{-}NO_3$ plots of 0.5 and 1.0, respectively (Kendall 1998; Finlay and Kendall 2007; Clague et al. 2015). This dual nitrate isotope enrichment has been interpreted over recent decades in numerous international and New-Zealand-based studies as being associated with denitrification.

However, based on subsequent studies, it has been recognised that, in aquatic environments, isotope fractionation during uptake by algae/plants can result in similar dual nitrate isotope enrichment as denitrification (Kendall et al. 2010). To date, no nitrate isotope reviews have been published that acknowledge this finding. The literature is not clear about how significant

the potential similarities in isotope fractionation are between denitrification and uptake in streams. Therefore, in the following sections, we interpret enrichment ratios of between approximately 1:2 and 1:1 as being indicative of denitrification, which is the currently accepted standard. We acknowledge that this approach may over-estimate denitrification in instances where substantial uptake occurs under conditions that would result in similar dual nitrate isotope enrichment as denitrification. Where available, we refer to supplementary information that supports the interpretation that denitrification is the dominant process (e.g. scarcity of plant biomass, redox indicators).

The nitrate isotope composition of groundwater and surface water in the New-Zealand-wide context is described and discussed in Rogers et al. (2023) in relation to the various nitrate sources and processes. The nitrate isotopes for the spring, seep and stream waters of the Pukekohe–Bombay area sampled in 2022 and 2023 are presented and discussed in Rogers (2024) in relation to general trends and isotope shifts. Rogers (2024) concludes that the waters in this area have a shared source of nitrate and are not significantly affected by denitrification processes. Most of the streams sampled plotted urine/urea or fertiliser (UUF) and soil N/Mixed UUF, and only three of the samples (Puk5, Te Hihi and Oira) had $\delta^{15}N\text{-}NO_3$ values >9‰.

Here, we present a detailed spatial analysis of the nitrate isotopes and concentration signatures of the spring, seep and stream waters of the Pukekohe–Bombay area to identify where denitrification processes are likely to occur. Figure 5.9 shows the spatial distribution of $\delta^{15}N\text{-}NO_3$, with a relatively clear pattern of heavier ^{15}N signatures downstream. This indicates that denitrification occurs in the water during its flow downstream, with the lighter nitrate isotopes preferentially consumed first, resulting in increasingly heavier isotope signatures in the remaining dissolved nitrate downstream. Figure 5.10 shows (a) the NO_3-N concentration and (b) $\delta\ ^{18}O\text{-}NO_3$ versus $\delta\ ^{15}N\text{-}NO_3$.

Trend vectors in a downstream direction are shown for stream sections with relatively consistent water sources (e.g. basalt discharges) and nitrate isotope trends. These are Mauku Stream, Whangamaire Stream and Whangapouri Creek samples 2–4 (sample 1 is from upstream of the confluence with Hickey Spring and is likely to reflect different nitrate sources and processes as captured by the Hickey-Spring-dominated flow at 2–4).

Hingaia Stream samples 1 and 2 are also from upstream of the confluence with the dominating Hillview Spring. Therefore, these likely capture different nitrate sources and processes than samples taken downstream of the confluence. Downstream from Hillview Spring, small decreases in nitrate concentration occur along the stream from sites 3 to 5, accompanied by small increases in nitrate isotope ratios. Vectors are also shown in Figure 5.10, generally mimicking the gradients of the other streams, but the changes were too small for meaningful comparison of gradients.

The nitrate isotope and concentration data for Ngakoroa Stream are highly variable. In its upper reaches, this stream receives some flow contribution from the basalt formation with market-gardening land use. However, most of its flow is gained from other areas, with variable nitrate sources and loads likely. Variable nitrate loads for Ngakoroa Stream are indicated by the high temporal variability of nitrate concentrations in this stream (Figure 5.8). Variable nitrate sources are likely to cause this variability in nitrate isotope signatures and concentrations. Oira Creek has similarly variable concentration, implying variable sources.

Another factor contributing to high longitudinal nitrate isotope variability in the streams not dominated by basalt discharges is the relatively low nitrate concentration of waters in these streams (Figure 5.10a). Low nitrate concentrations may result in denitrification reaching near-completion at sections of these streams. This would cause any small nitrate input downstream to dominate the isotopic signature in the stream water there and downstream, causing high variability of isotopic signatures from small local variable sources.

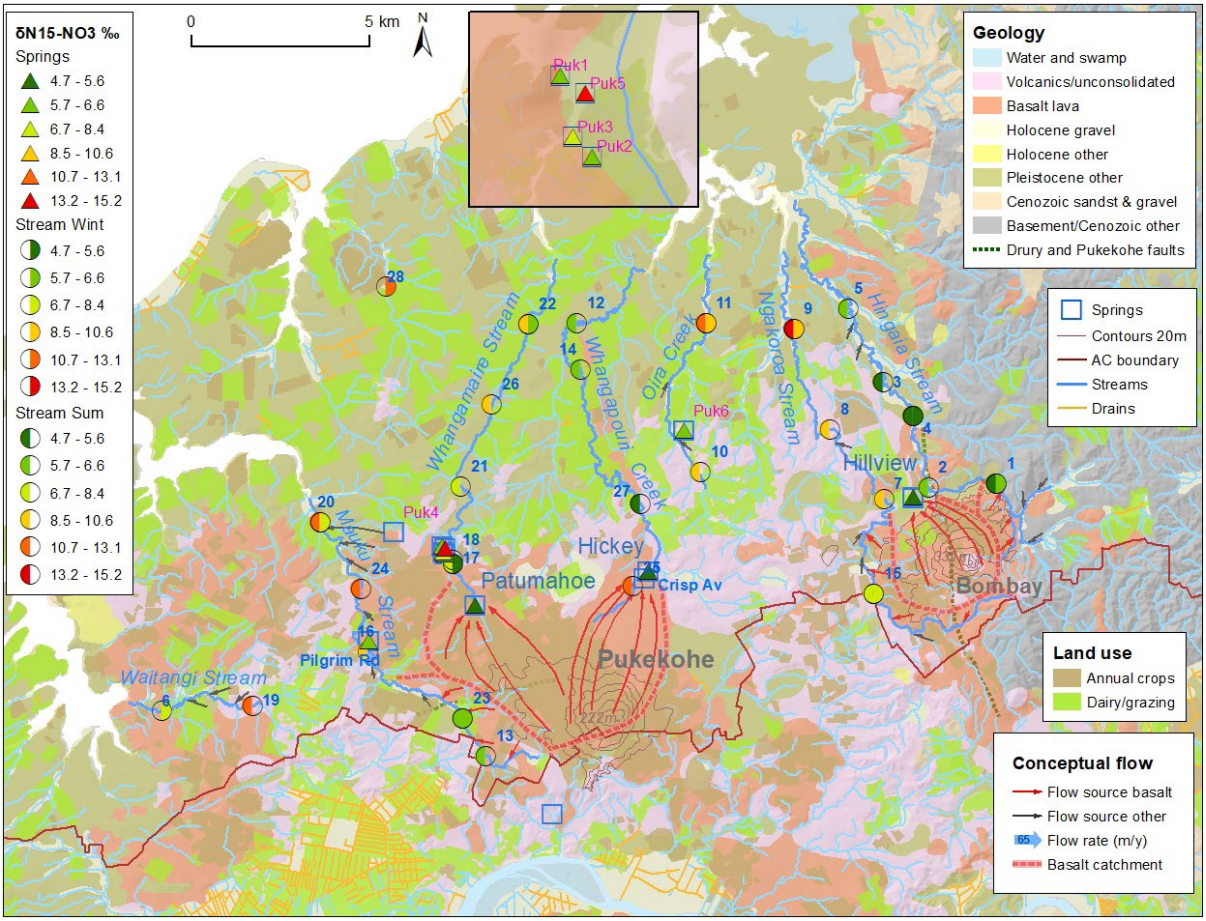


Figure 5.9 Spatial distribution of $\delta^{15}N\text{-}NO_3$. Conceptual flow is from Morgenstern et al. (2023). In addition to geology, market-gardening and dairy/grazing land uses are shown. The inset shows the cluster of springs and seeps near the upper Whangamaire Stream site 18.

For improved comparison of the gradients, Figure 5.10c shows the vectors for the three streams with robust isotope enrichment vectors shifted to the same origin. These gradients are all between the 1:2 and 1:1 linear relationship between $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$, indicating that denitrification is causing the decreases in nitrate concentrations. This agrees with other independent evidence. For example:

- Near-complete nitrate removal in a pond in absence of significant aquatic plant life (below).
- Anoxic conditions, favourable for microbial denitrification, measured in the top few centimetres of the sediments in the upper Whangapouri Creek.
- No obvious increases in nitrate loads during winter, which could be attributed to re-mineralisation of organic matter.

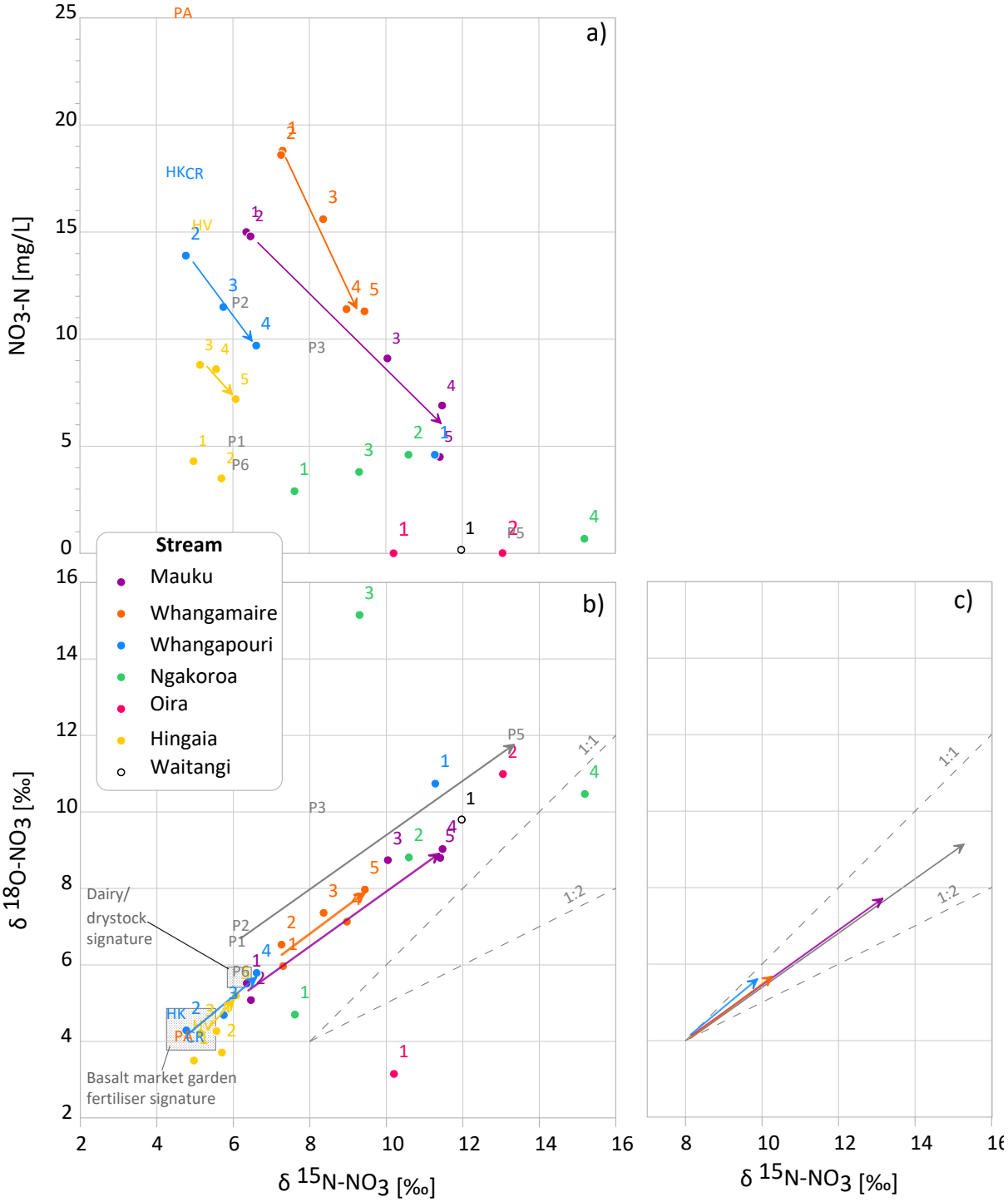


Figure 5.10 NO_3-N concentration (a) and $\delta^{18}O$-NO_3 (b) versus $\delta^{15}N$-NO_3 for the seven streams sampled in summer 2022 (2 February). Label numbers start with '1' at the most upstream sampling site and increase downstream. Vectors show the decreasing NO_3-N concentrations and increasing isotope ratios in a downstream direction for the streams with meaningful data (text). Gradients for 1:1 and 1:2 linear relationships between $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 are shown as dotted lines (Kendall et al. 2007) with arbitrary origin. The vectors are shifted to this origin in (c) for better comparison of their gradients. Magenta labels show data for the large springs sampled 7 April 2022 (PA = Patumāhoe; HK+CR = Hickey and Crisp Av; HV = Hillview). Grey labels show results for springs and seeps sampled 15 November 2023 (Puk1–6; 'P1-6' in figure).

In addition to the stream data, Figure 5.10 also shows data for the large springs (Patumāhoe; Hickey and Crisp Avenue; Hillview) and the springs/seeps Puk1–6 (P1-6). All of the large springs, and the origins of the vectors for Whangapouri Creek and Hingaia Stream, are plotted in a narrow range shown by the grey shaded box in Figure 5.10b. These groundwater discharges are oxic and therefore unlikely to be impacted by denitrification in the groundwater system. Therefore, the isotope range indicated by the grey box is likely to be the integrated nitrate isotope signature of groundwater recharged in the market-gardening-covered basalt lava at Pukekohe and Bombay.

The isotope and concentration signatures of the large springs are generally close to, or up-gradient of, the vectors of their respective streams. This shows that these spring signatures dominate the signatures of the water at these stream sites, which then become modified downstream.

The isotope and concentration data for Patumāhoe Spring plot a long distance upgradient of the origin of the vector for Whangamaire Stream (Figure 5.10a, b). This indicates that at the first stream sampling site significant amounts of nitrate from the spring had already been removed by denitrification. This agrees well with the fact that Patumāhoe Spring discharges into a large pond/wetland of approximately 100 m extension, likely enabling denitrification. By the time the water had reached the first stream sampling site, nitrate-N concentrations had already decreased from about 25 to 19 mg/L, with associated nitrate isotope enrichment. The degree of nitrate removal in this top part of the stream is similar to that along the entire stream section between sampling sites 1–5, in which nitrate-N concentrations decrease further from about 19 to 11 mg/L, with a similar associated nitrate isotope enrichment to the top part of the stream. The pond/wetland appears to be an efficient nitrate sink.

Minor springs Puk1 and 2 are likely to have their capture zones in a mixture of market-gardening and urban areas, with Puk1, located at the margin of the market-gardening area, being more dilute, as indicated by its lower nitrate concentration. Samples Puk1 and 2 (‘P1+2’ in Figure 5.10b) have very similar nitrate isotope signatures, indicating similar nitrate sources.

In contrast, Puk5 (‘P5’), from the outflow of a run-off collection pond, has a very low nitrate concentration of 0.7 mg/L NO_3-N despite the spring/seepage discharges into the pond likely containing relatively high nitrate concentrations (nearby springs Puk1–3 contain 5–12 mg/L NO_3-N). Low nitrate concentrations in the water after it has passed through the pond is likely the result of denitrification. This is indicated by nitrate isotope enrichment in this water. The vector from P1+2 to P5 is also shown in grey in Figure 5.10b and c. A gradient between the 1:2 and 1:1 linear relationship between $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ indicates denitrification. The pond appears to provide excellent conditions for denitrification.

An independent indication of denitrification, as opposed to uptake, in the pond is that there were no significant aquatic plants or algae visible in the pond (Figure A1.10) that could have taken up the nitrate.

There is a consistent pattern in that the samples with the lowest nitrate concentrations (Ngakoroa Stream 4, P2 and Waitangi Stream 1 in Figure 5.10a) have the highest nitrate isotope enrichments (Figure 5.10b).

Seep Puk3 has a slightly more enriched nitrate isotope signature than Puk1 and 2. This indicates partial denitrification, which is consistent with the brown staining at the seep and with the gas-tracer results indicating c. 20% of the water originating from anoxic flow paths (Section 5.4). Due to its very low flow, seep Puk3 is likely to have a very localised capture zone. The nitrate isotope signature is reflective of the lifestyle property it is located on.

Seep sample Puk4 is from a highly anoxic groundwater environment. A high ^{15}N ratio would be expected if some nitrate had remained in this water. However, no nitrate was found in this water – the nitrate isotope signature was lost due to complete denitrification.

The small spring Puk6 has only a drystock farm in its capture zone (Figures 5.9 and A1.11). The nitrate in this water has slightly higher isotope ratios compared to the nitrate in water recharged in the basalt market-gardening areas. This water is oxic and unlikely to have undergone denitrification. Therefore, with this flowing system providing an integrated tracer signature over time and space, this nitrate isotope signature is considered to be that of water recharged in the pastoral-grazing areas under oxic conditions.

5.9 Denitrification

Decreasing nitrate concentrations along streams associated with nitrate isotope enrichment, and near-zero nitrate concentrations in surface water and groundwater within areas of land use associated with high nitrate loading indicate that denitrification occurs in the Pukekohe–Bombay area. Denitrification is significant in streams and ponds/wetlands. It also occurs in anoxic groundwater of some geologic formations. This section aims to quantify denitrification in groundwater and surface water in the Pukekohe–Bombay area.

5.9.1 Groundwater

In groundwater, the main decay product of denitrification is nitrogen gas (dinitrogen, N_2). Groundwater is usually sealed from the atmosphere. Therefore, this excess-N_2, in excess to the intrinsic atmospherically derived N_2, accumulates along groundwater flow paths. This provides a quantitative measure of dissolved nitrogen gas originating from denitrification along the flow path (Section 3.1). We measured argon (Ar) and neon (Ne) concentrations in groundwater to isolate atmospherically derived intrinsic N_2 from denitrification derived N_2.

Deriving excess-N_2 only from N_2 and Ar data requires assumptions to be made about the recharge temperature or excess air in groundwater samples. Therefore, the results are only approximate and somewhat ambiguous (e.g. Stenger et al. 2018; Clague et al. 2019). This problem can be overcome by measuring further noble gases in the water, which makes it possible to constrain the free parameter. Neon analyses in groundwater have only recently become available in New Zealand (Section 3.1).

An Ar-N_2 plot was previously used by Morgenstern et al. (2023) for the Pukekohe–Bombay groundwater and major springs from the basalt formations to estimate excess-N_2. In Figure 5.11, the spring and seep data from the Pukekohe–Bombay area are shown in red. Derived recharge temperatures lie around the mean annual air temperature of 14.5°C. None of the samples shows a significant shift toward elevated N_2 concentrations (red arrow) of more than around 2.5 mg/L. This indicates that no significant excess-N_2 is present in these groundwaters, compared to high NO_3-N concentrations in the groundwater of 15–25 mg/L.

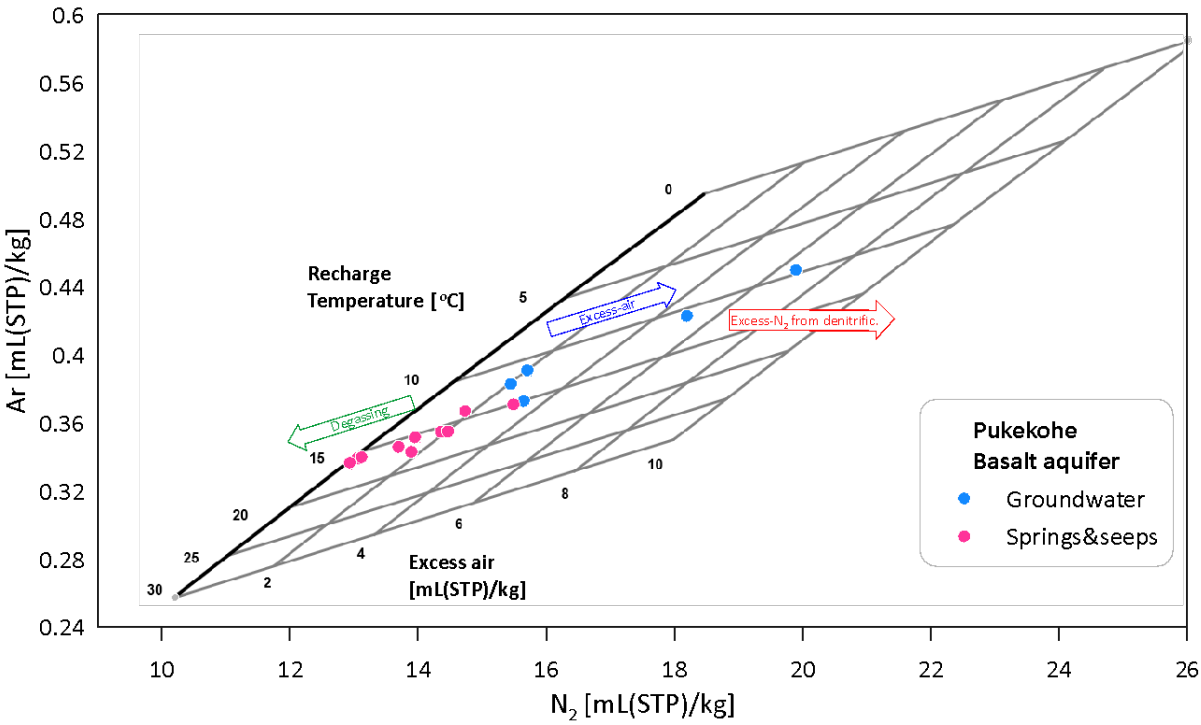


Figure 5.11 Plot of dissolved nitrogen (N_2) versus argon (Ar) concentrations, normalised to sea level. The positions of the samples within the grid indicate recharge temperatures and excess air concentrations (Heaton and Vogel 1981). The bold line on the left of the grid indicates gas concentrations in water in equilibrium with the atmosphere. Dissolved Ar, N_2 and excess air concentrations are expressed in millilitres of the respective gas at standard temperature and pressure (STP = 273.15 K, 101.325 kPa) per kilogram of water. Arrows indicate competing processes that can alter gas concentrations.

With the availability of Ne data, we were able to constrain groundwater recharge temperature and excess air, enabling more robust and accurate derivation of excess-N_2 concentrations. Excess-N_2 concentrations from N_2, Ar and Ne concentrations for the spring and seep samples are listed in Table 4.2.

The Ar-Ne derived low excess-N_2 concentrations confirm that denitrification is insignificant (<0.5 mg/L N_2) in the major springs from the basalt formation. An absence of denitrification in the basalt groundwater discharges is expected, as the groundwater throughout the basalt formation is oxic.

However, groundwater denitrification may occur within the Pleistocene and volcanic unconsolidated formations, as indicated by potentially anoxic groundwater discharges into the lower Mauku Stream and low nitrate concentrations in streams with capture zones mainly in pastoral land (Morgenstern et al. 2023). We searched for groundwater discharges in this area that could be sampled for excess-N_2. Unfortunately, the hydrogeology of the area is such that groundwaters discharge into the streams only via diffuse seepages, which are unsuitable for gas-tracer sampling. Therefore, it was not possible to quantify denitrification in a range of anoxic groundwater discharges typical for this area. It may be possible to measure excess-N_2 by intercepting groundwater seepages before they reach the streams; for example, using a push drill.

Springs and seeps with discrete outflows allowing for sampling of gas tracers were found at the boundary between the basalt formation and less hydraulically conductive formations (Puk1–3). As these are discharges from the basalt formation, they were found to be mainly oxic, containing insignificant excess-N_2 (<0.3 mg/L N_2).

However, groundwater sample Puk4 shows that denitrification in anoxic groundwater in this area occurs and that it can be quantitative, with nitrate completely removed. This groundwater discharges from a highly anoxic environment, as evidenced by its low concentration of dissolved oxygen and high methane concentration (Table 2.2), as well as the brown staining of the stream bed (Figure A1.9). The discharge is diffuse, but it was possible to sample for gas tracers by intercepting the seepage flow just before the pond through a small hole. This groundwater was found to contain 0.7 mg/L of excess-N_2, while its nitrate concentration was zero (Table 4.2). These results show that, initially, 0.7 mg/L NO_3-N were present in this water, which had been converted into 0.7 mg/L of excess-N_2 (benign nitrogen gas).

An initial nitrate-N concentration of 0.7 mg/L is unusually low given that market gardening occurs only a few hundred metres upgradient of the seep. However, this very shallow seep is likely to have its capture zone mainly in the bush-covered gully. Therefore, it does not represent market-gardening nitrate loading. Regardless of the low initial nitrate concentration, this result demonstrates that denitrification to completion does occur in this area in groundwater that passes through highly anoxic systems.

Sampling site Puk6 is located at the boundary between unconsolidated volcanics and less permeable formations. Land use within the capture zone of this spring is dairy/drystock grazing. The NO_3-N concentration of 3.9 mg/L is considered typical of water from such land use. As this water is oxic, no denitrification has occurred in the groundwater system. This is indicated by its excess-N_2 concentration of <0.3 mg/L N_2 (Tables 2.2 and 4.2).

5.9.2 Surface Water

In surface water, dissolved atmospheric gas concentrations as derived from groundwater (including N_2) quickly reach equilibrium concentration for water that is in contact with air. Therefore, it is not possible to derive the denitrification product excess-N_2 in surface water as a quantitative means of measuring denitrification.

However, it is possible to estimate in-stream nitrate removal in long sections of three of the sampled streams due to their unique settings. During summer baseflow, Whangamaire, Whangapouri and Ngakoroa streams receive most of their water and high nitrate loads in their upper reaches from the basalt formations (Figure 2.2). From there, these streams flow through Pleistocene deposits in which groundwater and associated nitrate flow paths are inactive during summer baseflow conditions (Morgenstern et al. 2023). We collected flow and nitrate data for these three streams from the upper and lower parts of their course through the Pleistocene formation. Table 5.1 lists flow and nitrate concentrations for these streams at summer baseflow in 2022 and for sections of other streams and a pond that allow for estimation of nitrate removal from surface waterways.

In the absence of gains of water and associated nitrate loads in sections of streams, the amount of nitrate being removed from the water in these stream sections can be estimated using a simple mass balance. Decreases of NO_3-N concentrations in percentage and removed NO_3-N in tons per season are listed in Table 5.1.

The dual nitrate isotope enrichments in three of the largest streams in this area (Whangapouri, Whangamaire, Mauku) indicate that the dominant process of nitrate removal is denitrification (Section 5.8). Despite the data being insufficient to constrain the specific dominant nitrate removal process for all streams, it is likely that the situation is similar in all streams in this area. Therefore, the NO_3-N removal rates in Table 5.1 are likely to be mainly due to denitrification.

Table 5.1 Stream flow, NO_3-N concentrations and ^{15}N ratios for selected streams and springs/seeps/pond. The ID, NO_3N and ^{15}N ratio data are from Morgenstern et al. (2023). 'NO_3N Concentration Decrease' is the decrease of the nitrate concentration in the stream along the relevant course or pond. 'NO_3N Load' is the amount of nitrate-N discharged via the stream, extrapolated to the three months of summer or winter. 'NO_3N Removed' is the amount of nitrate-N removed from the stream. '$\Delta\ \delta^{15}N$' is the shift in $\delta^{15}N$ caused by denitrification in the relevant section of the water way. GC = gas chromatography.

Stream Site	ID	Date	Stream Baseflow (L/S)	NO_3N Concentration (mg/L)	NO_3N Concentration Decrease (%)	NO_3N Load (tons/ season)	NO_3N Removed (tons/season)	$\delta^{15}N$ ‰	$\Delta\ \delta^{15}N$ ‰
Basalt Formation to Patumāhoe, Hickey, and Hillview Springs	-	-	-	-	0	-	0	5.08	0
Patumāhoe Spring	-	7 April 2022	-	25	-	-	-	4.7	-
Whangamaire Railway Culvert	17	2 February 2022	93	18.8	25	13.8	4.6	7.3	-
Whangamaire Ostrich Road	21	2 February 2022	116	15.6	-	14.3	-	8.36	-
Whangamaire Fantail	22	2 February 2022	128	11.3	28	11.4	2.9	9.44	1.1
Whangapouri Paerata Falls	27	2 February 2022	168	13.9	-	18.4	-	4.77	-
Whangapouri Pukekohe GC	12	2 February 2022	158	9.7	30	12.1	6.3	6.61	1.8
Ngakoroa Kern Road	8	2 February 2022	46	3.8	-	1.4	-	9.3	-
Ngakoroa Runciman Road	9	2 February 2022	41	0.7	82	0.2	1.2	15.2	-
Hingaia Maxter Road	4	2 February 2022	152	8.8	-	10.6	-	5.14	-
Hingaia Ararimu Road	3	2 February 2022	151	8.6	2	10.3	0.3	5.56	0.42
Hingaia Quarry Road	5	2 February 2022	182	7.2	16	10.4	-	6.07	-
Mauku Puni	13	2 February 2022	18	15		2.1	-	6.35	-
Mauku Wrights	24	2 February 2022	48	6.9	>54	2.6	-	11.47	-
Mauku Swede	20	2 February 2022	107	4.5	>35	3.8	-	11.41	-
Oira Swing Bridge Woodlyn Drive	11	2 February 2022	14	0	100	0	-	13.1	-
Oira Catchment	Puk6	15 November 2023	-	3.9	-	-	-	6.2	-
Oira Swing Bridge Woodlyn Drive	11	8 August 2023	209	0.6	85	1.0	5.4	9.6	-
Te Hihi Stream	28	8 August 2023	114	1.8	54	1.6	1.9	11.8	
Spring/seeps near Puk5	Puk1–3	15 November 2023	-	8.6	-	-	-	6.1	-
Collection pond	Puk5	15 November 2023	-	0.73	85	-	-	13.4	-

As shown in Table 5.1, along the course through the Pleistocene formation, the NO_3-N concentration of the water in:

- Whangamaire Stream reduces from 15.6 to 11.3 mg/L – a nitrate reduction of 28%. Extrapolated to baseflow through the summer months, this equates to an N removal from the stream water of about 2.9 tons per three summer months.
- Whangapouri Creek reduces from 13.9 to 9.7 mg/L – a nitrate reduction of 30%. Extrapolated to baseflow through the summer months, this equates to an N removal from the stream water of about 6.3 tons per three summer months.
- Ngakoroa Stream reduces from 3.8 to 0.7 mg/L – a nitrate reduction of 82%. Extrapolated to baseflow through the summer months, this equates to an N removal from the stream water of about 1.2 tons per three summer months.

Note that these nitrate concentration decreases and amounts of removed nitrogen refer only to the stream sections between the sampled sites through the Pleistocene formations. It is likely that additional significant denitrification also occurs in these streams above and below these sections, and therefore the total amount of nitrogen removed along the entire lengths of the streams is likely to be significantly higher.

For example, for the upper section of Whangamaire Stream between Patumāhoe Spring and Railway Culvert (17), assuming the nitrate concentration of Patumāhoe Spring is representative for the entire groundwater discharge into the stream through this section, the NO_3-N concentration of the water reduces from 25 to 18.8 mg/L – a nitrate reduction of 25%. Extrapolated to baseflow through the summer months, this equates to an additional N removal from the stream water in the upper section of Whangamaire Stream of about 4.6 tons per three summer months.

In contrast to the relatively high decreases in nitrate concentrations in the above streams, at Hingaia Stream downstream of Hillview Spring between sites 4 and 3, a section with no additional groundwater discharges, the NO_3-N concentration of the water reduces only from 8.8 to 8.6 mg/L (Table 5.1). This is a nitrate reduction of only c. 2% (0.3 tons N per three summer months), despite this section being a quarter of the length of Whangapouri and Whangamaire streams, where nitrate reductions of c. 30% occur. This low decrease in nitrate concentration may be due to conditions in this section of the streambed being less favourable for denitrification – this stream section is close to the hills and therefore likely to be steeper, with faster flow, and have less organic matter in the streambed compared to lowland sections of the streams.

Additional groundwater discharges (Figure 2.2) are likely to contribute further nitrate loads in the lowest sampled section of Hingaia Stream between sites 3 and 5. This is indicated by similar nitrate loads between the start and end of this section, despite NO_3-N concentrations decreasing from 8.6 to 7.2 mg/L. The 16% decrease in nitrate concentration is only a lower limit – the decrease would be higher without fresh nitrate inputs.

The nitrate decrease in the lowest sampled section of Hingaia Stream is similar to decreases in the lowland sections of Whangapouri and Whangamaire streams, indicating that the denitrification conditions in the lowland Hingaia Stream section are similar to those of the other streams.

Similar to Hingaia Stream between sites 4 and 3, an estimate of in-stream nitrate removal along Mauku Stream between sites 13 and 24 is prevented by further nitrate loads from groundwater discharges from basalt formations with the market-gardening land use. However, as land use along this stream course is relatively uniform market gardening, it can be assumed that these discharges have similar NO_3-N concentrations to those at site 13 (c. 15 mg/L). Therefore, the decrease in NO_3-N concentrations to 6.9 mg/L at site 24 indicates that nitrate reduction is at least 54%. It is likely to be higher without fresh nitrate inputs into the stream just above site 24.

In the lowest sampled section of Mauku Stream, between sites 24 and 20, the NO_3-N concentration decreases further to 4.5 mg/L. However, this decrease may partially be due to dilution by groundwater that has passed through anoxic systems – part of the denitrification may have occurred in the groundwater system.

Nitrate reduction through in-stream processes can also be estimated for Oira Creek, a stream draining mainly pastoral grazing land. Flow and nitrate concentrations for this creek are listed in Table 5.1. Oira Creek does not receive baseflow from basalt, so during summer its catchment discharge, from the Pleistocene formation, is largely inactive. At very low summer baseflow, an NO_3-N concentration of 0.0 mg/L was measured in this water, indicating that nitrate had been completely removed—regardless of the exact initial concentrations, the nitrate reduction was 100% (Table 5.1). Despite this, the mass of N removed from the stream was low because of the very low flow and N load during summer. Some of the nitrate from pastoral grazing land use may have been removed by uptake in the soil and denitrification near the redox interface.

At winter baseflow conditions, when Oira Creek's catchment discharges are active, the NO_3-N concentration downstream, measured at 0.6 mg/L, was very low for water with a capture zone in mainly pastoral grazing land. The average initial NO_3-N concentration of the water discharges from the pastoral land into the stream are not known. However, seep Puk6 is such a discharge, and it was sampled when the flow at Oira Creek at Swing Bridge was approximately 200 L/s, similar to the flow when Oira Creek was sampled in August 2023. Assuming the NO_3-N concentration of Puk6 (3.9 mg/L) is representative of the catchment, using this value as an initial nitrate concentration for the Oira Creek catchment results in a nitrate reduction of approximately 85% at winter baseflow conditions (Table 5.1). Despite only one measurement being available for such a land use, a nitrate reduction of >80% seems robust given such a low nitrate concentration in a stream discharging mainly dairy and drystock land.

The situation is likely to be similar at Te Hihi Stream. Assuming an input NO_3-N concentration of 3.9 mg/L for this mainly dairy/grazing-covered catchment, the stream NO_3-N concentration of 1.8 mg/L indicates a nitrate reduction of approximately 54% (1.9 tons N per three winter months) at winter baseflow conditions (Table 5.1). During summer, the nitrate reduction is likely to be 100%, as at Oira Creek.

Table 5.1 also shows an estimate of nitrate reductions for the run-off collection pond Puk5. The groundwater discharges into this pond are likely to have similarly high NO_3-N concentrations as springs and seeps Puk1–3. Using their average of 8.6 mg/L as an initial concentration into Puk5 leads to an estimate of 85% N reduction within this pond.

Figure 5.12 shows, together with the opposing trends of decreasing nitrate concentrations and increasing ^{15}N ratios, the estimates of nitrate reduction through denitrification within groundwater systems and N removal from stream sections where data is available for such estimates.

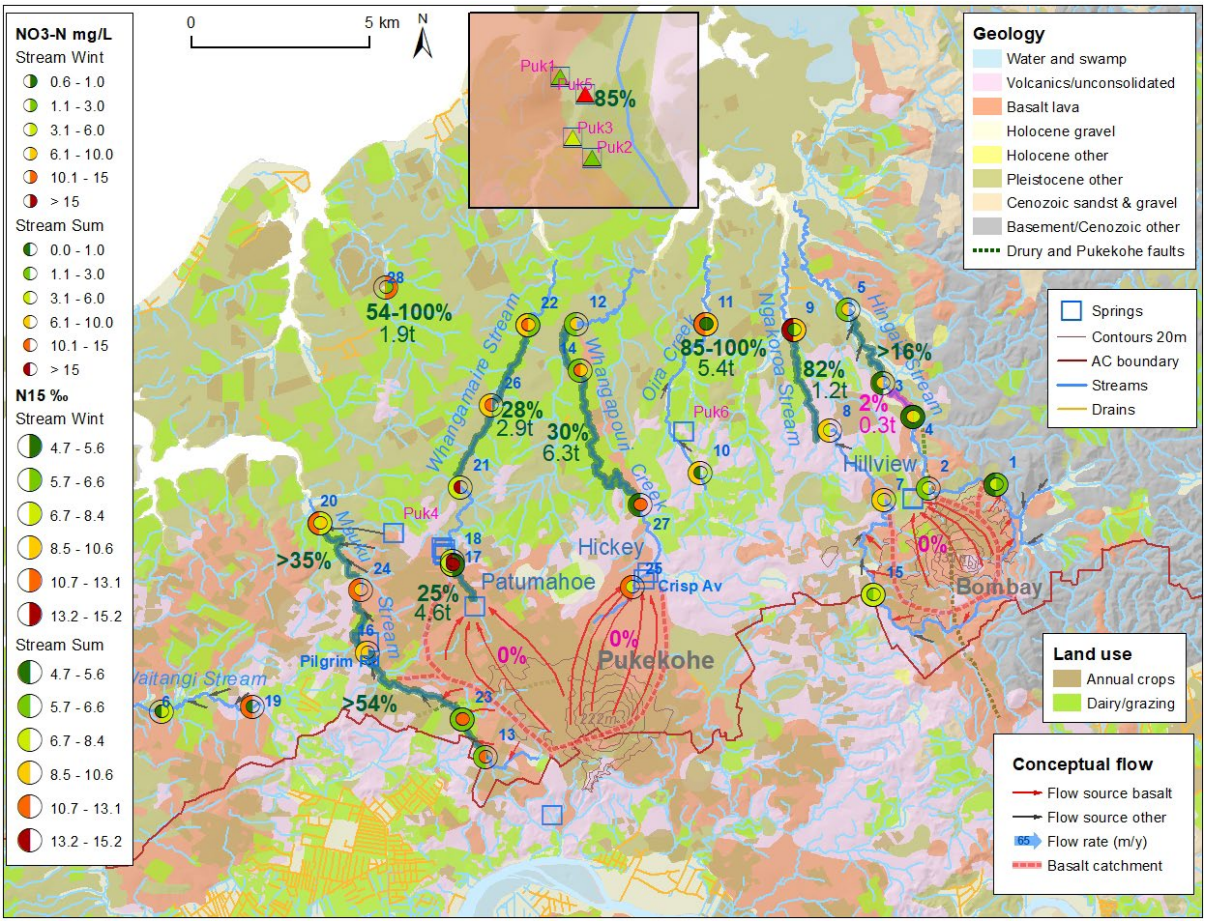


Figure 5.12 Estimates of nitrate reduction through denitrification in percentage and N removal from stream sections in tons per three months of summer or winter season (t). Green text and stream stretches are for high denitrification, red is for low denitrification. Also shown are nitrate-N (NO_3-N) (inner circles) and $\delta^{15}N$-NO_3 ratios (outer circles) for summer (left half of circles) and winter (right half of circles), with more detail in Figures 5.7 and 5.9. Conceptual flow is from Morgenstern et al. (2023).

Whangamaire Stream and Whangapouri Creek, along their sections passing through the Pleistocene formation without additional nitrate input, showed consistent trends of nitrate concentrations and nitrate isotope enrichments, indicative of denitrification. The shift in $\delta^{15}N$ along the streams – the difference between the upstream and downstream sites – is listed in Table 5.1 as $\Delta\ \delta^{15}N$. The data indicate that denitrification rates of around 30% are associated with a $\delta^{15}N$ increase of approximately 1.1 and 1.8 along these stream sections.

These shifts toward heavier N isotopes are expected to increase with progressing denitrification. With more data available, a correlation between $\Delta\ \delta^{15}N$ and percentage of nitrate reduction may enable a semi-quantitative measure of the amount of nitrate removed from stream water through microbial denitrification, based on $\Delta\ \delta^{15}N$, where dilution cannot be ruled out. Further research is required to test if such a correlation exists for different stream environments in different seasons and with interplay between nitrate removal and fresh inputs.

6.0 CONCLUSIONS

The main nitrate load in the Pukekohe–Bombay area, from market gardening, enters with infiltrating water into large groundwater stores in the basalt formation and discharges mainly through three large springs. Without denitrification in the groundwater system, these springs cause high nitrate concentrations in their receiving streams.

In the volcanics/unconsolidated formations, the presence of excess-N_2 in groundwater that has evolved to complete denitrification, as well as dilution of stream nitrate loads by potentially anoxic groundwater discharges, indicate that denitrification in groundwater systems occurs in these formations. However, it is not possible with the current data to estimate the extent of this groundwater denitrification.

Large nitrate sinks within the catchment were found to occur within surface waterways – in streams and ponds/wetlands. Nitrate loads were found to significantly decrease along the course of the streams. Due to the unique setting of several of these streams, with high nitrate loading in their upper reaches from the basalt springs and an absence of further significant nitrate loads within the lower reaches, the nitrate removal rate could be estimated. The dual nitrate isotope enrichment points to natural denitrification into nitrogen gas as the main process of nitrate removal. Ponds/wetlands and stream beds appear to be efficient nitrate sinks in this area.

In the Pleistocene formation, where land use is mostly pastoral dairy and drystock farming, nitrate is flushed out seasonally. These areas discharge water and nitrate loads mainly via shallow flow paths, which are not active in summer. Some streams in this area, despite discharging mainly pastoral grazing land, have near-zero nitrate concentrations in summer low-flows, indicating near 100% removal of nitrate load. Even in winter, when discharges are active, around 80% of the nitrate appears to be removed from these streams. In these catchments, nitrate removal may partially occur within the stream bed but could also have significant contributions within the soil and near the redox interface.

7.0 RECOMMENDATIONS

The tracer data collected from groundwater and stream water in the Pukekohe–Bombay area supports a relatively robust overall understanding of nitrate transport and sinks, including transmission of large nitrate loads from market-gardening land use through basalt aquifers in absence of nitrate sinks, discharge of these N loads through large springs into baseflow-controlled streams, partial nitrate removal through denitrification within these stream environments in the lowlands and seasonal flushing of nitrate from dairy/grazing-covered Pleistocene sediments with large fractions of the nitrate removed from the water through denitrification and or uptake. Results from samples collected from different sites, during different seasons and for various independent tracers – including hydrochemistry, isotopes and gases – indicate a consistent picture of processes involved. However, if resource management and remediation planning in particular stream environments requires a more detailed understanding of nitrate loads and sinks, we recommend the following investigations:

1. **Model timing of nitrate load response in springs discharging the basalt formations.** Management of nitrate loads in the basalt area may require better understanding of the timing of nitrate load response in the springs. Groundwater age distributions could be used to model nitrate load responses through the main spring discharges to source load changes in more detail (Morgenstern et al. 2015).
2. **Sample groundwater seepage in areas of anoxic groundwater discharge.** For better characterisation of groundwater denitrification, groundwater seepage should be sampled for excess air and age tracers in areas where anoxic groundwater discharges are expected (see Recommendations section in Morgenstern et al. [2023]). Push-drilling may enable sampling of groundwater seepage before the water reaches the streams to avoid contact with air. Many groundwater discharges mapped as springs appear to start as a pond. Obvious places to intercept the groundwater seepage into the ponds would be to push-drill next to the ponds on their upstream side. To identify where groundwater seepage into the streams is likely, higher-resolution stream gauging may be required.
3. **Conduct higher resolution sampling of N sinks.** Significant N sinks have been identified in surface water bodies in this area. Denitrification processes are considered to occur in 'hot spots and hot moments'. Higher-resolution sampling over space and time may enable identification of optimum conditions for denitrification, which may in turn inform engineered solutions to enhance denitrification. For example, nitrate appears to be removed very efficiently in Oira Creek, so investigating the ecological conditions that support instream N uptake in this environment may support the development of denitrification solutions to be applied elsewhere. Identification of boundaries of N uptake by algae and macrophytes versus denitrification would be informative to help avoid recycling of nitrogen via re-mineralisation of organic matter.
4. **Identify the medium where denitrification (or uptake) in streams occurs.** At this stage, denitrification is assumed to occur in the shallow stream sediments. Verify this by collecting water samples from the shallow water column and from anoxic shallow sediments that are in good hydraulic connection with stream water. Understanding optimum stream bed conditions for denitrification and nitrate uptake may enable replicating of those same conditions to other streams.
5. **Determine whether denitrification in surface water environments occurs to completion.** Collect water samples from the shallow water column and from the shallow sediments for excess-N_2 and nitrous oxide (N_2O) analysis to determine whether denitrification occurs to benign N_2 gas or only to N_2O, which is a potent greenhouse gas.

6. **Conduct further sampling in streams with highly seasonal nitrate loads.** Nitrate loads in some stream environments (Pleistocene sediments covered mainly with dairy/grazing) are highly seasonal. Currently, there are only two seasons measured, summer baseflow and winter baseflow after a prolonged wet period of 1.5 years. A better understanding of seasonal dynamics and flushing could be obtained by collecting samples from streams with highly seasonal nitrate loads three-monthly or more frequently, including high-frequency nitrate monitoring using optical sensors, over one year.
7. **Verify the efficiency of N sinks.** The pond and wetland at Patumāhoe Spring and a drainage pond Puk5 appear to be efficient N sinks. Such environments may provide efficient nitrate removal solutions that could be applied to other streams. Verify the efficiency of these N sinks by collecting samples from the water column and shallow sediments and at various places along the flow through these ponds.

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APPENDICES

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APPENDIX 1 PHOTOS OF SPRING AND SEEP SAMPLING



Figure A1.1 Crisp Avenue spring at downstream left bank of Whangapouri Creek, opposite Hickey Spring.



Figure A1.2 Patumāhoe Spring below road next to old well.



Figure A1.3 Hickey Spring at water supply works.



Figure A1.4 Hillview Spring at water-supply works.



Figure A1.5 Pilgrim Road domestic water-supply spring.



Figure A1.6 Puk1: Spring pool with visible discrete discharges (left). The siphoning tube was taped to a rock to enable positioning of the tubing inlet at a discrete discharge point without disturbing the sediment. The spring was cleared the evening before.



Figure A1.7 Puk2: Domestic supply spring. A flexible knee was taped onto the buried pipe to block the water and prevent air contact inside the pipe from which the water was siphoned to the sampling gear.



Figure A1.8 Puk3: Seep discharging low-dissolved-oxygen water. Seep flow was blocked with plastic foil, rocks and soil (left) to enable siphoning the water without air contact to the sampling gear (right).



Figure A1.9 Puk4: Duck pond with Bennett pump set up in small hole 1 m upstream, next to the pond that intercepts seepage into it (left); creek bed stained by iron hydroxide from anoxic water discharges (right).



Figure A1.10 Puk5: Collection pond with outflow pipe on left below track.



Figure A1.11 Puk6: Oira Creek riparian zones (left); log dump seep that was cleared and slightly dammed to enable siphoning the inflowing water below the surface (right).

APPENDIX 2 MAIN FARM TYPES IN THE PUKEKOHE VEGETABLE-GROWING AREA

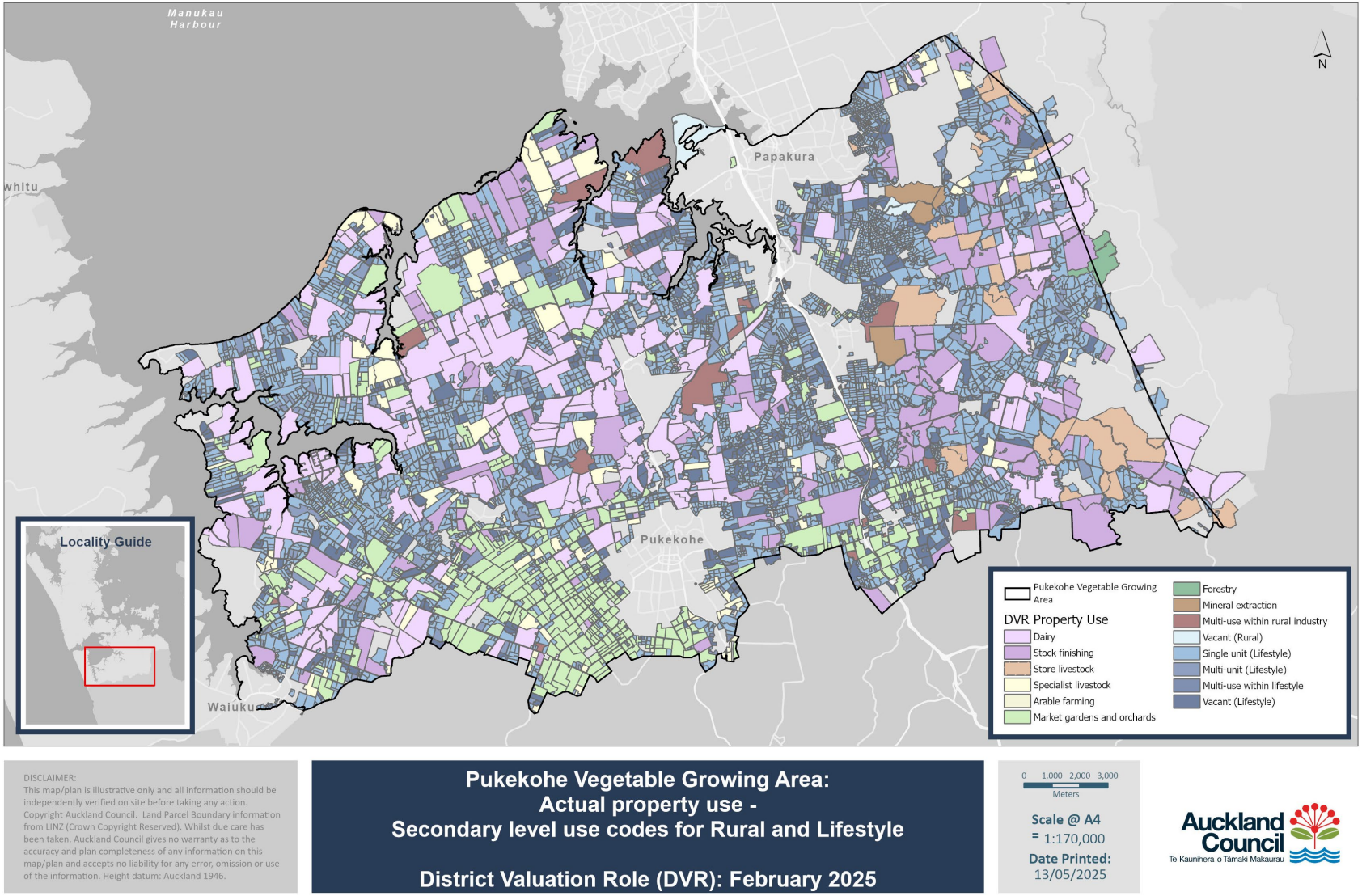


Figure A2.1 Main farm types in the Pukekohe vegetable-growing area. Image (sourced from Auckland Council [2025]) replaced in report in May 2025; update not considered large enough to require an official revised version of the report.

APPENDIX 3 ANALYSIS REPORTS AND DATA

The analysis reports and associated data are provided as digital file attachments.



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