

5 June 2020

Dear Editor,

5 Thank you for your work on this paper. The paper has been extensively revised in light of the referee's comments. Revised responses and an edited version of the paper are attached.

An approximate list of changes include (detail changes are given in the responses):

Abstract: Sentences added

- 10 1. Introduction: Extensive changes
2. Background: Values added, changes made
3. Methods: Many changes
4. Results: Sections shortened and revised
5. Discussion: Extensive revisions
15 6. Conclusions: Changes made
Appendices 2 and 3 added
References: New references added
Tables 1 and 4 revised

20 Code/Data availability

None

Author contribution

25 MKS had major responsibility for the paper, PLA-E responsibility for the research and report that the paper was based on

Competing interests

The authors have no competing interests.

30 The report below forms Supplementary Material for this paper:

Aitchison-Earl, P.: Sources of nitrate in groundwater in the Tinwald, Ashburton area. Environment Canterbury Report No. R19/85, 2019. <https://api.ecan.govt.nz/TrimPublicAPI/documents/download/3664244>

Yours faithfully,

35 Mike Stewart

Reply to Reviewer #1 (R1)

40 R1: The paper considers the contribution by irrigation return flow to high nitrate concentrations in groundwater and points out how this contribution of nitrate needs to be incorporated into assessment of nitrate load limits. The authors also note the occurrence of denitrification processes in a group of wells as indicated by N and O isotopes even though the levels of DO in those wells are not particularly low (up to 4 mg N/ L). This indicates that averaged DO concentrations may not exclude denitrification. The authors suggest denitrification may occur in localised areas with fine pores or reduced microsities even while average DO levels are higher than would be expected for denitrification to occur.

45 *Authors: We thank Reviewer #1 for constructive evaluation of our work.*

R1: Principal Criteria Scientific Significance: Good (2) The scientific significance is good – see summary above.

50 There is a discrepancy presented regarding the likely source or location of the denitrification. In the abstract, discussion and conclusions it is suggested that the denitrification may occur in localised areas with fine pores or reduced micro-sites, whereas in the results section (line 272 – 274) it states that the denitrification occurred “most probably within the soil the nitrate was leached from.”

55 *Authors: An important point. Our initial conception was that such denitrification would have been within the soil before leaching to the groundwater, but further consideration and perusal of the literature suggested that denitrification can occur in fine pores or reduced micro-sites in the vadose zone – groundwater continuum. We have amended the text to be more consistent with the latter explanation.*

R1: Scientific Quality: Good(2) Scientific method and approach are valid and are carried out well. The approach and conclusions could have been improved with the addition of excess N₂ data as this would have confirmed denitrification along the flow and added to the conclusions.

60 *Authors: We did not have excess N₂ data, but agree this could have strengthened the evidence for denitrification.*

R1: Presentation Quality: Excellent (1) The paper is written in a clear and readable fashion and is easy to follow. The number and quality of the figures and tables is good and adds to the presentation of information in the paper. Referee questions – all covered and good.

65 Specifics The final paragraph in the discussion section (lines 451 – 454) makes an observation about a dual porosity system in the groundwater at Tinwald which is consistent with the proposed site(s) for denitrification. Dual porosity has been studied in these alluvial gravel aquifers by, for example, Dann et al. 2009 and similar papers, and this paper(s) could usefully be incorporated to provide more context and insight to the discussion.

Authors: We agree and will add this reference. We think more evidence is needed here.

70 R1: Probable typo – In line 163-164 it gives the precision for the isotope analyses “except for samples below 100 mg/L NO₃-N.” All samples are below this level so I suspect the units or number is incorrect.

Authors: Yes, the number should have been 0.1 mg/L (100 µg/L)

R1: Typos: line 505. Denitrification spelt wrong.

Line 539. Canterbury spelt wrong. Line 545 review spelt wrong.

Authors: These have been corrected.

75

Reference:

Dann, R.L.; Close, M.E.; Flintoft, M.J.; Hector, R.; Barlow, H.; Thomas, S; Francis, G. (2009). Characterization and estimation of hydraulic properties in an alluvial gravel vadose zone. *Vadose Zone Journal* 8(3): 651-663.

80 Reply to Anonymous Referee #2 (R2)

R2: This paper looks at the impact of irrigation return waters in areas of intensive agriculture on nitrate concentrations and considers more broadly how we track the sources of nitrate via dual isotopes. The study itself is scientifically sound although I struggled in places with the text. Some of the sections are not very clearly written and the structure could be improved.

85 Specifically, both the introduction and discussion alternate between local and more global observations and the descriptions in parts of sections 4 & 5 are long. A few clearer statements around the global importance of the work would also improve its impact. I have made several comments below that I hope are useful in revising this paper.

Authors: We thank Referee #2 for helpful and constructive comments on our work.

90 R2: Specific comments: Abstract. The abstract is well-written and intelligible without having to refer to the rest of the paper. Having said this, it could be improved by:

1) Adding a sentence at the start to outline the motivation for the study

2) Adding a few key values (there are a fair number of qualitative terms here – high, low, relatively etc). A few specific values would convey more meaning.

Authors: We added sentences to the beginning of the abstract to address points 1) and 2) as follows:

95 “Nitrate concentrations in groundwater have been historically high ($N \geq 11.3$ mg/L) in an area surrounding Tinwald, Ashburton since at least the mid-1980s. The local community are interested in methods to remediate the high nitrate in groundwater. To do this they need to know where the nitrate is coming from.”

100 R2: Introduction The introduction sets the scene for the study. For a paper in an international journal such as HESS, it would be appropriate to add a few comments about how New Zealand compares to other intensive agricultural areas globally in terms of the scale of the problem. High nutrient loads are of global interest and this research will have broader interest, so some more comments here are warranted. The structure could be improved as it alternates between general and area-specific statements. Try to group these more. Some of the description of the issues around Tinwald could be in section 2.

105 Authors: We have referred to OECD reports (2013 and 2017), which place New Zealand’s intensive agricultural area management in the context of those of OECD member countries:

110 “Eutrophication causing hypoxia and algal blooms, due primarily to agricultural runoff of excess nutrients, is considered the most prevalent water quality problem globally (OECD, 2017). In New Zealand the N balance worsened (i.e. became more positive) more than in any other OECD member country between 1998 and 2009, almost entirely because of expansion and intensification of farming in New Zealand (OECD, 2013). (The N balance is the difference between N inputs to farming systems (fertiliser and livestock manure) and N outputs (crop and pasture production) - a positive N balance indicates increased potential for N pollution of soil, water and air. In fact, the increase of the positive N balance matched the increase of dairy farming in New Zealand.)”

Some description of issues around Tinwald has been moved to Section2.

R2: Lines39-43. What are the concentrations of nitrate in the groundwater and the river water?

115 Authors: Groundwater ($N \geq 11.3$ mg/L) and alpine river water ($N < 1$ mg/L). These numbers will be added to the text.

R2: Lines 44-48. This seems out of place in the description of the local setting. It would be better earlier where you discuss the general importance (especially as it refers to contaminants other than nitrate).

Authors: We couldn’t move this earlier because the term ‘irrigation return flow’ needed to be defined first.

120 R2: Lines 68-62. These references are a little dated. Can you point to some key recent studies, especially those that deal with the issues of irrigation return flows?

Authors: More recent references including two dealing with irrigation return flow as well as nitrate isotopes have been added (i.e. Wexler et al., 2014, Park et al., 2018, Spalding et al., 2019).

125 R2: Background As mentioned above, some of the detail from the introduction (eg the high nitrate, which is also covered in section 2.4) would be better here. This section is also long for the information it contains and probably it could be written more succinctly.

Authors: We have removed some of the detail from the introduction because it is given here.

130 R2: Lines 91-95 (and elsewhere). It would be preferable to use “residence times” not “ages”. Also, here and throughout suggest referring to the groundwater not the well (the well’s age is when it was installed, which is not what you mean).

Authors: These changes have been made.

R2: Line 125. MAV not defined (I think that it is the maximum WHO limit for nitrate in drinking water?). Is this the best value to use or should the lower NZ limit be used?

Authors: MAV is now defined in the introduction. We prefer to use MAV, but either limit could be used.

135 R2: Line 126-136. Adding values to the text would get the message across better (rather than the reader having to find them for their self).

Authors: Values have been added to the text.

140 R2: Methods Section 3.1 could use a few more details. a) Somewhere, the screened intervals should be notes as geochemical data from long screened production wells conveys different information to that from short-screened monitoring wells. b) In Table 1, is the depth the mid-screen? c) Were the wells purged or was sampling done from flowing wells? d) The Comments on groundwater levels and river flows is not very clear.

145 Authors: a) Screened intervals and mid-screen depths have been added to Table 1. b) The depths given were total depths, but we now use mid-screen depths instead where there were screens, and total depths where there were no screens. c) Field measurements had stabilised before sampling for all wells. 25 wells were purged of at least three well casing volumes before sampling, the 8 remaining wells were sampled by low flow methods (pumps were lowered into the wells and water was sampled after pipes were purged by three pipe volumes). d) This has been rephrased.

R2: Line 147. Field quality?

150 Authors: No, field quantity (quality means how good (the measurements) are, quantity means what the values are.)

R2: Lines 148-149. What are the criteria used for these groups? Results Section 4.1 is difficult to follow without some more details being reported in the text. At the moment, the reader has to keep looking at the data in the figures or tables to see what is being referred to (especially lines 186-192 and 193 to 200).

155 Authors: Groups A and B have low DO values (< 4 mg/L) with A having high $\delta^{15}\text{N}$ (> 15‰) and B moderate $\delta^{15}\text{N}$ (7-9‰). Groups C and D have high DO (> 8.2 mg/L) with C having the highest and D the lowest Cl and SO_4 concentrations. This description has been added to Section 3. The groups are clearly identified in Tables 1 and 2 and in many of the figures.

R2: Lines 217-223. You do not need the detail of the GMWL as it is well known. You could move the definition of the d excess to the methods.

160 Authors: This has been reduced.

R2: Lines 220-243. The description of the stable isotopes could be shorter (and clearer). There is a lot of text here to explain a relatively simple concept that samples with isotopic compositions to the right of the MWL are evaporated.

Authors: This has been rewritten.

165 R2: Lines 243-250. There are probably a reasonable number of uncertainties in these calculations (having to estimate the initial isotopic composition of the rainfall that recharges the groundwater, understanding the precise impacts of evaporation etc). Do you have any ideas of how those impact these calculations?

170 Authors: A mistake in this calculation has been corrected, Errors in measured quantities (δ) and estimated quantities (δ_b , h, temperature) do not change the fraction evaporated much when the fraction is small (5%) because of the form of the equation.

R2: Section 4.3. Again, this description is long in places and could be rationalised. The Raleigh equation (line 261) is reported later in the section - it might be better to report how the calculations were done in the methods which would let this section focus on the results (at the very least try to group the descriptions of the calculations and the outcomes more).

175 Authors: Rewritten – equation in Appendix 2.

R2: Section 5.1. Lines 330-364. Do you need all these calculations? It seems though the Cl mass balance together with the isotopic enrichment defines the recharge % well enough (it is the basis of an often-used recharge rate calculation after all). Could you start off with that and then report the results of the water mass balance as support? Also, the infiltration data look to be from a lysimeter, which may be less than total recharge (given that it is probably above the water table). Since you are interested in the chemistry of the recharging water it would be simpler to relate it to a recharge estimate based on the chemistry.

180 Authors: This has been rewritten.

R2: Section 5.2. The other aspect that is often ignored is that the source has to be there (regardless of the isotopic composition). The points made on lines 398-404 are correct but there are a fair few studies where the isotopic compositions point to stores that are not locally present. This more general discussion would be better in the conclusions.

185 Authors: Lines 398-404 are needed here for the logic of this section. A summary of this is already in the Conclusions (Lines 470-474).

R2: Lines 440-450. It is not clear whether these are general points or some things that may be related to your studies. If it is the latter, is there any evidence that they may apply? You make the point again in the next paragraph, so something to back it up would be good.

190 Authors: Lines 440-450 include one piece of evidence directly relevant to the study (Koba et al., 1997) and two pieces of evidence drawn from the study itself. As pointed out by Referee #1, other studies have shown the presence of at least two pore sizes in Canterbury gravels (Dann et al., 2009). This reference has been added to the paper.

R2: Conclusions The conclusions are reasonably area specific; however, there are several general points made in the discussion. It is preferable to have the conclusions outline the more general points (after the area-specific conclusions) – then the reader who skips the details gets the message!

195 Authors: The conclusions have been slightly revised.

R2: Appendix I am not sure what the rationale is for where the equations are presented. At the moment they are scattered throughout the text and in an appendix. You could look at whether they would all be better in the appendix or split between the appendix and the methods.

200 Authors: These equations have been put into Appendices 1-3

R2: Are the calculations in the Appendix the same as those from Gonfiantini (1986: Handbook of Environmental Isotope Geochemistry. Vol.2 the Terrestrial Environment. Elsevier, Amsterdam, 113-186) which are widely used?

205 Authors: The results would be very similar, but the calculations are based on the measurements and equations given by Stewart (1975), which also has been widely used and cited.

R2: Table 4. Standard deviations of the data would be useful

210 Authors: Standard deviations have been added to Table 4.

References

- Dann, R.L.; Close, M.E.; Flintoft, M.J.; Hector, R.; Barlow, H.; Thomas, S; Francis, G.: Characterization and estimation of hydraulic properties in an alluvial gravel vadose zone. *Vadose Zone Journal* 8(3): 651-663, 2009.
- 215 Park, Y., Kim, Y., Park, S-K., Shin, W-J., Lee, K-S.: Water quality impacts of irrigation return flow on stream and groundwater in an intensive agricultural watershed. *Science of the Total Environment* 630, 859–868, 2018.
- Spalding, R. F., Hirsh, A. J., Exner, M. E., Little, N. A., Kloppenborg, K. L.: Applicability of the dual isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to identify nitrate in groundwater beneath irrigated cropland. *Journal of Contaminant Hydrology* 220, 128–135, 2019.
- 220 Wexler, S. K., Goodale, C. L., McGuire, K. J., Bailey, S. W., and Groffman, P. M.: Isotopic signals of summer denitrification in a northern hardwood forested catchment, *Proc. Natl. Acad. Sci. U. S. A.*, 111(46), 16,413–16,418, 2014.

Irrigation return flow causing a nitrate hot spot and denitrification imprints in groundwater at Tinwald, New Zealand

Michael Kilgour Stewart¹, Philippa Lauren Aitchison-Earl²

¹Aquifer Dynamics and GNS Science, PO Box 30 368, Lower Hutt 5040, New Zealand

²Environment Canterbury, PO Box 345, Christchurch 8011, New Zealand

Correspondence to: Michael K. Stewart (m.stewart@gns.cri.nz)

Abstract. Nitrate concentrations in groundwater have been historically high ($N \geq 11.3$ mg/L) in an area surrounding Tinwald, Ashburton since at least the mid-1980s. The local community are interested in methods to remediate the high nitrate in groundwater. To do this they need to know where the nitrate is coming from. Tinwald groundwater exhibits two features stemming from irrigation with local groundwater (i.e. irrigation return flow). The first feature is increased concentrations of nitrate (and other chemicals and stable isotopes) in a 'hot spot' around Tinwald. The chemical concentrations of the groundwater are increased by recirculation of water already relatively high in chemicals. The irrigation return flow coefficient C (irrigation return flow/irrigation flow) is found to be consistent with the chemical enrichments. The stable isotopes of the groundwater show a similar pattern of enrichment by irrigation return flow of up to 40% and are also enriched by evaporation (causing loss of about 20% of the original water mass). Management implications are that irrigation return flow needs to be taken into account in modelling of nitrate transport through soil/groundwater systems and in avoiding overuse of nitrate fertilizer leading to greater leaching of nitrate to the groundwater and unnecessary economic cost. The second feature is the presence of 'denitrification imprints' (shown by enrichment of the $\delta^{15}N$ and $\delta^{18}O_{NO_3}$ values of nitrate) in even relatively oxic groundwaters. The denitrification imprints can be clearly seen because (apart from denitrification) the nitrate has a blended isotopic composition due to irrigation return flow and N being retained in the soil-plant system as organic-N. The nitrate concentration and isotopic compositions of nitrate are found to be correlated with dissolved oxygen concentration. This denitrification imprint is attributed to localised denitrification in fine pores or small-scale physical heterogeneity where conditions are reducing. The implication is that denitrification could be occurring where it is not expected because groundwater DO concentrations are not low.

1 Introduction

Excessive nitrate concentrations in groundwater are of great concern for human health and for the environment. New Zealand drinking-water standards set a Maximum Acceptable Value (MAV) for nitrate at 50 mg/L (equivalent to nitrate-nitrogen of 11.3 mg/L), based on the risk to bottlefed babies (Ministry of Health, 2008), in line with the WHO guidelines (WHO, 2016, 2017). Hereafter in this paper 'nitrate' is quantified as concentrations of nitrate-N in mg/L. Concerning health, the Canterbury Plains in New Zealand (Fig. 1a) has identified several "high-risk" areas where nitrate concentrations in shallow groundwater are above MAV most or all of the time (Scott and Hanson, 2015). Regarding the environment, eutrophication causing hypoxia and algal blooms, due primarily to agricultural runoff of excess nutrients, is considered the most prevalent water quality problem globally

(OECD, 2017). In New Zealand the N balance worsened (i.e. became more positive) more than in any other OECD member country between 1998 and 2009, almost entirely because of expansion and intensification of farming (OECD, 2013). The N balance is the difference between N inputs to farming systems (fertiliser and livestock manure) and N outputs (crop and pasture production) - a positive N balance indicates a build-up of N and increased potential for N pollution of soil, water and air. Such concentrations result from land use activities, including pastoral and arable farming, market gardening, application of nitrogenous fertilizers and industrial and sewage waste disposal (Laegreid et al., 1999). Pastoral farming has increased rapidly in recent years world-wide and especially in New Zealand. For example, dairy farming acreage on the Canterbury Plains in New Zealand (Fig. 1a) increased from 20,000 to 190,000 ha between 1990 and 2009 (Pangborn and Woodford, 2011). Arable farming has also increased and intensified. Health concerns of nitrate concentrations in drinking water relate to infant methaemoglobinaemia (WHO, 2016). The WHO guideline for maximum allowable nitrate concentration in freshwater is 50 mg/L or 11.3 mg/L of nitrate-N (WHO, 2017). Because N nitrate can also be toxic for aquatic life in groundwater-fed streams at lower levels than MAV, the New Zealand Government has set a maximum median for nitrate-N of 30.5 mg/L or 6.9 mg/L of nitrate-N for river systems. Hereafter in this paper 'nitrate' is quantified as concentrations of nitrate-N in mg/L.

Nitrate concentrations in groundwater in the Tinwald area have historically been high, commonly greater than 11.3 mg/L within an area approximately 3 km wide and 11 km long (Fig. 1b). This area of high nitrate was first identified by Hanson (2002), but nitrate was already elevated in the area in the 1980s (Aitchison-Earl, 2019). The high values are due to the history of land use in the overall area, but the Tinwald values are accentuated because the area is irrigated with local groundwater which has relatively high nitrate concentrations ($N \geq 11.3$ mg/L), whereas surrounding areas are irrigated with alpine river water with low nitrate concentrations ($N < 1$ mg/L). The terms 'irrigation return flow' (e.g. Chakraborty et al., 2015) and 'groundwater recirculation' (Brown et al., 2011) are often applied to situations where irrigation is from water that has been pumped from the underlying aquifer. This situation is common around the world sometimes with unrecognised effects on chemical concentrations (Sánchez Pérez et al., 2003, Park et al., 2018). An important and well-recognised example of the effects of irrigation return flow is non-point sourced arsenic pollution in the groundwater of the Bengal basin, regarded as one of the largest public health concerns in human history (Edmunds et al., 2015).

Irrigation return flow has important implications for water resources management as regards understanding and modelling of nitrate transport in groundwater systems. Much effort is being expended to model the effects of nitrate produced by farming practices in order to substantiate the introduction of appropriate controls on farming to protect the water supplies of downstream communities (e.g. Environmental Canterbury website, 2020). Irrigation return flow can seriously distort such modelling by extending the time scale of nitrate transport by abstracting water from groundwater downstream and applying it upstream, and also by adding nitrate on a second pass through the soil. This work examines the chemical and isotopic compositions of Tinwald groundwater to look for signatures attributable to irrigation return flow and how it contributes to the nitrate hot spot at Tinwald. Similar effects are expected to be important for many other locations in agricultural areas throughout the world.

Irrigation return flow also appears to contribute to an enhanced 'denitrification Imprint' in groundwater at Tinwald, where denitrification imprints are discernible in even reasonably oxic groundwaters. The stable isotopes of nitrate (^{15}N and ^{18}O) have often been used to investigate both the sources of the nitrate and its natural attenuation via denitrification (i.e. microbial reduction of nitrate) (e.g. Mariotti et al., 1988, Böhlke and Denver,

1995, Kendall, 1998, Wexler et al., 2014, Park et al., 2018, Spalding et al., 2019). Understanding the sources of nitrate is important for remediation of excessive nitrate concentrations as at Tinwald (Aitchison-Earl, 2019). Natural attenuation of nitrate via denitrification is a vital eco-service to the environment, and comparison of estimates of nitrate loss by leaching from the bottom of the root zone in catchments compared with the outflow of nitrate from streams shows that considerable attenuation of nitrate occurs in the vadose zone-groundwater continuum. However, little is known about the detailed processes affecting nitrate transport and fate in this region (Clague et al., 2015, Wells et al., 2016, Stenger et al., 2018, Burbery, 2018).

In summary, the objectives of this paper are to investigate the role of irrigation return flow in:

1. Accentuating the nitrate hot spot at Tinwald, and
2. Producing denitrification imprints in relatively oxic groundwaters.

2 Background

2.1 Geohydrologic setting

The study area centres around the small town of Tinwald (population 3000) situated on the south bank of the Hakatere/Ashburton River and located on the large coalescing alluvial plain known as the 'Canterbury Plains' (Fig. 1a). The Canterbury Plains were built up by rivers fed by glaciers over several million years. Deposition in the Tinwald area (Fig. 1b) was mainly by the South Branch Hakatere/Ashburton River and its ancestors (Barrell et al., 1996). The alluvial deposits are poorly stratified greywacke gravel dominated with silts and sands which become finer towards the coast. Oil well exploration drilling and seismic surveys of the Ashburton-Hinds areas indicate thicknesses of over 1000 m of alluvial gravels overlying marine sediments (Jongens et al., 2012).

Existing wells in the Tinwald study area are almost all less than 100 m, and over half are less than 40 m deep (Aitchison-Earl, 2019). Wells are generally screened within post-glacial (Holocene) or last glacial (Late Quaternary) deposits. Shallow wells and springs are common close to the river, within the Holocene age deposits. There is little geological impedance for movement of groundwater between shallower and deeper screened wells.

The regional groundwater flow direction is parallel to the Hakatere/Ashburton River. State Highway 1 runs through the study area (Fig. 1b) and was originally built to take advantage of drier conditions at the inland point of the old 'Hinds swamp'. The swamp has been largely drained but influences soil types, with deeper, poorly drained organic soils with less leaching and greater denitrification potential located coastwards of the highway. Soils are lighter and more freely draining with greater nitrate leaching risk inland of the highway and adjacent to the Hakatere/Ashburton River (Landcare Research, 2015).

In the Tinwald study area, groundwater in two wells with depths less than 50 m had mean ages-residence times of 12 and 63 years based on CFC and tritium measurements (Stewart et al., 2002; van der Raaij, 2013). Ages-Residence times generally increase with depth in other wells in the greater Ashburton area. A trial site for managed aquifer recharge (MAR) has been operating since 2016 just outside of the study area (Fig. 1b).

2.2 Hydrology

The closest long-term rainfall site is part of a climate station at Ashburton Council (Fig. 1b). Annual average rainfall at Ashburton Council is around 730 mm (measured between 1909-2017), ranging from 382 to 1147 mm.

There is little seasonality in rainfall, which averages 61 mm a month. Groundwater recharge was reported by

Thorpe and Scott (1999) based on lysimeter measurements of soil drainage at Winchmore (10 km north of Ashburton, Fig. 2). In the 10-year period (1961-1971), average recharge was 293.5 mm/year with average rainfall of 730 mm/year and PET of 765 mm/year. Average monthly recharge was much higher in winter months (April to September). Winchmore soil is described as Lismore Stony Silt Loam characteristic of that at Tinwald west of Highway 1, and much of the Canterbury Plains.

The Hakatere/Ashburton River has a north and south branch sourced from the Canterbury Ranges which converge at the north of the study area. The Hakatere/Ashburton River interacts with local groundwater, losing and gaining water along its length. Flow is lost to groundwater from the South Branch, and gains towards the confluence with the North Branch.

Springs and wetlands indicate areas where the water table is naturally close to the surface and groundwater discharge is occurring. Many springs are found in the Hakatere/Ashburton River catchment, and often occur in relict river channels (Aitchison-Earl, 2000). In the study area, Carters Creek and Laghmor Creek are both sourced from springs, and there are springs above Lake Hood that flow into the lake (Fig. 1b).

2.3 Land and groundwater use

Cropping has been a major land use in the Tinwald area since at least the early 1940s (Fig. 1b, Engelbrecht, 2005). Most of the area is not part of any of the major surface water irrigation schemes, so irrigation was developed from groundwater sources within the area from the 1980s. Cultivation and fertilizer practice in cropping has an impact on the amount of nitrate that is leached from the soil to the groundwater. Winter is the most likely time for leaching to occur due to saturated soils and less nitrogen being used by crops. Nitrogen-fixing clover crops have been used less over time with an increase in commercial fertilizers (predominantly urea). Point sources of nitrate and other contaminants include septic tanks (human effluent), dairy and other animal effluent, stormwater and contaminated water.

Groundwater use in the Tinwald area is mainly for irrigation, and for domestic and stock water supply. The Valetta Irrigation scheme extends to the edge of the study area in the north-west and sources water from the braided alpine Rangitata River to the south (Figs. 2 and 4).

2.4 Nitrate concentrations

Consistently high nitrate concentrations (greater than MAV of 11.3 mg/L) in groundwater were first identified in the Tinwald area in 2002 (Hanson, 2002). Maximum recorded nitrate concentrations from all samples between 1990 and 2017 are shown in Fig. 2. In general, lower nitrate concentrations occur close to the rivers and under and down-gradient of surface water irrigation schemes (~~less than 1/2 MAV of 5.6 mg/L~~). This is because of dilution by river-sourced water which is lower in nitrate. Nitrate concentrations are higher in areas with ~~more land-surface~~ local groundwater recharge ~~such as Tinwald (>11.3 mg/L)~~. Nitrate concentrations are lower towards the coast in the old Hinds swamp (southeast of SH1) (<5.6 mg/L), where the lower nitrate concentrations are driven by reducing conditions which facilitate denitrification (Hanson and Abraham, 2010). (Note that there are elevated nitrate levels (>11.3 mg/L) outside the study area from the east side of Ashburton to the coast, which are the result of historic leaching from meat processing plants. These are not part of this study.)

Nitrate concentrations have increased over time in the Tinwald area, with two long-term monitoring sites (Thews Road and Saleyards wells, Fig. 1b) having statistically significant ($P < 0.05$) upwards trends of 0.44 and 0.29 mg/L/year since monitoring began in 1995 (Aitchison-Earl, 2019).

375 3 Methods

3.1 Sampling

33 wells were sampled in the study area between 7 February and 14 March 2018 (Fig. 3). 13 of the wells had been sampled in 2004, and others were selected to fill gaps at a range of well depths. Groundwater levels were regionally high at the time of sampling following a sustained period of low levels at the time of sampling, related to high rainfall and river flows following a sustained period of low groundwater levels (Aitchison-Earl, 2019). A large rainfall event of over 100 mm occurred during the sampling period on 21 February, leading to an increase in river flow.

Information on the wells is given in Table 1. Screened intervals and mid-screen depths are given for screened wells, total well depths are given where the wells have no screens. 52% of the wells had short screens (average 2m length), 21% had long screens (average 10m length) and 27% had no screens. Field measurements had stabilised for all wells before sampling. 25 wells were purged of at least three well casing volumes before sampling, the 8 remaining wells were sampled by low flow methods (pumps were lowered into the wells and water was sampled after the pipes had been purged of three pipe volumes).

3.2 Chemical measurements

Samples were analysed for Environment Canterbury's standard suite of major ions through Hills Laboratories (Aitchison-Earl, 2019). Field measurements included dissolved oxygen (DO), pH, conductivity, temperature and depth to groundwater. A selection of the field quantity and ion concentration results are given in Tables 1 and 2. The samples have been ordered from lowest to highest DO concentrations, and four groups of samples (A to D) are identified to aid discussion. Groups A and B have low DO values (< 4 mg/L) with A having high $\delta^{15}\text{N}$ (15%) and B moderate $\delta^{15}\text{N}$ (7-9%). Groups C and D have high DO (> 8.2 mg/L) with C having the highest and D the lowest Cl and SO_4 concentrations.

3.3 Water Isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

Water samples were analysed on an Isoprime mass spectrometer; for $\delta^{18}\text{O}$ by water equilibration at 25°C using an Aquaprep device, for $\delta^2\text{H}$ by reduction at 1100 °C using a Eurovector Chrome HD elemental analyser. Results are reported with respect to VSMOW2. The analytical precision for this instrument is 0.2‰ for $\delta^{18}\text{O}$ and 2.0‰ for $\delta^2\text{H}$. Results are given in Table 1.

3.4 Nitrate isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}_{\text{NO}_3}$)

Nitrate samples (NO_3) were converted to nitrite (NO_2) using cadmium, then to nitrous oxide (N_2O) using sodium azide in an acetic acid buffer. The N_2O was then extracted from the water sample, passed through a series of chemical traps to remove H_2O and CO_2 , and cryogenically trapped under liquid nitrogen. After being cryofocused in a second trap, the N_2O passed through a GC column and into an Isoprime IRMS to determine its isotopic

signature of nitrogen and oxygen. Our method is modified from McIlvin and Altabet (2005), following personal communication with Mark Altabet. Results are reported with respect to AIR for $\delta^{15}\text{N}$ and VSMOW for $\delta^{18}\text{O}$. The analytical precision for these measurements is 0.3‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$, except for samples below ~~100~~0.1 mg/L $\text{NO}_3\text{-N}$ which may have lower precisions. Results are given in Table 1.

4 Results

4.1 Groundwater chemistry

DO concentrations in the Tinwald groundwaters range from 0.18 to 11.8 mg/L, although the majority are high and indicate relatively oxic groundwater. As noted above, the data in Tables 1 and 2 are ordered from lowest to highest DO values.

Chloride concentrations are useful to distinguish recharge sources. Chloride concentrations are highest in rainfall originating over the sea and near the coast, and generally decrease with distance inland. In particular, alpine rivers (with chloride values of 0-5 mg/L) and coastal rainfall-derived infiltration (with chloride ranging from 10-20 mg/L) can be clearly distinguished (Hayward, 2002; Stewart et al., 2002). However, chloride concentrations in the Tinwald area (Fig. 4a) are greater than expected even for coastal rainfall (most are >15 mg/L). The values are lower (0-10 mg/L) to the northeast side of the study area near the Hakatere/Ashburton River and to the southwest. Sulphate occurs naturally in groundwater and is present in fertilizers and fungicides, and so can be an indicator of human influence when concentrations are in excess of background levels as here (see Fig. 4b). As with chloride, levels in alpine river and low-altitude rainfall infiltration are very different, but in the case of sulphate the difference is caused by the nature of additions to the soils in the respective catchments rather than the concentrations in rainfall. Concentrations are lower on the northeast and southwest boundaries of the study area. Nitrate concentrations are shown in Fig. 4c. Nitrate concentration exceeds MAV (11.3 mg/L) in 17 of 33 wells sampled in the study area and is over 20 mg/L in four wells. The highest nitrate concentrations cluster inland of SH1 to the west and northwest of Tinwald and underlie an area of dominant cropping land use (Fig. 1b). Nitrate is lowest on the northeast boundary of the study area (near the Hakatere/Ashburton River) where it is generally below $\frac{1}{2}$ MAV, 5.65 mg/L, and lower but still over $\frac{1}{2}$ MAV on the southwest boundary.

To investigate possible irrigation return flow effects, we compare the concentrations of different solutes and isotopes and include the effect of evaporation as indicated by the stable water isotopes (Figs. 5a, b, c). Fig. 5a shows water $\delta^{18}\text{O}$ versus the chloride. Higher $\delta^{18}\text{O}$ correlates with higher chloride, but this is not due to evaporation (because the evaporation vector is not parallel to the trend). Instead the main influence is the source of the recharge because both chloride and $\delta^{18}\text{O}$ are higher in land surface recharge (e.g. Group C samples) and lower in alpine river recharge (Group D samples). There is no effect due to DO. Sample 21 shows an extra evaporation effect.

Fig. 5b shows chloride and sulphate are well correlated especially when the low DO samples are excluded. This trend is also due to the recharge sources (see Group C and D samples in the figure). ~~The trend is accentuated by evaporative enrichment (since the evaporation arrow is parallel to the trend in Fig. 5b).~~ Evaporative enrichment is slight. The low DO samples conform to the overall trend, but are more scattered than the other samples.

Fig. 5c shows nitrate and chloride are moderately correlated due to the recharge sources (see Group C and D samples), but there are other processes affecting the nitrate concentrations. ~~A small evaporation effect accentuates~~

445 ~~the trend.~~ The low DO waters have low nitrate concentrations indicating that they have been partially denitrified, ~~probably within the soil (see below).~~ Evaporation has an almost negligible effect.

The clear message from these results is that nitrate, sulphate and chloride concentrations are increased in areas irrigated by local groundwater compared to those irrigated by alpine river water.

4.2 Water Isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$

450 $\delta^{18}\text{O}$ values are useful as tracers of the sources of recharge to groundwater, because rainfall recharge and rivers from alpine catchments have different isotope ratio signatures. Scott (2014) reviewed $\delta^{18}\text{O}$ data for Canterbury and identified isotopic signatures in the Ashburton area. The Hakatere/Ashburton River has very negative $\delta^{18}\text{O}$ with a mean of -10.1‰ for the South Branch, and -10.7‰ for the North Branch. In contrast, rainfall recharge near the coast is less negative than -8‰, although it becomes more negative inland and is typically more negative than
455 -8‰ on the upper plains. The Rangitata River, the alpine source of Valetta and other irrigation schemes water, has a mean $\delta^{18}\text{O}$ of -9.8‰ (Taylor et al., 1989).

$\delta^{18}\text{O}$ data collected in the greater Ashburton area is shown in Fig. 6. The influence of more negative Rangitata River sourced water can be seen under the irrigation schemes. The $\delta^{18}\text{O}$ values are less negative (red and orange dots) in the Tinwald study area. More negative values (green dots) occur on the NE and SW boundaries of the
460 area, which are related to recharge from the South Branch Hakatere/Ashburton River and the Valetta scheme irrigation water. An area south of Tinwald near the coast (Eiffleton Irrigation Scheme) has less negative $\delta^{18}\text{O}$ values like those observed in the Tinwald study area for probably the same reasons (irrigation return flow).

We also sampled wells for $\delta^2\text{H}$ in 2018. ~~Plotting $\delta^2\text{H}$ and $\delta^{18}\text{O}$ against each other frequently gives a linear relationship following the equation~~

465
$$\delta^2\text{H} = 8.0\delta^{18}\text{O} + d. \quad (1)$$

~~On a global scale, d (called the deuterium excess) is equal to +10‰ on average, and the linear relationship is known as the Global Meteoric Water Line (Craig, 1961). A New Zealand Meteoric Water line with deuterium excess, d = +13‰ was established by Stewart and Taylor (1981), based on westerly-dominated zones of New Zealand (North Island and western parts of the South Island). However, Scott (2014) and previous workers found that data from Canterbury fitted local meteoric lines with d = +10‰ for the Waimakariri Zone and d = +11‰ for the Selwyn Te Waihora Zone. Scott (2014) noted a lack of paired $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data in the Ashburton area, but
470 available evidence supports a local meteoric water line (LMWL) for Canterbury with intercept d = +10‰ (Stewart and Taylor, 1981; Taylor et al., 1989; Stewart and Morgenstern, 2001; Scott, 2014; Stewart et al., 2018). i.e. the LMWL is This is taken as the LMWL below.~~

475
$$\delta^2\text{H} = 8.0\delta^{18}\text{O} + 10. \quad (1)$$

Paired $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data for the Tinwald study are plotted in Fig. 7. The Tinwald data plot below the LMWL and have a linear best-fit line (excluding sample 21, which has been affected by extra evaporation) given by:

$$\delta^2\text{H} = 6.3\delta^{18}\text{O} - 7.2 \quad (2)$$

The slope of less than 8 for this line ~~suggests/indicates~~ that the waters have been affected by evaporation. A ratio of about 5 in the ^2H and ^{18}O enrichments is expected for evaporation at ambient temperatures (Stewart, 1975). It is ~~expected/likely~~ that the isotopic compositions of the water would have been enriched by evaporation and/or evapotranspiration during the irrigation return flow process. Estimates of the isotopic enrichments required to explain the displacement of the average isotopic compositions of the group from the LMWL are shown by the red

485 arrow with slope of 5 in Fig. 7. The average isotopic composition of the samples except sample 21 (Table 1) was
(-8.58, -61.2), where the bracket represents ($\delta^{18}\text{O}$, $\delta^2\text{H}$). The average initial composition of the samples would
then have been (-9.43, -65.4), i.e. where the red arrow with a slope of 5 meets the LMWL (marked by the small
red circle in Fig. 7). This degree of isotopic enrichment is obtained by evaporation of approximately ~~205~~205% of the
water according to both isotopes (see the calculation in ~~the a~~Appendix 1 based on Stewart, 1975). ~~Uncertainty in
this fraction evaporated is small because the isotopic composition of the remaining water changes rapidly with
the degree of evaporation due to the form of the equation, so considerable changes of isotopic composition do not
change the fraction evaporated much. Recharge would be a mix of rainfall and irrigation water which would be
evaporated. The effects would be expected to be variable from well to well as observed.~~

490
In addition, the difference in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of Groups C and D is attributed to their different irrigation
sources (local groundwater or alpine river water) as observed for the chemical compositions. Assuming that both
495 groups are affected by evaporation to the same extent, the difference between the groups compared to the
difference between the irrigation sources will give an approximate measure of the irrigation input. The $\delta^{18}\text{O}$
difference between Groups C and D is 0.63‰ (Table 4) and that between the sources is 1.63‰, giving irrigation
input of 39%. For $\delta^2\text{H}$ it is 4.1‰ compared to 10.2‰ giving 40% irrigation input. These are likely to be
overestimates because Group C waters may be more affected by evaporation than Group D waters. (The
500 compositions of the irrigation sources are taken as local rainfall (-8.17, -58.7) and alpine river (-9.80, -68.9)).

4.3 Nitrate isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$

The nitrate isotope results are given in Table 1 and plotted in Fig. 8a. The samples have symbols depending on
their DO concentrations, as in previous figures. The figure displays two important features:

1. There is a very good linear relationship between the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values of the nitrate,
- 505 2. Their positions along the line depend on their DO concentrations.

The first feature is the linear relationship between the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values of the nitrate (except sample 06
and to a smaller extent samples 02 and 03). Denitrification causes increased δ values of nitrate, along with decrease
of nitrate concentration. The slope of the isotopic enrichments caused by denitrification (i.e. enrichment in
 $\delta^{18}\text{O}_{\text{NO}_3}$ /enrichment in $\delta^{15}\text{N}$) has been reported to be in the range 0.48 – 0.77 (Kendall, 1998; Burns et al., 2011;
510 Kaushal et al., 2011; Zhang et al., 2019). The line shown in Fig. 8a has a slope of 0.68 and was calculated to
simulate the effect of denitrification using the Rayleigh formula to represent the process (Kendall, 1998). Similar
denitrification line slopes of 0.73 and 0.75 were observed by Clague et al. (2015) and Stenger et al. (2018)
respectively. The individual denitrification calculations for each of the isotopes are plotted in Figs. 8b and c (see
515 ~~explanation below~~Appendix 2 and Table 3). The starting point for the denitrification lines was chosen to be the
average of the Group C samples. The linear relationship shows that either the various sources of nitrate all produce
nitrate with the same isotopic δ -values (which is contrary to what we know) or more probably nitrate leaching
from the soil is blended by processes in the soil (Wells et al., 2015) and by irrigation return flow. The exceptions
are sample 06 and to a lesser extent samples 02 and 03, their isotopic compositions (Fig. 8a) suggest that they
initially had higher $\delta^{15}\text{N}$ than the other samples and therefore a greater proportion of effluent nitrate.

520 The second feature of the figure is surprising. Denitrification is only expected to take place where DO levels are
very low (e.g. < 0.5 mg/L, McMahon and Chapelle, 2008). But here denitrification effects are observed even when
the DO concentrations in the groundwaters are much higher. ~~This must mean that the denitrification occurred~~

~~during the past histories of the nitrates, most probably within the soil the nitrate was leached from.~~ The lowest DO range in Table 1 (with DO < 4 mg/L, samples 01-09) includes Group A waters which have the lowest DOs and most marked denitrification effects (with $\delta^{15}\text{N}$ values from 15 to 20‰), Group B waters with DO from 1.36 to 3.39 mg/L and $\delta^{15}\text{N}$ values from 7 to 9‰, and one other well (07) that in contrast shows only minor denitrification ($\delta^{15}\text{N}$ is 5‰) despite its relatively low DO (2.68 mg/L). The intermediate DO group (4 < DO < 8.2 mg/L) has intermediate nitrate concentrations and shows smaller denitrification effects ($\delta^{15}\text{N}$ values from 3.5 to 6.0‰, samples 10-14). The highest DO group (with DO > 8.2 mg/L) ~~are-is~~ nearly saturated with oxygen and shows minimal denitrification effects ($\delta^{15}\text{N}$ values from 1.7 to 4.8‰, samples 15-33).

Fig. 8b shows the natural log of the nitrate concentrations versus $\delta^{15}\text{N}$ values, the natural log is used because the denitrification line will be linear on this type of plot according to the Rayleigh formula (Appendix 2). The grey bands show approximate values of the $\delta^{15}\text{N}$ values of possible nitrate sources (i.e. natural soil with $\delta^{15}\text{N}$ of -3 to 7‰, inorganic fertilizer with -3 to 3‰, and effluent with 9 to 25‰, Fogg et al., 1998; Stewart et al., 2011). The Ln (NO_3) values they are plotted at are schematic, we normally expect background nitrate concentrations from natural sources in soil to be about < 0.7 to 1 mg/L (Close et al., 2001; Daughney and Reeves, 2005). Nitrogen-fixing clover is a possible source of nitrate with an isotopic composition like that of soil nitrate in pasture in Canterbury (Trevis, 2012). ~~But~~ we think its contribution is not large, because the abundance of clover has decreased over the years as fertilizer use (particularly urea) has increased.

The approximate Rayleigh formula used is

$$\delta = \delta_a + \epsilon \cdot \ln(f) \quad (3)$$

~~where δ is the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ value of the nitrate remaining after the microbes have catalysed partial denitrification, and δ_a is the initial composition of the nitrate. ϵ is the enrichment factor for the reaction and f is the fraction of nitrate remaining after the reaction. Results of the calculation are given in Table 3.~~

The enrichment factors producing the denitrification lines in Figs. 8b and c are $\epsilon(^{15}\text{N}) = -3.0\text{‰}$, $\epsilon(^{18}\text{O}) = -2.1\text{‰}$ (Table 3). These are similar to the ranges determined by Clague et al. (2015) ($\epsilon(^{15}\text{N}) = -1.1$ to -9.6‰ , $\epsilon(^{18}\text{O}) = -1.0$ to -7.2‰), and values by Stenger et al. (2018) ($\epsilon(^{15}\text{N}) = -2.0\text{‰}$, $\epsilon(^{18}\text{O}) = -1.3\text{‰}$), while Mariotti et al. (1988) gave an $\epsilon(^{15}\text{N})$ range from -5 to -8‰. Other authors (Kendall, 1998, and references therein) gave much larger negative values. Mariotti et al. (1988) suggested that low values may occur if denitrification occurs in dead-end pores causing a non-fractionating sink for nitrate by diffusion. Stenger et al. (2018) considered that small-scale physical heterogeneity, including the localised distribution of resident electron donors and the effect of lateral flows, was a more likely cause with their coarse-textured ignimbrite materials.

Fig. 8c shows the natural log of the nitrate concentrations versus $\delta^{18}\text{O}_{\text{NO}_3}$ values. As with Figs. 8a and b, the denitrification line through Groups C and B wells project to sample 01. This well is located south of Tinwald near Lagmhor Creek in the Hinds swamp denitrification area. Group A wells show the greatest denitrification effects, the other samples in the group (02, 03 and 06) lie to the right of the denitrification line in Fig. 8b indicating that they have larger proportions of effluent than the rest of the samples. Samples 02 and 03 occur downgradient of the old Tinwald Saleyards, sample 06 is northwest of SH1 in an area of lifestyle blocks adjacent to the major cropping area. It is probable that the effluent source is providing a source of dissolved organic carbon to fuel denitrification reactions in Group A wells.

Group B wells (showing moderate denitrification) are located closest to the Hakatere/Ashburton River. One sample (04) is in the cropping area, the others (05, 08, 09) are in areas with lifestyle blocks, which could contribute both septic tank and animal effluent to assist denitrification.

565 Group C wells (representative of wells irrigated by local groundwater) are distributed through the central part of the high nitrate hot spot. They plot in the upper part of the cluster of green points in Fig. 8a, and to the right in Figs. 8b and c.

Group D wells (representative of wells irrigated more by alpine river water) are located on the southwest boundary of the study area. They plot in the lower part of the green point cluster in Fig. 8a, and to the left in Figs. 8b and c. The green points in Fig. 8 have $\delta^{15}\text{N}$ values that are mostly within the soil nitrate or inorganic fertilizer ranges and show little evidence of denitrification. Natural soil nitrate alone does not account for the slightly elevated nitrate concentrations in these wells, making inorganic fertilizer (or rather organic-N derived from it, see discussion below) the likely dominant source.

570 A mixing curve between two nitrate source end members (soil nitrate and fertilizer/effluent mixture nitrate) has been fitted to the solid green points (Appendix 3 not shown). The equation of the curve (Kendall, 1998) is:

575
$$\delta^{15}\text{N} = b - a/C_N \quad (4)$$

where a describes the shape of the curve, b is the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}_{\text{NO}_3}$ value of the total (blended) nitrate source, and C_N is the nitrate concentration. The best-fitting curves give $\delta^{15}\text{N} = 3.64.1\%$, $\delta^{18}\text{O}_{\text{NO}_3} = -0.20.0\%$ for the blended nitrate source. This indicates that the source is dominated by inorganic fertilizer but has a small proportion of effluent source based on ^{15}N (it is assumed that the highest nitrate concentrations are little affected by denitrification).

580

5 Discussion

5.1 Irrigation return flow effects on chemical and isotopic concentrations

Fertilizers have been applied to much of the area between the Ashburton and Hinds Rivers not just to the Tinwald study area, and rainfall applies to the whole area with contours of the δ values in rainfall decreasing inland from the coast (Stewart et al., 2002). Yet the Tinwald area shows elevated nitrate concentrations (and chloride, sulphate, etc.) compared to the surrounding areas (see Fig. 2). The difference is that the Tinwald study area is irrigated by groundwater from shallow local wells with high solute concentrations, whereas much of the rest of the area is irrigated by alpine river water with low concentrations of solutes. This has affected the chemical and water isotope concentrations.

590 The irrigation return flow process is illustrated schematically in Fig. 9. Dewandel et al. (2007) defined an irrigation return flow coefficient C equal to the recharge from irrigation (i.e. irrigation return flow, IRF, divided by the irrigation flow itself, I , so that $C = \text{IRF}/I$). C is equal to the overall recharge rate for rainfall and irrigation in our system (we omit surface runoff and lateral seepage in this treatment because both are expected to be small). (Note that drains in the area are fed mainly by groundwater.) C is used to quantify the effect of irrigation return flow on the water balance.

595

The average chemical concentrations of Groups C and D are taken as representative of the Tinwald hot spot and outside groundwaters respectively (average values and standard deviations for each chemical are given in Table 4). The table also gives the enrichment factors and irrigation return flow coefficients between Groups C and D

600 derived from each chemical; the enrichment factor is equal to $1/C$ assuming that chemicals put in via rainfall and
 605 irrigation are concentrated into the recharge fraction, i.e. are concentrated by the loss of AET. Cl mass balance
 has often been used to estimate recharge because it is conservative, here the enrichment factor is 3.2 and
 coefficient C obtained is 31%. The SO_4 enrichment factor is very large (7.0) suggesting greater fertilizer input
 into the Group C area soil than into the Group D area soil. The HCO_3 factor is small (1.2) probably because of
 chemical re-equilibration as water passes through the soil in both areas. The average enrichment factor is 2.4 and
 coefficient C is 42% for all of the chemicals except SO_4 and HCO_3 . The coefficient C can be compared with
 lysimeter measurements of recharge fraction from the nearby research station of Winchmore (Thorpe and Scott,
 1999, Fig. 2); the recharge fraction is recharge divided by input (i.e. rainfall plus irrigation). Thorpe and Scott
 found that the recharge fraction at Winchmore was 43% for the average irrigation input of 300 mm/year, in
 approximate agreement with the chemical results above.

610 Recharge to groundwater (RGW) is given by

$$RGW = R + I - AET \quad (5)$$

where R is rainfall, I is irrigation input and AET is actual evapotranspiration (all in mm/year). Surface runoff and
 lateral seepage are neglected in this treatment as both are expected to be small. (Note that drains in the area are
 fed mainly by groundwater.) Thorpe and Scott (1999) reported on many years of lysimeter measurements of
 recharge at the nearby research station of Winchmore. They found that

615 $RGW = 0.80(R + I) - 380 \quad (6)$

for pasture, while for bare soil it was

$$RGW = 0.77(R + I) - 244 \quad (7)$$

The recharge fraction (RGW%) is the ratio of recharge to incident rainfall plus irrigation applied, i.e.

620 $RGW\% = RGW / (R + I) \quad (8)$

Dewandel et al. (2007) defined an irrigation return flow coefficient C equal to the recharge from irrigation (i.e.
 irrigation return flow, IRE) divided by the irrigation flow itself (I). C is the same as the recharge %, i.e.

$$C = \frac{IRE}{I} = \frac{I \times RGW\%}{I} = RGW\% \quad (9)$$

625 if the recharge rate is assumed to be the same for both rainfall and irrigation. C is used to quantify the effect of
 irrigation return flow on the water balance.

Equations (6) and (7) can be used to determine the coefficient C for Tinwald. Assuming that $I = 200$ mm, C is
 $364/930 = 39\%$ for pasture, and 51% for bare soil. These give predicted chemical enrichment factors ($1/C$) of 2.6
 for pasture and 2.0 for bare soil (if chemicals put in via rainfall and irrigation are concentrated into the recharge
 fraction, i.e. are concentrated by the loss of AET). The pasture value may be the most appropriate to compare with
 630 the observed values in Table 4 for the different chemicals. The observed values are very scattered, but are similar
 on average to the predicted value of 2.6. Chloride is the most conservative element and its enrichment factor (3.2)
 is a little higher than the predicted value. The sulphate enrichment factor is very large suggesting greater fertilizer
 input into the Group C area soil than into the Group D area soil. The bicarbonate factor is small perhaps because
 of chemical re-equilibration as groundwater passes through the soil in the Group C area.

635 The $\delta^{18}O$ and δ^2H values of Groups C and D are affected by the different irrigation water sources (local
 groundwater or alpine river water) and by evaporation as described in Section 4.2. An irrigation input of up to
 40% is indicated by the mean isotopic compositions of groups C and D (Section 4.2). Evaporation is indicated by

displacement of the sample points from the LMWL in Fig. 7. An approximate calculation given in ~~the~~ Appendix 1 shows that evaporation of about 205% of the water can explain the average displacement of the points.

640 Irrigation return flow has important implications for management of nitrate in agriculture. An important aspect of water resources management is understanding and modelling of nitrate transport in water systems (in this case groundwater). Much effort is being expended to model the effects of nitrate produced by farming practices in order to introduce and substantiate appropriate controls on farming to protect the water supplies of downstream communities (e.g. Environmental Canterbury website, 2020). Irrigation return flow can seriously distort such
645 modelling by lengthening the time scale of nitrate transport by abstracting water from groundwater downstream and applying it upstream and by adding nitrate on a second pass through the soil.

Another effect of irrigation return flow is distortion of tracer age dating results. Tritium concentrations will not be reset by interaction with the atmosphere when irrigation water is applied to the soil, so the tritium ages-residence times of groundwater affected by irrigation return flow will appear to be older than they really are. In contrast-,
650 CFC/SF₆ ages-residence times will be reset to zero in the soil and groundwater ages-residence times will reflect time since recharge. This appears to be the case for data in the Tinwald area, although data is scarce (Stewart et al., 2002).

A practical consideration is that if irrigation water already contains nitrate then too much fertilizer could be applied leading to unnecessary economic cost and greater nitrate leaching potential, if the nitrate in the groundwater is not
655 accounted for by nutrient budgeting (e.g. Flintoft, 2015).

5.2 Nitrate dual isotope concentrations

5.2.1 Nitrate source identification

Nitrate isotope results that have not been affected by denitrification (i.e. usually the oxic samples) potentially give information on the nitrate sources and also on the starting points for denitrification vectors. Numerous studies of
660 the $\delta^{15}\text{N}$ values produced by different nitrate sources have identified ranges which have differed under local conditions (e.g. Kendall, 1998; Fogg et al., 1998; Stewart et al., 2011, Fig. 8b). Results for oxic samples from recent New Zealand studies are given in Fig. 10. The rectangles show source signature fields resulting from urea fertilizer/soil N/ruminant excreta at Toenepi Catchment (Clague et al., 2015), urine/urea/soil N at Harts Creek (Wells et al., 2016), low intensity animal grazing (soil N/manure) at Waihora wellfield (Stenger et al., 2018), two
665 sources (inorganic fertilisers/manure and piggery effluent) at Waimea Plains (Stewart, 2011), and inorganic fertiliser/urea/manure at Tinwald (Groups C and D, this work). Despite the variety of nitrate sources, the $\delta^{15}\text{N}$ values generally show overlapping ranges as illustrated in Fig. 10 (except for the Waimea Plains piggery effluent source).

Use of $\delta^{18}\text{O}_{\text{NO}_3}$ in combination with $\delta^{15}\text{N}$ to identify nitrate sources has not been very successful, as illustrated in
670 Fig. 10 where the $\delta^{18}\text{O}_{\text{NO}_3}$ values overlap each other. On the other hand, the combination has proven to be effective for detecting the occurrence of processes in the nitrogen cycle, such as nitrification and denitrification (Aravena and Robertson, 1998). The only distinctive source $\delta^{18}\text{O}_{\text{NO}_3}$ values are those expected for nitrate fertilizer (see 'nitrate fertilizers' box in Fig. 10, Xue et al., 2009, Wells et al., 2015). Many researchers have looked for such $\delta^{18}\text{O}_{\text{NO}_3}$ values and generally failed to find them (Kloppman et al., 2018). Instead the values observed in
675 groundwaters are usually characteristic of soil nitrate or effluent (as illustrated in Fig. 10).

The probable answer to this failure to observe the expected high $\delta^{18}\text{O}_{\text{NO}_3}$ values in groundwater is that inorganic fertilizer-derived nitrate is not directly and rapidly transferred to groundwater but is retained in the soil-plant system as organic-N, and only later mineralised and re-oxidised thereby becoming available for leaching to the groundwater (Somers and Savard, 2009, Wells et al., 2015, Kloppmann et al., 2018). The process of mineralisation and re-oxidation resets the $\delta^{18}\text{O}_{\text{NO}_3}$ and also changes the $\delta^{15}\text{N}$. The time delays in this process can be considerable (as much as several decades, Sebilo et al., 2013). This means that there will be a legacy of organic-N built up in the Tinwald soil from past applications of fertilizer in addition to past soil management practices. This time delay is in addition to the time delay due to the mean residence time of the groundwater. Others have previously identified the importance of organic-N in the soil (variously known as soil organic matter (SOM, Somers and Savard, 2009) or soil organic nitrogen (SON, Wells et al., 2015)) as the pool of nitrogen within the soil controlling the rate and timing of nitrate releases to groundwater. The transfer to organic-N is most efficient at times of high microbial activity (spring/summer growth) and much less in low microbial activity (winter), when increased nitrate leaching to the groundwater is likely (Mengis et al., 2001; Somers and Savard, 2009).

The nitrate isotopes (Fig. 8a) show an unexpected blending of the isotopic compositions of the nitrate in the groundwater (and therefore the soil/vadose zone). This blending is considered to be due to irrigation return flow in conjunction with the action of organic-N in mediating and retaining N in the soil. This has allowed the denitrification process to be identified and explored in this study, and the enrichment factors for denitrification to be determined.

5.2.2 Denitrification imprint in oxic groundwater

The nitrate isotopes show clearly that denitrification is important in the Tinwald soil and vadose zones groundwater (Fig. 8). Firstly, the nitrate isotopes show that the nitrate sources are blended within the soil and that inorganic fertilizers are dominant with minor effluent input. Secondly, the nitrate concentration and isotopic compositions are correlated with the DO concentrations, despite most of the groundwaters having DO concentrations greater than the levels at which denitrification can occur (McMahon and Chapelle, 2008; Rivett et al., 2008).

The correlations are displayed in Figs. 11a-c. The relationship between DO and nitrate is approximately linear (Fig 11a) with the nitrate concentrations being more scattered at the high DO end related to the recharge sources (Groups C and D, see earlier results). The line fitted to samples with DO < 8.2 mg/L and Group C samples shows an average trend reflecting denitrification. Figs. 11b and c showing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ plotted against $\ln(\text{DO})$ also have average linear trends fitted to them related to denitrification.

Stenger et al. (2008) pointed out a similar situation where denitrification was inferred by unexpectedly low nitrate concentrations, but DO concentrations although varied were not particularly low. There was, however, an approximate correlation of nitrate and DO, as here. Manganese (Mn) and Iron (Fe) are other indicators of reducing conditions. Both cases (Stenger et al. and Tinwald) show the expected patterns of low nitrate concentrations when Mn and Fe are elevated (indicating very reducing conditions) and higher nitrate concentrations when Mn and Fe are very low (indicating oxidising conditions).

Several factors suggest that the denitrification imprint arises from localised denitrification in fine pores where conditions are reducing. 1. Koba et al. (1997) showed that denitrification can occur in anaerobic pockets within otherwise oxic sediments or water bodies. 2. The low values of $\epsilon(^{15}\text{N})$ and $\epsilon(^{18}\text{O})$ observed here indicate that denitrification occurs in fine pores or small-scale physical heterogeneity. 3. The occurrence of the denitrification

715 imprint in moderately oxic waters (in which denitrification could not have occurred) means that the denitrification must have occurred in parts of the system which were much more reducing. Logically these are fine pores or inhomogeneities containing electron donors with heterotrophic bacteria.

The Tinwald study area is not in an area where the groundwater is generally reducing (Close et al., 2016), but nevertheless ~~groundwater from~~ some wells show the denitrification imprints. It would appear that denitrification imprints in moderately oxic groundwater should be common, but many more nitrate isotope measurements would be required to show this.

As a final comment, there appear to be two types of pore space in the gravels at Tinwald, i.e. larger pores with mobile water and finer pores with almost stagnant water, that communicate by diffusion (e.g. Dann et al., 2009). This is likely to cause slowing of nitrate transport ~~and decrease of nitrate within through~~ the system as nitrate is ~~retained is~~ transferred to the finer pores (~~together with and partially denitrified some denitrification~~).

6 Conclusions

Chemical measurements at Tinwald corroborated previous indications of an area of high nitrate concentration in the groundwater, which ~~partly~~ results from irrigation return flow in the area. During the recirculation process by spray irrigation of local groundwater, the chemical composition of the groundwater is enriched by recirculation of water already relatively high in chemicals, along with enrichment by gain of chemicals from the soil ~~and evaporation~~. The irrigation return flow coefficient (C) of about 0.4 indicates a chemical enrichment factor of close to 2.6, in approximate agreement with the observed chemical enrichment factors for different elements. The stable isotopes of the groundwater show enrichment by evaporation, which can be accounted for by an average evaporative loss of about ~~20~~5% compared with the rainfall source of the water. Comparison of the isotopic compositions of groundwater in the Tinwald hot spot and outside it ~~suggest indicate~~ that the irrigation input to recharge is ~~up to~~about 40% ~~in agreement with the chemical and recharge measurements~~. The effects of irrigation return flow are not often described but have considerable management implications, e.g. modelling of nitrate transport through soil/groundwater systems could be highly unrealistic if irrigation return flow effects are disregarded. In addition, too much fertilizer could be applied leading to unnecessary economic cost and greater leaching of nitrate to groundwater if nitrate in irrigation water is not accounted for.

Irrigation return flow also appears to have caused a blending of the nitrates from different sources in the soil as shown by their nitrate isotope compositions. The blended source is dominated by fertiliser which has been transformed by the soil-plant system into organic-N which acts as the important soil N reservoir from which N is mineralised and oxidised during leaching, with effluent contributing to a minor extent. The blending of the different nitrate sources allowed clear identification of the denitrification process in this study. Denitrification enrichment factors of $\epsilon(^{15}\text{N}) = -3.0\text{‰}$, $\epsilon(^{18}\text{O}) = -2.1\text{‰}$ were determined. The nitrate concentration and isotopic compositions were found to be correlated with the DO concentrations because of denitrification, despite most of the groundwaters having DO concentrations greater than the levels at which denitrification can occur. This denitrification imprint is attributed to localised denitrification in fine pores where conditions are reducing, aided by the irrigation return flow process. The implication is that denitrification could be occurring where it is not expected because groundwater DO concentrations are not low.

Appendix 1: Isotopic effect of evaporation on water

The fraction of water evaporated (f) is estimated by applying equation 3a from Stewart (1975):

$$\delta = \delta_{end}(1 - f^\beta) \quad (A1)$$

755 where δ is the enrichment due to evaporation, and δ_{end} and β are given by

$$\delta_{end} = \gamma(\delta_b + 1) - 1 \quad (A2)$$

$$\beta = \frac{1 - \alpha_p \alpha_k (1-h)}{\alpha_p \alpha_k (1-h)} \quad (A3)$$

Here

$$\gamma = \frac{\alpha_p h}{1 - \alpha_p \alpha_k (1-h)} \quad (A4)$$

760 and δ_b is the isotopic composition of the atmospheric vapour relative to the initial composition of the water, α_p and α_k are the equilibrium and kinetic fractionation factors respectively between water and vapour, and h is the relative humidity.

Assuming the water composition increases from (-9.43, -65.4) to (-8.58, -61.2) due to evaporation, where the brackets signify ($\delta^2\text{H}\%$, $\delta^{18}\text{O}\%$), the isotopic enrichment relative to the initial composition of the water is (0.86, 4.5). δ_b and h were estimated to be (-12, -90) and 70%, respectively. With average temperature of 15°C, f was calculated to be 0.79-95 (or fraction of water evaporated (f) was 0.2405).

765

Chemical enrichment due to evaporation is given by

$$C = C_o/f \quad (A5)$$

where C_o and C are the initial and final concentrations of the chemical.

Appendix 2: Isotopic effect of denitrification on nitrate

770 The approximate Rayleigh formula (Kendall, 1998) was used to calculate the isotopic effects of denitrification on nitrate. This formula is

$$\delta = \delta_o + \epsilon \cdot \ln(f) \quad (A6)$$

775 where δ is the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}_{\text{NO}_3}$ value of the nitrate remaining after the microbes have catalysed partial denitrification, and δ_o is the initial isotopic composition of the nitrate. ϵ is the enrichment factor for the reaction and f is the fraction of nitrate remaining after the reaction. Results of the calculation are given in Table 3.

Appendix 3: Isotopic effect of mixing of two sources of nitrate

A mixing curve between two nitrate source end members (soil nitrate and fertilizer/effluent mixture nitrate) has been fitted to the solid green points (not plotted in the figures). The equation of the curve (Kendall, 1998) is:

$$\delta = b - a/C_N \quad (A7)$$

780 where δ is the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}_{\text{NO}_3}$ value of the sample nitrate, b is the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}_{\text{NO}_3}$ value of the fertilizer/effluent nitrate, a describes the shape of the curve, and C_N is the sample nitrate concentration. The best-fitting curves give $\delta^{15}\text{N} = 4.1\%$, $\delta^{18}\text{O}_{\text{NO}_3} = 0.0\%$ for b (the fertilizer/effluent nitrate).

785 **References**

- Agribase, 2016. Assure Quality, s.l.: s.n.
- Aitchison-Earl, P.: Springs of the Ashburton Catchment. Environment Canterbury Technical Report U04/79, 2000.
- Aitchison-Earl, P.: Sources of nitrate in groundwater in the Tinwald, Ashburton area. Environment Canterbury Report No. R19/85, 2019.
790 <https://api.ecan.govt.nz/TrimPublicAPI/documents/download/3664244>
- Aravena, R. and Robertson, W.: Use of multiple isotope traces to evaluate denitrification in groundwater: study of nitrate from a large-flux septic system plume. *Groundwater*, 36(6), 975-982, 1998.
- Barrell, D., Forsyth, P., and McSaveney, M.: Quaternary geology of the Rangitata Fan, Canterbury Plains, New Zealand. Institute of Geological and Nuclear Sciences Report 96/23, 1996.
795
- ~~Böhlke, J. K., and Denver, J. M.: Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. *Water Resources Research*, 31, 2319-2339, 1995.~~
- Brown, K. B., McIntosh, J. C., Rademacher, L. K., and Lohse, K. A.: Impacts of agricultural irrigation recharge on groundwater quality in a basalt aquifer system (Washington, USA): a multi-tracer approach. *Hydrogeol. J.*, 19 (5), 1039-1051. DOI 10.1007/s10040-011-0736-z, 2011.
800
- Burbery, L.: Nitrate reactivity in groundwater: a brief review of the science, practical methods of assessment, and collation of results from New Zealand field investigations. *J. Hydrol. (NZ)*, 57(2), 41-69, 2018.
- Burns, D. A., Boyer, E. W., Elliott, E. M., and Kendall, C.: Sources and transformations of nitrate from streams draining varying land uses: Evidence from dual isotope analysis. *J. Environ. Qual.* 38, 1149-1159, 2011.
805
- Clague, J. C., Stenger, R., and Clough, T. J.: Evaluation of the stable isotope signatures of nitrate to detect denitrification in a shallow groundwater system in New Zealand. *Agric. Ecosyst. Environ.* 202, 188-197, 2015.
- Close, M. E., Rosen, M. R., and Smith, V. I.: Fate and transport of nitrates and pesticides in New Zealand's aquifers. In M. R. Rosen, and P. A. White, *Groundwaters of New Zealand* (pp. 185-220). Wellington: New Zealand Hydrological Society, 2001.
810
- Close, M. E., Abraham, P., Humphries, B., Lilburne, L., Cuthill, T., and Wilson, S.: Predicting groundwater redox status on a regional scale using linear discriminant analysis. *J. Contam. Hydrol.*, 191, 19-32, 2016.
- ~~Chakraborty, M., Mukherjee, A., and Ahmed, K. M.: A review of groundwater arsenic in the Bengal Basin, Bangladesh and India: from source to sink. *Current Pollution Reports*, 1: 220.
815 <https://doi.org/10.1007/s40726-015-0022-0>, 2015.~~
- Craig, H.: Isotopic variations in meteoric waters. *Science* 133 (3465), 1702-1703, 1961.
- ~~Dann, R.L., Close, M.E., Flintoft, M.J., Hector, R., Barlow, H., Thomas, S., and Francis, G.: Characterization and estimation of hydraulic properties in an alluvial gravel vadose zone. *Vadose Zone Journal* 8(3), 651-663, 2009.~~
820
- Daughney, C. J. and Reeves, R. R.: Definition of hydrochemical facies in the New Zealand National Groundwater Monitoring Programme. *J. Hydrol. (NZ)*, 44, 105-130, 2005.

Formatted: Font: 10 pt

Formatted: Font: 10 pt

Formatted: Font: 10 pt

- 825 Dewandel, B., Gandolfi, J. M., de Condappa, D., and Ahmed, S.: An efficient methodology for estimating irrigation return flow coefficients of irrigated crops at watershed and seasonal scale. *Hydrol. Process.* 22, 1700-1712, 2007.
- Edmunds, W. M., Ahmed, K. M., and Whitehead, P. G.: A review of arsenic and its impact in groundwater of the Ganges-Brahmaputra-Meghna delta, Bangladesh. *Environ. Sci. Proc. Impact*. doi:10.1039/c4em00673a, 2015.
- Engelbrecht, R. L.: Land use history - Ashburton District, s.l.: Report prepared for Environment Canterbury, 2005.
- 830 Environmental Canterbury: <https://www.ecan.govt.nz/get-involved/news-and-events/2017/waimakariri-groundwater-investigation-suggests-long-term-increase-in-nitrates/>. Accessed 7 February 2020.
- Flintoft, M.: Nitrogen Recycling from St Leonards Drain. Report for Canterbury Regional Council, 2015.
- Fogg, G. E., Rolston, D. E., Decker, D. L., Louie, D. T., and Grismer, M. E.: Spatial variation in nitrogen isotope values beneath nitrate contamination sources. *Groundwater*, 36(3), 418-426, 1998.
- 835 Hanson, C. R.: Nitrate concentrations in Canterbury groundwater - a review of existing data. Environment Canterbury Technical Report R02/17, 2002.
- Hanson, C. and Abraham, P.: Nitrate contamination and groundwater chemistry - Ashburton-Hinds plain. Environment Canterbury Technical Report R10/143, 2010.
- Hayward, S.A.: Christchurch-West Melton groundwater quality: A review of groundwater quality monitoring data from January 1986 to March 2002. Environment Canterbury Technical Report U02/47, 2002.
- 840 Jongens, R., Barrell, D., Campbell, J., and Pettinga, J.: Faulting and folding beneath the Canterbury Plains identified prior to the 2010 emergence of the Greendale fault. *NZ J. Geol. and Geophys.* 55(3), 169-176, 2012.
- Kaushal, S. S., Groffman, P. M., Bland, L. E., Elliott, E. M., and Shields, C. A., and Kendall, C.: Tracking non-point source nitrogen pollution in human-impacted watersheds. *Environ. Sci. Technol.* 45, 8225-8232, 2011.
- 845 Kendall, C.: Tracing nitrogen sources and cycles in catchments. In C. Kendall, and J. J. McDonnell, *Isotope tracers in catchment hydrology*. Elsevier Science, 519-576, 1998.
- Kloppmann, W., Otero, N., Mayer, B., Sebilo, M., Goody, D.C., Lapworth, D., Surridge, B., Petelet, E., Flehoc, C., and Baran, N.: Limitations of the isotopic composition of nitrates as a tracer of their origin. *Geophys. Res. Abst.* 20, EGU2018-2617, 2018.
- 850 Koba, K., Tokuchi, N., Wada, E., Nakajima, T., Iwatsubo, G.: Intermittent denitrification: The application of a ¹⁵N natural abundance method to a forested ecosystem. *Geochim. Cosmochim. Acta*, 61, 5043-50, 1997.
- Laegreid, M., Bockman, O. C., and Kaarstad, O.: *Agriculture, Fertilizers and the Environment*. CABI Publishing, Wallingford, UK 294 pp., 1999.
- 855 Land Information New Zealand (LINZ): Website: www.linz.govt.nz, 2019.
- Landcare Research.: *Soils and climates in Canterbury: Clusters for matrix for good management Project*. Prepared for Environment Canterbury, 2015.
- 860 Mariotti, A., Landreau, A., and Simon, B.: ¹⁵N isotope biogeochemistry and natural denitrification process in groundwater: Application to the chalk aquifer of northern France, *Geochim. Cosmochim. Acta*, 52, 1869-78, 1998.

- McIlvin, M. R. and Altabet, M. A.: Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Anal. Chem.*, 77 (17), 5589–5595, 2005.
- 865 McMahon, P. B. and Chapelle, F. H.: Redox processes and water quality of selected principal aquifer systems. *Ground Water*, 46, 259-271, 2008.
- Mengis, M., Walther, U., Bernasconi, S.M., and Wehrli, B.: Limitations of using $\delta^{18}\text{O}$ for the source identification of nitrate in agricultural soils. *Environ. Sci. Technol.*, 35, 1840-1844, 2001.
- [Ministry of Health: Drinking-water Standards for New Zealand 2005. revised 2008. Wellington: Ministry of Health, 2008.](#)
- 870 [OECD: OECD Compendium of Agri-environmental Indicators, OECD Publishing, Paris. DOI: https://dx.doi.org/10.1787/9789264181151-en, 2013.](#)
- [OECD: Water resources management, in OECD Environmental Performance Reviews: New Zealand 2017, OECD Publishing, Paris. DOI: https://dx.doi.org/10.1787/9789264268203-11-en, 2017.](#)
- 875 Pangborn, M. C. and Woodford, K. B.: Canterbury dairying – A study in land use change and increasing production. Congress Proceedings: 18th International Farm Management Congress, Methven, New Zealand, 81-87. <http://ifmaonline.org/contents/pr-canterbury-dairying-a-study-in-land-use-change-and-increasing-production-p8187/>, 2011.
- [Park, Y., Kim, Y., Park, S-K., Shin, W-J., Lee, K-S.: Water quality impacts of irrigation return flow on stream and groundwater in an intensive agricultural watershed. Science of the Total Environment 630, 859–868, 2018.](#)
- 880 Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N., and Bemment, D. B.: Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Research*, 42, 4215-4232, 2008.
- Sánchez Pérez, J. M., Antiguédadb, I., Arratec, I., and Garcia-Linares, C.: The influence of nitrate leaching through unsaturated soil on groundwater pollution in an agricultural area of the Basque country: a case study. *Science of the Total Environment*, 317, 173–187, 2003.
- 885 Scott, L.: Review of Environment Canterbury's oxygen-18 data. ECan Technical Report R14/128, 2014.
- [Scott, L., Hanson, C.: Risk maps of nitrate in Canterbury groundwater. ECan Technical Report R15/xx, 2015.](#)
- Sebilo, M., Mayer, M., Nicolardot, B., Pinay, G. and Mariotti, M.: Long-term fate of nitrate fertilizer in agricultural soils. *Proc Natl Acad Sci USA*, 110(45):18185-18189, 2013.
- 890 Somers, G. and Savard, M. M.: Stable ifcsotopes of nitrate reveal the important role of soil organic matter in mediating nitrogen transfer to groundwater with implications for consequences of climate change. *GeoHalifax2009*, 2009.
- [Spalding, R. F., Hirsh, A. J., Exner, M. E., Little, N. A., Kloppenborg, K. L.: Applicability of the dual isotopes \$\delta^{15}\text{N}\$ and \$\delta^{18}\text{O}\$ to identify nitrate in groundwater beneath irrigated cropland. Journal of Contaminant Hydrology 220, 128–135, 2019.](#)
- 895 Stenger, R., Barkle, G., Burgess, C., Wall, A. and Clague, J.: Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone-aquifer continuum. *J. Hydrol.(NZ)*, 47(1), 1-24, 2008.
- 900 Stenger, R., Clague, J. C., Morgenstern, U., and Clough, T. J.: Vertical stratification of redox conditions, denitrification and recharge in shallow groundwater on a volcanic hillslope containing relict organic matter. *Science of the Total Environment*, 639, 1205-1219, 2018.

- Stewart, M. K., Morgenstern U., Tsujimura, M., Gusyev, M. A., Sakakibara, K., Imaizumi, Y., Rutter, H., van der Raaij, R. W., Etheridge, E., Scott, L., and Cox, S. C.: Mean residence times and sources of Christchurch springs. *J. Hydrol. (NZ)*, 57(2), 81-94, 2018.
- 905 Stewart, M. K.: Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops: Applications to atmospheric processes and evaporation of lakes. *J. Geophys. Res.*, 80(9), 1133-1146, 1975.
- Stewart, M. K. and Morgenstern, U.: Age and source of groundwater from isotope tracers. In *Groundwaters of New Zealand*, M. R. Rosen and P. A. White (eds). New Zealand Hydrological Society Inc., Wellington. Pp. 161-183, 2001.
- 910 Stewart, M. K., Stevens, G., Thomas, J., van de Raaij, R., and Trompetter, V.: Nitrate sources and residence times of groundwater in the Waimea Plains, Nelson. *J. Hydrol. (NZ)*, 50(2), 313-338, 2011.
- Stewart, M. K. and Taylor, C. B.: Environmental isotopes in New Zealand hydrology. Part 1. Introduction: The role of oxygen-18, deuterium and tritium in hydrology. *NZ J. Sci.*, 24, 295-311, 1981.
- 915 Stewart, M. K., Trompetter, V., van de Raaij, R., 2002. Age and source of Canterbury plains groundwater. Environment Canterbury Report U02/30.
- Taylor, C. B., Wilson, D. D., Brown, L. J., Stewart, M. K., Burdon, R. J., and Brailsford, G. W.: Sources and flow of North Canterbury Plains groundwater, New Zealand. *J. Hydrol.*, 106, 311-340, 1989.
- Thorpe, H. R. and Scott, D. M.: An evaluation of four soil moisture models for estimating natural ground water recharge. *J. Hydrol. (NZ)*, 38(2), 179-209, 1999.
- 920 Trevis, I. A.: Assessing and tracking nitrate contamination from a point source and the effects on the groundwater systems in Mid Canterbury, New Zealand. Christchurch, New Zealand: MSc Thesis, University of Canterbury, 2012.
- van der Raaij, R. W.: Groundwater age determination of Ashburton District Council water supply wells. GNS Science Consultancy Report 2013/80, 2013.
- 925 Wells, N. S., Baisden, W. T., and Clough, T. J.: Ammonia volatilisation is not the dominant factor in determining the soil nitrate isotopic composition of pasture systems. *Agric. Ecosyst. Environ.* 199, 290-300. doi.org/10.1016/j.agee.2014.10.001, 2015.
- Wells, N. S., Baisden, W. T., Horton, T., and Clough, T. J.: Spatial and temporal variations in nitrogen export from a New Zealand pastoral catchment revealed by stream water nitrate isotopic composition. *Water Resour. Res.*, 52, 2840-2854, 2016.
- 930 [Wexler, S. K., Goodale, C. L., McGuire, K. J., Bailey, S. W., and Groffman, P. M.: Isotopic signals of summer denitrification in a northern hardwood forested catchment, *Proc. Natl. Acad. Sci. U. S. A.*, 111\(46\), 16,413–16,418, 2014.](#)
- 935 World Health Organization.: Nitrate and nitrite in drinking-water: Background document for development of WHO Guidelines for drinking-water quality. World Health Organization, Geneva, 2016.
- World Health Organization.: Guidelines for drinking-water quality, 4th edition, incorporating the 1st addendum. World Health Organization, Geneva, 2017.
- Xue, D. J., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., and Boeckx, P.: Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. *Water Research*, 43(5), 1159-1170, 2009.
- 940

Zhang, Y., Shi, P., Song, J., and Li, Q.: Application of nitrogen and oxygen isotopes for source and fate identification of nitrate pollution in surface water: A review. *Appl. Sci.*, 9, 18, 2019.

945 Table 1: Sample and well information, field dissolved oxygen concentration (DO) and isotopes of water and nitrate. The wells are ordered from lowest to highest DO concentrations, and four groups of samples (A to D) are identified for discussion (below).

Well No.	ID	Group	Date	Screen Length (m)	Mid-Screen Depth (m)	DO mg/L	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	$\delta^{15}\text{N}_{\text{NO}_3}$ ‰	$\delta^{18}\text{O}_{\text{NO}_3}$ ‰
K37/0702	01	A	28/03/18	1.5	33.3	0.18	-8.3	-58.6	20.4	11.8
K37/3114	02	A	15/03/18	1.5	35.3	0.45	-8.59	-61.4	16.6	7.8
K37/1806	03	A	15/03/18	27.0	42.5	0.67	-8.47	-58.4	15.7	7.8
K37/2977	04	B	8/02/18	3.0	47.5	1.36	-8.83	-64.2	7	3.1
K37/1014	05	B	22/02/18	1.5	8.8	1.68	-8.75	-62.9	7.2	3.3
K37/0819	06	A	22/02/18	1.5	39.3	2.44	-8.5	-60.9	20	6.5
K37/0147	07		7/02/18	ns ¹	10	2.68	-8.18	-60.2	5	0.7
K37/1862	08	B	15/03/18	1.5	35.3	2.95	-8.84	-62.1	8	3.9
K37/0336	09	B	9/04/18	ns	7	3.39	-8.74	-61.6	8.7	4
K37/3052	10		22/02/18	ns	15	4.11	-8.8	-63.5	4.2	0.2
K37/1012	11		15/03/18	2.0	29.6	6.34	-8.38	-58.7	6	2.8
BY21/0125	12		28/03/18	1.0	28.5	6.73	-8.53	-59.8	3.5	0.3
BY21/0184	13		7/02/18	6.0	7.5	7.76	-8.18	-59.1	4.5	1.2
K37/0088	14		12/03/18	3.6	8.2	8.05	-8.48	-61.4	5.9	1.8
K37/1972	15	C	7/02/18	ns	20	8.29	-8.35	-59.3	3.7	1.1
K37/0961	16		8/02/18	6.0	55.5	8.37	-8.52	-60.6	4.1	1
K37/0697	17		14/03/18	1.5	21.3	8.65	-8.6	-60.5	3.3	0.1
K37/2347	18		12/03/18	3.0	58.5	8.76	-8.57	-62	2.5	-0.1
K37/1767	19		28/03/18	2.0	28.5	9.18	-8.49	-59.6	2.2	-0.4
K37/2301	20		9/04/18	ns	25	9.25	-8.76	-61.5	4.8	1
K37/3049	21		22/02/18	ns	15	9.36	-7.71	-54.4	1.8	-1.2
K37/1807	22		14/03/18	1.5	23.3	9.39	-8.56	-62	3	-0.3
K37/0968	23	C	10/04/18	5.0	7.5	9.54	-8.19	-60.2	2.6	-0.5
K37/1479	24		9/02/18	12.5	66.3	9.6	-8.64	-61.3	2.2	-0.2
K37/1603	25	D	9/02/18	6.0	59.7	9.6	-8.8	-63.9	2.2	-0.8
BY21/0306	26		17/04/18	ns	14	9.68	-8.83	-63.5	3.8	0.8
BY21/0307	27	C	17/04/18	ns	13	9.85	-8.47	-61	3.3	-0.5
K37/1661	28	C	8/02/18	ns	11	9.9	-8.36	-59.7	3.7	-0.1
K37/1939	29	D	9/04/18	1.5	38.4	10.3	-9.17	-64.3	1.7	-1.1
K37/3146	30	D	14/03/18	3.0	52.5	10.3	-8.94	-64.4	1.8	-0.8
K37/0502	31		8/02/18	1.1	21.9	10.4	-8.47	-61.6	4.5	1
K37/0685	32		14/03/18	1.0	17.0	11.6	-8.51	-60.2	3.5	0.6
BY20/0151	33		9/04/18	6.0	39.0	11.8	-8.66	-61.3	2.2	-0.9

¹ns means no screen. Depths for wells with no screens are total depths.

Formatted Table

950 **Table 2: Major ion chemistry of water samples.**

ID No.	Group	DO mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	SO ₄ mg/L	HCO ₃ mg/L	NO ₃ mg/L
01	A	0.18	11.9	1.02	18.8	6.6	18	11.6	78	0.064
02	A	0.45	15.5	1.49	27	10.5	18.1	17.5	102	5.8
03	A	0.67	13.2	1.41	23	8.5	17.6	15.3	92	2.5
04	B	1.36	11.1	1.02	18.8	7.5	12.1	13.6	76	3
05	B	1.68	18.5	1.25	29	10.4	17.7	35	97	4.3
06	A	2.44	12.5	1.08	20	7.6	17.1	19	76	1.43
07		2.68	15.2	1.71	35	8.2	20	27	75	11.8
08	B	2.95	15.7	1.39	24	9	17	25	85	4.5
09	B	3.39	18.4	1.32	28	9.4	18.1	34	102	3.9
10		4.11	16.7	1.74	29	9.3	16.4	27	64	12.9
11		6.34	18.1	1.64	27	10	26	26	57	10.9
12		6.73	14.8	1.47	29	10.3	17.2	17.1	78	13.1
13		7.76	15.9	1.71	24	8.3	20	29	54	7.7
14		8.05	17.2	1.71	30	9.7	21	22	64	13
15	C	8.29	17.7	1.28	35	12.4	26	36	55	17.4
16		8.37	14.7	1.59	30	9.4	19.3	22	66	14
17		8.65	16.5	1.37	24	8	17.6	24	60	9.2
18		8.76	16	1.5	28	9.6	16.3	21	57	13.9
19		9.18	17.9	1.63	33	11.2	21	25	71	15.7
20		9.25	14.4	1.39	30	10	15.3	22	61	17.1
21		9.36	14.9	1.53	29	9	18.5	29	69	7.7
22		9.39	17.5	1.77	36	11	19.6	26	60	21
23	C	9.54	18.4	1.56	31	9.8	23	30	63	15
24		9.6	14.5	1.6	32	9.3	14.9	18.4	49	22
25	D	9.6	10.3	1.19	16.9	5.3	9.2	5	48	9.3
26		9.68	15.2	1.52	32	8.8	21	27	82	9.5
27	C	9.85	21	2.3	43	11.4	23	39	53	26
28	C	9.9	18	1.72	38	11.9	22	33	53	25
29	D	10.3	9.2	1.1	14.9	4.1	6	5.8	49	6.7
30	D	10.3	9.5	1.1	14	4.4	7.1	3.8	49	7.3
31		10.4	15.3	1.63	35	10.5	13.2	23	77	18.5
32		11.6	17.7	1.77	34	10.5	21	27	77	12.8
33		11.8	14.8	1.5	28	7.9	13.4	18	61	16.8

Table 3: Results of calculations of the $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ values of nitrate affected by denitrification. The initial nitrate concentration was 19 mg/L, and the δ_0 values were $\delta^{15}\text{N} = 3.1\%$, $\delta^{18}\text{O}_{\text{NO}_3} = 0.0\%$. The enrichment factors used were $\epsilon(^{15}\text{N}) = -3.0\%$, $\epsilon(^{18}\text{O}) = -2.1\%$.

f	NO ₃ mg/L	Ln (NO ₃)	$\delta^{15}\text{N}$ ‰	$\delta^{18}\text{O}_{\text{NO}_3}$ ‰
1.0	19	2.94	3.1	0.0
0.7	13.3	2.59	4.2	0.7
0.5	9.5	2.25	5.2	1.4
0.3	6.65	1.89	6.7	2.5
0.2	3.8	1.34	7.9	3.3
0.1	1.9	0.64	10.0	4.7
0.04	0.76	-0.27	12.8	6.6
0.02	0.38	-0.97	14.8	8.0
0.01	0.19	-1.66	16.9	9.4
0.004	0.076	-2.58	19.7	11.3

955

Table 4: Average chemical and isotopic concentrations of Groups C and D. Enrichment factors and IRF coefficients (C) for the chemicals, and isotopic differences and irrigation inputs for the isotopes are given.

Quantity	Group D	Group C	Enrichment Ffactor	Coefficient C (%)
Cl (mg/L)	7.4 ± 1.1	23.5 ± 1.3	3.2	31
SO ₄ (mg/L)	4.9 ± 0.7	34.5 ± 3.0	7.0	—
HCO ₃ (mg/L)	48.7 ± 0.4	56 ± 3.7	1.2	—
NO ₃ (mg/L)	7.8 ± 1.0	20.9 ± 4.2	2.7	37
Na (mg/L)	9.7 ± 0.4	18.8 ± 1.2	1.9	53
K (mg/L)	1.13 ± 0.04	1.72 ± 0.33	1.5	67
Ca (mg/L)	15.3 ± 1.0	36.8 ± 3.9	2.4	42
Mg (mg/L)	4.6 ± 0.4	11.4 ± 0.9	2.5	40
Mean			2.84	42
			Difference	Irrigation input
$\delta^{18}\text{O}$ (‰)	-8.97 ± 0.13	-8.34 ± 0.09	0.63	39
$\delta^2\text{H}$ (‰)	-64.2 ± 0.2	-60.1 ± 0.6	4.1	40

960

Formatted: Normal

Formatted Table

Captions

- Figure 1: a. New Zealand map showing locations of Tinwald and other areas mentioned in the text. b. Tinwald study area with simplified land usage (Agribase, 2016). Base map containing road and stream information © LINZ (2019).
- 965 Figure 2: Maximum nitrate concentrations in the greater Ashburton area 1990 to 2017. Base map © LINZ (2019).
- Figure 3: Wells sampled in the Tinwald study area for this study. Base map © LINZ (2019).
- Figure 4: a). Chloride, b). Sulphate, c). Nitrate concentrations in the Tinwald study area (the smaller dots indicate maximum concentrations measured prior to the 2018 investigation). Base maps © LINZ (2019).
- 970 Figure 5: Plots of: a. chloride versus water $\delta^{18}\text{O}$, b. chloride versus sulphate, and c. chloride versus nitrate concentrations. Groups C (with land surface irrigation recharge) and D (alpine river recharge) are circled. The red arrow shows the predicted effect of evaporation.
- Figure 6: $\delta^{18}\text{O}$ in the Ashburton area at groundwater and surface water sites. Data outside of the Tinwald study area is mean $\delta^{18}\text{O}$ from all available measurements, inside the study area $\delta^{18}\text{O}$ is the single result from the current sampling. Base map © LINZ (2019).
- 975 Figure 7: Paired $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data in the Tinwald study area. The average initial composition of the well waters is indicated by the small red circle. Groups C and D samples are circled.
- Figure 8: a. Plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{ONO}_3$. Groups A and B are circled, C and D indicated by letters. b, c. Plots of $\delta^{15}\text{N}$ and $\delta^{18}\text{ONO}_3$ versus the natural log of the nitrate concentration.
- Figure 9: Schematic view of recharge and irrigation return flow in the Tinwald hot spot.
- 980 Figure 10. Plot of the nitrate isotopic source signatures from several New Zealand studies. Red rectangle – 0.4 m suction samples at Toenepi Catchment (Clague et al., 2015), purple rectangle - stream samples from Harts Creek (Wells et al., 2016), blue rectangle – oxic water samples from Waihora wellfield northwest of Lake Taupo (Stenger et al., 2018), orange double arrows - $\delta^{15}\text{N}$ values only from groundwater in the Waimea Plains (Stewart et al., 2011), and oxic waters (Groups C and D) from the present investigation.
- 985 Figure 11: a. Plot of DO versus nitrate concentration. b, c. Plots of $\text{Ln}(\text{DO})$ versus $\delta^{15}\text{N}$ and $\delta^{18}\text{ONO}_3$.

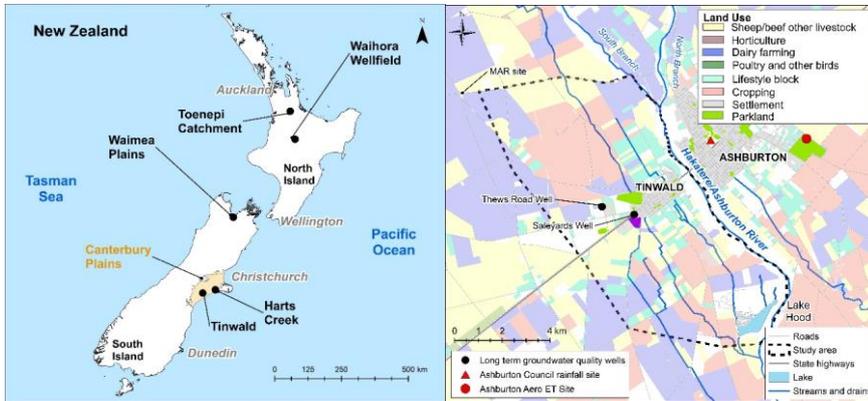
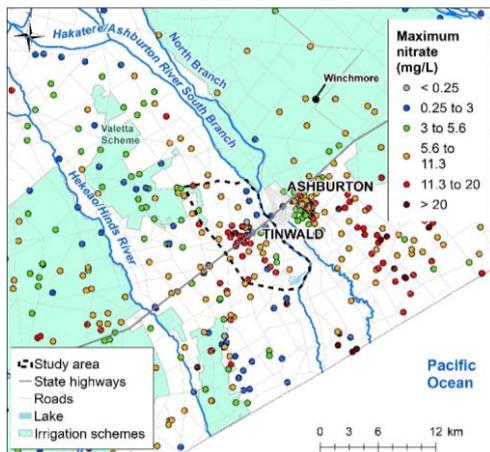


Figure 1: a. New Zealand map showing locations of Tinwald and other areas mentioned in the text. b. Tinwald study area with simplified land usage (Agribase, 2016). Base map containing road and stream information © LINZ (2019).

990



995 Figure 2: Maximum nitrate concentrations in the greater Ashburton area 1990 to 2017. Base map © LINZ (2019).

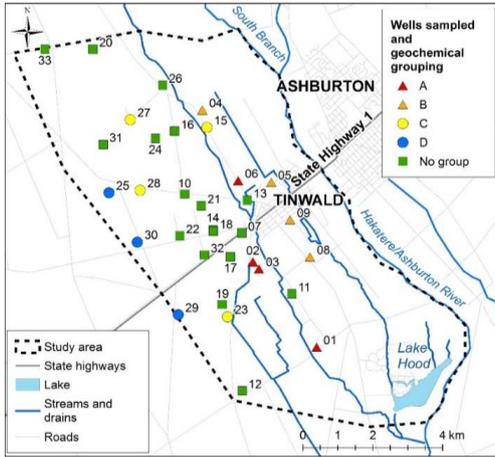


Figure 3: Wells sampled in the Tinwald study area for this study. Base map © LINZ (2019).

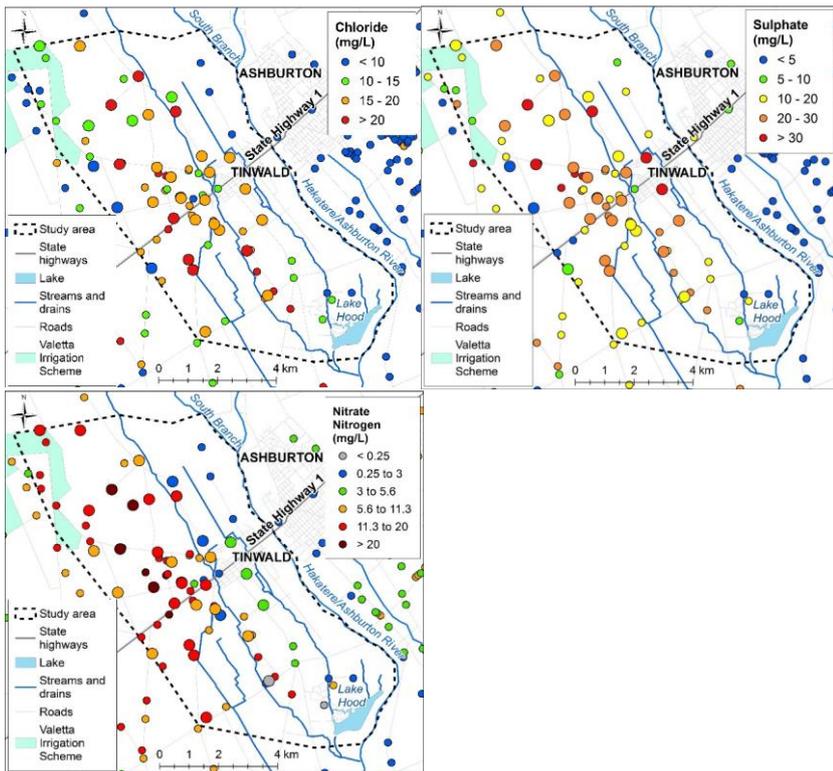
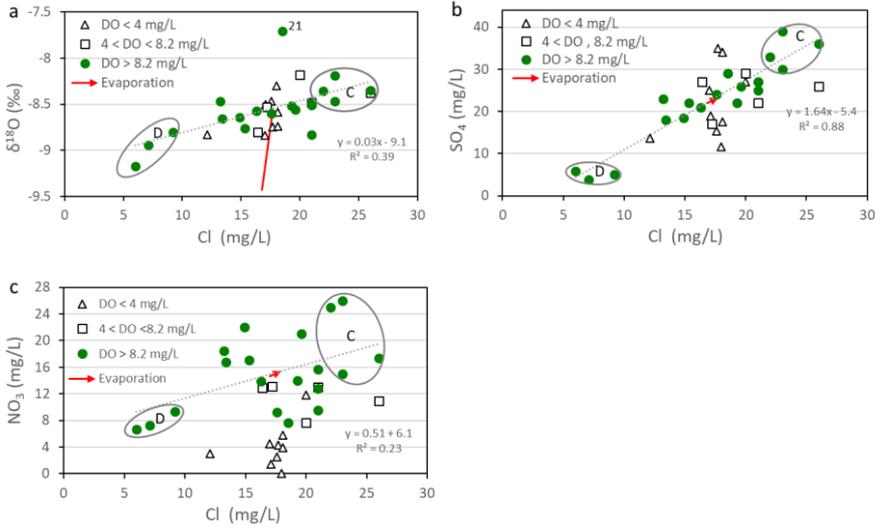
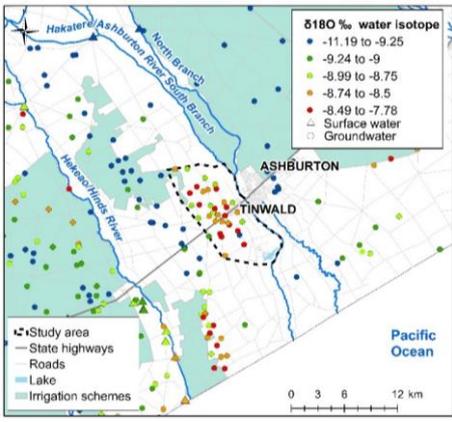


Figure 4: a). Chloride, b). Sulphate, c). Nitrate concentrations in the Tinwald study area (the smaller dots indicate maximum concentrations measured prior to the 2018 investigation). Base maps © LINZ (2019).



1005

Figure 5: Plots of: a. chloride versus water $\delta^{18}\text{O}$, b. chloride versus sulphate, and c. chloride versus nitrate concentrations. Groups C (with land surface irrigation recharge) and D (alpine river recharge) are circled. The red arrow shows the predicted effect of evaporation.



1010

Figure 6: $\delta^{18}\text{O}$ in the Ashburton area at groundwater and surface water sites. Data outside of the Tinwald study area is mean $\delta^{18}\text{O}$ from all available measurements, inside the study area $\delta^{18}\text{O}$ is the single result from the current sampling. Base map © LINZ (2019).

1015

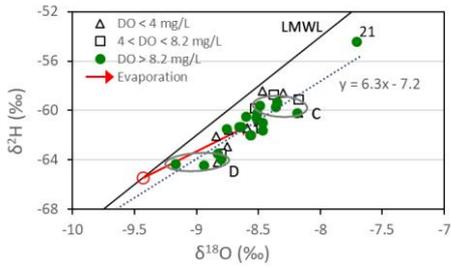


Figure 7: Paired $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data in the Tinwald study area. The average initial composition of the well waters is indicated by the small red circle. Groups C and D samples are circled.

1020

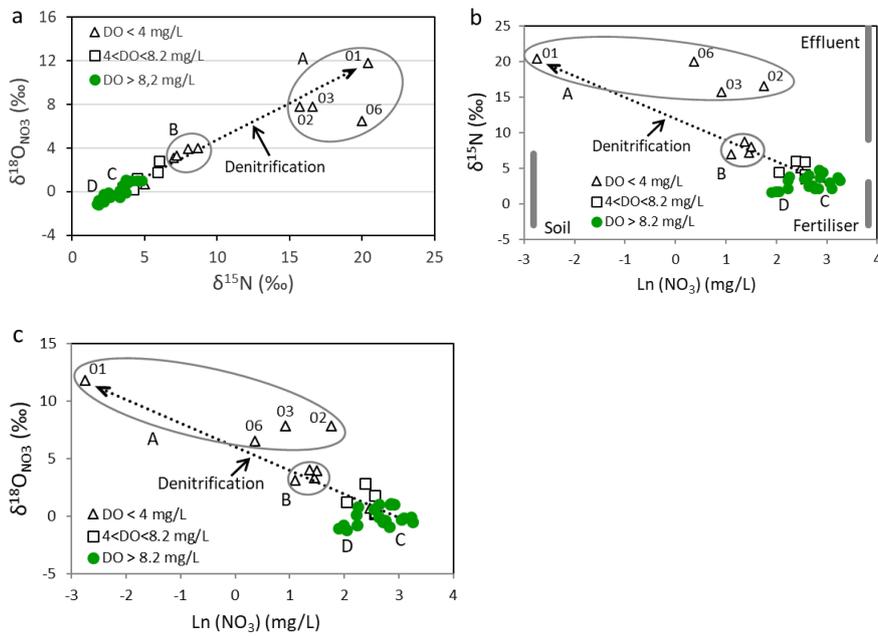


Figure 8: a. Plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}_{\text{NO}_3}$. Groups A and B are circled, C and D indicated by letters. b, c. Plots of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ versus the natural log of the nitrate concentration.

Formatted: Subscript
Formatted: Subscript

1025

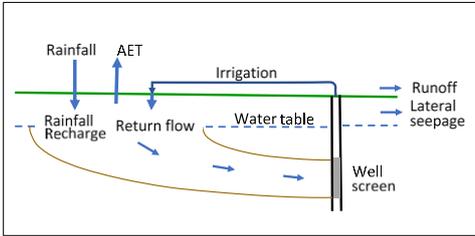


Figure 9: Schematic view of recharge and irrigation return flow in the Tinwald hot spot.

1030

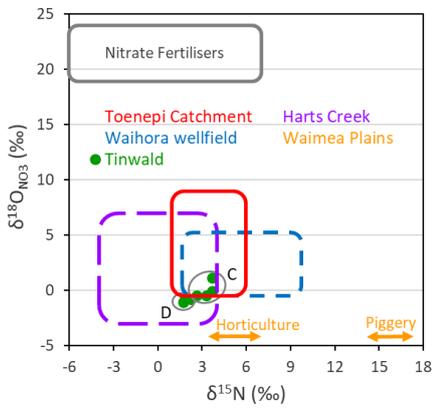


Figure 10. Plot of the nitrate isotopic source signatures from several New Zealand studies. Red rectangle – 0.4 m suction samples at Toenepi Catchment (Clague et al., 2015), purple rectangle - stream samples from Harts Creek (Wells et al., 2016), blue rectangle – oxic water samples from Waihora wellfield northwest of Lake Taupo (Stenger et al., 2018), orange double arrows - $\delta^{15}\text{N}$ values only from groundwater in the Waimea Plains (Stewart et al., 2011), and oxic waters (Groups C and D) from the present investigation.

1035

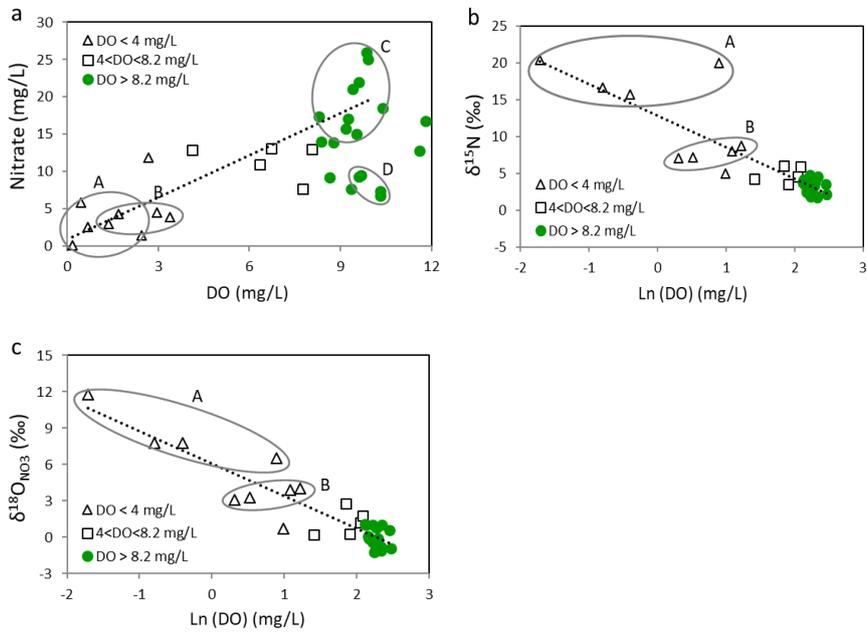


Figure 11: a. Plot of DO versus nitrate concentration. b, c. Plots of Ln(DO) versus $\delta^{15}N$ and $\delta^{18}O_{NO_3}$.