High-frequency NO_3^- isotope ($\delta^{15}N$, $\delta^{18}O$) patterns in groundwater recharge reveal that short-term changes in land use and precipitation influence nitrate contamination trends

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Abstract

Poultry manure is the primary cause of nitrate (NO_3^-) exceedances in the transboundary Abbotsford-Sumas Aquifer (Canada-USA) based on synoptic surveys two decades apart, but questions remained about seasonal and spatial aspects of agricultural nitrate fluxes to the aquifer to help better focus remediation efforts. We conducted over 700 monthly $\delta^{15}N$ and $\delta^{18}O$ of nitrate assays, focusing on shallow groundwater (<5 yr.-old) over a five-year period to gain new insight on spatiotemporal sources and controls of groundwater nitrate contamination. NO_3^- concentrations in these wells ranged from 1.3 to 99 mg N L^{-1} (n=1041) with a mean of 16.2 ±0.4 mg N L^{-1}. The high-frequency ^{15}N and ^{18}O isotope data allowed us to identify 3 distinctive NO_3^- source patterns; i) primarily from synthetic fertilizer; ii) dynamic changes in nitrate due to changes in land use; and iii) from a mix of poultry manure and fertilizer. A key finding was that the source(s) of nitrate in recharge could be quickly influenced by short-term near-field management practices and stochastic precipitation events, which ultimately impact long-term nitrate contamination trends. Overall, the isotope data affirmed a subtle decadal-scale shift in agricultural practices from manure increasingly towards fertilizer nitrate sources; nevertheless poultry-derived N remains a predominant source of nitrate contamination. Because the aquifer does not generally support denitrification, remediation of the Abbotsford-Sumas aquifer is possible only if agricultural N sources are seriously curtailed, a difficult proposition due to longstanding high-value intensive poultry and raspberry and blueberry operations over the aquifer.

1. Introduction

The global widespread use and over-application of synthetic and manure N-nutrients in agriculture has caused widespread groundwater nitrate (NO_3^-) contamination in surficial aquifers around the world (Hasleur et al., 2005; Hamilton and Helsel, 1995; Spalding and Exner, 1993). Furthermore, with global trends towards increased agricultural intensification, threats to groundwater quality are correspondingly heightened (Vorosmarty et al. 2000; Böhlke, 2002). In agricultural settings, elevated groundwater NO_3^- concentrations typically reflect a supply of N from manure, synthetic fertilizer or soil organic matter which exceeds, or is poorly synchronized with crop N requirements (Canter, 1997). The risk of NO_3^- contamination is especially high in phreatic aquifers comprised of coarse grained permeable soils with minimal propensity for natural attenuation and remediation processes such as microbial denitrification. Studies have used stable isotopes of nitrate ($\delta^{15}N$, $\delta^{18}O$) to differentiate different source inputs (Mitchell et al., 2003; Wassenaar et al., 2006; Xue et al., 2009, Pasten-Zapata et al. 2014), while others have used $\delta^{15}N$ and $\delta^{18}O$ to examine the anaerobic remediation of nitrate by microbial denitrification (Böhlke et al. 1995; Kellman and Hillaire-Marcel, 2003). Others used isotopes of nitrate to assess soil N transformations (Savard et al. 2010) or temporal variations in agricultural leachate to groundwater (Ostrom et al. 1998; Loo et al. 2017; Savard et al. 2007).

Concentrations of non-agricultural NO_3^- in aquifers that are low (<1 mg N L^{-1}) and below drinking water standards are usually attributed to atmospheric N deposition, organic N from plant decomposition or land breakage, and geological sources that are mobilized due to disruptions in water recharge fluxes such as introduction of irrigation (Canter, 1997). Choi et al. (2003) suggests low groundwater NO_3^- concentrations consistently below 3 mg N L^{-1} with $\delta^{15}N$ values between +5 and +8 ‰, are likely derived from natural soil or organic N

sources (average $\delta^{15}N$ +5 ‰). Loo et al. (2017) reported non-agricultural soil $\delta^{15}N$ nitrate ranges between +3.7 to +4.9 ‰ in our study area (Table 1).

Sources of nitrate from animal waste arise from dispersed agricultural field applications and/or point-source manure storage facilities (liquid and solid). Under aerobic soil conditions, NO_3^- quickly forms from oxidation of NH_4^+ after manure application (Aravena et al, 1993). Due to preferential volatilization of ^{14}N in gaseous NH_3 from NH_4^+ during wet storage and/or application of manure, manure-derived NO_3^- is accordingly enriched in ^{15}N (Kendall 1998). Nitrate derived from manures or septic waste can have $\delta^{15}N$ values between +10 to +25 ‰, (Wassenaar, 1995; Kreitler, 1975; Heaton, 1986; Aravena and Robertson, 1998), generally revealing little distinctive ^{15}N isotopic resolution between these two organic N waste sources. Poultry manure solids have average $\delta^{15}N$ values of approximately +7.9 ‰ in the study area (Loo et al., 2017; Wassenaar, 1995). In North America, Urea ($CO(NH_2)_2$) (Nitrogen, Phosphorus, Potassium (N-P-K): 46-0-0), is one of the most common forms of synthetic fertilizers used (Overdahl et al., 2007). Other forms of synthetic fertilizers include ammonium-nitrate (NH_4-NO_3) (34-0-0) and ammonium-sulfate (NH_4-SO_4) (22-0-0), as shown in Table 1. Each of these are manufactured by fixation of atmospheric N ($\delta^{15}N$ = ~0 ‰), resulting in $\delta^{15}N$ values from -2.8 to +0.3 ‰ (Loo et al., 2017). In the Abbotsford-Sumas aquifer area, berry-specific fertilizer blends are commonplace (Table 1), where N is derived from one of the above sources (Loo et al., 2017; Wassenaar, 1995).

The $\delta^{18}O$ values of synthetic fertilizer derived NO_3^- typically range between +18 to +22 ‰, because the oxygen in nitrate originates from air O_2 ($\delta^{18}O$ = +23.5 ‰) and ^{18}O depleted H_2O (Amberger and Schmidt, 1987). Nitrate derived from NH_4-NO_3 fertilizers,

where 50 % of the oxygen is from nitrification of NH_4 fertilizer and 50 % is from synthetic NO_3^- fertilizer, have reported $\delta^{18}O$ values around +13 ‰ (Aravena et al. 1993). In this study, the $\delta^{18}O$ of ground water is relatively uniform (-11.1 ±0.4 ‰; Wassenaar, 1995), which would result in $\delta^{18}O$ values around zero ‰ for NO_3^- derived only from the nitrification of soil or organic N or ammonium sources.

In the phreatic transboundary Abbotsford-Sumas Aquifer (ASA) (Canada-USA, Figure 1), long-term nitrate contamination trends and isotopic studies have been conducted over several decades. The isotopic apportionment of NO_3^- sources in the aquifer was based on two summertime synoptic isotopic studies spanning a full decade, that revealed that poultry manure was the predominant source of NO_3^-, with localized long-term shifts towards inorganic fertilizer sources (Wassenaar, 1995, Wassenaar et al. 2006) due to changes in agricultural practices (Zebarth et al. 2015). These agricultural changes include: decadal shifts from beef and dairy feed production to lower N uptake berry production; changes in irrigation methods from sprinklers to low pressure drip fertigation; planting of cover crop for berry alley management; and a slow transition from raspberries to blueberries. One critique of the previous synoptic isotope studies was that sampling (and hence interpretations) was prejudiced to summer 'snapshots', and thereby could be biased, especially for the numerous shallow and highly responsive water table wells spanning the aquifer and winter-biased recharge (Environment Canada, 2014). The seasonal dynamics of NO_3^- sources and fluxes and the potential for isotopic changes due to soil and unsaturated zone NO_3^- cycling were not fully evaluated, and need to be considered to improve surface nutrient applications and agricultural management practices.

To address this knowledge gap, we conducted high-frequency (monthly) NO_3^- concentration and isotope analysis of the ASA over a 5-year period, with a focus on shallow

wells having groundwater residence times of <5 years as determined by ^{3}H-He age dating. Our aim was to determine whether high-frequency (monthly) nitrate and isotope (δ^{15}N, δ^{18}O) sampling improved upon previous interpretations of N sources and processes, and whether important seasonal changes in the proportion of NO_3^- sources recharging to groundwater were overlooked by synoptic snapshots. Our goal was to gain improved insight on the spatiotemporal sources and controls of groundwater-nitrate dynamics, and thereby to help better inform agricultural nutrient management practices and potential NO_3^- remediation efforts in the aquifer.

2. Materials and Methods

2.1   Study Area and Hydrogeologic Setting

The Abbotsford-Sumas aquifer is a shallow phreatic transboundary aquifer located in southwestern British Columbia, Canada, and northwestern Washington State, USA (Figure 1). The ASA is the most intensively studied nitrate-contaminated aquifer in Canada (Zebarth, 1998, 2015), and covers an area of about 200 km^2, with approximately 40 % of the total surface area in Canada (Cox and Kahle, 1999). Our study area encompassed approximately 40 km^2 on the Canadian side of the aquifer, between the Abbotsford International Airport and the Canada-USA border (Figure 1). Land use on the aquifer is predominantly commercial raspberry and blueberry production, mixed with intensive commercial poultry barn operations (Figure 1) and is <5 % rural residential; (BC Ministry of Agriculture, unpublished data).

The aquifer is typically 10-25 m thick, but reaches 70 m thickness towards the south-east portion (Cox and Kahle, 1999). The aquifer comprises coarse glacio-fluvial sand and gravel with minor till and clayey silt lenses (Armstrong et al. 1965), with glacio-marine clays confining the aquifer below (Halstead, 1986). The high sand and gravel content results in a

high transmittance of water, with mean hydraulic conductivities (K) of 1.6×10^{-3} m s^{-1} (Chesnaux et al. 2007) to 9.5×10^{-4} m s^{-1} (Cox and Kahle, 1999). The thin organic-poor soils (0-70 cm) are medium-textured aeolian deposits, moderately-well to well-drained, and are classified as Orthic Humo-Ferric Podzols (Luttermerding, 1980).

Average annual precipitation across the aquifer (1981-2010) is 1538 mm, of which 70 % falls between October and March (Environment Canada, 2014). Annual recharge estimates range from 850 to 1100 mm (Zebarth et al. 2015), and water table depths typically vary widely between 2 to 20 m below surface depending on the location and season. Annual water table fluctuations average ~3.6 m (Scibek and Allen, 2006). The overall flow direction in the aquifer is south (Figure 1), southeast, and southwest at linear velocities of up to 450 m yr^{-1} (Liebscher et al. 1992; Cox and Kahle, 1999).

The aquifer is highly vulnerable to surface derived NO_3^- and other contamination because of: i) intensive agricultural activity, ii) highly permeable soil, coarse sand and gravel lithology, and iii) high precipitation amounts in the fall and winter when nutrient uptake by crops is lowest and the NO_3^- leaching potential is greatest (Kohut et al. 1989; Liebscher et al. 1992). Elevated groundwater-nitrate concentrations exceeding drinking water guidelines are observed since the 1970's (Zebarth et al. 2015). Mitchell et al. (2003) and others (Wassenaar et al. 1995) showed vertical stratification of nitrate in groundwater was linked to agricultural practices, with greatest nitrate concentrations (>20 mg N L^{-1}) occurring in shallow water table regions (<10 mbgs), while average groundwater-nitrate concentrations (<10 mg N L^{-1}) in deep wells (>10 m screen depth below average static water level) were lower and relatively stable over time. Based on Environment and Climate Change Canada (ECCC) monitoring, the highest seasonal and temporal variations in NO_3^- are found in wells screened near the water table. Both seasonal and long-term temporal variations in groundwater-nitrate over

decadal timeframes are well documented (Liebscher et al. 1992; Graham et al., 2015). The aquifer has little widespread intrinsic capacity to sustain microbial denitrification (self-remediation) because of largely aerobic conditions and the low organic content of the aquifer materials (Wassenaar, 1995), but it can occur in localized pockets around riparian discharge zones.

2.2 Sample Collection and Analysis

Monthly groundwater samples (*n*=56 per well) were collected from 19 selected monitoring wells from September 2008 to March 2013. These wells were selected based on the following criteria: 1) ground water having a <5-year residence time based on ^{3}H-He age-dating (Wassenaar et al. 2006); 2) representative spatial coverage within the monitoring network; and 3) wells representing aerobic groundwater where denitrification does not occur (Tesoriero, 2000; Wassenaar et al. 2006). These criteria helped to ensure that high-frequency nitrate and isotopic patterns stem from short-term nitrate responses unaffected by historical or subsurface biogeochemical processes or mixing with deeper water, and could therefore be more explicitly linked to contemporary landscape and agricultural activities and practices happening roughly within a 5-year timeframe.

Static water level measurements were taken prior to pumping and were reported in meters above mean sea level (masl). Groundwater was sampled from the wells using a Grundfos® stainless steel submersible pump, Teflon® lined LDPE tubing, and stainless-steel fittings and valves. Well water was pumped through a flow-through cell housing a calibrated YSI® multi-probe sonde (temperature, pH, specific conductance, oxidation reduction potential (ORP), and dissolved oxygen (DO)). General chemistry, and NO_3^- isotope water samples were collected after at least three well volumes were purged and the YSI® field parameters were stabilized. All bottles were rinsed 3x with sample water prior to filling.

Water samples for major ion and nutrient concentrations were taken in 1 L LDPE bottles, filtered through 0.45 µm cellulose acetate membrane filters, stored at 5°C and analyzed within 5 days for nitrate using standard ion chromatography techniques. Nitrate concentrations were determined at the Pacific-Yukon Laboratory for Environmental Testing in North Vancouver, BC, Canada. Nitrate results are reported as mg N L^{-1} with a minimum detectable limit of 0.02 mgL^{-1}.

Samples for nitrate isotope analyses (δ^{15}N, δ^{18}O) were field filtered through 0.45 µm cellulose acetate membrane filters and frozen (-40 °C) in 125 ml HDPE bottles. Nitrate isotope assays were conducted by the University of Calgary Stable Isotope Laboratory, using a microbial reduction to N$_2$O described elsewhere (Casciotti et al. 2002; Sigman et al. 2001). All δ^{15}N values are reported relative to the atmospheric air reference (Mariotti, 1983) and normalized by analyzing reference materials IAEA-N3 (δ^{15}N$_{AIR}$ = +4.7 ‰), USGS32 (δ^{15}N$_{AIR}$ = +180 ‰), USGS34 (δ^{15}N$_{AIR}$ = -1.8 ‰), USGS35 (δ^{15}N$_{AIR}$ = +2.7 ‰) along with samples. The analytical uncertainty for δ^{15}N was ±0.5 ‰. The δ^{18}O values were reported relative to the VSMOW reference (Coplen, 1994) and determined by analyzing reference materials IAEA-N3 (δ^{18}O$_{VSMOW}$ = +25.6 ‰), USGS32 (δ^{18}O$_{VSMOW}$ = +25.7 ‰), USGS34 (δ^{18}O$_{VSMOW}$ = -27.9 ‰), and USGS35 (δ^{18}O$_{VSMOW}$ = +57.5 ‰). The analytical uncertainty for δ^{18}O was ±1.0 ‰.

Nitrate and chloride concentrations were log-transformed prior to analysis to ensure normal distributions and were evaluated using Principal Component Analysis (PCA) and Factor Analysis. Statistical analyses (at the 95 % confidence level), including multivariate time series analyses were conducted using the Kruskall-Walis methods for determining seasonality, log-normal transformations, Mann-Kendall trend analyses and Gaussian mixture

and Bayesian clustering models using WQHydro®, ProUCL 5® and XLSTAT® (Lettenmaier, 1988; Thas et al. 1998). Seasonal Mann-Kendall trend analysis were deemed inappropriate for evaluating nitrate concentration seasonality as the repeating periods were correlated to precipitation patterns instead of calendar month, and because peak nitrate concentration timings varied from year to year, resulting in a determination of non-seasonality.

3. Results and Discussion

3.1 Groundwater Nitrate Concentrations

Results of monthly nitrate concentrations in the water table wells in the aquifer over the 5-year sampling period ranged from 1.3 to 99.0 mg N L^{-1} (n=1041), having a mean concentration ($\pm$ SE) of 16.2 $\pm$0.1 mg N L^{-1}. Approximately 76 % of the shallow groundwater locations (16 of 19 sites) exceeded the maximum allowable concentration (MAC) of 10 mg N L^{-1} in the Canadian Drinking Water Guidelines (Health Canada). These nitrate exceedances were consistent with previous observations of high nitrate concentrations in shallow wells in the aquifer (Hii et al. 1999). Previous studies reported NO_3^- concentrations exceeding the MAC in 58 %, 69 % and 59 % of wells (Wassenaar 1995, Zebarth et al. 1998, Wassenaar et al. 2006), respectively. The current study only had ~50 % monitoring wells in common with previous investigations because early studies also sampled deeper monitoring wells containing older groundwater.

A time-series analysis showed that overall NO_3^- concentrations steadily increased from 14.1 to 18.4 mg L^{-1} in the targeted shallow wells over our 5-year study period, which contrasted with long-term declines observed for a wider depth variety of wells in the Canadian portion of the aquifer (Zebarth et al. 2015). Graham et al. (*2015)* identified several key drivers causing the short-term (intra- and inter-year) nitrate trends (increases or declines) that contrasted with the long-term (inter-decadal) declines. These key drivers were primarily

stochastic rainfall patterns (wet vs. dry years, with first major rainfalls occurring in October) and short-term land-use change factors. The overall increasing nitrate trend in the 19 wells could be attributed to the marked increases in NO_3^- concentrations in three of the wells occurring in the second half of our study, without which the average NO_3^- concentration in the remaining 16 wells (15.5 mg L^{-1}), did not change. These nitrate increases were attributed to i) clearing of an adjacent woodlot, and the subsequent application of large quantities of poultry manure as a soil amendment up-gradient of PC-25 and PC-35 in 2011, and ii) a raspberry field up-gradient of US-02 that underwent a renovation cycle (described in Zebarth et al. 2015) which likely also included soil organic amendments. Wells 94Q-14, PA-25 and PA-35 did not exceed the nitrate MAC because these sites were located up-gradient of the most intensive agricultural production areas.

Almost half the 19 shallow monitoring wells (47 %) showed NO_3^- seasonality, with maximum concentrations usually occurring in the springtime. Nitrate accumulates in the soil and root zones over the summer, and a large proportion of nitrate flushing to the water table happens with the first major recharge events in the fall and winter rainy season (Kowalenko, 2000). Subsequent recharge typically has lower nitrate concentrations as the availability of dissolved soil nitrate drops. Previous evidence of NO_3^- flushing in the fall is shown by Wassenaar (1995) and Zebarth et al. (1998), when precipitation, recharge rates, and soil-NO_3^- are at their peak. Coupled with vadose zone infiltration lag-times of several months, which do not vary significantly between sites (Herod et al. 2015), accordingly peak NO_3^- concentrations reaching the water table are usually observed in the springtime.

All wells have aerobic groundwater (mean = 8.9 mg O_2 L^{-1} ; Supplementary Table), however, two sites (ABB-03 and US-02) showed short intervals of lowered DO levels (<1 mg L^{-1}) in the winter months, coinciding with higher water tables. Chloride levels were on

average 8.7 ± 3.0 mg L^{-1}. At 6 sites (91-10, 91-15, PA-25, PA-35, US-02, and US-05), NO$_3^-$ and Cl concentrations exhibited a covariance (Pearson's R correlation coefficients >0.5), suggesting similar sources. Three sites (PC-25, FT5-12 and FT5-25), exhibited an offset between NO$_3^-$ and Cl, however, the Cl peaks usually lagged behind NO$_3^-$ peaks by 1-3 months, which is inconsistent with the conservative properties of Cl$^-$. This was also observed by Malekani (2012), and may be caused by differences in timing of NO$_3^-$ and Cl availability in combination with growing season leaching under drip irrigation, or variable transit times though the unsaturated zone. The remaining sites exhibited limited seasonal nitrate and chloride variability or showed no correlation between these variables, suggesting more mixing within local groundwater and possibly longer transit times in the unsaturated zone.

3.2   Nitrate N and O Isotopes

Overall, the mean ($\pm$SE) groundwater nitrate δ^{15}N value from the 19 study wells was $+7.9 \pm 0.1$ ‰ (*n*=717), which was consistent with positive δ^{15}N values of local poultry manure solid sources (Wassenaar, 1995; Loo et al. 2017) as summarized in Table 1. Higher δ^{15}N source values were observed in nitrate extracted from soil below former manure stockpiles and ranging up to +14 ‰, due to ammonia volatilization (Wassenaar, 1995). Mean nitrate δ^{18}O was -1.7 $\pm$0.1 ‰ (*n*=717), which was typical of values derived during the nitrification of manure or synthetic fertilizers (Xue et al. 2009). Previously measured groundwater δ^{18}O$_{H2O}$ in the aquifer ranged between -10 to -12 ‰ and coupled with O derived from air (+23.5 ‰), the current nitrate δ^{18}O values were comparable with earlier δ^{18}O values (Wassenaar 1995) of -1.0 $\pm$ 0.3 ‰ (*n*=16) and +0.5 $\pm$ 0.8 ‰ (*n*=40) a decade later (Wassenaar et al., 2006).

To further assess sources and seasonality of groundwater nitrate from these 19 shallow wells, the results were evaluated using nitrate concentrations and isotopic compositions. A Keeling plot of $1/NO_3^-$ vs $\delta^{15}N$ (Figure 2A), supported by a Gaussian mixing model, suggests three main nitrate groupings with the following proportions and interpretation: i) a historical mixing (47 %) trend between high NO_3^- and high $\delta^{15}N$ (manure-derived) and intermediate NO_3^- and low $\delta^{15}N$ values (fertilizer-derived), ii) fertilizer and soil N dominant (47 %) low-intermediate NO_3 and low $\delta^{15}N$ (+2 to +4‰), iii) intermediate NO_3^- and intermediate $\delta^{15}N$ (+8 ‰), mixed source of manure/soil N/fertilizer (6 %). A Bayesian VVV clustering model (which considers the volume, shape and orientation of data points) using $\delta^{15}N$ and NO_3^- suggested 5 possible groupings (Figure 2B), with means shown in Table 2. These findings altogether suggest that field-scale agricultural management practices up-gradient of the monitoring wells resulted in 4 quantifiably distinctive nitrate isotopic clusters (Table 3 - Source Grouping). The first two Bayesian groups were amalgamated as they suggested the same isotopic source, but with partial isotopic enrichment.

Another clustering approach, based on $\delta^{15}N$ trends and seasonality in the 19 wells over the course of the study was also evaluated. In this case, sites were separated into 4 clusters (Table 3 - Trend Grouping) as follows: A) No trend with stable $\delta^{15}N$ values (SD < ±1.0 ‰); B) No trend with variable $\delta^{15}N$ values (SD> ±1.0 ‰); C) ^{15}N enrichment trends; D) ^{15}N depletion trends.

3.3.1   Nitrate Isotopic Variations

Considering the Bayesian and Gaussian clustering approaches altogether, we separated the nitrate and isotope data into 4 distinctive groups (Figure 3) based on their

isotopic values (3 primary groups and 1 sub-group), both in relation to each other and to well-known NO_3^- sources.

Group 1a groundwater was impacted by synthetic fertilizer and/or organic N and showed little isotopic variability, while Group 1b was similar but impacted by clear short-term spikes in $\delta^{15}N$ and NO_3^-. Group 2 was dominated by poultry manure with some influence of ^{15}N depleted sources, while Group 3 was dominated solely by poultry manure N.

The four wells categorized into Group 1a, with $\delta^{15}N$ values of +3 to +8‰ representing 21 % of the 19 sites (PA-25, PA-35, 91-07, and US-04), had a mean $\delta^{15}N$ value of +5.0 ‰. The N isotope distribution of these samples suggests they were dominated by synthetic fertilizers and natural (background) soil N sources ($\delta^{15}N$ of -1.0 ‰ and +4.0 ‰, respectively). Loo et al. (2017) reported that weighted $\delta^{15}N$ of fertilizer treatment leachate in the ASA is +3.2 ± 2.3 ‰. Sampling wells in this group did not exhibit large seasonal swings in NO_3^- concentration or $\delta^{15}N$ values, although strong seasonality was found for NO_3^- in wells PA-25 and PA-35. These isotope data suggest a combination of annual synthetic fertilizer applications with occasional poultry manure application as a soil amendment, which is a common agricultural practice in this area, particularly with blueberry crops.

The Group 1b wells were distinctive because the mean nitrate $\delta^{15}N$ value was more depleted than poultry manure (+6.7‰), but spanned a wider $\delta^{15}N$ range from +2 to +16‰, but representing only 2 wells (PC-25 and PC-35). In addition, both exhibited nitrate ^{18}O enrichment, coupled with increasing $\delta^{15}N$ values (Figure 3A) and NO_3^- concentrations. Well PC-25 was likely subjected to localized and temporal root zone denitrification since some $\delta^{18}O$ values increased above +5 ‰, however, groundwater DO values were never below 8.8

mg L^{-1}, suggesting groundwater microbial denitrification process were unlikely in the aquifer. The positive $\delta^{15}N$ values coupled with elevated NO_3^- (Figure 3B) concentrations were more likely the result of soil amendment practices whereby poultry manure is applied to fields during crop replacement cycles to augment soil carbon and nitrogen content (Zebarth et al. 2015). As previously indicated, this site may also have been affected by recent adjacent woodlot clearing and poultry manure application following planting of a new blueberry crop in 2011-2012. If the elevated $\delta^{15}N$ values after January 2012 are omitted from these two wells, the mean $\delta^{15}N$ value drops to +4.2 ‰, which corresponds to Group 1a. Furthermore, most of the Group 1a/1b wells fall along the same groundwater flow path (Figure 1).

Wells categorized as Group 2 had a mean $\delta^{15}N$ of +7.8 ‰, which corresponded to both leachate from manure treated fields (+7.3 ± 1.2 ‰; Loo et al., 2017) and poultry manure in general (~+7.8 ‰). The more ^{15}N depleted samples were likely influenced by synthetic fertilizers or residual soil N, while ^{15}N enriched samples represented temporal soil zone denitrification. Group 2 wells include: 91-03, 91-15, 94Q-14, ABB-02, ABB-03, ABB-05, FT5-12, FT5-25, PB-20 and PB-35. Wells in this group were in the majority, representing 53 % of the sites, and as with Group 1 did not exhibit large seasonal or inter-annual swings in NO_3^- concentrations or their $\delta^{15}N$ values, other than both NO_3^- concentrations and $\delta^{15}N$ values were more elevated compared to Group 1. Based on these results, it appeared that poultry manure applications, or excess residual soil N from historical poultry manure applications influenced the nitrate contamination level in these wells.

The Group 3 wells (91-10, US-02 and US-05) had a mean $\delta^{15}N$ value of +12.6 ‰ and a $\delta^{15}N$ range of +9 to +16 ‰, which was more ^{15}N-enriched than local poultry manure or manure leachates (Table 1). These ^{15}N enriched results likely resulted from ammonia

volatilization of the source poultry manure and temporal soil zone denitrification. Ammonia volatilization occurs in poultry manure piles and during field application. The mineralized residual ammonium can have $\delta^{15}N$ values up to +25 ‰, but is dependent on pH, temperature, humidity and other environmental factors (Kendall, 1998). Group 3 sites are all located down-gradient of current and former poultry barns or known locations of on-field poultry storage piles, which was shown by Wassenaar (1995) to result in ^{15}N-enriched values in soil N from +7.5 to +13.6 ‰ that are transported to the aquifer.

3.3.2   5-Year Isotopic Trends

The 19 monitoring wells were evaluated based on their nitrate $\delta^{15}N$ and $\delta^{18}O$ isotopic trends over the 5-year study period. The trend evaluation was conducted using Mann-Kendall (monthly data) and Seasonal Kendall (bi-monthly data) non-parametric tests for detection of upward or downward trends in a time series at the $p>0.05$ level of significance. For individual wells, if there was insufficient evidence to detect a trend, individual well results were grouped as being 'stable' or 'variable', depending on whether the $\delta^{15}N$ standard deviation was < or > 1.0 ‰, respectively. Wells exhibiting seasonality were identified as Group B. The analysis showed no statistically significant temporal trend in $\delta^{15}N$ during the study period, however, if results from the three nitrate 'spiking' sites (US-02, PC-25 and PC-35) were removed, a statistically significant $\delta^{15}N$ depletion trend was observed over the 5 year period, with $\delta^{15}N$ declining from +9.1 to +7.4‰. This finding corresponded to the previously reported finding of a decadal-scale nitrate ^{15}N depletion trend in the aquifer, which was attributed to a long-term shift from manure to fertilizer use (Wassenaar et al. 2006).

Four wells (91-15, ABB-02, ABB-05 and FT5-12) were classified into Trend Group A, where analyses did not support a significant upward or downward $\delta^{15}N$ trend and ±SD ≤1.0 ‰ (Figure 5A). All four wells (21 %) were from Distribution Group 2, where $\delta^{15}N$ were +6 to +10 ‰. Interestingly, all Group A sites exhibited appreciable NO_3^- variability, but only FT5-12 depicted any seasonality, with peak nitrate concentrations occurring in winter, likely the result of organic soil N mobilization following higher precipitation periods. Average NO_3^- concentrations were 16.1± 6.4 mg N L^{-1}. The de-coupling of $\delta^{15}N$ from NO_3^- suggested a consistent isotopic NO_3^- source, with limited residual buildup of enriched ^{15}N, where concentrations were likely driven by seasonal periods of enhanced recharge.

Trend Group B comprised 6 wells (91-10, PA-25, PA-35, PB-20, US-02 and US-05) with no significant $\delta^{15}N$ trend over the study period (Figure 5B), but exhibiting high $\delta^{15}N$ variability around the mean (±SD ≥1.0 ‰). The degree of $\delta^{15}N$ and NO_3^- variability differed for most wells in this group; however, all sites exhibited strong $\delta^{15}N$ and NO_3^- coupling, with at least a 5 ‰ change in $\delta^{15}N$ and 15 mg N L^{-1} fluctuation in NO_3^- concentrations. Decreasing DO concentrations in US-02 were associated with increasing $\delta^{15}N$ values; however, in this case NO_3^- and Cl concentrations (Supplementary Table) were synchronous, suggesting the same source. In fact, the up-gradient field of this well had undergone a renovation cycle in the preceding months, where old raspberry plants were removed followed by a poultry manure soil amendment prior to replanting. Sites 91-10 and US-05 showed similar $\delta^{15}N$ and NO_3^- fluctuations, albeit smaller in magnitude, with corresponding increases in chloride and elevated DO concentrations. Sites 91-10 and US-05 are close to each another (<200 m apart) along a similar groundwater flow path,

suggesting these variations are linked. No other sites in this group were spatially proximal. Sites PB-20, PA-25 and PA-35 exhibited varying degree of coupled $\delta^{15}N$ and NO_3^- seasonality, suggesting nitrate leaching was the primary driver of NO_3^- variability. For PA-25, increasing NO_3^- concentrations with ^{15}N enrichment (although variable in degree) were systematically observed each winter, suggesting nitrate mobilization occurred during peak winter rainfall periods.

Six sites were identified as Trend Group C, with increasing $\delta^{15}N$ trends (91-03, 91-07, FT5-25, PC-25, PC-35, and US-04). These sites were evenly distributed between Distribution Groups 1a (3) 1b (2) and 2 (1), suggesting one driver controlling local NO_3^- concentrations and $\delta^{15}N$ values. Enriching ^{15}N trends (often along a flow path) are usually associated with progressive microbial denitrification, however, all sites had high DO aerobic concentrations (>8 mg L^{-1}). Sites PC-25 and PC-35, which exhibited some degree of coupled $\delta^{15}N$ and $\delta^{18}O$ enrichment at a 2:1 ratio, also showed increasing NO_3^- concentrations, suggesting heavy loading of poultry manure. Prior to the marked increase of NO_3^- and $\delta^{15}N$ in the spring of 2012, PC-25 and PC-35 exhibited a significant, albeit gradual, increasing ^{15}N trend (Figure 5C). This revealed a second subtle driver – the increased precipitation that occurred between 2008-2011 (Environment and Climate Change Canada, 2014) and its effect on groundwater nitrate concentrations, as shown by Graham et al. (2015). Wells 91-03, FT5-25, and US-04 did not undergo any up-gradient crop replacement or soil amendments, and exhibited various degrees of NO_3^- and $\delta^{15}N$ seasonality, further strengthening the precipitation link as a potential driver. The $\delta^{15}N$ trend could be linked to the enhanced mobilization and infiltration of ^{15}N depleted organic soil N.

Group D exhibited a ^{15}N depletion trend (Figure 5D), and consisted of monitoring wells 94Q-14, PB-35 and ABB-03, and had a negative δ^{15}N shift of 1-3 ‰, and δ^{15}N values between +6 to +10 ‰ (Group 2). Well 94Q-14 showed δ^{15}N seasonality, but not in NO_3^-, with concentrations mostly below the MAC. PB-35 showed small seasonality in NO_3^- concentrations but none in δ^{15}N, indicating possible mixing and dilution due to a shift in nitrogen sources. Wassenaar et al. (2006) suggested that a negative δ^{15}N shift may be attributed to the longer-term change in nitrogen sources used from poultry manure to synthetic fertilizers. Lastly, ABB-03 showed no significant trend in NO_3^- concentrations or in δ^{18}O of nitrate, however, δ^{15}N and δ^{18}O were correlated, while δ^{15}N and NO_3^- were inversely correlated. Furthermore, ABB-03 exhibited 3-4-month intervals of lower than usual DO conditions ($\Delta \geq 4$ mg L^{-1} compared to other seasons; Supplementary Table that corresponded to periods of ^{15}N enrichment and decreasing NO_3, suggesting localized denitrification, which were repeatable to various degrees on a seasonal basis, but was most prominent in 2011 (Supplementary Table). These findings suggest localized and temporally limited denitrification may be occurring in the soil root zone in some areas, contributing to ^{15}N enrichment and variability of NO_3^- concentrations. Site ABB-03 was not near Fishtrap Creek (Figure 1) which Tesoriero (2000) and Wassenaar et al. (2006) identified as a localized riparian denitrification hot spot. Enrichment in ^{15}N of nitrate at these sites appeared to be from temporal drivers that could be overlooked in one-time synoptic sampling (Wassenaar, 1995).

4.0 Conclusions and Outlook

This study represents an unprecedented high-frequency 5-year seasonal spatiotemporal study of water table well with over 700 nitrate isotopic assays, revealing the

dynamics of nitrate recharging the transboundary Abbotsford-Sumas aquifer. The high (monthly) temporal frequency of nitrate and isotopic data aimed to address concerns that infrequent nitrate isotopic or concentration synoptic samplings of shallow ground water overlooks important factors of seasonality that may be key drivers of nitrate sources and fluxes to shallow aquifers. Indeed, our study revealed new important scientific information not previously seen in the synoptic surveys that will help managers better tackle nutrient management strategies to help reduce ground water pollution.

Overall, and unsurprisingly, we found the predominant perennial source of nitrate to the aquifer at all spatiotemporal scales within the 5-year intensive sampling period was animal waste (poultry) sources, which was already known for decades. Nitrate concentrations in young (<5 yr.-old) and shallow groundwater was persistently high in nitrate, ranging from 1.3 to 99 mg-N L^{-1}, with a mean of 16.2 mg-N L^{-1}, and well in exceedance of the Canadian drinking water MAC of 10 mg-N L^{-1} for 76 % of the wells. The study also verified a postulated and subtle decadal-scale shift towards ^{15}N depleted nitrate sources, likely reflecting systematic changes in agriculture practices from the early days of indiscriminate manure disposal towards more targeted use of synthetic fertilizers, or from changes in crop types and associated nutrient practices, as evidenced by the mean $\delta^{15}N$ value for nitrate of +7.9 ± 3.0 ‰ compared to +10.2 ± 4.0 ‰ in the 1990s. Synthetic fertilizer and soil N represent a comparatively higher N loading in the central portions of the ASA, but are flanked on both sides by higher poultry manure dominated N loadings (Figure 4). The high nitrate concentrations in contemporary recharging groundwater and lack of targeted nitrogen reduction measures, means widespread nitrate contamination of the aquifer is likely to persist into the foreseeable future, and our data affirm little evidence for persistent or widespread natural attenuation of nitrate by subsurface denitrification processes, at any time of the year.

Nitrate remediation of the aquifer will only be possible if agricultural N sources are dramatically reduced or eliminated.

In some wells we found that localized agricultural practices (i.e. nearby organic N soil amendment) had a nearly immediate multi-year negative impact, mainly exhibited by marked increases of poultry-derived N, and lasting for several years and across seasons. This common practice at field renovation and post woodlot clearing, resulted in spatial clustering and differing short-term trends for water table nitrate and its isotopes across the aquifer (Figure 4 and 6), further revealing that infiltrating NO_3^- and its isotopic composition can change quickly in direct response to contemporary near-field practices. Conversely, this suggests N source cutoff as a ground water remediation effort could be similarly as effective. Despite 53 % of shallow wells showing no isotopic trends, 47 % showed an ^{15}N enrichment or depletion trend in nitrate, and about half of the wells exhibited nitrate seasonality in NO_3^- concentrations and/or $\delta^{15}N$ values controlled by temporal infiltration of residual mineralized N or weak, short-term denitrification.

Due to the rapid shift in NO_3^- and isotopic values of recharging groundwater immediately following field renovation and soil amendment practices, this study reinforces the importance of designing and conducting appropriate spatio-temporal nitrate sampling to reduce the risk of misinterpreting nitrate concentrations and its isotopic data through the more common practice of occasional synoptic surveys. The dynamics of nitrate in younger (<5 yr.-old) water table wells, however, also imply it would be prudent to monitor deeper, older groundwater which smooth out short-term fluctuations and hence record longer-term and aquifer-wide trends.

For the ASA agricultural area specifically, measuring the impact of changes in nutrient management practices associated with the switch from raspberry to blueberry

crops or field renovation is required to determine its impacts on groundwater nitrate dynamics. Decisions on future groundwater aquifer nitrate management need to take into consideration permanent or cyclical changes in the planned crop types, and the associated nutrient management practices involved with them. Subtle shifts in nitrate in the ASA may be unexpectedly influenced by the recent increased planting of blueberries in place of raspberries, which may to be less reliant of cyclical poultry manure soil amendments.

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Figure 1: Location of the Abbotsford-Sumas aquifer (ASA), southwestern B.C., Canada and northwestern Washington State, USA, along with simplified agricultural land-use and sampling locations with ground water mean residence times (MRT) of < 5 years. Arrows show the approximate groundwater flow direction.
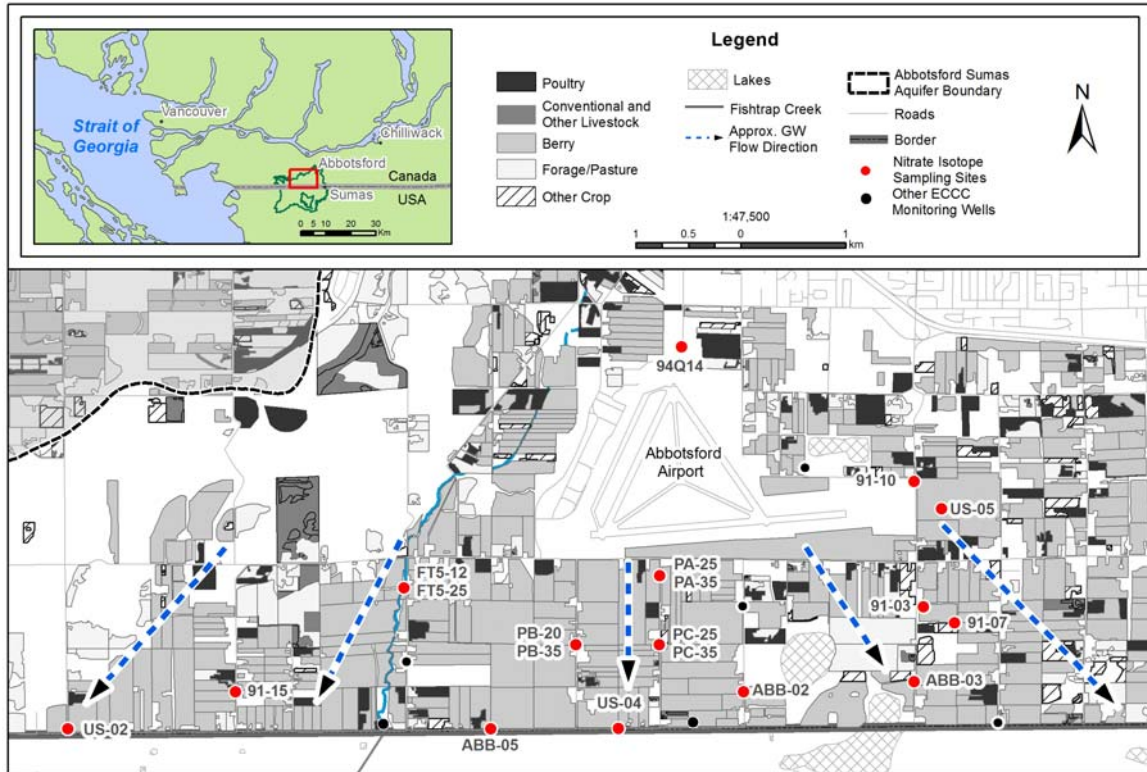
Figure 2: A) Keeling plot of $1/NO_3$ (x-axis) vs. $\delta^{15}N$ (y-axis). Three distinct groups are i) Arrow represents mixing line between fertilizer and enriched manure endmembers, ii) (Bottom) wide range NO_3 (mineral fertilizer leachate and Soil N), iii) (Middle group) manure/fertilizer mixture. $\delta^{15}N$ reference sources (Wassenaar, 1995, Loo et al. 2017). B) $\delta^{15}N$ vs. Nitrate Bayesian clustering model suggest 5 distinct groupings.
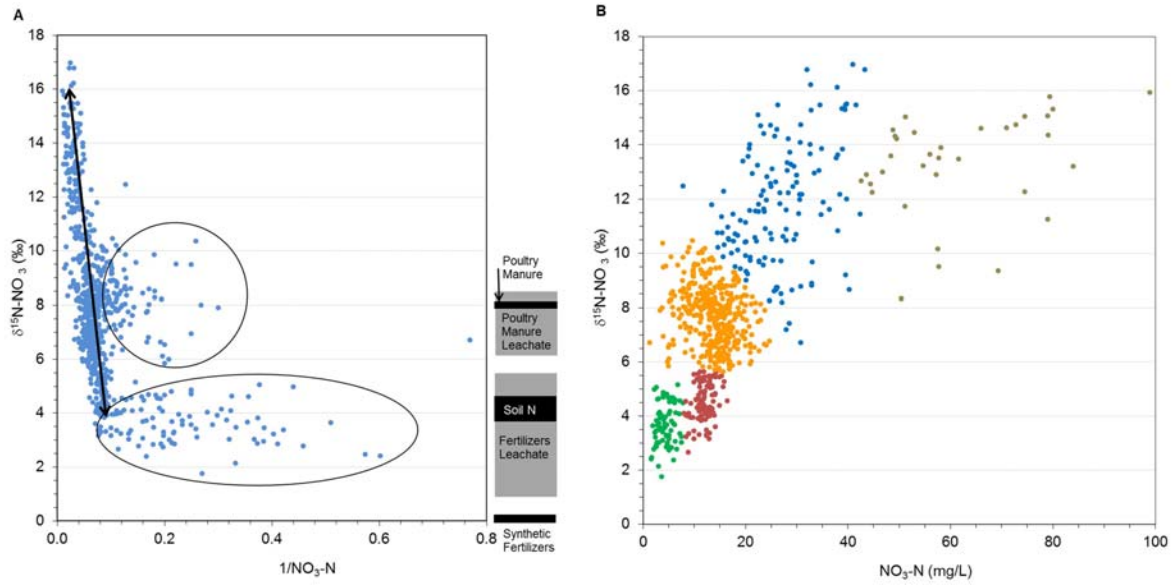
Figure 3: A) Nitrate $\delta^{18}O$ vs $\delta^{15}N$ cross-plot. B) Distribution of 19 well sites grouped by $\delta^{15}N$ range and $\delta^{18}O$. Group 1a: $\delta^{15}N$ range (3 to 8‰). Group 1b: $\delta^{15}N$ range (+2 to +16‰) $\delta^{18}O$ full range. Group 2: $\delta^{15}N$ range (+6 to +10‰). Group 3: $\delta^{15}N$ range (+9 to +16‰).
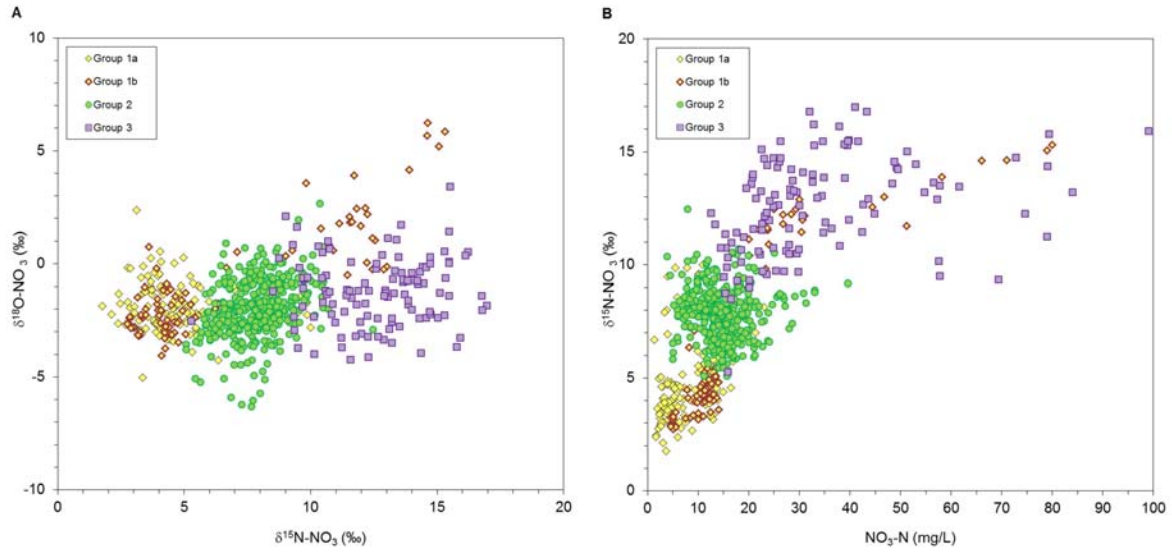
Figure 4: Spatial distribution of δ^{15}N source groupings, along with agricultural land-use.
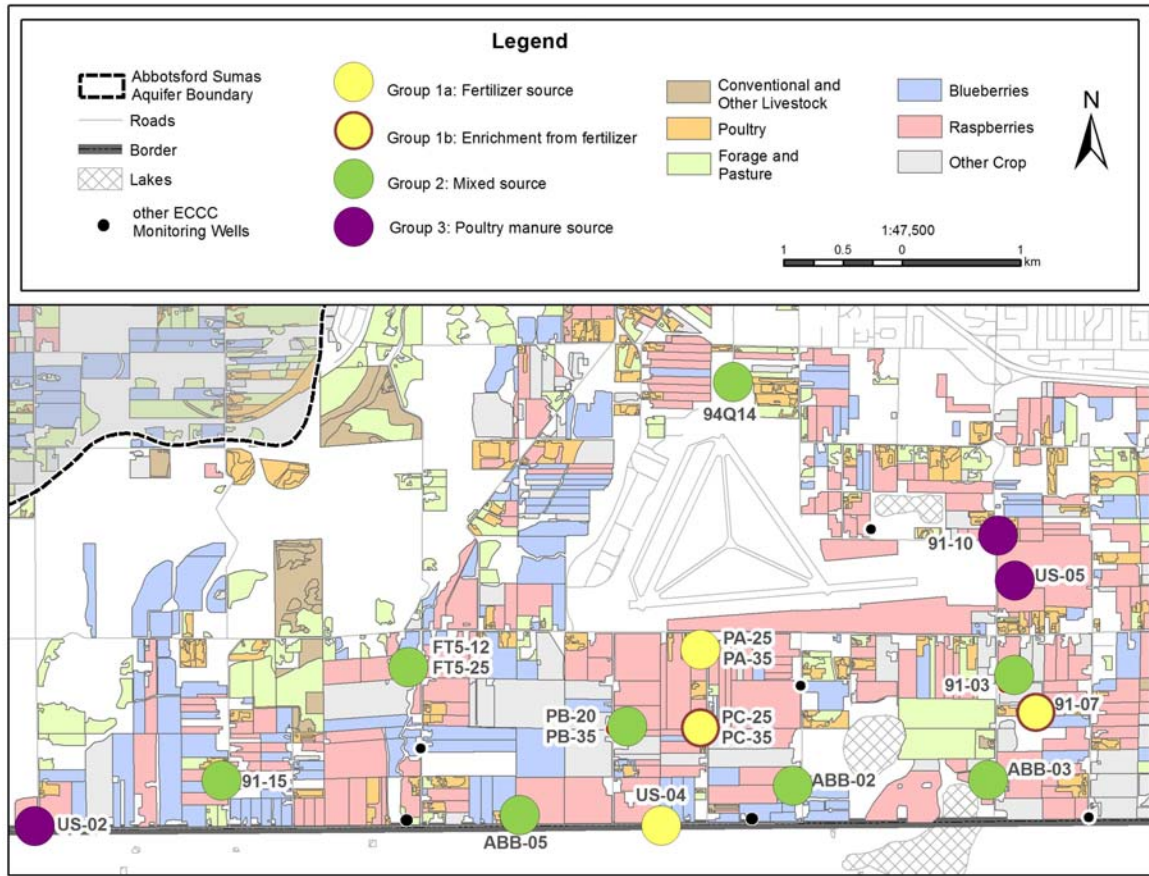
Figure 5: $\delta^{15}N_{-NO3}$ time series plots: A) No trend - stable (SD<±1.0), B) No trend - variable (SD>±1.0), C) Enrichment trend, D) Depletion trend.
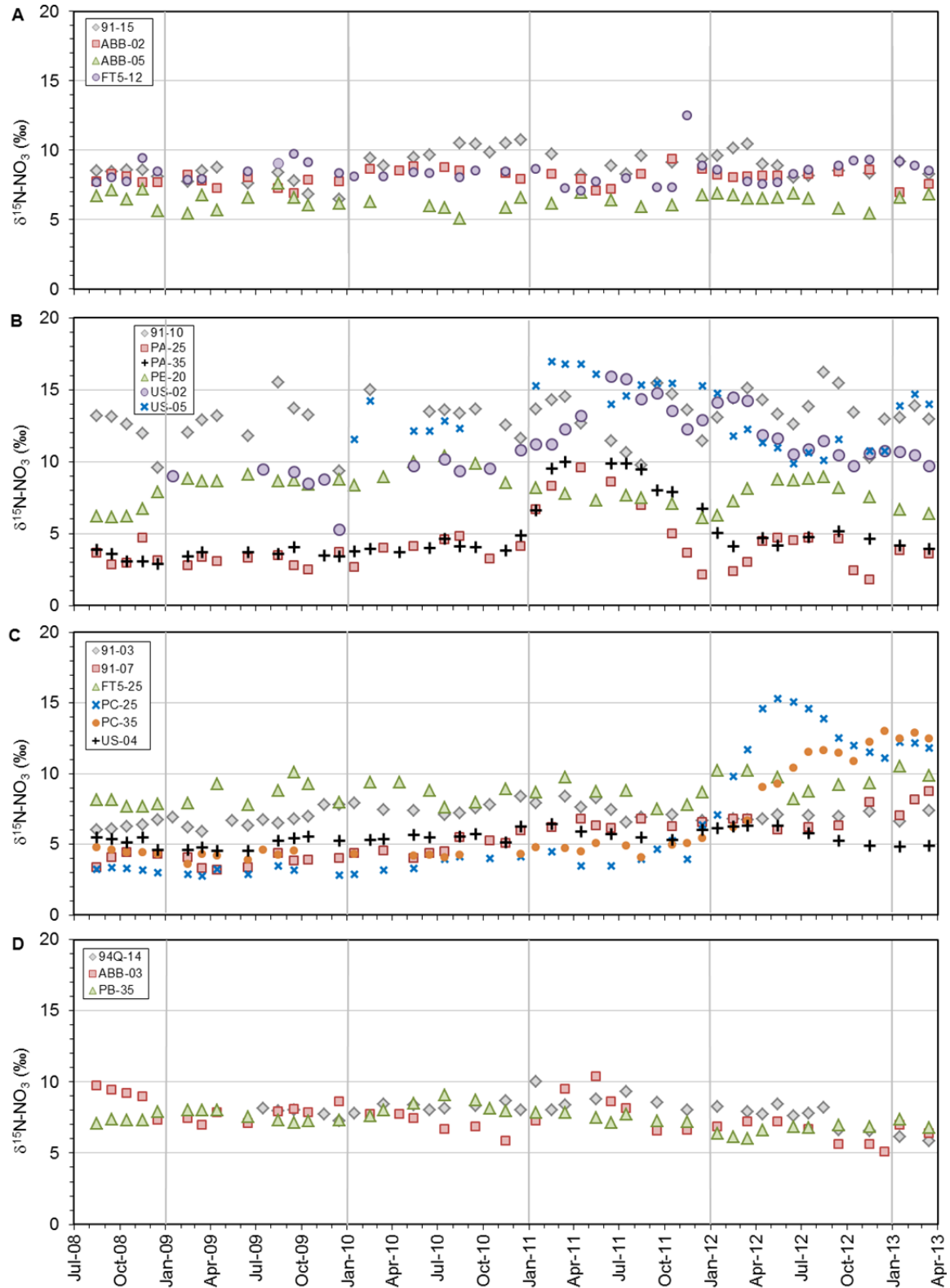
Figure 6: Spatial distribution of $\delta^{15}N$ trend groupings, along with agricultural land-use.
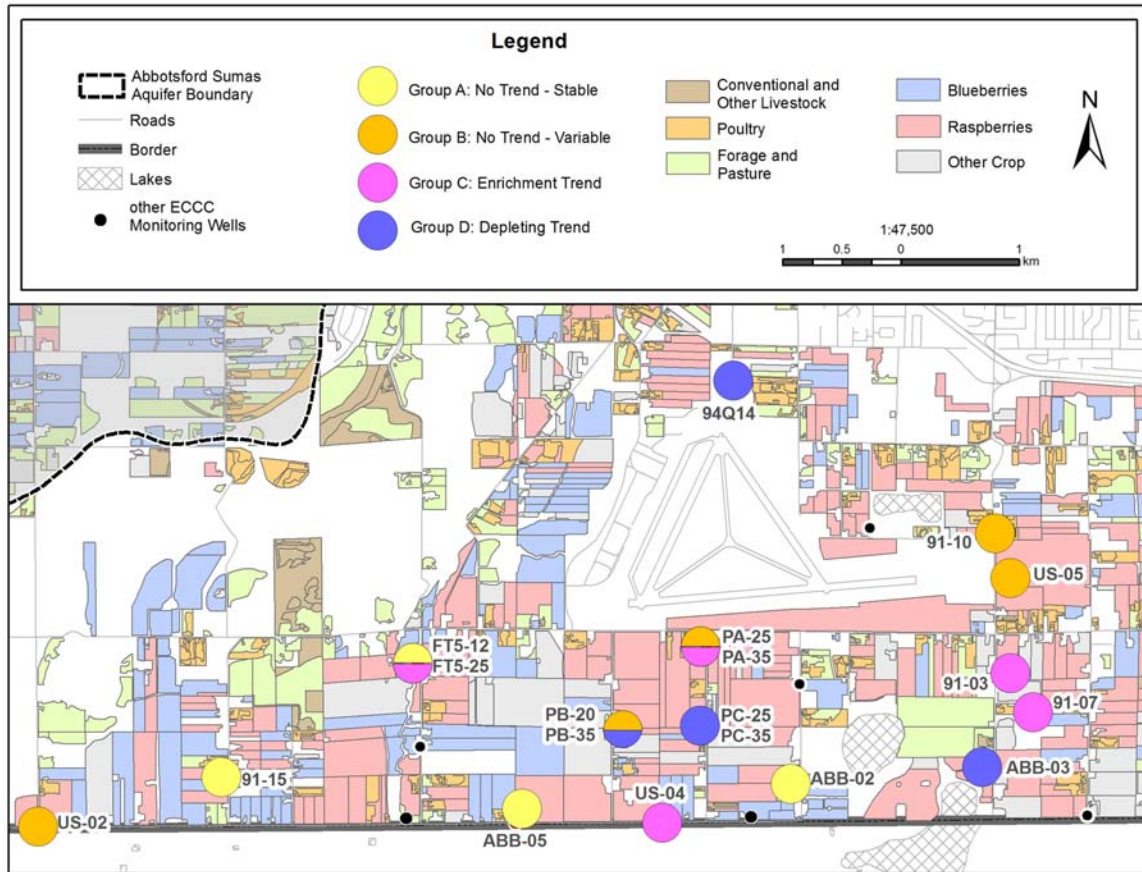
Table 1: Local synthetic fertilizer, poultry manure, soil N and leachate δ^{15}N values used in the Abbotsford area.

Source	δ^{15}N (AIR, ‰)	Reference
Poultry Manure (total N)	+7.9	Loo et al., 2017
Poultry Manure (total N)	+8.1	Wassenaar, 1995
Poultry Manure (total N)	+7.9	Wassenaar, 1995
Urea (total N)	-0.7	Loo et al., 2017
NH_4-NO_3 (total N)	-2.8	Loo et al., 2017
NH_4-SO_4 (total N)	+0.3	Loo et al., 2017
Urea (total N)	-0.6	Wassenaar, 1995
NH_4-SO_4 (total N)	-0.9	Wassenaar, 1995
Soil N (total N)	+3.8 to +4.6	Loo et al., 2017
Soil N (total N)	+3.7 to +4.1	Wassenaar, 1995
Irrigation water - average (NO_3-N)	+9.0	Loo et al., 2017
Weighted fertilizer treatment leachate (NO_3-N)	+3.2±2.3	Loo et al., 2017
Weighted manure leachate (NO_3-N)	+7.3±1.2	Loo et al., 2017

Table 2. Bayesian clustering model of NO_3-N and $\delta^{15}N$ means by class.

Class	1	2	3	4	5
Mean (NO_3^-)	4.4	13.2	13.5	22.9	55.2
Mean ($\delta^{15}N$)	3.7	5.4	7.9	10.7	13.2

Table 3: Nitrate isotopic Distribution and Trend grouping classification.

	Source Grouping		δ^{15}N Trend Grouping
1a	δ^{15}N range (+3 to +8‰), δ^{18}O range (-5 to +2‰)	A	No trend - stable (SD< ±1.0 ‰)
1b	δ^{15}N range (+2 to +16‰), δ^{18}O (-7 to +7‰)	B	No trend - variable (SD> ±1.0 ‰)
2	δ^{15}N range (+6 to +10‰), δ^{18}O range (-5 to +2‰)	C	Enrichment
3	δ^{15}N range (+9 to +16‰), δ^{18}O range (-5 to +2‰)	D	Depletion

Table 4: Results summary with $^3H/^3He$ groundwater ages in years (Wassenaar et al., 2006); Average water column height (meters; mid-screen depth below average static water level); Isotopic Distribution and Trend groupings; NO_3-N, $\delta^{15}N$ and $\delta^{18}O$ values (mean, standard deviation, and confidence intervals ($\alpha=0.05$)).

Site ID	$^3H/^3He$ Age (yrs.)	Average Water Column Height (m)	Source Group	Trend Group	NO_3^- mg N L^{-1} Mean	SD	CI	$\delta^{15}N_{AIR}$ ‰ Mean	SD	CI	$\delta^{18}O_{VSMOW}$ ‰ Mean	SD	CI
91-03	3.5	2	2	C	17.2	3.8	1.0	7.0	0.6	0.2	-2.0	1.0	0.3
91-07	2.7	1.8	1a	C	13.2	3.3	0.9	5.4	1.5	0.5	-2.6	0.8	0.3
91-10	3.2	3	3	B	33.2	11.6	3.0	13.1	1.6	0.5	-0.9	1.4	0.4
91-15	5.94	7.2	2	A	12.1	3.7	1.0	8.9	1.0	0.3	-1.4	0.8	0.3
94Q-14	4.2	6.3	2	D	7.7	1.9	0.5	8.0	0.8	0.3	-0.9	0.8	0.3
ABB-02	5.5	5	2	A	14.0	3.4	0.9	8.0	0.5	0.2	-3.5	1.4	0.4
ABB-03	0.9	5.2	2	D	12.4	3.9	1.0	7.5	1.2	0.4	-1.3	1.6	0.5
ABB-05	4.3	6.7	2	A	16.2	2.3	0.6	6.4	0.6	0.2	-2.6	0.9	0.3
FT5-12	N/A	2	2	A	16.1	6.4	1.7	8.4	0.9	0.3	-1.9	1.0	0.3
FT5-25	N/A	5.6	2	C	13.1	2.6	0.7	8.8	0.9	0.3	-1.5	1.0	0.3
PA-25	4.2	2.9	1a	B	5.8	3.4	0.9	4.1	1.8	0.6	-1.7	1.1	0.4
PA-35	4.7	6.7	1a	B	4.6	2.2	0.6	5.1	2.2	0.7	-1.4	0.8	0.3
PB-20	1.3	2.4	2	B	18.9	5.1	1.3	8.0	1.1	0.4	-2.1	1.2	0.4
PB-35	4.8	6.7	2	D	17.0	3.7	1.0	7.4	0.7	0.2	-2.1	0.9	0.3
PC-25	1.5	2.2	1b	C	17.5	19.6	5.1	6.8	4.5	1.4	-0.3	3.0	0.9
PC-35	4.4	6.3	1b	C	14.9	7.0	1.8	6.6	3.3	1.0	-1.4	1.6	0.5
US-02	1	4.6	3	B	38.6	22.8	6.0	11.4	2.3	0.7	-1.7	1.7	0.5
US-04	5	6.9	1a	C	13.2	2.0	0.5	5.4	0.5	0.2	-2.2	0.7	0.2
US-05	<1	1	3	B	27.3	10.1	3.2	13.4	2.2	0.8	-1.3	1.2	0.4

Supplementary Table: Abbotsford-Sumas analytical results: date (dd/mm/yyyy), well ID, water table elevation (meters above sea level), dissolved oxygen (mg L^{-1}), chloride concentration (mg L^{-1}), nitrate concentrations (mg N L^{-1}) and isotopic composition of nitrate (δ^{15}N and δ^{18}O).