FRASER RIVER ACTION PLAN

Evaluation of the Origin and Fate of Nitrate in the Abbotsford Aquifer Using the Isotopes of ^{15}N and ^{18}O in NO_3^-

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Leonard I. Wassenaar

Environmental Sciences Division
National Hydrology Research Institute
11 Innovation Blvd.
Saskatoon, Saskatchewan
S7N 3H5

EVALUATION OF THE ORIGIN AND FATE OF NITRATE IN THE ABBOTSFORD AQUIFER USING THE ISOTOPES OF ^{15}N and ^{18}O in NO_3

A Final Report to
B.C. Ministry of the Environment
Fraser River Action Plan

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Executive Summary '

Evaluation of the Origin and Fate of Nitrate in the Abbotsford Aquifer using the Isotopes of ^{15}N and ^{18}O in NO_3

- **54% of 117 domestic, municipal, and monitoring wells sampled in the Abbotsford aquifer in B.C. and Washington State in 1993 exceeded the maximum permissible drinking water limit of 45 mg/L as NO_3**

- **The Abbotsford aquifer is extensively contaminated with NO_3 Interpolation of the NO3 data suggested about 80% of groundwater in the Abbotsford aquifer in 1993 had concentrations exceeding 40 mg/L NO_3**

- **The potential nitrate sources in the forms of poultry manure N and ammonium fertilizers were isotonically distinctive in their $\delta^{15}N$ composition.**

- **Groundwater nitrate $\delta^{15}N$ values were mostly in the range of NO_3 derived from poultry manure N, and to a lesser extent from ammonium based fertilizers.**

- **The $\delta^{15}N$ and $\delta^{18}O$ values of groundwater nitrate indicated conclusively that no significant groundwater denitrification is occurring in the Abbotsford aquifer.**

- **The $\delta^{18}O$ nitrate and $\delta^{18}O$ water data suggested vitrification of manure and fertilizer occurred in the summer months, and is flushed into the aquifer in the fall. Attempts should be made to minimize or eliminate soil and root zone nitrate levels, particularly in the fall.**

- **The Abbotsford aquifer does not sustain denitrification, therefore the only viable form of cleanup is the elimination of nitrate at the source and continual flushing from natural recharge. Nevertheless, because the residence time of groundwater in the Abbotsford aquifer is on the order of decades, high levels of nitrate will persist for many years even if the nitrate sources were eliminated.**

Abstract

Extensive nitrate contamination of groundwater **in the Abbotsford aquifer to levels above drinking water limits is a major problem in the Fraser Lowlands of southwestern British Columbia. Nitrate concentrations in the aquifer ranged from O** to 151 **mg/L NO$_3$ with a median concentration of 46 mg/L NO$_3$. Of 117 wells sampled, 54% had nitrate concentrations exceeding the drinking water limit. Approximately 80% of the study area had groundwater nitrate concentrations exceeding 40 mg/L N0$_3$-. Potential nitrate source materials were poultry manure N and ammonium based fertilizers. The δ^{15}N of solid poultry manure samples ranged between +7.9 and +8.6 o/oo. Four brands of synthetic fertilizers commonly used had δ^{15}N values between -1.5 and -0.6 O/oo. Ammonia volatilization caused the δ^{15}N of groundwater nitrate produced from poultry manure N to range between +8 and +16 O/oo. The δ^{18}O values of groundwater nitrate, by contrast, mostly ranged between +2 and +5 O/oo. This narrow range of δ^{18}O values fell within the expected range of nitrate produced by vitrification of reduced nitrogen forms such as poultry manure N an-d ammonium fertilizers, and had a similar range of δ^{18}O values as nitrate in the upper part of the unsaturated zone below raspberry fields and beneath former manure piles. The δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ data indicated nitrate in the aquifer was predominantly derived from poultry manure and to a lesser extent from ammonium based fertilizers. The δ^{18}O-NO$_3^-$ data suggested the vitrification process occurred mainly in the summer months, with the soil nitrate produced subsequently flushed into the aquifer during fall recharge. The δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ data further indicated that no significant bacterial denitrification is taking place in the Abbotsford aquifer.**

Introduction

The Abbotsford aquifer' (Figure 1) is an important **source of water for industrial, municipal, irrigation, and domestic uses in the Fraser Lowlands both in southwestern British Columbia (B.C.), Canada, and northern Washington State, U. S. A., and is one of the largest groundwater reserves in the Lowlands. The Abbotsford aquifer, however, is extremely susceptible to surface derived contamination because of its largely unconfined nature and highly permeable sands and gravels. In the past decade the aquifer has become the focus of public concern. This concern has resulted from widespread nitrate contamination, from the detection of agricultural pesticides, and from increased pressures for urban development above the aquifer. Furthermore, flow of groundwater in the aquifer is southerly from British Columbia into Washington State, thereby raising the possibility of cross-border groundwater contamination.**

Nitrate contamination of groundwater in the Abbotsford aquifer to levels well above national drinking water standards (>45 mg/L NO$_3$) is a major problem both in B.C. (Kwong, 1986; Kohut et al., 1989; Liebscher et al., 1992) and in Washington State (S. Cox, USGS, pers. comm.). Many wells in the aquifer show marked seasonal variations in water table nitrate concentration, with highest concentrations occurring during the fall and winter recharge period. Other wells exhibit slightly decreasing or variable nitrate concentrations over the past ten years. Of greater concern is that nitrate concentrations in some wells are steadily increasing since nitrate measurements began in the early 1970s (Kwong, 1986; Liebscher et al., 1992).

The source of nitrate contamination in the Abbotsford aquifer is not unequivocally known, but is attributed to long-term agricultural land use practices, such as poultry manure stockpiling and the spreading of poultry manure and fertilizer directly above the permeable sands and gravels of the aquifer, particularly on the B.C. side **of the International border (Kohut et al., 1989; Zebarth et al., 1994). Land use above the**

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[1] **The Abbotsford aquifer is the name given to the deposit in Canada.** In Washington State the equivalent **deposit is known as the Sumas aquifer. The term Abbotsford aquifer,** or the aquifer, applies to both for **the purposes of this report.**

aquifer is primarily agricultural with intensive raspberry farming and poultry production accounting for much of the agricultural activity in Canada (Nelson, 1992). The manure produced from the numerous poultry operations are generally stored in large piles, uncovered and without leachate liners for several days, or stored in a similar fashion at raspberry growers before spreading on fields. Some manure piles are left uncontained above the aquifer for more than a month before spreading (Nelson, 1992). Chemical nitrogen fertilizers are typically applied in April and May at rates of 50 to 70 kg N/ha, often above the 55 kg N/ha recommended for raspberries (BCMAFF,1994), with additional poultry manure N spread between raspberry rows at rates of up to 1½ dump truck loads per acre every 1 to 3 years (Nelson, 1992). Manure and fertilizers are usually cultivated into the soil, but manure is sometimes left on the land surface (Nelson, 1992). A nitrogen budget for a 17 km^2 agricultural zone in the Abbotsford area by Zebarth et al (1994) suggested a 7-fold excess of nitrogen over what is required is applied to the fields in the forms of manure and fertilizer. In contrast, less intensive pasture and dairy production account for most of the land use in Washington State. A number of liquefied manure pits exist to contain cattle manure, with liquid manure spreading to the fields (S. Cox, USGS, pers. comm.).

Stable isotope ratios of nitrogen ($^{15}N/^{14}N$)[2] in NO_3^- are often used to aid in distinguishing various sources of nitrate in groundwater (Kreitler and Jones, 1975; Kreitler, 1979; Gormly and Spalding, 1979; Flipse and Bonner, 1985; Kaplan and Magaritz, 1986; Wells and Krothe, 1989; Exner and Spalding, 1994). $\delta^{15}N$ values can be used to distinguish between inorganic fertilizer derived nitrate ($\delta^{15}N \approx -1$ to +2 O/oo) and animal waste sources or sewage ($\delta^{15}N \approx +8$ to +16 O/oo) derived nitrate. A disadvantage to the single isotope approach to groundwater nitrate studies is that ammonia volatilization can lead to significant and variable enrichments of ^{15}N in the residual ammonium source material and nitrate subsequently produced, especially in areas like the Abbotsford aquifer where poultry manure is routinely used. Thus, a wide range in $\delta^{15}N$ values of nitrate could be produced from nitrification of poultry manure

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[2] Stable isotope ratios are typically expressed in delta permil notation (δ) relative to an internationally accepted standard, where, for example, $\delta^{15}N = [(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard} -1] \times 1000$.

and animal waste sources (Kreitler, 1975; Gormly and Spalding, 1979). Furthermore, groundwater denitrification, a beneficial microbially mediated process that converts nitrate to N_2O and N_2 causes isotopic enrichments of ^{15}N in residual nitrate from its original isotopic signature (Mariotti et al., 1988). Thus the considerable variations **in $\delta^{15}N$ of groundwater nitrate can be difficult to interpret without additional supporting evidence (Korom, 1992).**

Bacterial denitrification is often limited by nutrient availability and lability of electron donors such as dissolved organic carbon (Starr and Gillham, 1993), sedimentary organic matter (Hendry et al., 1984; Postma et al., 1991), or reduced sulfur forms (Kolle et al., 1987; Bottcher et al., 1990). Denitrification has been documented in a number of groundwater systems (Howard, 1985; Trudell et al., 1986; Kolle et al., 1987; Mariotti et al., 1988; Smith **and Duff, 1988; Bottcher et al., 1990; Postma et al., 1991; Spalding et al., 1993). In general, microbial denitrification tends to occur in anaerobic aquifers with shallow water tables and sufficient supplies of electron donors (see review by Korom, 1992).**

Recent studies suggest that the oxygen isotope content of groundwater nitrate may be a good tracer of nitrate source, particularly where nitrate based fertilizers are used. Further, the $\delta^{18}O$ isotopic composition of nitrate provides a more reliable indicator for the denitrification process than $\delta^{15}N$ (Amberger and Schmidt, 1987; Bottcher et al., 1990). Nitrate derived from mineralization of reduced nitrogen forms (ammonium, nitrite) in the unsaturated zone have only 2 possible sources of isotonically distinctive oxygen, atmospheric oxygen and associated meteoric waters. The aerobic vitrification pathway from ammonium to nitrate results in one third of the oxygen in the nitrate being derived from air and two thirds being derived from water (Aleem et al., 1965; Anderson and Hooper, 1983; Hollocher, 1981; Yoshinari and Wahlen, 1985). Therefore, nitrate produced from vitrification of manure or fertilizer should have a relatively narrow range of oxygen isotope values, with most of the variability attributed to the isotopic composition of the meteoric waters involved. Inorganic nitrate fertilizers, on the other hand, are manufactured using solely air oxygen, and their isotopic composition is similar to air (Amberger and Schmidt, 1987).

Denitrification also causes oxygen isotope enrichment **in** the **residual nitrate (Bottcher et al., 1990).** However, if oxygen and nitrogen isotopes of groundwater **nitrate were used together, a more reliable means could be** used to establish the source(s) and **processes leading to nitrate contamination, as well as the occurrence of bacterial denitrification. To date, however, only a few studies have used the** $\delta^{18}O$ **signature of nitrate in field applications (Amberger and Schmidt, 1987; Bottcher et al., 1990; Aravena et al., 1993).**

The objective of this study was to use the $\delta^{15}N$ **and** $\delta^{18}O$ **stable isotopic composition of groundwater nitrate to** 1 **) evaluate the origin of nitrates in the Abbotsford aquifer system, and 2) to ascertain whether natural remediation of nitrate in the aquifer by bacterial denitrification is occurring. The objective was met by analyzing** $\delta^{15}N$ **and** $\delta^{18}O$ **in nitrate from groundwater samples and from unsaturated zone porewater profiles, and analyzing the** $\delta^{15}N$ **of potential nitrate contamination source materials (manure, fertilizers). Additional data were collected to augment the nitrate isotope data. These included water chemistries, stable isotopes** $(\delta^{18}O, \delta^{2}H)$ **of water and tritium (3H). A large database of complete water chemistry was also available from previous studies (Gartner-Lee, 1993).**

HYDROGEOLOGY AND HYDROCHEMISTRY

The Abbotsford aquifer encompasses an area of about 200 km^2 in the Fraser Lowlands of southwestern British Columbia and northern Washington State, U.S.A. (Figure 1) The aquifer is largely unconfined, and is comprised of Late Wisconsinan glacial-fluvial coarse sands and gravels that were deposited as outwash during the retreat of Sumas ice (Armstrong, 1980). The sands and gravels are up to 60 m in thickness. The upper boundary of the aquifer is the water table, which ranges from near ground surface to more than 40 m depth. The aquifer is confined below by glaciomarine clays (Halstead, 1986). The soil zone is thin and well drained due to the coarse texture of the sediments. The water table commonly varies by 3 m during the year, with highest water levels following fall and winter rains. Water table levels

correlate directly with precipitation in the fall and winter (Kohut, 1987; Kahle, 1990; Liebscher et al 1992). The recharge rate has been estimated to range **between 37 and 81 percent of the annual precipitation** of **about 1500 mm/yr. (Kohut, 1987). Hydraulic head is measurably invariant with depth in multi-level piezometers, indicating that flow is predominantly horizontal. General flow directions are towards the south, southwest and southeast (Figure 1) at estimated average linear velocities up to 450 m/yr. (Liebscher et al 1992). Groundwater is a calcium -bicarbonate type with TDS ranging between 70 and 300 mg/L. Otherwise good water quality is seriously deteriorated with high nitrate concentrations in many domestic and municipal wells. DOC levels are low, and typically less than 1.0 mg C/L (Liebscher et al., 1992).**

MATERIALS AND METHODS

Water samples from piezometers, domestic and municipal wells in the Abbotsford aquifer (n=l 17) and from a creek and gravel pit (n=2) were collected on two occasions in February 1993, and in August 1993. Groundwater samples were collected after wells had been pumped for at least 15 minutes (domestic) or three well volumes removed (piezometers). Water samples for nitrate, chloride and sulfate ion analyses were 0.45 μm field filtered, collected in 50 mL plastic bottles, stored at 5°C, and analyzed using standard ion chromatographic techniques at NH RI. The ion analyses were augmented with water chemistry conducted by Gartner-Lee (1993). Samples for $\delta^{18}O$ and&H (n=l 19) were collected in 10 mL plastic bottles. Water samples for enriched tritium analyses were collected in 1 L plastic bottles.

Frozen samples of representative poultry manure (n=3) from the Abbotsford area were provided by the B.C. Ministry of Agriculture, Fisheries and Foods (BCMAFF). Fifty mg subsamples of the manure solids were freeze dried **for nitrogen isotopic analyses. Four samples of inorganic fertilizer used locally on raspberry fields were also provided by BCMAFF. Fertilizer grains were separated by colour (green and white) for nitrogen isotopic analyses (n=8). XRD analyses were performed on various fertilizer grains to determine the nitrogen and mineral forms.**

Soil and unsaturated zone leachable nitrate samples were collected at four locations at several depths (n=8). Sediments were taken using a hand auger to a maximum depth of 1 m. **Two** profiles were sampled from underneath 2 different raspberry fields, and **2 profiles were sampled from beneath recently cleared poultry manure stockpiles. Due to the presence of coarse gravel and large cobbles it was not possible to hand auger deeper than 1 m. One kg soil samples were leached in Milli-QTM deionized water (1:2 ratio) to extract water soluble nitrate. The supernatant was 0.45 μm filtered and the nitrate was then processed to the KNO_3 salt form as described below.**

Soil samples from six sites were taken to determine $\delta^{15}N$ on total soil organic nitrogen (n=l 2). At three sites soil samples were taken from below former poultry manure stockpiles. At the other three sites samples were taken from A and B horizons in "undisturbed", non-agricultural settings. Soil samples were immediately frozen upon collection. 100 mg subsamples were oven dried (80°C) and analyzed for $\delta^{15}N$ using the method of Kendall and Grim (1990).

Sufficient groundwater (1 -5 L) was collected from wells and piezometers to yield 80 to 100 mg of NO_3^-. All samples were 0.45 μm field filtered into 1 L polyethylene bottles, transported to NHRI and stored at 5°C until further processing. Nitrate was converted into a KNO_3 /KC1 salt for $\delta^{15}N$ analyses, and into pure $AgNO_3$ salt for $\delta^{18}O$ analyses, as described below.

A modification of the procedure described by Amberger and Schmidt (1 987) was used for the conversion of dissolved nitrate to $KN0_3$ salt. For all samples with greater than 10 mg/L S04, the S04 was removed by precipitation with excess $BaCl_2$ and the supematant re-filtered. This step removed oxygen bearing anions such as S04 or PO_4. One Liter groundwater and surface water samples were then passed through a 100 mL column of activated carbon to remove low molecular weight dissolved organic carbon (DOC). Cations in the sample were then exchanged with H^+ by applying the sample to a 200 mL cation exchange resin column (BioRad AG 50W-X4, H^+ form, 20~50 mesh). Following this step the sample was at pH 2-3 and composed of dilute HNO_3 and HCl. Although DOC in the groundwater was very low, as an additional step, samples were

passed through a 100 ml XAD-8TM column to ensure removal of the high molecular weight DOC fraction (Thurman and Malcolm, 1981). DOC was removed because it can contain up to 20 wt.‰oxygen that could interfere with the nitrate oxygen isotope analysis. The samples were then placed in a 1 L beaker and titrated to neutral pH with 0.1 N KOH using a Metrohm™ auto-titrator. The samples were placed in Teflon™ beakers and dried at 90"C in a convection drying oven. Samples, composed of variable proportions of KNO_3 and KCl, were then homogenized by grinding in an agate mortar and stored in glass vials in a vacuum desiccator for later conversion and analysis for $\delta^{15}N$. XRD analysis of selected samples confirmed that only KNO_3 and KCl were present.

It was found in our laboratory experimentation that the earlier method for oxygen isotopes in nitrate using mercuric chloride combustion (Amberger and Schmidt, 1987) resulted in nonquantitative conversions of nitrate oxygen to CO_2(<60-80 ‰) In addition, the use of mercuric cyanide was not preferred because of it hazardous nature, and because mercury from the combusted samples was found to migrate into the high vacuum sample preparation system. Silver cyanide was substituted for mercuric cyanide and sample yields improved to between 90-100% (using $700°C$ combustion) and eliminated the Hg problem. However, although consistent $\delta^{18}O$ values and better sample yields were attained when using the similar sample weights ($\approx$15 mg KN03), a 5 ‰ $\delta^{18}O$ enrichment trend was found over a KNO_3 sample weight range of 15 mg to 5 mg. Because the stoichiometry of the combustion reaction is essentially unbalanced for K using the Amberger and Schmidt (1 987) method and AgCN, it was thought that possibly K_2O was formed, or that KCl reacted with Vycor above $700°C$. As a result, this technique was abandoned and the KNO_3 and KCl salt mixtures were converted to pure $AgNO_3$ using the procedure developed by Silva et al (1994), described below.

Because $AgNO_3$ is light sensitive the conversion from the KNO_3 salt mixture was done without preparatory delay (Silva et al., 1994). Sufficient sample of the KNO_3 (65 mg as NO_3^-) and KCl mixture was re-dissolved in 40 mL of Mini-Q water. Samples were applied to a 5 mL BioRad Ag 2-X8 (Cl form, 20-50 mesh) ion exchange column to extract the nitrate. The column was rinsed with deionized water and nitrate was
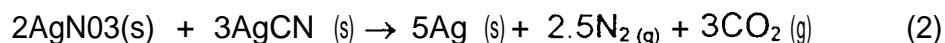
eluted from the column with 15 mL 3M HCl in 5 mL increments, and immediately neutralized by slowly adding 7 g of 99%+ Ag_2O (Alfa Inc.). The chloride from the HCl precipitated as AgCl salt, leaving only $AgNO_3$ in solution. The slurry was then filtered (0.45 pm) and rinsed with 15 mL deionized water. The filtrate was placed in a 200 mL glass beaker and frozen. When frozen, the samples were freeze dried in the dark to avoid light exposure. The pure AgNO3 salt was then transferred to glass vials and stored in a dark vacuum desiccator until preparation for combustion to CO_2.

Nitrogen isotopic analyses of KNO_3 samples were conducted by conversion to N_2 gas using the CaO sealed tube combustion technique described by Kendall and Grim (1990). The pure dinitrogen gas produced from the combustion was directly analyzed on the mass spectrometer for $\delta^{15}N$. Intercomparison $\delta^{15}N$ samples from the International Atomic Energy Agency (N1, N2, N3), and the NBS (USGS 32, USGS 25) were used to check for accuracy. Two 50 mg aliquots of KNO_3 reference materials N3 and USGS 32 were converted to $AgNO_3$, as described above, for $\delta^{18}O$ analyses.

Oxygen isotopic analyses of the $AgNO_3$ samples were conducted using minor modifications of the technique described by Silva et al (1994). Ten mg $AgNO_3$ samples were weighed into a 6 mm prebaked Vycor™ boat along with 2 mg of graphite (99.9 % Aldrich) powder (1.5 x stoichiometric excess). It was found that 18 mg 99.9% AgCN (Fluka) (1.5x stoichiometric excess) could be substituted for graphite, the advantage being AgCN was much easier to handle and weigh than graphite. The disadvantage of AgCN is that the N_2 could not be used for $\delta^{15}N$, as was the case with graphite. The 6 mm sample boat was then loaded into a pre-baked 22 cm long 9mm O.D. Vycor™ breakseal tube. The sample vessel was then "necked down" and attached to a high vacuum line and evacuated to c 10'5 atm (or =1 hour). Samples were enclosed in black paper jackets during evacuation to avoid exposure to light. After flame sealing the vessels, the samples were placed in a cold programmable muffle furnace, brought to 900°C, and immediately cooled to room temperature at a rate of 1 "C /min. The stoichiometry of the combustion was;

$$2 AgNO_3 (s) + 3C (s) \rightarrow 2Ag (s) + N_2 (g) + 3CO_2 (g) \qquad (1)$$

and

$$2AgNO3(s) + 3AgCN_{(s)} \rightarrow 5Ag_{(s)} + 2.5N_{2(g)} + 3CO_{2(g)} \qquad (2)$$

The resulting CO_2 gas was cryogenically separated from the nitrogen and analyzed on the mass spectrometer. Quantitative sample yields ranged between 98-100 %. Although there are no accepted international standards for $\delta^{18}O$ in NO_3, $\delta^{15}N$ standards N3 and USGS 32 (KNO3) and a KNO3 working standard were dissolved and converted , to AgNO3 as a check on reproducibility.

Isotopic analyses of water ($\delta^{18}O, \delta^2H$) were conducted using standard techniques. For $\delta^{18}O$ water samples were equilibrated with CO_2 using a commercial water equilibrator (VG Isoprep-18TM). For δ^2H water samples were converted to hydrogen gas using the standard zinc reduction technique. Three μL water samples were injected into evacuated 6 mm O.D. Pyrex breakseal tubes via individual injection ports in a heated manifold. The Pyrex tubes contained 120 mg of degassed zinc reagent (Biogeochemical Laboratories, Indiana State University). The water was frozen onto the zinc with liquid nitrogen, the nitrogen replaced with cold methanol (-80°C), and non-condensable gases were pumped away. The sample tube was then flame sealed and placed in a block heater at 495°C for 30 min. The hydrogen gas produced was directly analyzed on the mass spectrometer.

All isotopic analyses were performed using a VG Optima™ or VG 602™ isotope ratio mass spectrometer at NH RI. Stable isotope ratios are expressed in the usual delta permil (δ º/oo) notation relative to the international standard (Fritz and Fontes, 1981). Actual sample reproducibility (incl. sample preparation and analysis) for nitrate isotopes based on 12 duplicate field samples was better than 0.3 for $\delta^{15}N$ and 0.5 for $\delta^{18}O$. External precision was better than 0.20100 for 5180-water and 1.5 º/oo for δ^2H-water. Enriched tritium analyses were analyzed by Alberta Environment (Vegreville Laboratory, Alberta) and are reported in T. U., with a detection limit of 0.8 T.U.

Sampling wells were numbered and are shown in Figure 2. Groundwater was sampled from 74 piezometers and monitoring wells, from 43 domestic or municipal

wells (Canada and USA), and from a gravel pit (site 76) and Fishtrap Creek (site 77) (groundwater discharge zones). Thirteen of the monitoring wells were multi-levels, screened from near the water table to a maximum depth of 30 m. The well names (Table 1) corresponded to those used in earlier reports (Gartner-Lee, 1993, Liebscher et al., 1992). The "BC" series and the "FT1 -6" piezometers were sampled on both trips.

RESULTS AND DISCUSSION

Water Chemistry and Isotope Hydrology

Groundwaters area calcium bicarbonate type, with TDS ranging from 70 to 300 mg/L. Groundwater pH ranged from 6-8, and speciation calculations done using a revised WATEQF (Plummer et al., 1991) on groundwater chemistry data from Gartner-Lee (1993) showed water in the aquifer was undersaturated with respect to major ' mineral phases such as calcite, dolomite, silicates, and sulfates. Gartner-Lee (1993) showed that nitrate was the predominant nitrogen form in the-aquifer, with ammonium at, or below, the limit of detection.

$\delta^{18}O$ and δ^2H data for groundwater from wells sampled in the Abbotsford aquifer are listed in Table 1 and plotted in Figure 3. All data plot within a narrow range of values (e.g. -10 to -12 ^{O}/oo for $\delta^{18}O$), and plot along the local meteoric water line for Victoria, B.C. (Fritz et al., 1987). The stable isotope data confirmed that groundwater in the Abbotsford aquifer is primarily recharged from the late fall rains. Most of the precipitation that recharges the aquifer in the Abbotsford area occurs between October and February (Figure 4).

Tritium samples were collected from three multi-level piezometers (Table 2). All samples were tritiated, indicating groundwater in the Abbotsford aquifer was recharged since 1953. Measured TU'S from 3 to 11 were in the range of precipitation over the past 10 years. Over a vertical depth range from 7 m (water table) to 18 m tritium values were relatively low and constant (3-5 TU), which suggested that groundwater in the

upper part of the aquifer was well mixed and less than about 10 years old. This agreed with the estimated recharge rates for the Abbotsford aquifer of up to 1.2 m/yr. (Kohut, 1987). The deepest wells (25m) had slightly higher TU'S, which were consistent with tritium in water recharged in the mid-1 970's. Using estimated horizontal Darcy flow velocities of up to 450 m/yr. (Liebscher et al., 1992), the residence time of groundwater in the entire aquifer system from north to south could be as little as 20 years, or based on presence of tritium, a maximum of 40 years.

Nitrate Contamination

Nitrate concentrations in the Abbotsford aquifer ranged from O to 151 mg/L NO_3^-, with a median concentration of 46 mg/L NO_3^- for the time period sampled (Table 1). Of a total of 117 wells sampled, 54% of the wells had nitrate concentrations exceeding accepted drinking water limit of 45 mg/L $NO3$. Only a few of the deeper multi-level piezometers had no measurable nitrates, particularly those located on the uncultivated flood plain of Fishtrap Creek (wells south of #76). All domestic wells sampled had NO_3 present. Of 43 domestic or municipal wells sampled, 56 % had nitrate concentrations exceeding the maximum permissible drinking water limit of 45 mg/L NO_3 Many domestic wells exceeded the limit by a factor of 2-3, the highest nitrate concentration in a domestic well being 151 mg/L NO_3^-. There was no overall trend in nitrate concentration versus depth in the Abbotsford aquifer (Figure 5), and wells as deep as 50 m had nitrate levels above 20 mg/L NO_3. Most of the multi-level piezometers (except for 32) showed no trend in nitrate concentration with increasing depth. Piezometers that were repeated had similar nitrate concentrations in February and August. Fishtrap Creek and a gravel pit, which are groundwater discharge zones, also had high nitrate levels comparable to those found in wells (Table 1). These findings were consistent with earlier surveys conducted on the Canadian side of the border (Liebscher et al., 1992). In a study of recent and historic nitrate data Liebscher et al (1992) noted that nitrate in some wells increased since the early 1970's, whereas in others the nitrate levels are seasonally variable or decreasing.

The nitrate concentrations for the sampling period were kriged and plotted as iso-them lines in Figure 6. Because not all wells were completed at the same depth, either below ground surface or below the water table, the kriging could not accurately account for three dimensional variability in nitrate concentration. Thus, Figure 6 can only be used in a general sense to provide some indication of the extent of nitrate contamination. For multi-level wells only the uppermost piezometer nitrate data were used in kriging (SurferTM 5.0). The data in Figure 6 indicate the areal extent of nitrate contamination. Approximately 80% of the groundwater in the study area had nitrate concentrations above 40 mg/L NO_3^-, whereas about 20% of groundwater in the study area had nitrate concentrations below this value. The highest nitrate concentrations (i.e. >100 mg/L NO_3^-) occur in the agricultural south-central and south-western parts of the Abbotsford aquifer. It should be emphasized, however, given potential variability in nitrate inputs and high groundwater velocities in the aquifer, the trends in Figure 6 are transient, do not consider 3 dimensional variability, and would likely change overtime. Nevertheless, a similar plot by Liebscher et al (1992) based on data from many of the same wells throughout the 1 980s showed similar zones of high nitrate concentrations, but it appeared that the high nitrate zone (e.g. 100 mg/L contour) in the south-central part of the aquifer could have moved south by about 500 m.

Nitrate Sources

Manure and Fertilizers

The $\delta^{15}N$ of potential nitrate source materials in the forms of manure and inorganic fertilizers are summarized in Table 3. The $\delta^{15}N$ of bulk poultry manure samples (Organic N plus NO_3^--N) ranged between +7.9 and +8.6 ^{O}/oo. Four different brands of inorganic fertilizers used on raspberry fields were composed of white and green and orange grains containing urea, ammonium sulfate, ammonium phosphate or potassium chloride. The four fertilizer mixes ranged in $\delta^{15}N$ between -1,.5 and -0.6 ^{O}/oo. Thus, the $\delta^{15}N$ of fertilizers are isotonically depleted from the manure by at least 8 ^{O}/oo.

The isotopic signatures of the manure and fertilizers are in keeping with published data (Hubner, 1986; Kreitler, 1975). Fertilizers composed of nitrate salts were not used for agricultural purposes in the Abbotsford area (Geoff Hughes-Games, pers. comm.).

Vitrification of ammonia and ammonium from manure and fertilizer under aerobic conditions in the soil or unsaturated zone leads to nitrate formation by the reactions;

$$NH_3 \rightarrow NH_4^+ \rightarrow NO_2^- \quad \text{and} \quad NO_2^- \rightarrow NO_3^- \tag{3}$$
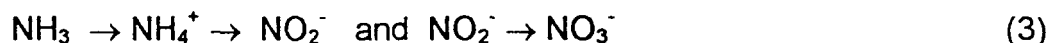
In aerobic coarse textured soils and the unsaturated zone (3) proceeds quickly to completion with little nitrogen isotopic fractionation (Exner and Spalding, 1994). No measurable nitrite or ammonium was in groundwater of the Abbotsford aquifer (Gartner-Lee, 1993), suggesting this reaction was completed in the soil and unsaturated zone. Soil zone denitrification is thought to be insignificant due to the coarse and welldrained nature of the soil (Zebarth et al., 1994). Thus, the $\delta^{15}N$ of nitrate in groundwater derived solely from ammonium fertilizers should range between about O and -2 o/oo. The $\delta^{15}N$ of nitrate derived from poultry manure, however, could deviate from the $\delta^{15}N$ of the solid manure as a result of nitrogen isotopic fractionation during ammonia volatilization. Ammonia volatilization favours off-gassing of 14NH3, leaving the residual ammonia enriched in 15N relative to the solid manure source material. Thus, the $\delta^{15}N$ of nitrate in the aquifer derived from poultry manure should be at least +8 o/oo, and from other studies of nitrate from animal wastes, could vary from +8 to +16 o/00 (Kreitler, 1975; Kreitler and Jones, 1975; Lindau and Spalding, 1984).

Contaminated and Non Contaminated Soils

Samples of soil were collected from poultry manure contaminated soil and non-agricultural soil and analyzed for $\delta^{15}N$ of total N. Samples were taken from sites immediately outside the study area shown in Figure 2, due to limited site availability during the sampling period. However, the sites were typical of those above the aquifer (Geoff Hughes-Games, BCMAFF, pers. comm.). The results (Table 4) indicated a

distinctiveδ^{15}N difference between soil N from a non-contaminated setting and soil N from beneath former poultry manure stockpiles. lδ^{15}N f soil N beneath poultry stockpiles was isotonically enriched, ranging from +7.5 to +1 3.6 o/oo.δ^{15}N of non-contaminated soil ranged between +3.7 and +4.9 ^{O}/oo. The δ^{15}N of soil N from manure stockpile sites indicates that nitrate mineralized from residual manure and subsequently flushed through the unsaturated zone to the aquifer could range from about +8 to +14 ^{O}/oo. As indicated above, this δ^{15}N range was also in agreement with earlier findings of nitrates derived from manure and sewage sources (Kreitler, 1975; Kreitler and Jones, 1975; Spalding et al., 1993).

Soil and Unsaturated Zone Porewater Nitrate

Nitrate, nitrite and selected anions were extracted from the soil and unsaturated zone porewater to further provide a clearer indication of the isotopic composition of nitrate percolating through the unsaturated zone into the Abbotsford aquifer (Table 5). Samples of nitrate extracted from soil beneath former manure stockpiles had δ^{15}N values' ranging between about +14 and +16 o/oo1 whereas, nitrates from soil beneath one raspberry field had δ^{15}N values between about +9 and +12 ^{O}/oo (Table 5). There was a distinct difference in the δ^{18}O of nitrate from soil beneath manure piles and nitrate from soil under raspberry fields (+4.7 to +5.7 ^{O}/oo vs. +2.2 to +2.8 ^{O}/oo) . The lesser δ^{15}N values beneath the raspberry field likely resulted from a more diffuse nitrate source and possible mixture of manure and synthetic fertilizers. The δ^{18}O of nitrate from soil beneath the raspberry field (+2 to +3) was in keeping with nitrate oxygen derived from air (+22 ^{0}/oo) and precipitation in Abbotsford (-9 to -6 ^{O}/oo; Figure 3) in a ratio of 1/3 to 2/3 (Hollocher, 1981; Anderson and Hooper, 1983). The nitrate samples from beneath the manure pile had slightly heavier δ^{18}O values than expected, which suggested that either water in the manure pile was from 1-2 ^{O}/oo heavier in δ^{18}O than precipitation as a result of some evaporation, or that minor isotopic enrichment due to denitrification had occurred in the manure pile. The cause of the 6180 enrichment

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below manure stockpile sites could not be further explained on the basis of the existing data.

Estimated nitrate concentrations in soil porewater ranged from about 600 mg/L NO_3 in the upper 15 cm of soil below raspberry fields, up to 18,000 mg/L NO_3 in the upper 15 cm of soil beneath former manure piles. Below 15 cm depth soil porewater nitrate concentrations were lower in both settings, ranging from about 360 mg/L beneath raspberry fields, to 6000 mg/L beneath former manure piles (Table 5). The lower values observed at depth beneath the raspberry fields were in keeping with nitrate concentrations of 600 to 1300 mg/L NO_3 estimated for an integrated 90 cm depth interval for manured fields in the Abbotsford area (Chipperfield, 1992). Nitrite was only found in soil porewater beneath former manure piles, suggesting some minor denitrification had occured. Chloride concentrations were high, which suggested additional chloride in the aquifer was derived both from animal waste sources or from potash used in fertilizers. The variable and temporal input of chloride to the aquifer either from manure, potash or precipitation suggested NO_3/Cl ratios could not be reliably used as an indicator of denitrification.

In summary, the soil and unsaturated zone of the Abbotsford aquifer provide a large reservoir of nitrate. Nitrates leaching to the aquifer have potential $\delta^{15}N$ values ranging between O and +16 o/oo and $\delta^{18}O$ values of about +2 to +5 ^{0}/oo. The manure, soil and soil porewater chemical and isotope data were used as constraints to interpret nitrate isotopes in groundwater, as discussed below.

$\delta^{15}N$ and $\delta^{18}O$ in Groundwater Nitrate

The nitrogen and oxygen isotopic compositions of nitrates in the Abbotsford aquifer are listed in Table 1. The $\delta^{15}N$ of nitrates ranged between +2 and +23 ^{0}/oo (Figure 7). No groundwater samples had $\delta^{15}N$ values within the range of fertilizers commonly used (-2 to O ^{0}/oo). Of 98 groundwater samples' less than 10% had $\delta^{15}N$

values less than +5 o/oo, whereas 80°A had $\delta^{15}N$ values between +7 and +16 ^{O}/oo. Less than 9% of groundwater samples had $\delta^{15}N$ greater than +16 ^{O}/oo (Figure 7).

The $\delta^{15}N$ data supported the view that poultry manure ($\delta^{15}N > +8$) **was** the primary **source of nitrate to the Abbotsford aquifer. Fertilizers did not appear to be a significant contributor, although $\delta^{15}N$ values** between +2 and +8 ^{O}/oo suggested a **mixture of manure and fertilizer nitrate. There was no correlation between $\delta^{15}N$ and NO3 (Figure** 8**), or between $\delta^{15}N$ and depth in the aquifer (not shown). Only two multi-level piezometers indicated a slight trend of more enriched values at depth (23 and 24). These samples with $\delta^{15}N$ values >+18 ^{O}/oo had the lowest NO$_3$ concentrations, which could be interpreted as minor denitrification. Overall, however, the data suggested that denitrification did not occur to any extent in the deeper portions of the aquifer. $\delta^{15}N$ values were kriged and contoured in Figure 9. Less than 10% of groundwater nitrate in the study area had δ15N values less than +6 ^{O}/oo, and these were confined to several agricultural zones south of the Abbotsford airport (Figure 9). More than 80% of groundwater nitrate in the study area had $\delta^{15}N$ values above +7 ^{O}/oo, which (in the absence of denitrification) suggested that most of the nitrate in the Abbotsford aquifer was derived from manure sources (Figure 9). Zones of $\delta^{15}N$ values greater than +12 ^{O}/oo suggested a greater input of nitrate derived from poultry manure.**

Oxygen isotope data for nitrates in the Abbotsford aquifer are plotted in Figure 10. The $\delta^{18}O$ values of nitrate plotted in a narrow range, with 81940 of nitrate samples having $\delta^{18}O$ values between +2 and +5. This narrow range of values lies within the range of nitrate produced by vitrification of ammonium, and had a similar range of $\delta^{18}O$ values as nitrate in the upper part of the unsaturated zone (Table 5). The $\delta^{18}O$ values of nitrate could not be kriged **because there was no significant oxygen isotopic variation in nitrate across the study area. A plot of $\delta^{18}O$ vs $\delta^{15}N$ of nitrate is shown in Figure 11. Had denitrification occurred, the** ti15N **and $\delta^{18}O$ values of the residual nitrate would have shifted in a positive direction in about a 2:1 isotopic ratio (Bottcher et al., 1990). Because more than 90% of the groundwater nitrate samples had $\delta^{18}O$ values less than +5 ^{O}/oo, the oxygen isotopic data provided conclusive evidence that no**

significant denitrification was taking place. Only a few (<5%) of groundwater nitrates appeared to trend in a direction suggesting denitrification, and a few samples with low $\delta^{15}N$ and higher $\delta^{18}O$ values (=3%) suggested a possible mixture of manure derived nitrate with synthetic nitrate. **The lack of denitrification is likely due to the lack of labile or sufficient supplies of electron donors. DOC levels of less than 1 mg C/L, for example, could not support microbial denitrification in the Abbotsford aquifer (cf Starr and Gillham, 1993).**

Thus, the $\delta^{15}N$ and $\delta^{18}O$ of groundwater nitrate indicated conclusively that no significant denitrification was taking place in the Abbotsford aquifer, and that the nitrate in the aquifer was predominantly derived from poultry manure nitrogen forms and to a lesser extent from ammonium fertilizers.

Vitrification of Manure and Fertilizers

The $\delta^{18}O$ -N 0 3 data provided a further indication of when the process of vitrification occurred. As shown earlier, the $\delta^{18}O$ of groundwater in the aquifer plotted within a relatively narrow range of values, between about -10 to -12 O/oo (Figure 3). Had the water oxygen involved in vitrification solely been that represented by groundwater, the expected $\delta^{18}O$ values of NO_3 in the aquifer resulting from vitrification would be between -1 to +1 O/oo, if one third of the oxygen in the nitrate been derived from air (+22 O/oo) and two thirds derived from groundwater (-1 2 to -10 O/oo) (Aleem et al., 1965; Anderson and Hooper, 1983; Hollocher, 1981). However, all the $\delta^{18}O$ -NO_3- values were slightly isotonically heavier, and mostly ranged between +2 and +5 O/oo. This apparent discrepancy suggested that the water involved in the nitrification process was not that which recharged the aquifer.

The requirement of slightly enriched $\delta^{18}O$ in the water involved in vitrification was not unexpected. Manure and fertilizers are typically applied to the fields in spring and early summer. Thus, because vitrification is a fast reaction, it would most likely be summer rains with isotonically heavier $\delta^{18}O$ values (-1 O and -6 O/oo; Figure 3; Fritz et al., 1987) rather than fall rains that provided the water oxygen source to vitrification. In

this case, about 75°A of the $\delta^{18}O$ -NO_3 data could be explained by the involvement of meteoric waters with $\delta^{18}O$ values of -10 to -6 o/oo   This range of $\delta^{18}O$ in water would produce nitrate with $\delta^{18}O$ values between about O and +4.0 O/oo. Thus, the data suggested that the vitrification process predominantly occurred in the summer months. The nitrate produced **in the soil zone during the summer was subsequently flushed through the unsaturated zone into the aquifer during fall recharge, as indicated by $\delta^{18}O$ of groundwater.**

[t should be noted, however, that about 25% of the groundwater nitrates had $\delta^{18}O$ values greater than +4 o/oo. This required, **in the absence of denitrification, the involvement of water in the vitrification process with $\delta^{18}O$ values beyond the range of values observed in precipitation** (Fritz et al., 1987). As **shown earlier, nitrates from soil beneath former manure piles had $\delta^{18}O$ values that were slightly heavier than from beneath fields (Table 5). This suggested that the water involved in vitrification beneath, or within, manure piles was either subjected to some evaporation, contained some $\delta^{18}O$ enriched waters as poultry urine, or the nitrate produced was subjected to some minor denitrification near the manure pile. Although none of these possibilities could be fully resolved on the basis of the existing data set, the presence of some nitrite beneath the former manure piles supported the hypothesis that some minor denitrification had occurred.**

In summary, the nitrate oxygen isotope data suggested that most of the NO_3 in the aquifer was produced by vitrification of manure N and ammonium fertilizers in the soil zone during the summer months. The nitrate produced was then subsequently flushed to the groundwater during fall recharge, as indicated by groundwater $\delta^{18}O$ values similar to that of fall rains.

CONCLUSIONS

Extensive nitrate contamination of groundwater in the Abbotsford aquifer to levels above national drinking water standards is a major problem in British Columbia

and Washington State. Nitrate concentrations in the Abbotsford aquifer ranged from O to 151 mg/L NO_3, with a median concentration of 46 mg/L NO_3 for the time period sampled. Of 117 wells sampled, 54°A had nitrate concentrations exceeding accepted drinking water limit of 45 **mg/L N0$_3$. From a land use perspective, approximately 80°A of the study area had groundwater nitrate concentrations exceeding 40 mg/L N0$_3$.**

Potential nitrate source materials were poultry manure and inorganic fertilizers. The $\delta^{15}N$ of solid poultry manure (organic and ammonia-N forms) ranged between +7.9 and +8.6 o/oo, with the $\delta^{15}N$ of the resulting nitrate ranging between +8 and +16 O/oo. Four brands of inorganic fertilizers commonly used had $\delta^{15}N$ values between -1.5 and -0.6 O/oo. Thus, the $\delta^{15}N$ of fertilizers were isotonically distinctive from the manure by at least 8 O/oo. The $\delta^{18}O$ values of groundwater nitrate, in contrast, plotted in a narrow range with most N0$_3$ samples having $\delta^{18}O$ values between +2 and +5. This narrow range of $\delta^{18}O$ values lies within the range of nitrate produced by vitrification of manure N and fertilizer ammonium, and had a similar range of $\delta^{18}O$ values as nitrate in the upper part of the unsaturated zone below fertilized and manured raspberry fields and beneath former manure piles. The $\delta^{15}N$ and $\delta^{18}O$ stable isotope data together indicated nitrate in the Abbotsford aquifer was predominantly derived from poultry manure and to a lesser extent from ammonium based fertilizers. The $\delta^{18}O$ nitrate data further suggested vitrification occurred in the summer months, with the nitrate produced during the summer subsequently flushed through the unsaturated zone and into the aquifer during fall recharge. A plot of $\delta^{15}N$ versus $\delta^{18}O$ showed conclusively that no significant natural remediation by bacterial denitrification was taking place in the Abbotsford aquifer.

The results of the study infer that widespread nitrate contamination of the Abbotsford aquifer will continue, unless agricultural land management practices are dramatically changed. The findings of this study suggest that attempts should be made to eliminate or minimize the residual nitrate levels in the soil and root zone, particularly in the fall and winter when soil nitrate is recharged to the aquifer. Nevertheless, because the residence time of groundwater in the Abbotsford aquifer is on the order of

decades, and because the aquifer does not appear to sustain any significant bacterial denitrification, the high nitrate concentrations currently observed in the aquifer will likely persist for decades **even if the surficial nitrate** sources were eliminated. **Because of the apparent lack of bacterial denitrification, the only form of nitrate removal from the aquifer will be through continued flushing from recharge.**

ACKNOWLEDGMENTS

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Figure1. Location of Abbotsford aquifer, southwestern B.C. and northern Washington State. Dashed line denotes approximate aquifer outline. Piezometric contours, adapted from Liebscher et al (1992) indicates groundwater **flow directions.**

Figure 2. Well sampling locations in Abbotsford aquifer. Numbers refer to wells listed in Table 1. Dashed line as in Figure 1.

Figure 3. $\delta^{18}O$ and δ^2H composition of groundwater in the Abbotsford aquifer. Victoria local meteoric water line is from Fritz et al., 1987.

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Figure 8. Crossplot of $\delta^{15}N\text{-}NO_3^-$ versus NO3 concentration.

Figure 9. Contour of $\delta^{15}N\text{-}NO3$ over the study area. Contour interval is 3 permil.

Figure 10. Frequency histogram of $\delta^{18}O$ in groundwater nitrate. Bars show potential $\delta^{18}O$ range for nitrate derived from vitrification of reduced N forms, and for manufactured NO3 fertilizer as given by Amberger and Schmidt (1986). Directional trends to the right could indicate mixing and denitrification.

Figure 11. Crossplot of $\delta^{18}O\text{-}NO_3^-$ versus $\delta^{15}N\text{-}NO_3^-$. The two lines encompass the denitrification trend in 2:1 isotopic enrichment ratio as reported byBottcheretal(1990). Arrow indicates direction of mixing with commercial NO3 fertilizers. The data indicate no significant denitrification is taking place.
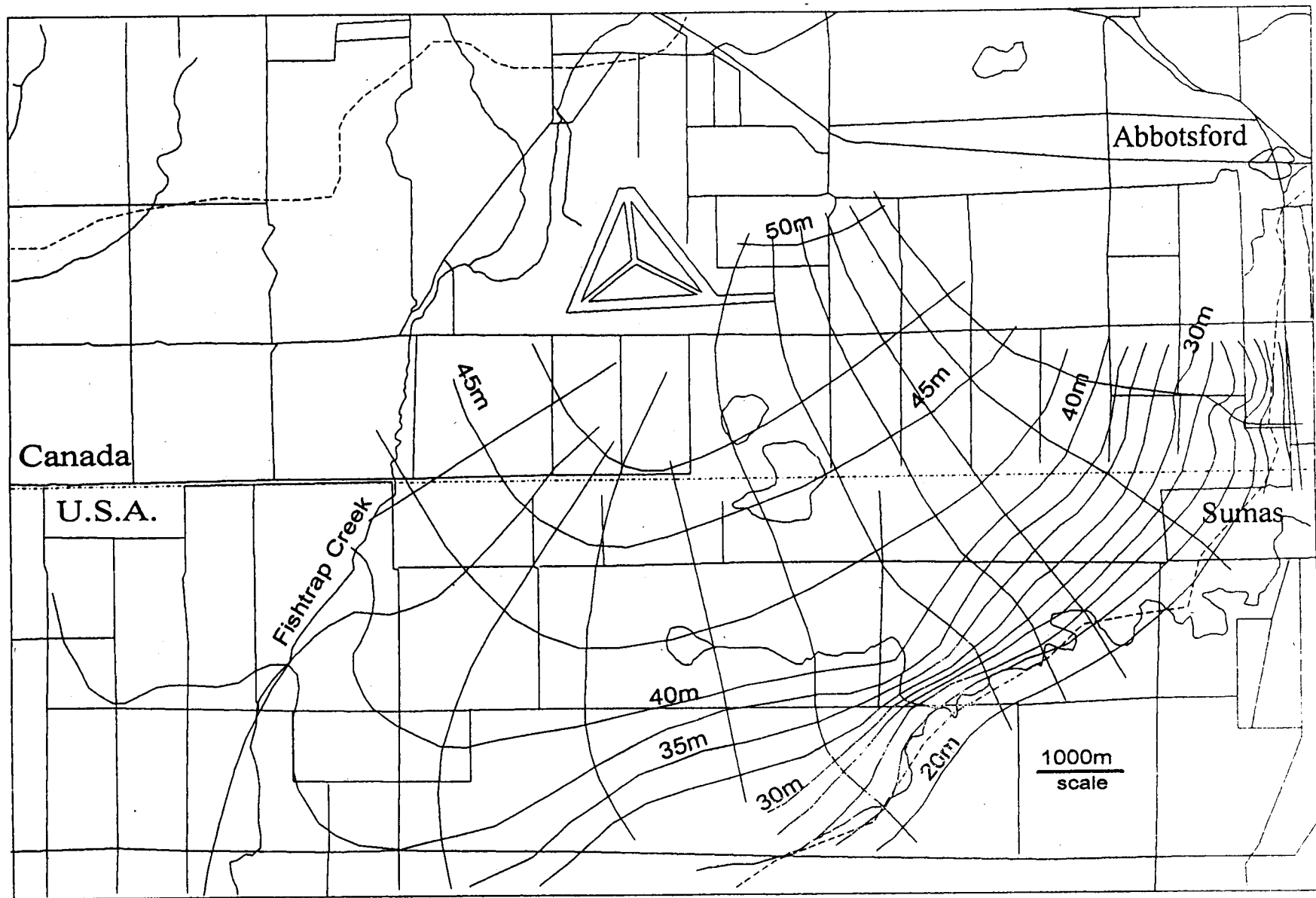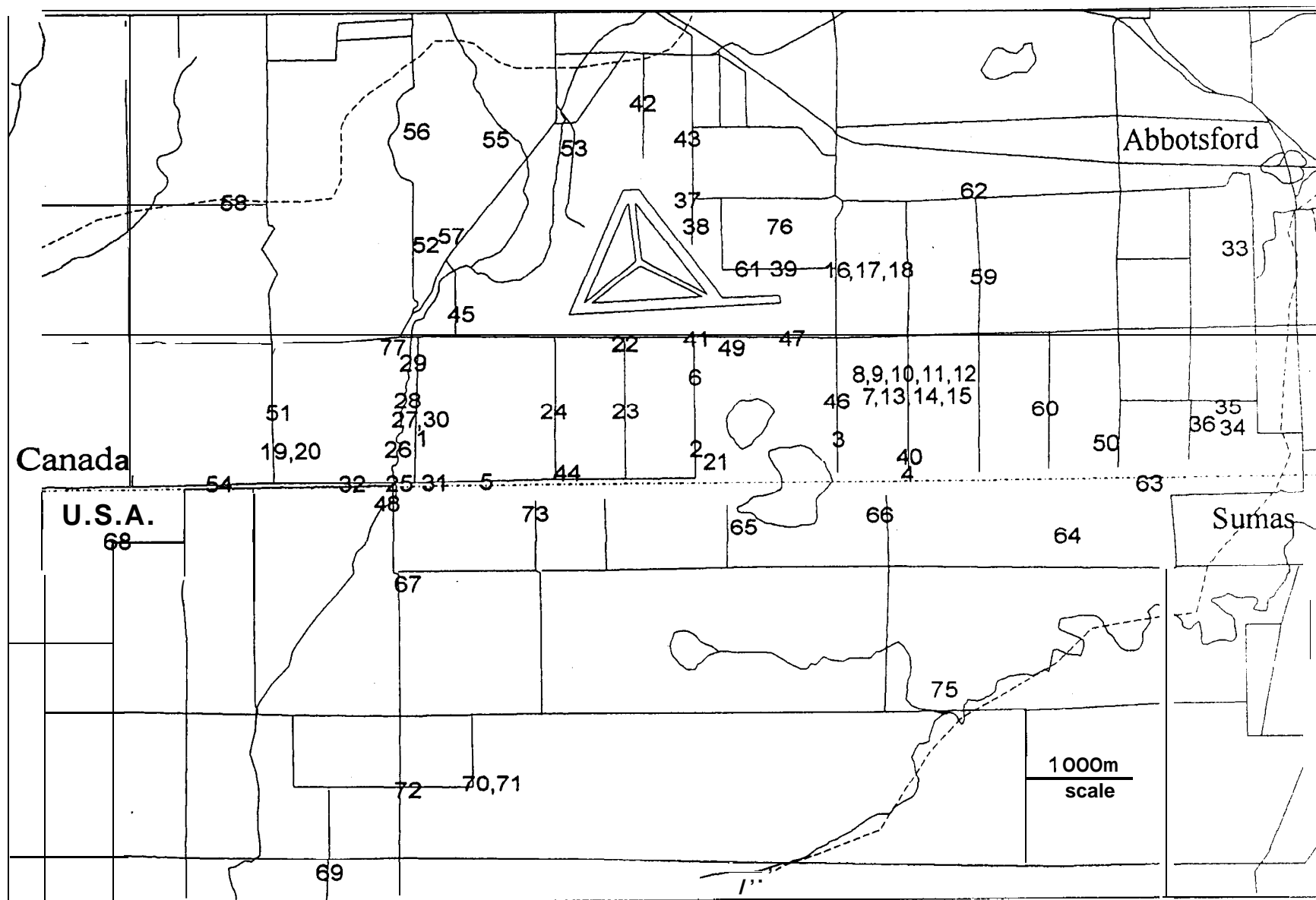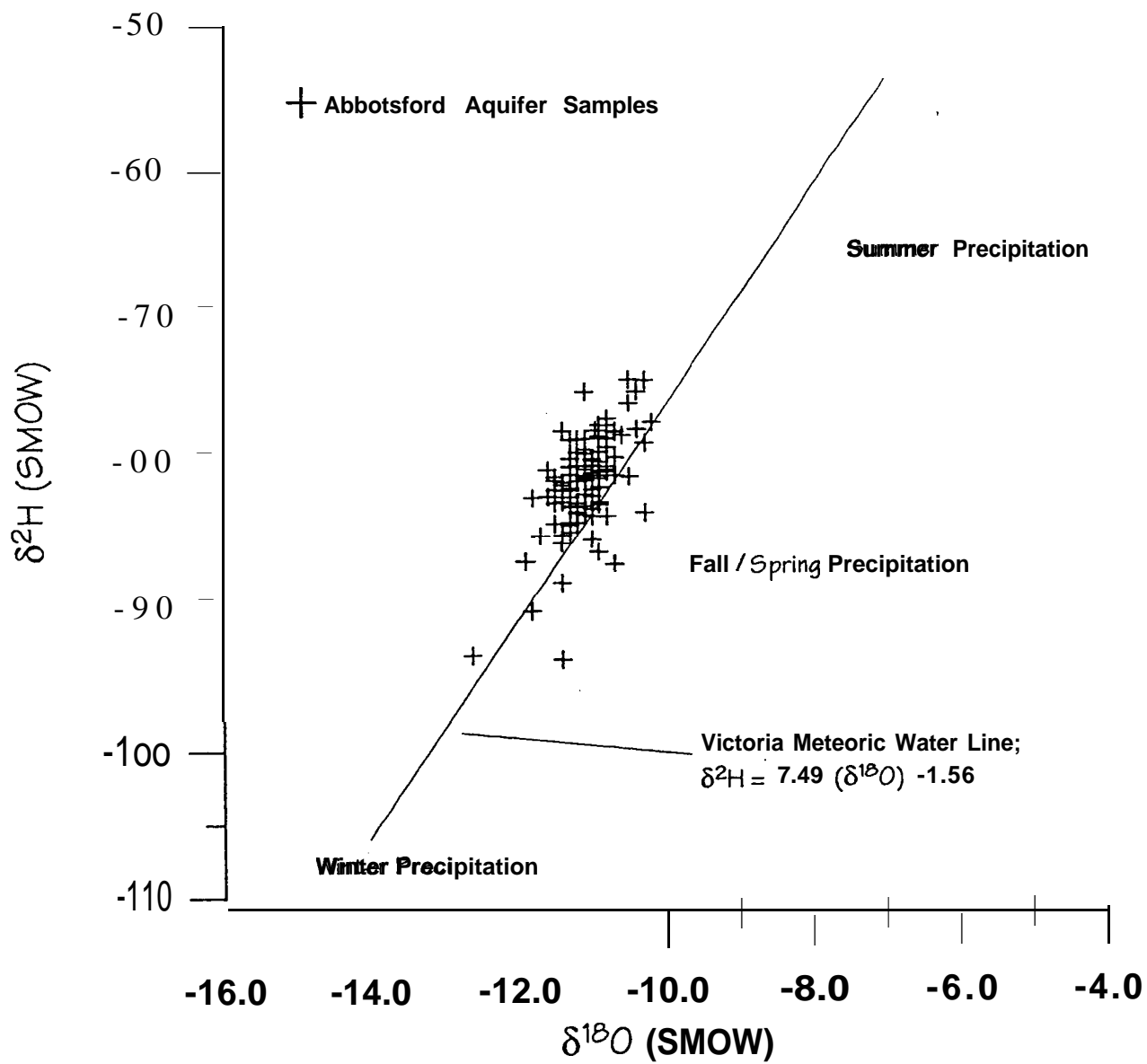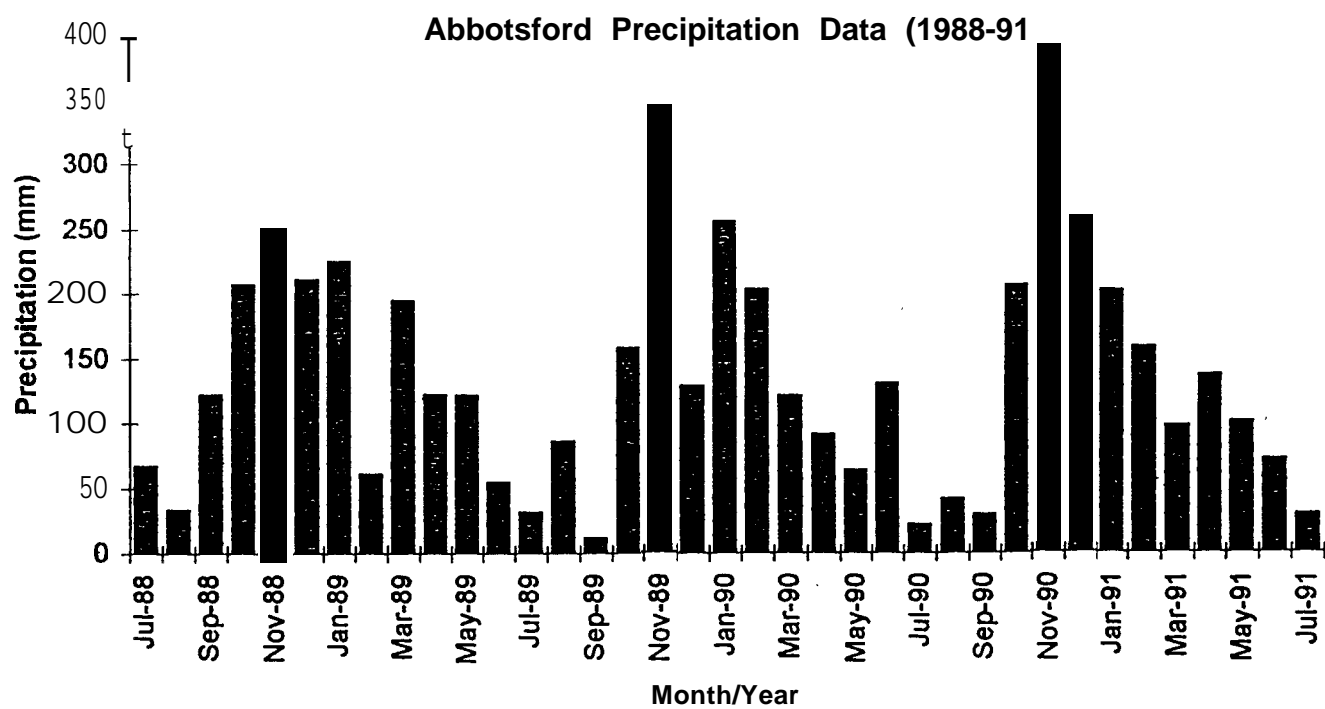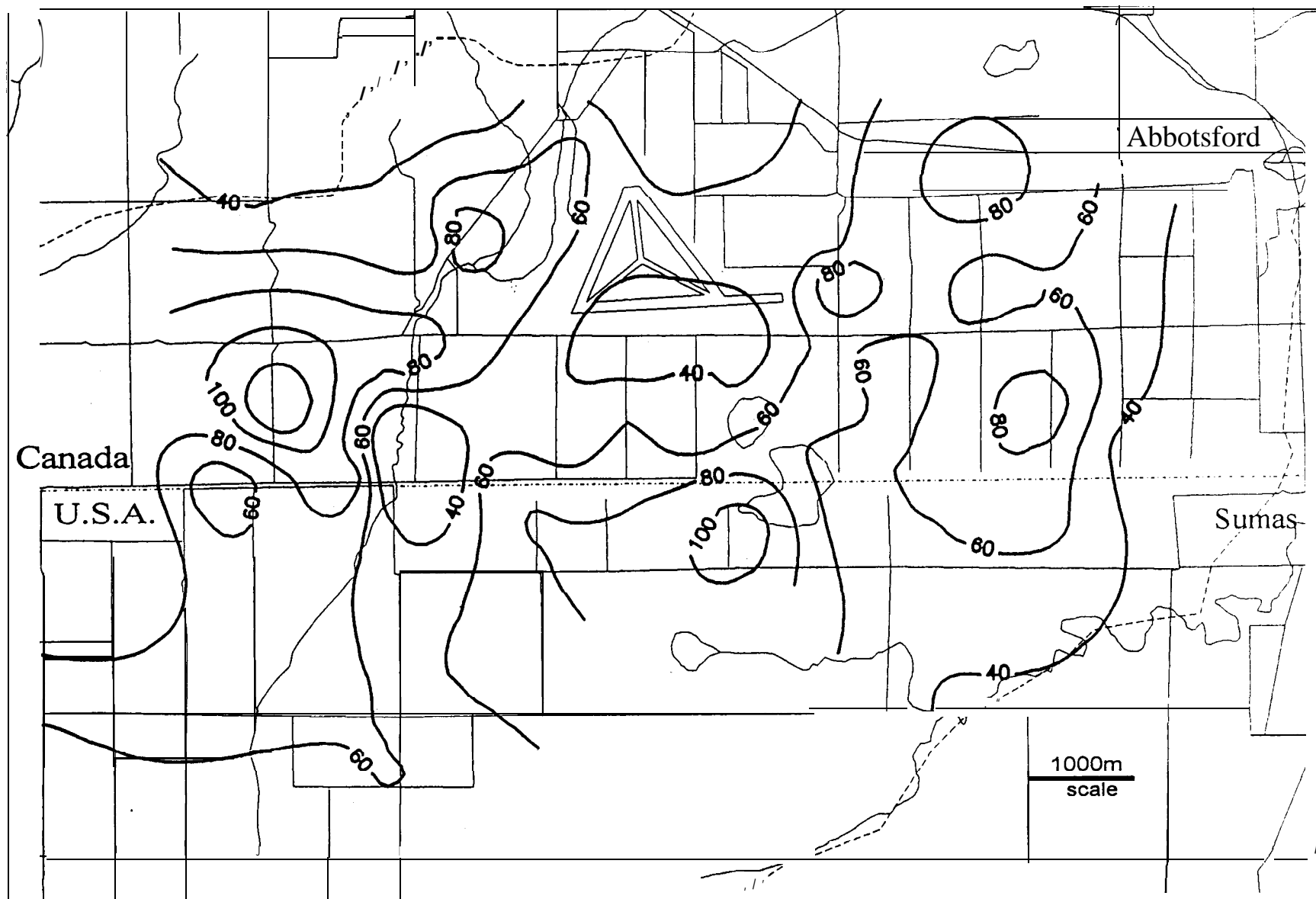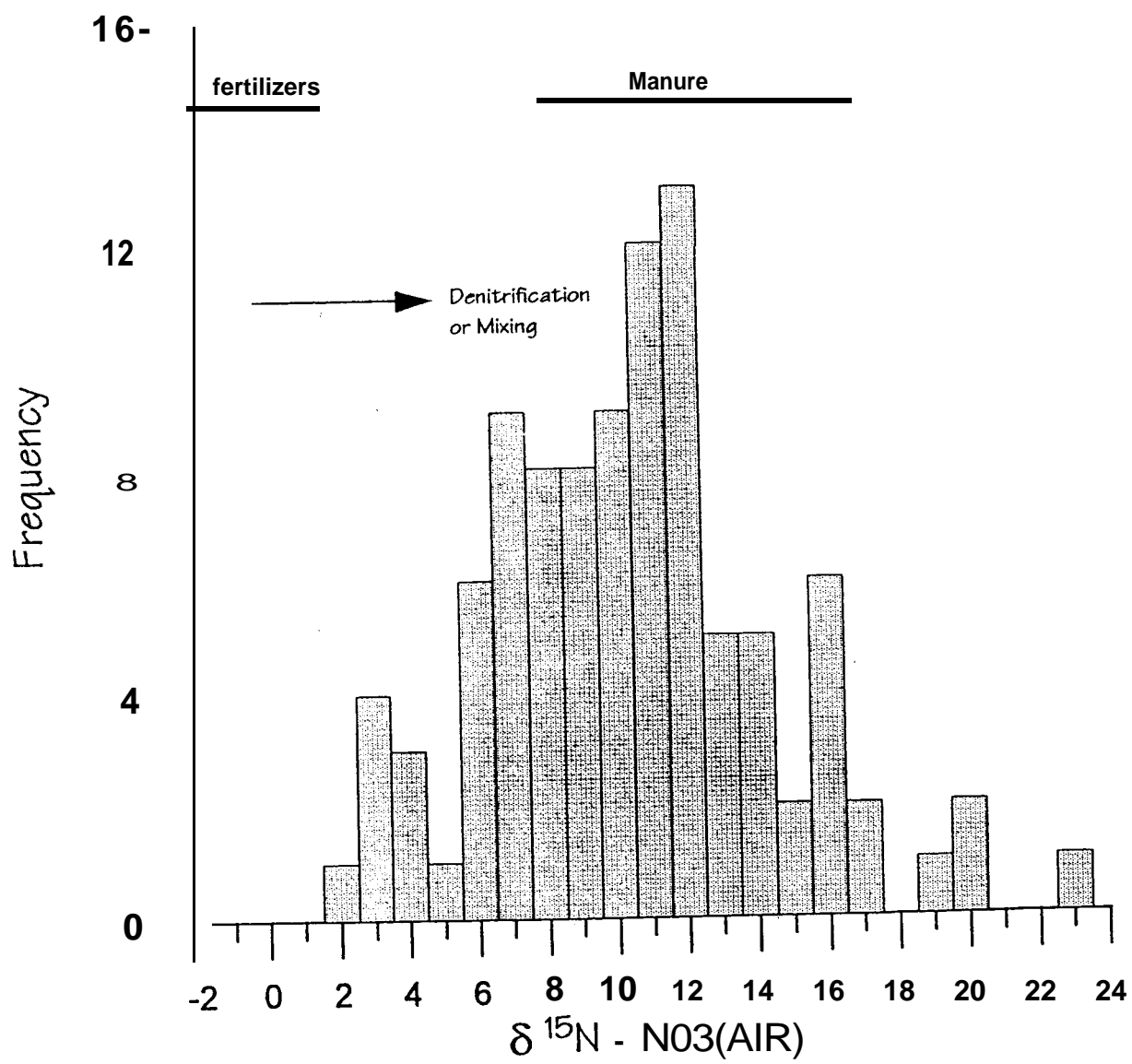
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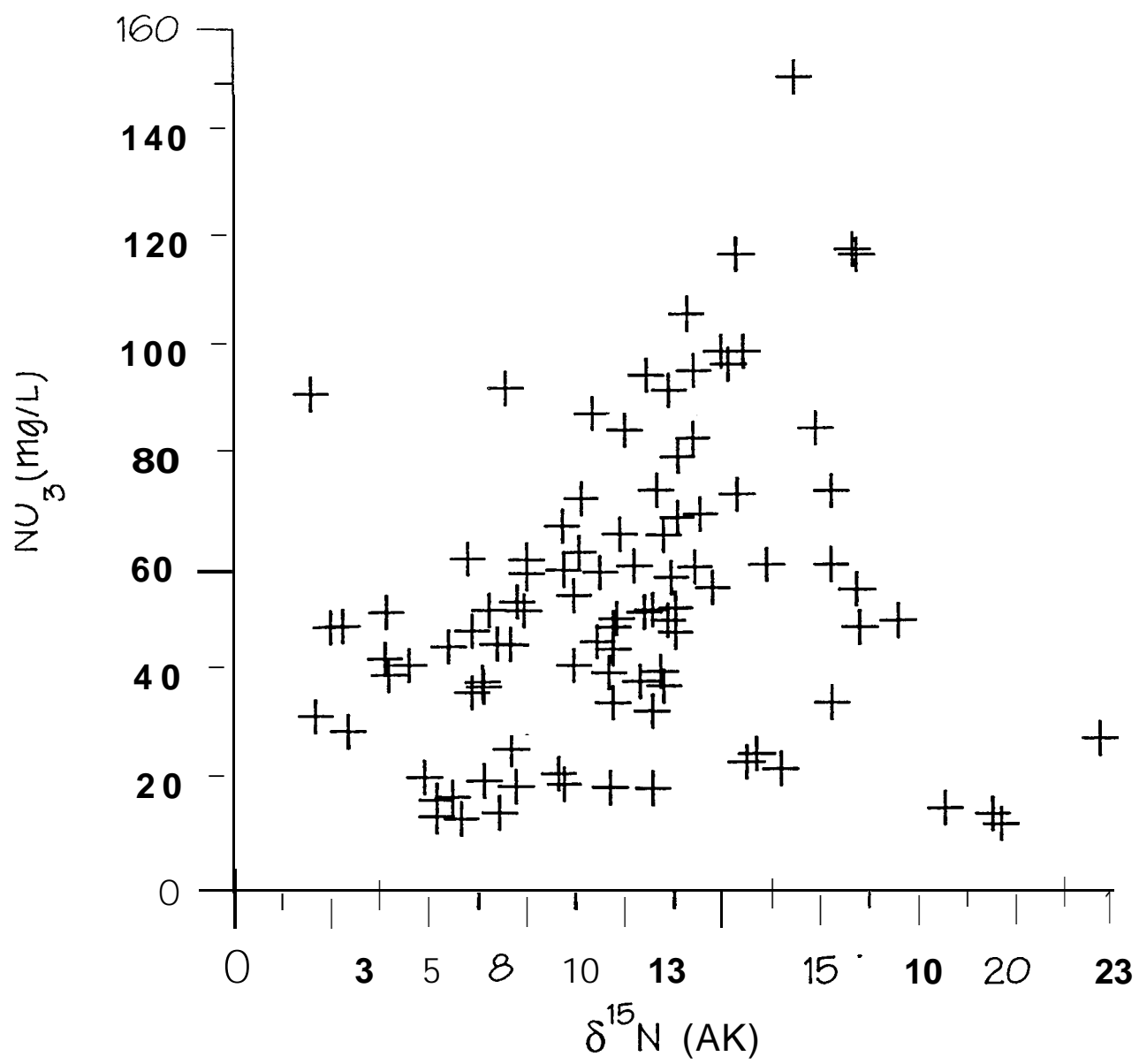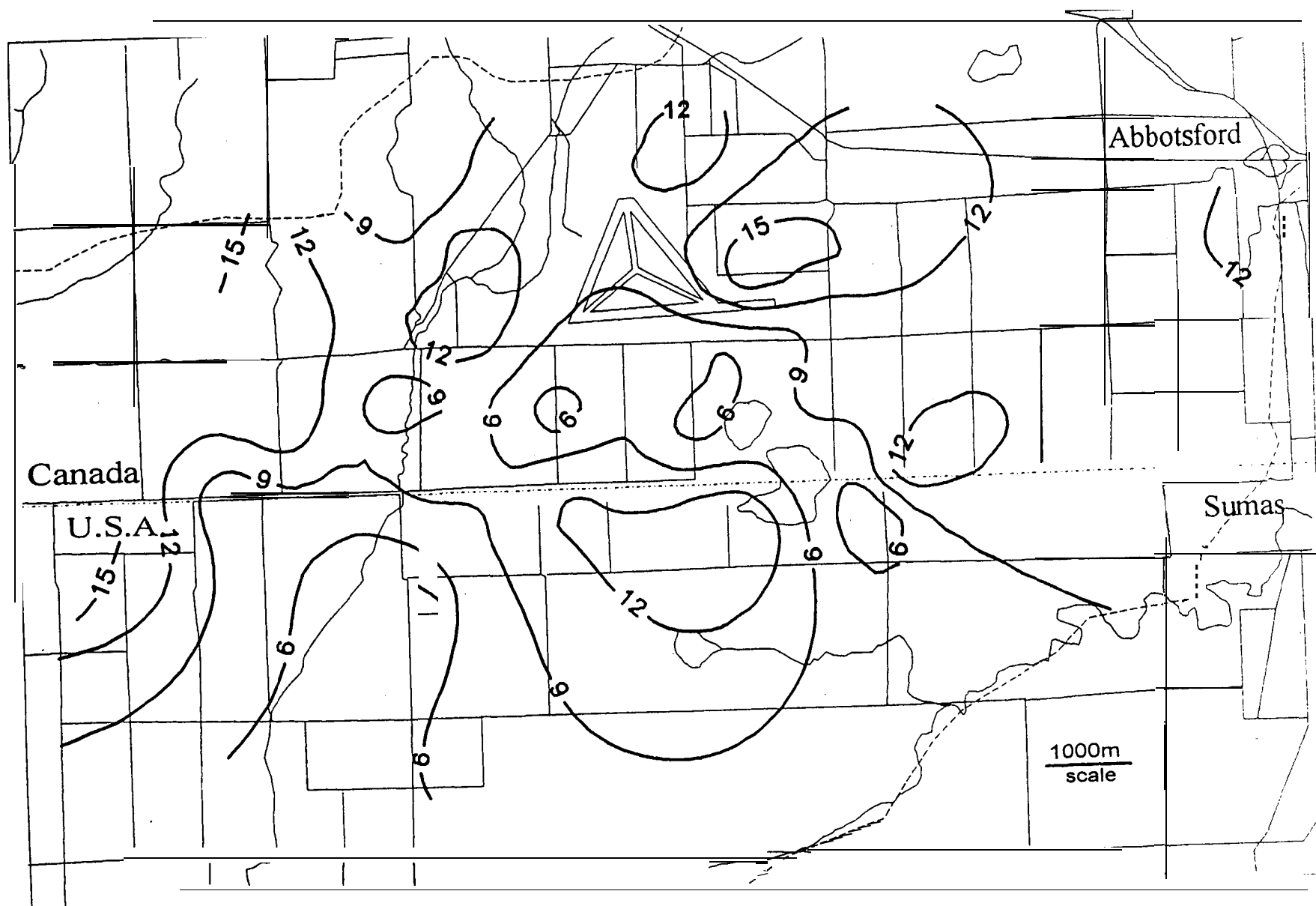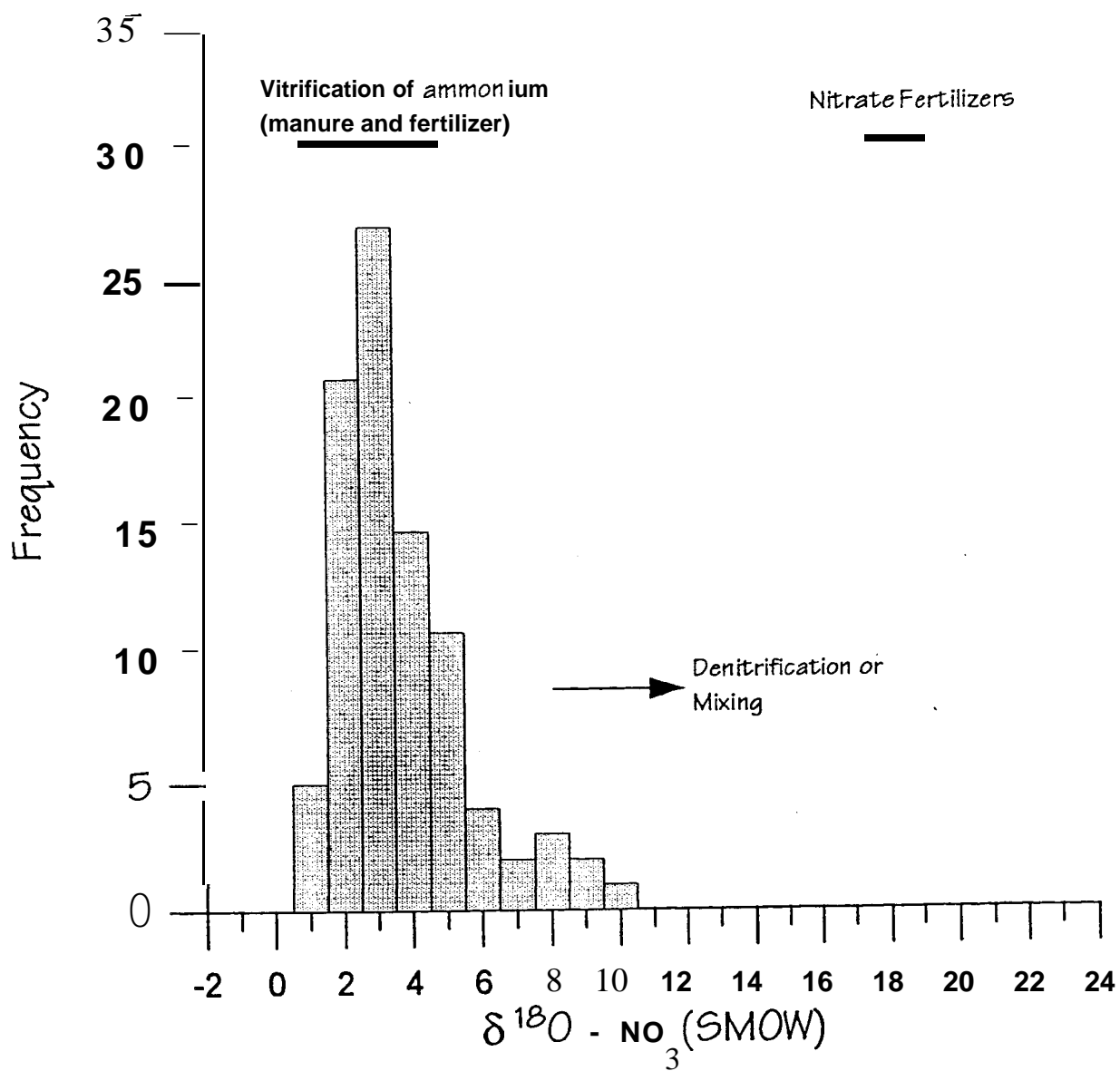**Figure 5**
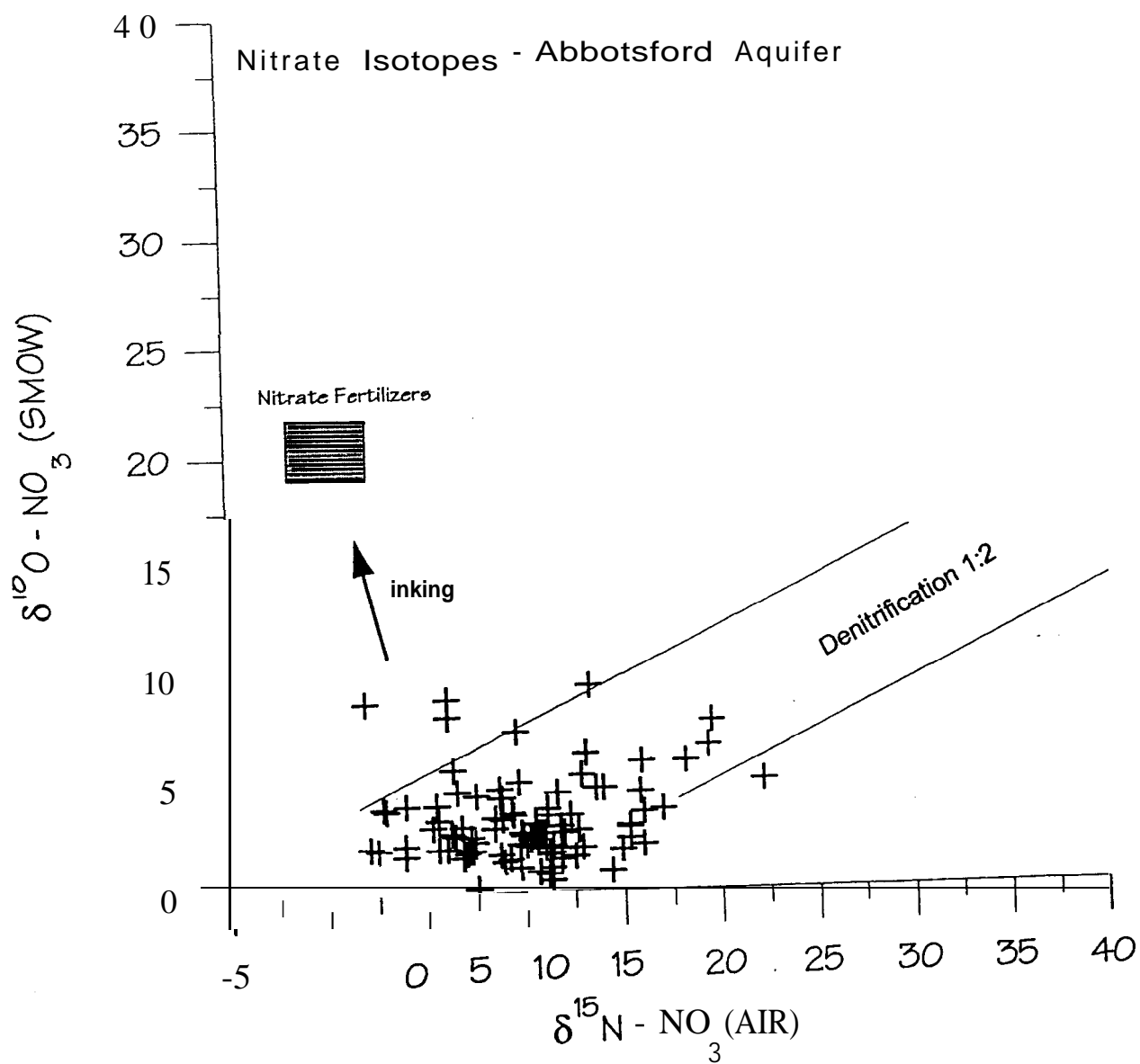
Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

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Table 1. Well site data, depth, location, and isotopic composition of water and nitrate in Abbotsford aquifer. Map # refers to location on Figure 1. Water isotopes and nitrate oxygen isotope data are normalized relative to the VSMOW-VSLAP scale. $\delta^{15}N$ of nitrate is relative to Air standard.

Map #	Well Name	Date	Easting (m)	Northing (m)	Well Depth (m)	$\delta^{18}O$ water	δ^2H water	NO_3^- mg/L	$\delta^{15}N$ NO_3^-	$\delta^{18}O$ NO_3^-
	Groundwater Piezometers									
1	ABB1	22/02	543665	5428349	8.0	-10.8	-83.9	21.2	+14.0	+4.7
2	ABB2	22/02	546883	5428062	7.8	-11.1	-83.2	61.5	+7.5	+0.2
3	ABB3	22/02	548514	5428161	18.0	-11.0	-83.4	45.4	+5.5	+4.0
4	ABB4	22/02	549310	5427765	30.0	-10.8	-80.7	85.8	+14.9	+1.9
5	ABB5	22/02	544471	5427708	9.5	-10.9	-81.9	72.7	+8.9	+1.4
6	ABB6	22/02	546878	5428879	10.0	-10.9	-81.1	48.3	+6.1	+8.8
7	91-6-1	22/02	548904	5428725	29.1	-11.1	-81.5	52.2	+10.7	+2.7
	91-6-2	22/02	548904	5428725	26.8	-11.1	-81.5	51.7	+10.5	+3.1
	91-6-3	22/02	548904	5428725	25.2	-11.1	-81.2	46.3	+9.3	+3.6
	91-6-4	22/02	548904	5428725	23.1	-11.1	-81.3	50.6	+9.9	+2.7
8	CDA1	22/02	548758	5428903	20.7	-11.1	-81.1	59.5	+8.4	+3.4
9	CDA2	22/02	548863	5428905	22.3	-10.8	-79.2	41.9	+8.7	+4.3
10	91-1	22/02	548600	5428883	10.0	-11.0	-83.9	56.2	+12.3	+3.5
11	91-2	22/02	548606	5428883	36.0	-11.2	-83.3	69.1	+11.4	+0.5
12	91-3	22/02	548602	5428877	24.4	-11.0	-82.5	65.9	+11.0	+2.7
13	91-4	22/02	548917	5428725	21.4	-11.2	-83.0	49.0	+9.7	+5.0
14	91-5	22/02	548908	5428725	45.3	-11.1	-82.4	58.1	+11.2	+1.7
15	91-7	22/02	548900	5428725	22.0	-11.1	-81.1	44.9	+9.7	+1.1
16	91-8	22/02	548514	5430084	33.5	-10.3	-78.9	60.5	+15.3	+3.0
17	91-9	22/02	548514	5430079	28.0	-10.9	-81.3	73.4	+12.9	+5.3
18	91-10	22/02	548514	5430076	13.5	-10.7	-78.2	118.0	+12.9	+2.0
19	91-13	22/02	542035	5428064	20.8	-10.7	-79.9	92.9	+11.2	+0.8
	91-14	22/02	542035	5428064	4.8	-10.6	-78.4	88.6	+9.2	+1.5
20	91-15	22/02	542035	5428061	11.4	-10.7	-79.9	80.4	+11.4	+2.1
21	91-16	22/02	546882	5428067	14.4	-11.0	-82.1	42.0	+4.5	-
22	BC-A-25	22/02	546075	5429250	7.6	-11.1	-81.4	19.6	+8.8	+4.3
	BC-A-35	22/02	546075	5429250	10.7	-10.9	-80.8	13.3	+6.2	+2.7
	BC-A-55	22/02	546075	5429250	16.8	-11.3	-83.2	19.2	+7.6	-
	BC-A-75	22/02	546075	5429250	22.9	-11.3	-84.5	26.0	+7.5	-
23	BC-B-20	22/02	546075	5428500	6.1	-10.2	-77.5	62.8	+8.8	+3.3
	BC-B-35	22/02	546075	5428500	10.7	-10.8	-80.9	74.1	+10.8	+2.7
	BC-B-55	22/02	546075	5428500	16.8	-11.1	-83.8	50.3	+11.1	+3.8
	BC-B-75	22/02	546075	5428500	22.9	-11.4	-81.6	15.1	+18.2	+5.9
24	BC-C-25	22/02	545251	5428500	7.6	-11.0	-85.5	36.9	+6.1	+8.0
	BC-C-35	22/02	545251	5428500	10.7	-10.7	-81.1	67.6	+8.4	+2.9
	BC-C-55	22/02	545251	5428500	16.8	-11.3	-84.4	33.4	+10.7	+0.9
	BC-C-75	22/02	545251	5428500	22.9	-11.4	-85.2	12.1	+19.6	+7.7
25	FT1-8	22/02	543477	5427693	2.4	-10.4	-75.4	0.0	-	-
	FT1-24	22/02	543477	5427693	7.3	-10.9	-79.5	0.0	-	-
	FT1-40	22/02	543477	5427693	12.2	-11.1	-75.4	0.0	-	-
26	FT2-9.9	22/02	543469	5428073	3.0	-10.8	-77.7	0.0	-	-
	FT2-21	22/02	543469	5428073	6.4	-11.3	-82.0	0.0	-	-
	FT2-31	22/02	543469	5428073	9.4	-11.4	-82.9	0.0	-	-
27	FT3-26	22/02	543552	5428412	7.9	-11.0	-80.5	0.0	-	-
	FT3-38	22/02	543552	5428412	11.6	-10.9	-80.2	1.3	-	-
28	FT4-12	22/02	543580	5428636	3.7	-10.4	-78.0	49.3	+2.8	+3.9
	FT4-25	22/02	543580	5428636	7.6	-10.8	-78.6	43.2	+3.9	+1.7

	FT4-40	22/02	543580	5428636	12.2	-11.1	-80.7	0.0	-	-
29	FT5-12	22/02	543642	5429055	3.7	-10.5	-76.2	95.7	+10.6	+2.4
	FT5-25	22/02	543642	5429055	7.6	-11.0	-80.1	65.9	-	-
	FT5-40	22/02	543642	5429055	12.2	-11.3	-82.6	0.0	-	-
30	FT6-26	22/02	543527	5428414	7.9	-11.2	-83.6	0.0	-	-
	FT6-38	22/02	543527	5428414	11.6	-11.5	-84.4	0.0	-	-
	FT6-59	22/02	543527	5428414	18.0	-11.3	-84.3	0.0	-	-
31	FT7-22	22/02	543888	5427700	6.7	-10.8	-77.3	0.0	-	-
	FT7-32	22/02	543888	5427700	9.8	-10.8	-80.5	0.0	-	-
	FT7-56	22/02	543888	5427700	17.1	-11.4	-82.6	0.0	-	-
32	FT8-12	22/02	542936	5427693	3.7	-	-	107.0	+11.7	+4.5
	FT8-39	22/02	542936	5427693	11.9	-11.0	-80.0	92.4	+2.0	+8.7
	FT8-59	22/02	542936	5427693	18.0	-11.9	-87.0	45.9	+6.8	+3.0
	FT8-79	22/02	542936	5427693	24.1	-11.5	-83.0	0.0	-	-
22	BC-A-25	25/08	546075	5429250	7.6	-11.3	-83.3	17.3	+6.0	-
	BC-A-35	25/08	546075	5429250	10.7	-11.4	-81.8	20.9	+5.3	+3.0
	BC-A-55	25/08	546075	5429250	16.8	-11.5	-81.2	20.3	+6.8	+1.6
	BC-A-75	25/08	546075	5429250	22.9	-11.6	-82.6	27.8	+22.2	+5.0
23	BC-B-20	25/08	546075	5428500	6.1	-11.1	-79.4	59.1	+9.4	+3.5
	BC-B-35	25/08	546075	5428500	10.7	-11.0	-78.1	85.4	+10.0	+2.1
	BC-B-55	25/08	546075	5428500	16.8	-11.3	-81.1	52.5	+11.3	+1.1
	BC-B-75	25/08	546075	5428500	22.9	-11.4	-85.8	14.1	+19.4	+6.6
24	BC-C-25	25/08	545251	5428500	7.6	-11.1		40.2	+4.0	+4.0
	BC-C-35	25/08	545251	5428500	10.7	-11.1	-80.7	58.9	+7.5	+4.4
	BC-C-55	25/08	545251	5428500	16.8	-11.2	-84.3	35.0	+9.7	+2.2
32	FT8-39	25/08	542936	5427693	11.9	-10.9	-86.4	93.2	+7.0	+1.8
	FT8-59	25/08	542936	5427693	18.0	-11.7	-85.2	52.2	+6.5	+4.6

Domestic /
Municipal Wells

33	77	23/08	553100	5430300	18.3	-11.2		21.5	+8.7	+1.7
34	78	23/08	553000	5428400	44.2	-11.8	-82.6	19.0	+10.0	-
35	79	23/08	553000	5428500	47.2	-11.3	-85.0	24.3	-	-
36	80	23/08	552700	5428300	40.5	-11.5	-81.5	24.0	+13.4	+9.4
37	90	23/08	546800	5430900	26.7	-11.5	-82.1	38.9	+10.4	+2.6
38	91	23/08	546900	5430600	18.8	-11.0		69.8	+12.0	+2.7
39	226	23/08	547900	5430100	19.8	-10.7	-87.2	48.9	+16.0	+3.6
40	228	23/08	549300	5427800	39.9	-10.8	-78.7	60.5	+13.6	+4.7
41	231	23/08	546900	5429300	11.6	-11.2		14.4	+7.2	+2.5
42	232	23/08	546300	5432000	13.7	-11.2	-79.6	18.8	+11.1	+3.5
43	233	23/08	546800	5431600	25.6	-11.0	-81.0	13.7	+5.6	+3.3
44	234	23/08	545400	5427800	13.1	-11.2	-81.5	60.0	+11.8	+1.5
45	235	23/08	544200	5429600	7.6	-11.4	-78.1	74.0	+15.3	+2.9
46	237	23/08	548500	5428600	16.0	-10.9	-81.9	97.7	+12.7	+2.8
47	238	23/08	548000	5429300	31.1	-11.3	-80.0	53.7	+7.3	+1.9
48	239	23/08	543400	5427600	8.7	-11.4	-88.5	-	-	-
49	240	23/08	547300	5429200	18.6	-11.3	-82.2	16.7	+5.6	+2.0
50	241	23/08	551600	5428100	17.7	-11.6	-	38.1	+11.0	+2.0
51	243	23/08	542100	5428500	4.6	-10.9	-77.7	151.0	+14.4	+0.9
52	244	23/08	543800	5430400	33.5	-11.2	-78.7	40.5	+9.6	+7.3
53	245	23/08	545500	5431500	10.7	-11.6	-80.7	66.2	+9.9	+2.6
54	246	23/08	541400	5427700	14.6	-10.5	-81.2	38.8	+6.4	+5.6
55	247	23/08	544600	5431600	10.8	-11.2	-80.5	40.7	+10.9	-
56	248	23/08	543700	5431700	50.6	-11.8	-90.5	32.6	+2.1	+2.1
57	249	23/08	544100	5430500	18.0	-12.6	-93.5	100.0	+13.1	-

58	250	23/08	541600	5430900	29.0	-11.3	-78.7	34.8	+15.3	+2.4
59	252	23/08	550200	5430000	49.7	-11.3	-80.6	48.0	+11.3	+1.8
60	253	23/08	550900	5428500		-11.4	-82.2	96.6	+11.8	+2.0
61	254	23/08	547500	5430100	30.2	-10.6	.-	50.0	+17.0	+3.7
62	255	23/08	550100	5431000	26.8	-11.1	-79.7	100.0	+12.5	+1.6
63	Sumas #4	24/08	552092	5427637	21.0	-11.4	-93.8	26.4	-	-
64	May Rd. #3	24/08	551147	5427039	21.9	-11.2	-83.7	60.3	+10.3	+2.4
65	Holmquist	24/08	547422	5427161	11.3	-10.7	-78.1	118.0	+16.0	+2.1
66	Jahns	24/08	548986	5427297	24.4	-10.3	-83.6	29.9	+2.9	+3.8
67	Honcoop	24/08	543572	5426540	8.8	-10.9	-83.1	51.9	+3.9	+2.2
68	Assink	24/08	540232	5427038	7.6	-10.5	-74.6	119.0	+15.9	+4.5
69	Helgath	24/08	542638	5423265	8.8	-10.9	-82.9	49.1	+2.5	+2.0
70	Gilmore	24/08	544321	5424267	11.0	-11.1	-78.6	45.7	+7.1	+1.9
71	Gilmore #2	24/08	544402	5424268	13.4	-11.0	-80.4	52.1	+7.4	+2.3
72	Covenant	24/08	543546	5424195	9.1	-10.8		61.6	+6.0	+2.0
73	Coon	24/08	545029	5427330	7.6	-10.9	-78.5	83.9	+11.8	+3.0
74	Heeringa	24/08	539378	5424752	6.4	-10.3	-74.7	54.8	+8.7	+4.7
75	McAbee	24/08	549714	5425302	8.5	-10.9	-79.5	38.0	+6.4	+2.6

Surface Waters

76	Gravel Pit	22/02			-	-10.3		55.8	+16.0	+5.9
77	Fishtrap Creek	22/02			-	-10.8		22.5	+13.2	+6.3

Table 2. Enriched tritium data from
multilevel piezometers in Abbotsford
aquifer, August 1993.

Well #	Depth (m)	Tritium (TU)
22	8.3	dry
	11.7	4.3
	18.3	4.7
	25.0	10.7
23	6.7	4.3
	11.7	4.7
	18.3	5.3
24	8.3	3.1
	11.7	3.1
	18.3	7.7
	25.0	11.3

Table 3. $\delta^{15}N$ isotopic composition of representative nitrate source materials in Abbotsford area.

Sample	Composition	$\delta^{15}N$ (AIR)
Manure		
Turkey manure	total organic	+8.6
Poultry manure	total organic	+8.1
Poultry manure	total organic	+7.9
Inorganic Fertilizers		
Berry Mix 1		
white	urea	-0.6
green	ammonium sulfate, ammonium phosphate	-0.9
Berry Mix 2		
white	urea	-0.8
green	ammonium sulfate, ammonium phosphate	-0.7
Berry Mix 3		
white	urea	-0.8
green	ammonium sulfate, ammonium phosphate	-1.0
Berry Mix 4		
white	urea	-0.4
green	ammonium sulfate, ammonium phosphate	-1.5

Table 4. $\delta^{15}N$ of shallow soil samples from representative poultry stockpile sites and uncontaminated sites in Abbotsford area.

Soil Sample	Depth/Horizon	$\delta^{15}N$ (AIR)	Comment
A	0-15 cm	+12.2	Beneath poultry manure stockpile
	15-30	+13.6	
B	0-15 cm	+3.9	Beneath poultry manure stockpile
	15-30	+7.4	
C	0-15 cm	+12.1	Beneath turkey manure stockpile
	15-30	+8.4	
D	Ap	+4.9	Non-contaminated soil
	B	+3.9	
E	Ap	+4.5	Non-contaminated soil
	B	+4.8	
F	Ap	+3.7	Non-contaminated soil
	B	+4.4	

Table 5. Concentration of nitrate, nitrite, chloride, sulfate, and $\delta^{15}N$ and $\delta^{18}O$ of nitrate from soil and unsaturated zone samples above Abbotsford aquifer. Ion concentrations are in mg/L in porewater. Calculated from soil extracts and assuming a soil density of 2.7 g/cm^3, 30% porosity, and a soil moisture content of 10%.

Soil/Site	Depth (cm)	NO$_3$	NO$_2$	Cl	SO$_4$	$\delta^{15}N$	$\delta^{18}O$
A - Manure	0-15	18,648	270	1531	1171	-	+5.7
Stockpile	15-30	3,423	<	90	360	+14.0	+2.9
B - Manure	0-15	5,405	3,603	2,162	1,081	+16.4	+4.8
Stockpile	15-75	1.981	90	180	180	+15.2	+4.7
32 - Raspberry	0-15	13,963	<	2,225	630	+9.2	+2.2
Field	15-75	6,036	<	270	811	+12.4	+2.8
18 - Raspberry	0-40	630	<	<	360	-	-
Field	100-150	360	<	<	270	-	-