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ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · AUGUST 2006

Impact Factor: 5.33 · DOI: 10.1021/es060724w · Source: PubMed

3 AUTHORS:


Leonard I. Wassenaar
International Atomic Energy Agency (IAEA)


M. Jim Hendry
University of Saskatchewan


Nikki Harrington
Flinders University

Decadal Geochemical and Isotopic Trends for Nitrate in a Transboundary Aquifer and Implications for Agricultural Beneficial Management Practices

LEONARD I. WASSENAAR,*,† M. JIM HENDRY,‡ AND NIKKI HARRINGTON§

Environment Canada, 11 Innovation Boulevard, Saskatoon, Saskatchewan, Canada, S7N 3H5, Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, S7N 5E2, and Department of Water, Land, and Biodiversity Conservation, 11 Helen Street, P.O. Box 1246, Mount Gambier, South Australia 5290, Australia

Nitrate contamination of aquifers is a global agricultural problem. Agricultural beneficial management practices (BMPs) are often promoted as a means to reduce nitrate contamination in aquifers through producer optimized management of inorganic fertilizer and animal manure inputs. In this study, decadal trends (1991−2004) in nitrate concentrations in conjunction with $^3H/^3He$ groundwater ages and nitrate stable isotopes ($\delta^{15}N$, $\delta^{18}O$) were examined to determine whether BMPs aimed at reducing aquifer-scale nitrate contamination in the transboundary Abbotsford-Sumas aquifer were effective. A general trend of increasing nitrate concentrations in young groundwater (<∼5 yr) suggested that voluntary BMPs were not having a positive impact in achieving groundwater quality targets. While the stable isotope data showed that animal manure was and still is the prevalent source of nitrate in the aquifer, a recent decrease in $\delta^{15}N$ in nitrate suggests a BMP driven shift away from animal wastes toward inorganic fertilizers. The coupling of long-term monitoring of nitrate concentrations, nitrate isotopes, and $^3H/^3He$ age dating proved to be invaluable, and they should be considered in future assessments of the impact of BMPs on nutrients in groundwaters. The findings reveal that BMPs should be better linked to groundwater nutrient monitoring programs in order to more quickly identify BMP deficiencies, and to dynamically adjust nutrient loadings to help achieve water quality objectives.

Introduction

Groundwater contamination stemming from longstanding agricultural practices is a global problem with adverse economic and health effects (*1*). Of all agricultural contaminants, nitrate (NO_3^-) is the most widespread in exceeding national drinking water standards in groundwater (*2*, *3*). In agricultural areas of North America, for example, between 5 and 46% of domestic water wells exceed the 45 mg/L (as NO_3^-) drinking water quality standard (*3*, *4*). Generally, nitrate in aquifers originates from long-term or historical point (waste lagoons and storage) and nonpoint (fertilizers, manure spreading) nutrient sources associated with agricultural practices. The origin, fate, and transport of nitrate in groundwater has been extensively studied over the past decades (*2*−*6*).

In response to nitrate contamination of aquifers, agricultural nutrient management programs have been increasingly implemented since the 1990s with the goal to reduce the environmental impact of agricultural nutrients on ground and surface water quality. These programs, termed agricultural beneficial management practices (BMPs), focus on fine-tuning producer nutrient inputs to meet the minimum crop requirements and prevent nutrient leaching into receiving waters. BMPs generally attempt to strike a balance between (1) optimizing crop nutrient uptake efficiency, (2) eliminating leaching of residual nitrate, and (3) providing agronomic efficiencies as a benefit to producers (*7*, *8*). Increasingly complex theoretical “systems models” are being advanced to help guide agricultural BMP development at watershed and landscape scales (*7*−*9*).

While optimized nutrient management may provide agronomic benefits to producers, there is little documentation in the scientific literature that BMPs have successfully remediated extensive nitrate contamination of aquifers. Of the few studies available, groundwater nitrate concentrations increased or remained constant despite the implementation of BMPs (*10*−*15*), or declined when all fertilizer nitrogen inputs were eliminated and forage was cyclically removed from the landscape (*16*). Thus, the efficacy of BMP approaches to remediate nitrate contaminated aquifers remains to be demonstrated. Further, BMP implementation needs to be quantified and periodically field tested to determine whether long-term nutrient reductions in critical areas of the receiving environment have occurred. This knowledge is required to forecast when pollution abatement in groundwater may be expected to occur, and to adaptively adjust BMPs and related monitoring strategies to help achieve water quality objectives in a reasonable time frame.

Ideally, to assess whether BMPs are successful in reducing nitrate contamination in an aquifer, the aquifer should be regional in extent (as opposed to conducting plot scale leaching studies) and BMPs aimed at reducing groundwater nitrate contamination should have been in place for several years prior to the evaluation. Furthermore, long-term and frequent monitoring of groundwater quality, both before and after the implementation of BMPs, should be available. Few groundwater systems in the world are suited to studying the long-term impact of BMPs on improving groundwater quality, mainly due to incomplete or short-term monitoring records. The Abbotsford-Sumas aquifer, located in the Fraser Lowlands of British Columbia (Canada) and Washington State (USA), meets these evaluation criteria.

The Abbotsford-Sumas aquifer is a highly permeable sand and gravel aquifer that serves as a major water supply for over 100 000 people in Southwestern B.C, Canada, and Washington State, U.S.A. (see Supporting Information). Since water quality monitoring began in the early 1970s, otherwise excellent water quality has been extensively degraded with nitrate. Currently, nitrate contamination is widespread in the aquifer, with concentrations in many wells exceeding drinking water standards (*6*, *17*−*20*). As a result, nitrate contamination in this aquifer remains a long-term international transboundary water quality concern in B.C. and

* Corresponding author phone: (306) 975-5747; e-mail: len.wassenaar@ec.gc.ca.
† Environment Canada.
‡ University of Saskatchewan.
§ Department of Water, Land, and Biodiversity Conservation.

10.1021/es060724w CCC: $33.50
Published on Web 06/30/2006

Washington State decades after extensive nitrate contamination was first identified.

On both sides of the Canada−U.S.A. border, agricultural land use is dominated by raspberry fields (~80% of land use), intensive poultry operations, and dairy farms (*17*). Previous investigations revealed that nitrate contamination in the aquifer derives from decades of poor agricultural practices such as roadside and uncovered animal manure stockpiling, and over-fertilization of raspberry fields with manure (*6, 21*). A nitrogen budget in the 1990s (*21*) estimated that a 7-fold excess of N was routinely applied to raspberry fields in the form of animal manure and fertilizers, with leaching of residual soil nitrates into the aquifer during fall and winter rains. Furthermore, nitrates entering the Abbotsford-Sumas aquifer undergo little biogeochemical transformation because the aquifer has almost no intrinsic capacity to support geomicrobial denitrification (*6, 22*). Thus, remedial action plans for this aquifer required major changes to historically acceptable land use practices; changes aimed at greatly reducing or eliminating the excess nitrogen leaching to the groundwater.

In 1992, the government of British Columbia legislated a regulatory Code of Agricultural Practice for Waste Management (*23*) aimed at preventing the leaching of nitrates into surface and groundwaters. This regulatory code required that animal waste be stored in contained facilities, onsite waste storage be less than two weeks, and outside waste storage be covered during the October−March rains to prevent nitrate leaching, producer applications of manure and fertilizers be optimized to closely meet crop requirements, and that agricultural practices not cause contamination of receiving waters. To promote this regulatory objective, a number of stewardship programs were established over the past decade to encourage adoption of BMPs (e.g., B.C. Environmental Farm Plan Program). Key BMPs include the voluntary Abbotsford Aquifer Groundwater Protection Program begun in the 1990s by local poultry producers to develop alternate markets for manure that was traditionally disposed of on the ground surface. Similarly, the raspberry industry implemented a BMP approach to reduce residual fertilizer and waste nitrate leaching into the aquifer during late summer by planting between-row cover crops, switching from manure to inorganic fertilizers, and by crop diversification to blueberries because of their lower nutrient requirements.

Despite a decade of stewardship programs and various voluntary BMPs, a 2005 B.C. government regulatory compliance report (*24*) revealed that 76% of farms operating on top of the Abbotsford-Sumas aquifer still do not have a nutrient management plan. Most of the concerns identified in the report were related to the key contributors of groundwater nitrate contamination; the improper storage and inappropriate spreading of solid and liquid animal manure. Of all commercial operations, 86% were in compliance, compared to 50% compliance for hobby farms. The relative contribution of either type of operation to nitrate leaching into the aquifer remains unknown.

In this study aquifer nitrate contamination was examined by interpreting trends and changes in sources of nitrate in the Abbotsford-Sumas aquifer after a decade of voluntary BMP efforts (1993−2004). Very few studies have examined the long-term (decadal) impact of BMPs to improve groundwater quality at the scale of an aquifer. Geochemical and isotopic techniques were employed to examine current sources of nitrate in the aquifer, comparative and long-term nitrate trends, and to establish the age of the groundwater associated with nitrate contamination. The sample collection methods for geochemical, isotopic, and noble gas assays are fully described in the Supporting Information. The geochemical and isotopic data collected were compared with the data set collected from the same wells in 1993 (*6*). Results of this study should provide information to resource managers to help focus efforts in promoting adoption of BMPs, and to target adoption of management strategies most likely to result in remediation of groundwater. The approach used in this investigation−the coupling of geochemistry, monitoring data, stable isotopes, and $^{3}H/^{3}He$ age dating−provides unique insight into the issue of nitrate contamination trends and should be considered in future aquifer BMP assessments.

Results and Discussion

Changes in Nitrate Concentrations between 1993 and 2004. As a first step to examine temporal changes, the nitrate concentration data were compared from wells sampled in 1993 (*6*) and 2004 (Table S-1). Overall, of 31 monitoring wells re-sampled, 64% showed an increase in nitrate concentrations between 1993 and 2004. The increase in concentration ranged from a minimum of 0.4 mg NO_3/L to a maximum of 67 mg NO_3/L. The average increase in nitrate concentration was 28 mg NO_3/L for research monitoring wells. Of the monitoring wells that showed a decrease in nitrate levels (36%), the decrease ranged from a minimum of 0.3 mg NO_3/L to a maximum of 41 mg NO_3/L. Overall, nitrate concentrations in the monitoring wells increased by an average of 14 mg NO_3/L over the decade.

In contrast to data from monitoring wells, the majority of 25 domestic wells re-sampled (72%; Table S-1) showed a decline in nitrate concentrations over the decade, with individual well decreases ranging from 2.4 to 139 mg NO_3/L. Of seven domestic wells (28%) that showed an increase in nitrate concentration over the decade, increases ranged from 0.4 to 62 mg NO_3/L with an average overall increase of 30 mg NO_3/L. On average, the nitrate concentrations in domestic wells decreased by only 12 mg NO_3/L over the decade. Two local surface water samples from Fishtrap Creek and a local gravel pit showed minor declines in NO_3 over the decade.

For domestic and monitoring wells combined, and when restricted to where there were directly comparative 1993−2004 data (Table S-1), the data yielded an average overall nitrate increase ~3.0 mg NO_3/L in the aquifer. However, this difference in nitrate concentrations between 1993 and 2004 was not significant ($p > 0.1$, $n = 56$, paired Student's t-test). When additional groundwater monitoring wells installed since 1993 were included, and where there were no directly comparative well data, the average nitrate levels in the aquifer were 60 mg NO_3/L and 54 mg NO_3/L in 2004 and 1993, respectively. This represents an average, but statistically insignificant, increase of ~6 mg NO_3/L over the decade. The average nitrate concentrations for both 2004 and 1993 exceed Canadian and U.S. drinking water guidelines by more than 15%.

The percentage of domestic and monitoring wells that exceeded nitrate drinking water standards was 59% in 2004, unchanged from 58% in 1993. The maximum single well drinking water standard exceedance was by a factor of 6.4 (285 mg/L NO_3; monitoring well US4) in 2004. In 2004, no statistically significant trends in NO_3 concentration in the aquifer with well depth were observed, as in 1993. Nitrate concentrations were spatially variable across the aquifer in both 1993 and 2004. This was attributed to rapid groundwater flow and spatially varying nitrate inputs across the landscape and vadose zone.

Changes in the δ^{15}N of Nitrate from 1993 to 2004. It was previously shown, using stable isotopes, that the majority of nitrate in the aquifer in 1993 could be attributed to animal manure sources (*6*). The δ^{15}N of nitrate derived solely from locally used NH_4-based inorganic fertilizers should range between about 0 and −2 ‰ (*6*). The δ^{15}N of nitrate derived from animal wastes in the Abbotsford area, however, should be +8 ‰ or higher(*6*), and from other studies of nitrate derived from animal wastes, could vary between +8 and +16

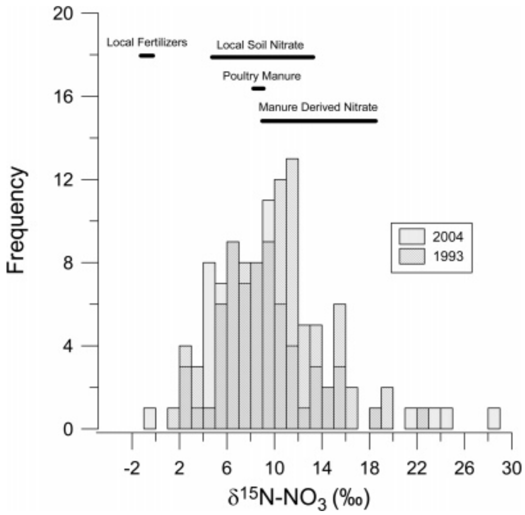

FIGURE 1. Comparative frequency histogram of δ^{15}N (‰) for nitrate samples from the Abbotsford-Sumas aquifer in 2004 and 1993. Nitrate source ranges and that of nitrate in soil leachate are given by the bars at the top of the graph.

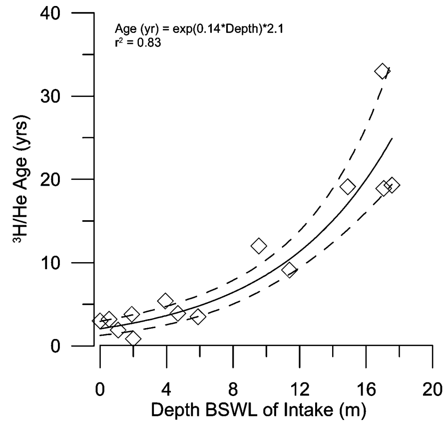

FIGURE 2. ^{3}H−^{3}He groundwater ages in the Abbotsford-Sumas aquifer from selected monitoring wells. Ages are reported in Table S-1. BSWL is sample depth below static water level in meters. Dashed lines are 95% CI of the fit.

‰ due to ammonia volatilization during storage and transformation in soils (*25−27*).

Histograms comparing nitrate δ^{15}N in the aquifer in 2004 and 1993 are presented in Figure 1, and data are reported in Table S-1. The mean (±SD) δ^{15}N in the aquifer was +10.1 ± 9.0 ‰ ($n = 70$) and +10.2 ± 4.0 ‰ ($n = 56$) in 2004 and 1993, respectively, suggesting little, if any, change in the prevailing nitrogen source(s) of nitrate contamination in the aquifer. Where well data was directly comparable, a Student's t-test showed no significant difference in the mean δ^{15}N between 1993 and 2004 ($p > 0.1$, $n = 53$). The 2004 δ^{15}N data supported the 1993 interpretation (*6*) that animal manure (δ^{15}N > +8 ‰) was and still is the prevailing source of nitrate in the aquifer (Figure 1). Ammonium-based or nitrate inorganic fertilizers do not appear to be a major contributor to extensive nitrate contamination (but see below), although the δ^{15}N values between +2 and +8 ‰ found in soil leachate extracts suggested a mixture of manure and fertilizer NO_3^-. As in 1993, no significant correlation between δ^{15}N and nitrate or between δ^{15}N and depth was found in the aquifer.

Establishing Groundwater Ages. Although the nitrate and its δ^{15}N values suggest that sources of contamination have not changed significantly over the past decade, the lack of water quality improvements cannot be interpreted as a failure of the BMPs without knowing the residence time of groundwater associated with nitrate. It is possible that many wells contain nitrate that entered the groundwater system long before BMPs were initiated, and hence could result in misleading conclusions about the success or failure of voluntary BMPs.

To resolve this, ^{3}H/^{3}He analyses were used to precisely age-date groundwater samples from 18 research and monitoring piezometers installed in the aquifer (Table S-1). The ^{3}H/^{3}He age dating method was chosen because of its ability to accurately (±0.5 y) age water that has entered aquifers within the past 40 years (*28*). These assays allowed the nitrate trends and isotopic assessments to be bracketed to those times before and after the voluntary BMPs were introduced. The ^{3}H/^{3}He age dating technique does not account for the residence time of water in the unsaturated zone, which owing to relatively shallow water tables and high rates of recharge, is believed to be less than 2−3 years (*18, 29*). Groundwater ages in the aquifer ranged from 0.9 to 33 years old. A cross-plot of ^{3}H-^{3}He groundwater age versus depth of the well intake zone below static water level in the well is shown in Figure 2. These data show an exponential increase in groundwater age with depth below static water level ($r^2 = 0.83$), indicating that deep groundwater experiences significantly longer flow paths than shallow groundwater. This observation is in keeping with hydrological information that groundwater flow in the aquifer is strongly dominated by lateral flow in a north to southwardly direction (*17*), and improves on previous assessments of groundwater ages in this aquifer (*22*).

If voluntary BMPs introduced over the past decade were working as anticipated, there should be a measurable positive impact (i.e., reduced nitrate concentrations) in wells where the groundwater is, at most, 5 years old, allowing for 2−3 years of travel time through a variable thickness unsaturated zone. Detection of water quality improvements resulting from BMPs was not expected in groundwater that is a decade or older, other than by changes in naturally occurring intrinsic biogeochemical processes such as in situ denitrification.

Nitrate and δ^{15}N Trends with Groundwater Age. Long-term trends in monthly nitrate concentrations were examined on two groups of research piezometers: (1) those with groundwater ages determined using ^{3}H/^{3}He to be older than 10 years ($n = 3$; 22 (deep), 81, 82 (deep) see Supporting Information), and (2) those piezometers with groundwater ages that were less than about 5 years old ($n = 3$; 2, 5, 82 (shallow)). For wells with groundwater ages less than 5 years old, the assessment was again split by (1) using all of the available monthly long-term nitrate monitoring data collected by Environment Canada between 1991 and 2004, and (2) by bracketing nitrate trends in groundwater since September 1999, a time frame where the BMPs could reasonably be expected to have shown a positive impact.

For monitoring wells where groundwater ages were determined using ^{3}H/^{3}He to be older than 10 years old, and where the impact of BMPs was not expected to occur, a Mann−Kendall nonparametric test for detection of trends in a time series (*30, 31*) exhibited no significant trends upward or downward in nitrate concentrations over the past decade ($p > 0.1$). Similarly, a least squares regression showed no significant temporal linear trend ($r^2 < 0.001$, Figure 3). For monitoring wells where groundwater was under 5 years old, the Mann−Kendall test on monthly nitrate data from 1991 to 2004 showed no trend in nitrate concentrations over the decade ($p > 0.5$). Similarly, a least squares regression suggested no significant linear temporal trend ($r^2 < 0.02$). However, when these same wells were bracketed for concentration trends since September 1999, the Mann−Kendall test showed a small but significant increase in nitrate concentrations over the past 5 years ($p < 0.05$), an upward trend that is supported by the least squares linear regression (presented graphically in Figure 3; $r^2 = 0.2$). When these same

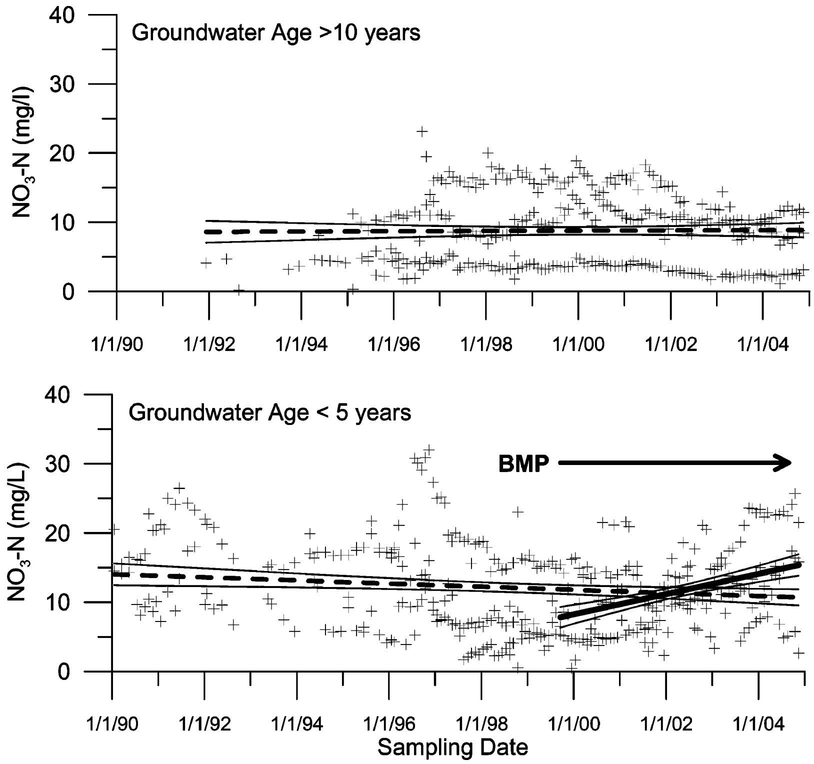

FIGURE 3. Long-term time series for nitrate from selected monitoring wells where ^3H-^3He groundwater ages were determined. Upper panel is >10 year old groundwater. The lower panel is <5 year old groundwater. BMP trend is for samples constrained from September 1999 to September 2004. Dashed and solid lines denote least squares regression and 95% CI of the fit.

data sets were examined for seasonal bias using the Mann–Kendall test for seasonality, the trend of increasing nitrate over the past 5 years was strongly weighted to those groundwater samples collected during the months of September–December, and to a lesser extent, the growing season months. This finding supports the observation that heavy fall and winter rains likely cause rapid leaching of nitrate into the aquifer.

From the $^3H/^3He$ data presented in Figure 2, and if BMPs were collectively having a positive effect on groundwater quality, a reduction of nitrate levels was expected to be evident in monitoring wells with intake zones ≤4 m below the water table. Unfortunately, other than those wells examined above, no long-term nitrate time-series data were available for observation or domestic wells in the aquifer that met this criterion. Nevertheless, these findings suggest that assessing the impact of BMPs in this aquifer could be greatly improved by expanding the current groundwater quality monitoring network to include a wider range of monitoring wells with intake zones ≤4 m below ground surface.

If the past five years represent a reasonable time frame where improvements in water quality may be expected following a decade of various BMPs, then the trend of increasing nitrate concentrations in young groundwater indicate BMPs are not having the desired effect. The recent trend of increasing nitrate levels may be interpreted in light of changes in nitrate sources stemming from BMPs. In Figure 4, young groundwater nitrate $\delta^{15}N$ data from 2004 and 1993 are plotted along with the isotopic composition of local nitrogen sources of animal waste and fertilizers reported by others (*6*). Of eight monitoring wells that met the young groundwater age criteria, five showed an increase in nitrate concentrations along with a corresponding decrease in the $\delta^{15}N$ values, suggesting that a decadal change in nitrate concentration corresponds with a source shift away from animal wastes toward inorganic fertilizers. Well BC-A-25 showed no decrease in nitrate, but a decrease in $\delta^{15}N$,

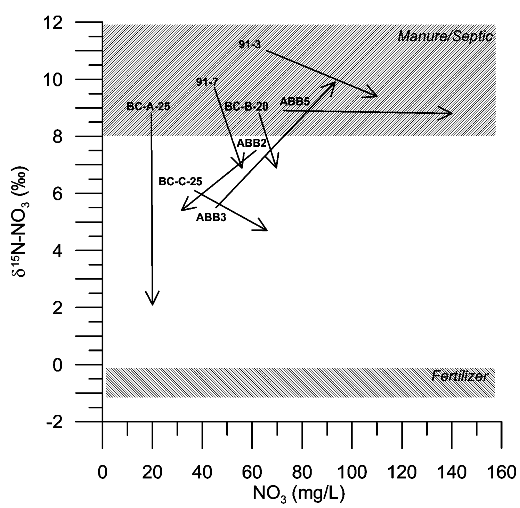

FIGURE 4. Comparative nitrate and $\delta^{15}N$ trends between 1993 and 2004 for shallow monitoring wells (<5 m depth) and whose groundwater ages were determined to be <5 years old using ^3H-^3He, in relation to $\delta^{15}N$ range for local nitrogen sources. Wells are listed in Table S-1. Start of arrow is 1993 and end is 2004.

suggesting a shift from animal waste toward inorganic fertilizer nitrate sources. One well (ABB3) exhibited an increase in nitrate with a large positive change in $\delta^{15}N$, suggesting this well had a comparative shift toward a greater animal waste nutrient source.

The observed nitrate source shift between 1993 and 2004 was unexpected, as adoption of various BMPs was anticipated to result in an overall decrease in nitrate flux to the aquifer. However, the past decade has seen a BMP driven shift away from the use of animal manure as fertilizer on the land surface toward managed and plant optimized nutrient applications through the use of inorganic fertilizers (*23*, *32*, *33*). Over the same time frame, poultry and manure production in the area

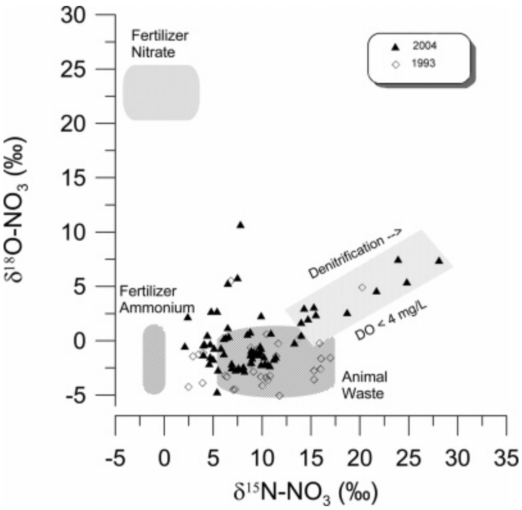

FIGURE 5. Comparative cross plot (1993−2004) of $\delta^{18}O$ versus $\delta^{15}N$ l nitrate in the aquifer, and plotted with respect to range for local nitrogen sources. Trend for denitrification (dotted) is limited to those samples with dissolved oxygen <2 mg/L.

has increased by 50%, indicating that the observed relative reduction in manure-derived nitrate to recent groundwater was likely achieved through improved animal waste management and removal practices. Studies have shown that inorganic fertilizer application has potential to allow for more rapid leaching of residual soil inorganic nitrogen into groundwater (*34*) since these chemicals do not possess the N cycling and soil conditioning properties of manure. In an earlier study (*6*), it was shown that the $\delta^{15}N$ of nitrate extracted from soils beneath selected raspberry fields in the Abbotsford area were considerably lower than nitrates extracted from soil beneath manure piles. Thus, the 1993−2004 nitrate $\delta^{15}N$ comparisons for young groundwater, though few, suggest that a shift from animal waste disposal and fertilization toward inorganic fertilizer application may be leading to enhanced leaching of excess nitrogen during fall and winter rains.

Dual Nitrate Isotopes: Source Identification and Denitrification. A number of previous investigations used dual-isotopic analyses of nitrate ($\delta^{18}O$, $\delta^{15}N$) to better assess the sources of nitrate in aquifers and to provide an indicator of whether the process of denitrification is occurring (*6*, *25*, *35*−*38*). The $\delta^{18}O$ and $\delta^{15}N$ analyses from the Abbotsford-Sumas aquifer in 2004 and 1993 are plotted in Figure 5 along with nitrate isotope ranges expected for various local nitrogen sources were constructed from data presented in the 1993 study (*6*), but the $\delta^{18}O$ values of the nitrate source components were adjusted to reflect the potential oxygen isotopic variability that was measured in gaseous and dissolved O_2 and water H_2O (*39*).

The majority of the $\delta^{18}O$ values of nitrate were in a relatively narrow range between −5 ‰ and +1.5 ‰. This covers the expected range of values for nitrate derived from nitrification of local inorganic fertilizer and animal manure sources. The cross-plot of nitrate $\delta^{18}O$ versus $\delta^{15}N$ shown in Figure 5 shows that most of the nitrate in the aquifer originated from a mixture of animal waste and ammonium inorganic fertilizer sources. Fewer than 9% of the values were between +1.5 and +12 ‰ for $\delta^{15}N$, and 0 and +5 ‰ for $\delta^{18}O$, a window suggestive of a 3-component mixture of inorganic fertilizer nitrate and ammonium, and animal manure. Although fewer samples were analyzed for dual nitrate isotopes in 1993 ($n = 36$) versus 2004 ($n = 66$), a comparison of these data from 1993 and 2004 revealed a statistically significant shift in $\delta^{15}N$ toward ammonium-based inorganic fertilizers over the decade, as discussed above.

Previous studies (*6*) concluded that geomicrobial denitrification is not a widespread intrinsic remediation process in the Abbotsford-Sumas aquifer. Others found that, while denitrification occurs in the aquifer (*22*), it is spatially restricted to deep, low oxygenated groundwater in the aquifer, or to denitrifying zones around riparian discharge zones. This study reaffirms that denitrification is a spatially insignificant natural remediation process in the aquifer. The 2004 data (Figure 5) support this assertion; only 10 groundwater nitrate samples had $\delta^{15}N$ and $\delta^{18}O$ values that trend in a positive direction signifying the process of denitrification and having the expected slope of about 0.5 (*35*, *40*, *41*). All of these samples were taken from the deepest wells or from riparian zones where dissolved oxygen concentrations were <2 mg/L. Unfortunately, it was not possible to determine or apply known nitrate isotope enrichment factors to the isotope data to quantify the denitrification process, due to the fact samples in this study were not collected along discrete flow paths, and because spatially variable nitrate and source inputs have likely occurred over many years (*42*). The lack of widespread geomicrobial denitrification, however, is clear, and can be attributed to the fact that the aquifer is highly oxygenated and lacks sufficient supplies of electron donors such as dissolved organic carbon (*43*). Overall, dissolved organic carbon levels in the aquifer are less than 0.5 mg/L and, combined with rapid groundwater flow rates, is insufficient both spatially and temporally to facilitate geomicrobial respiration to achieve anaerobic conditions required for subsurface denitrification communities (*43*, *44*). Thus, the dual-isotope nitrate isotope results reaffirm denitrification is a spatially ineffective remediation process in the aquifer, and that the prevailing sources of nitrate in the aquifer are a changing mixture of animal waste and fertilizers.

Previously (*6*), it was noted that domestic septic systems exist above the aquifer. It has since been suggested that rapid urban growth in the Abbotsford area over the past decade could represent an ever increasing source of nitrate to the aquifer. This appears unlikely because human waste and septic sources produce nitrate is isotopically indistinguishable from animal waste (*25*), and the nitrogen isotope data suggest a recent shift toward inorganic fertilizers, not toward animal or human organic wastes. Others have determined by mass-balance calculations that <4% of nitrate in the aquifer could be derived from septic wastes (*18*).

Nitrate Status of the Abbotsford-Sumas Aquifer. Following a decade of various voluntary agricultural BMPs aimed at reducing nitrate contamination in the Abbotsford-Sumas aquifer, the evidence presented here indicates that nitrate contamination levels in the aquifer have not significantly changed. The monitoring data from young groundwaters revealed a trend of increasing nitrate levels over the past 5-year period, corresponding with a $\delta^{15}N$ shift in nitrogen sources away from manure sources toward inorganic mineral fertilizers. Comparative dual-isotope nitrate analyses also reflected this decadal shift in nitrogen sources away from animal manure toward inorganic fertilizers. This $\delta^{15}N$ shift may be attributed to a BMP driven change in practices away from the use of animal manure as fertilizer toward the use of inorganic chemical fertilizers in raspberry production. These findings, along with an apparent increase in nitrate in shallow wells, implies that fertilizer application practices may be resulting in more directly and easily leachable residual inorganic N in the soil. Further, due to the fact that the aquifer sediments are coarse and subjected to strong fall and winter rains, the groundwater is exceptionally vulnerable to the leaching of residual surface-derived inorganic nutrients. It is conceivable that the best managed agricultural BMPs may be largely ineffective at reducing or preventing widespread nitrate contamination in the Abbotsford-Sumas aquifer. Despite the promulgation of voluntary agricultural BMPs and various governmental efforts to encourage their adoption, the findings here present a challenge to current approaches to achieving drinking water quality objectives in this aquifer. Although the immediate impact of wider BMP adoption on nitrate contamination in the aquifer cannot be predicted, and given BMP efforts are not being quantified on the landscape, it appears that current agricultural practices remain largely ineffective at preventing leaching of nitrate into the aquifer.

Observations on the Efficacy of BMPs to Reduce Nitrate Concentrations. The efficacy of BMPs to reduce nitrate contamination at aquifer scales has yet to be widely demonstrated. Ideally, BMPs aimed at reducing nitrate contamination ought to be developed as part of comprehensive agricultural and environmental nutrient utilization and flux monitoring program. BMPs should be quantifiable and co-developed in consort with groundwater quality monitoring programs that include temporal, spatially representative, monitoring of soil and vadose zone residual N levels, concurrently with monitoring of targeted shallow groundwater wells. Deficiencies in BMPs to prevent nutrient leaching through the soil and vadose zone would be more quickly identified, and inputs of agricultural nutrients appropriately adjusted in consultation with local agricultural producers to achieve environmental and agronomic objectives. New technologies such as soil nitrogen inhibitors designed to increase the residence time and uptake of nutrients in the soil zone could be explored in some situations (*45*). However, the potentially high cost of achieving groundwater quality objectives in agricultural landscapes is documented in a BMP modeling study conducted in Europe. There it was determined that drinking water standards in several watersheds could not be achieved through BMPs without a significant *reduction* in agricultural productivity (*7*). Finally, as noted by others (*12*), the commonplace practice of voluntary participation in BMPs may lead to noncompliance issues such as those identified in the Abbotsford-Sumas aquifer (*24*). Noncompliant "offenders" in highly vulnerable settings have the potential to endanger overall environmental and water quality objectives.

Acknowledgments

Environment Canada, Agriculture and Agri-Foods Canada, the Natural Sciences and Engineering Research Council of Canada, and the Canadian Water Network provided funding for this project. Thanks to R. Kirkland, B. Hii, and S. Cox for field and logistical support. We thank K. Solomon for providing tritium−helium age dates.

Supporting Information Available

Full descriptions of the aquifer hydrogeology, materials, and methods, a site map, and a table of data used in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 27, 2006. Revised manuscript received May 18, 2006. Accepted May 29, 2006.

ES060724W