Ground Water Quality

Nitrate Distributions and Source Identification in the Abbotsford–Sumas Aquifer, Northwestern Washington State

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ABSTRACT

The Abbotsford–Sumas Aquifer is a shallow, predominantly unconfined aquifer that spans regions in southwestern British Columbia, Canada and northwestern Washington, USA. The aquifer is prone to nitrate contamination because of extensive regional agricultural practices. A 22-month ground water nitrate assessment was performed in a 10-km^2 study area adjacent to the international boundary in northwestern Washington to examine nitrate concentrations and nitrogen isotope ratios to characterize local source contributions from up-gradient sources in Canada. Nitrate concentrations in excess of 10 mg nitrate as nitrogen per liter (mg N L^{-1}) were observed in ground water from most of the 26 domestic wells sampled in the study area, and in a creek that dissects the study area. The nitrate distribution was characteristic of nonpoint agricultural sources and consistent with the historical documentation of agriculturally related nitrate contamination in many parts of the aquifer. Hydrogeologic information, nitrogen isotope values, and statistical analyses indicated a nitrate concentration stratification in the study area. The highest concentrations (>20 mg N L^{-1}) occurred in shallow regions of the aquifer and were linked to local agricultural practices in northwestern Washington. Nitrate concentrations in excess of 10 mg N L^{-1} deeper in the aquifer (>10 m) were related to agricultural sources in Canada. The identification of two possible sources of ground water nitrate in northwestern Washington adds to the difficulty in assessing and implementing local nutrient management plans for protecting drinking water in the region.

THE ABBOTSFORD–SUMAS AQUIFER lies within the agriculturally productive Fraser–Whatcom lowlands that straddle the U.S.–Canada boundary (Fig. 1). Intensive agricultural practices in the lowlands, combined with high precipitation and well-drained soils, make the unconfined aquifer susceptible to nitrate (NO$_3^-$) contamination (Tesoriero and Voss, 1997). In addition to land use in northwestern Washington, agricultural practices in British Columbia, Canada are affecting water quality in the northwestern Washington area because ground water in the aquifer flows south. Nitrate concentrations exceeding the USEPA maximum contaminant level (MCL) of 10 mg nitrate as nitrogen per liter (mg N L^{-1}) have persisted in ground water and surface water in northwestern Washington, despite the implementation of best management practices (BMPs) over the past

two decades (Wills, 1998). This is problematic because the aquifer serves as a drinking water supply for rural residents and small communities in both the USA and Canada (Hii et al., 1999). In a step to improve water quality, in April 1998 the State of Washington signed into law the Dairy Nutrient Management Act. This law requires all dairy farms to develop and implement a dairy nutrient management plan by December 2003. Since agribusiness is an important economic base in this region, differentiating sources of NO$_3^-$ to the aquifer is essential in the design and management of agricultural loading in northwestern Washington, both from a public health and economic standpoint.

Ground water NO$_3^-$ contamination in shallow unconfined aquifers due to agricultural practices is a worldwide problem. Excess N in the form of NO$_3^-$ accumulates in the soil when land application of animal manures and inorganic, commercial fertilizers exceed the N agronomically required by crops. The mobile NO$_3^-$ ion is easily leached to the ground water during precipitation events and irrigation, especially in areas with well-drained soils and shallow water tables. Numerous studies have documented the extent of the problem and the relationship between agricultural activities and NO$_3^-$ leaching in shallow aquifers (e.g., Power and Schepers, 1989; Spalding and Exner, 1993; Stuart et al., 1994; Puckett et al., 1999; Nolan and Stoner, 2000; Nolan, 2001). Nitrate contamination in the Abbotsford–Sumas Aquifer is unique because it spans extensive agricultural regions in both British Columbia and northwestern Washington, making it difficult to manage.

A section of the Abbotsford–Sumas Aquifer in southern British Columbia, referred to here as the British Columbia study area (Fig. 1), has been the subject of a number of studies in the last two decades because of its high density of agricultural land use. It is called the "raspberry capital of Canada" and also contains a large number of poultry farms and processing plants (Hii et al., 1999). Researchers have reported NO$_3^-$ concentrations in the study area exceeding the 10 mg N L^{-1} MCL (Liebscher et al., 1992; Wassenaar, 1995; Zebarth et al., 1998; Hii et al., 1999). Most recently, Hii et al. (1999) summarized NO$_3^-$ results from piezometers sampled between 1991 and 1997 in the British Columbia study area and documented persistent high concentrations of NO$_3^-$ in both shallow and deep samples in the aquifer. Wassenaar (1995) analyzed N and O isotope data for NO$_3^-$ from 117 ground water samples predominantly

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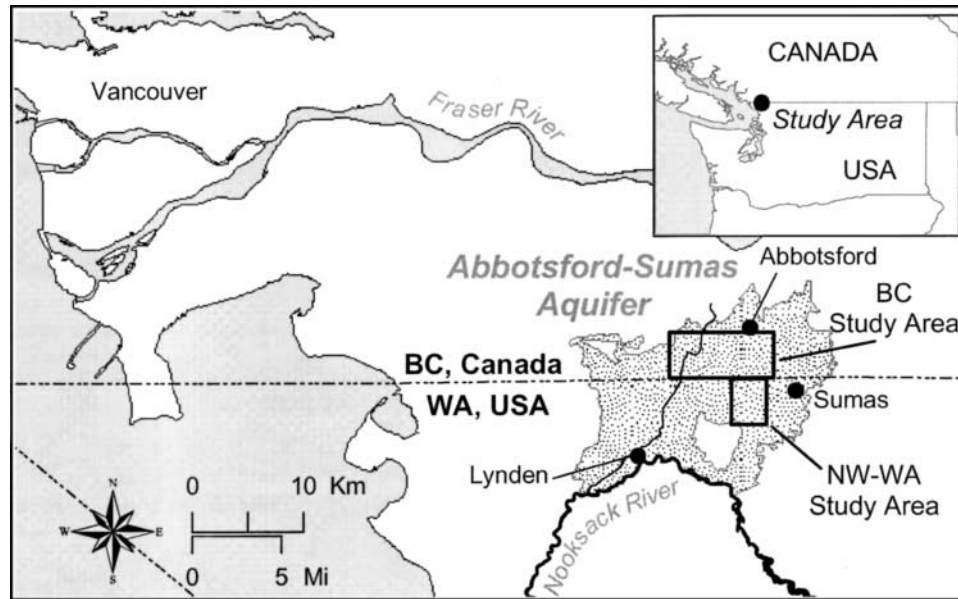**Abbreviations:** DBWT, depth below the water table; MCL, maximum contaminant level.

Fig. 1. Location of the Abbotsford–Sumas Aquifer, the British Columbia (Canada) study area, and the northwestern Washington (USA) study area.

from the British Columbia study area and concluded that the primary British Columbia source for NO_3^- in the aquifer is poultry manure, and to a lesser extent inorganic, commercial fertilizers. Poultry manure was also indicated as the dominant N source to the British Columbia aquifer by Zebarth et al. (1998).

Like the British Columbia study area, agricultural land use in northwestern Washington is also contributing NO_3^- to the aquifer. This region is the largest producer of raspberries (*Rubus* spp.) in the state of Washington and has many dairy farms; therefore, fertilization practices include a mix of inorganic, commercial fertilizers and animal manure (J. Gillies, personal communication, 1998). Nitrate concentrations above the 10 mg N L^{-1} MCL have been reported at a number of locations in the aquifer in northwestern Washington (e.g., Erickson, 1998; Cox and Kahle, 1999). In addition, degraded surface water quality in the region also suggests contamination due to land use (Wills, 1998; Butkus et al., 2000). Because ground water flows south from British Columbia, accurate knowledge of NO_3^- concentrations and source separation in the aquifer is important to manage agronomic loading adequately in northwestern Washington and to protect drinking water in the region. Nitrate concentrations in the northwestern Washington portion of the aquifer have not been comprehensively examined previously to assess this issue.

The objectives of this study were to (i) characterize the extent of ground water NO_3^- contamination in a study area of the Abbotsford–Sumas Aquifer in northwestern Washington, and (ii) distinguish NO_3^- sources originating up-gradient in British Columbia from sources localized in northwestern Washington. These objectives can be achieved by evaluating the horizontal and vertical variability of ground water NO_3^- concentrations and N isotope values in a portion of the aquifer using domestic wells and linking them to land use information. We assume that deep wells in the study area are a proxy

for ground water age and withdraw ground water derived up-gradient in British Columbia. Nitrate data from shallow wells and a surface water stream in the study area will be used as an indicator of localized sources of NO_3^-.

STUDY AREA

Hydrogeologic Setting

The study area encompasses approximately 10 km^2 of the Abbotsford–Sumas Aquifer in northwestern Washington, beginning at the international boundary (Fig. 2). Regionally, the Abbotsford–Sumas Aquifer is predominately unconfined and covers an area of about 200 km^2 (Liebscher et al., 1992). The aquifer is comprised largely of glacial outwash sand and gravel deposits with lenses of sand, silt, and clay deposited during the Sumas stage (11 000–10 000 yr ago) of the Fraser glaciation (Easterbrook and Hansen, 1974). The thickness of the unconfined aquifer is typically about 15 to 25 m, but can range from 5 to 70 m (Cox and Kahle, 1999). Because of the high percentage of sand and gravel, the aquifer has a large capacity to transmit water. Cox and Kahle (1999) used data from 170 completed wells in the aquifer to estimate a mean hydraulic conductivity of 82 m d^{-1} that ranged from 2 to 2380 m d^{-1}. They also estimated a median lateral ground water velocity of 0.75 m d^{-1} and a range from 0.06 to 8.8 m d^{-1}. These ranges of values are consistent with values determined for the British Columbia study area by Liebscher et al. (1992) and Hii et al. (1999), and by Stasney (2000) for our study area. Underlying the Abbotsford–Sumas Aquifer is a confining unit, primarily clay with an unsorted mixture of pebbly silt of glaciomarine origin (13 500–11 000 yr ago). The clay layer is believed to be continuous at depth and is interpreted as Bellingham glaciomarine drift (Easterbrook, 1976) in northwestern Washington and as the Fort Langley Formation (Halstead, 1986) of glaciomarine origin to the north in British Columbia. The dominant soil types in the study area include the Kickerville silt loam (coarse-loamy, isotic, mesic Typic Haplorthod), Jug very gravelly loam (sandy-skeletal, mixed, frigid Andic Haplohumod), and Skipopa silt loam (fine, isotic, mesic Aquandic Haploxer-
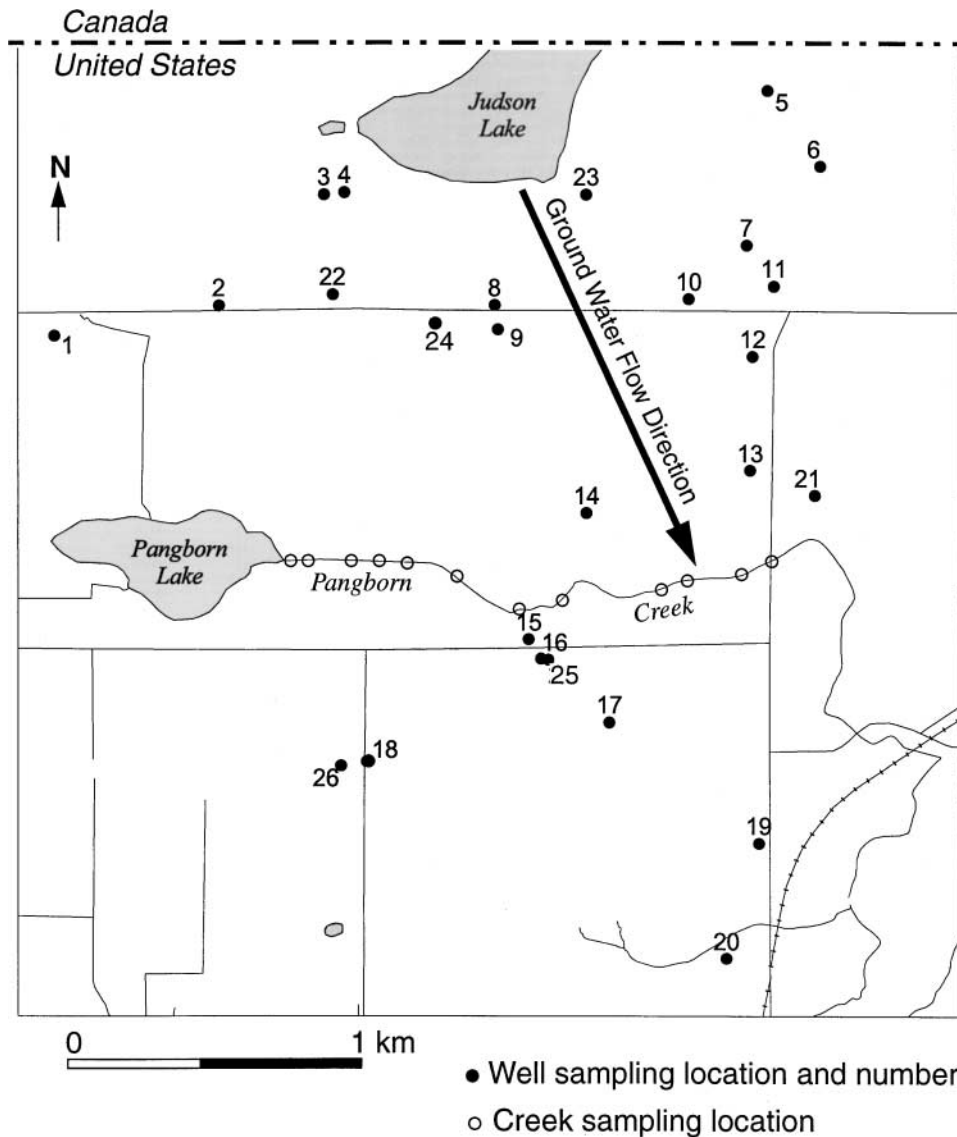
Fig. 2. Detail of the Abbotsford–Sumas Aquifer in northwestern Washington, and domestic well and surface water sampling sites in the northwestern Washington study area.

alf) (USDA, 1992). The soils are thin (0–70 cm) with permeabilities generally greater than typical precipitation rates (Cox and Kahle, 1999). Recharge to the aquifer is primarily by precipitation, of which 70% typically occurs between October and March. Because of the permeable soils and coarse-grained aquifer material, recharge is on the order of 60% of the annual precipitation (Cox and Kahle, 1999). The 30-yr rainfall average at the Clearbook, WA weather station near our study area is 1160 mm, annually. Yearly rainfall for 1997 and 1998 were 1.56 and 1.17 m, respectively (Stasney, 2000). Irrigation is also common in the summer months in many parts of the region and is typically on the order of 0.30 to 0.45 m (J. Gillies, personal communication, 2001). Discharge regions are small creeks, lakes, and streams. Water level measurements indicate that the water-table depth fluctuated from season to season in the study area and showed the largest variations between the spring and fall seasons of 1997–1999 (Stasney, 2000). The largest overall average variation in water table levels was approximately 2 m in the northern half of the study area and 1 m in the southern half.

Land Use

Land use in the study area is dominated by agriculture. In 1998, 57% of the study area was comprised of berry fields, dairies, corn (*Zea mays* L.) fields, and grasslands; raspberries occupied 50% of that area (Nanus, 2000). Most of the raspberry fields are fertilized by inorganic, commercial fertilizers and may require irrigation between bloom and post-harvest (May–August) due to the decreased precipitation during these months (Menzies, 1999). Fields are irrigated by drip tape, which is buried in the soil along the edge of each row of berries, or by overhead sprinkler irrigation systems. Because the study area also has a high concentration of dairy farms, considerable amounts of animal waste are produced. Corn and grasses, grown by dairies for feed purposes, are typically fertilized by spraying liquid manure from dairy lagoons (J. Gillies, personal communication, 1998). Land use north of the study area, in the British Columbia study area (Fig. 1), is dominantly raspberry fields with numerous commercial poultry barns dispersed throughout the region (Zebarth et al.,

1998). The British Columbia region is fertilized primarily by poultry manure (Wassenaar, 1995).

Well Locations

We measured water levels and collected water samples from 26 domestic wells (Fig. 2). The selection of the well locations depended partly on the permission of landowners and wells were chosen to span a distribution along roads in the study area. Most wells were located down-gradient from raspberry fields and dairy operations. Surface locations of wells were established with a global positioning system (±3–5 m) in the field. Elevations of well casings were surveyed to ±0.003 m above mean sea level with a rod and level (Stasney, 2000). Driller-well logs were analyzed to determine the depths and screen interval lengths of the sampling wells.

MATERIALS AND METHODS

Water Level Measurements

The depth to water was measured monthly for 22 months at accessible wells, before any water was removed from the well, with a depth-to-water meter with an electrical sounding tape. The corrected static water level (CSWL) represents the median measured depth to the water table with respect to the ground surface. The CSWL also represents the median vadose zone thickness. The depth below the water table of the sampling location was estimated by subtracting the CSWL from the well depth and represents the approximate depth below the water table (DBWT) from which a sample was collected. Data from well logs and information from a local drilling company (D. Hayes, personal communication, 2002) indicate that the well screen lengths are typically 1.5 m or less. Due to the inability to measure water levels in several wells, the DBWT was estimated for these wells using information from drilling well logs, topographic maps, reported well depths, and static water-level measurements from wells in the general area.

Water Sampling

Twenty domestic wells were sampled monthly between April 1997 and January 1999 to characterize spatial and temporal water quality parameters in the study area (Fig. 2). Six additional domestic wells (Wells 6, 16, 24, 25, and 26; Fig. 2) were sampled intermittently. Sampling of Wells 6 and 24 through 26 depended on permission from landowners, and Well 16 was replaced by deep Well 25 in August of 1998. Water samples were collected consistently from the same location, which was the closest tap to the well. After static water levels were measured, the wells were purged at the standpipe for approximately 10 min, or until the specific conductance stabilized to remove any stagnant water. A 1-L flow-through cell was used to minimize atmospheric interactions. Water samples were collected in 500-mL, 2 *M* hydrochloric acid-washed Nalgene bottles (Nalge Nunc International, Rochester, NY) for nitrate + nitrite and nitrite (NO_2^-) analyses. All bottles were rinsed three times with the sample before collection, then placed in an iced cooler for transport.

Surface water samples were collected in November 1997 and February and May 1998, at 12 locations along a 2.4-km reach of Pangborn Creek, which dissects the central portion of the study area (Fig. 2). Pangborn Creek is a discharge zone for the Abbotsford–Sumas Aquifer and also receives runoff from nearby croplands. Samples for laboratory analysis were collected at each site by placing a 250-mL acid-washed Nalgene bottle at elbow depth in the water. The bottles were rinsed three times with stream water before collection, then placed

in an iced cooler for transport. To assess NO_3^- sources in the study area we analyzed N isotopes sampled from ground water at nine wells and two surface water sites. Wells 2, 5, 7, 9, 10, 13, 14, 17, and 18 were selected because they represent a spatial distribution in the study area and had high NO_3^- concentrations that would improve the likelihood of identifying the source of contamination. We sampled each of the nine wells and two surface water sites in February, June, and October 1998. Water samples were collected in 1-L Nalgene bottles, which contained acid before collection to fix the solution, and then placed in an iced cooler for transport.

Laboratory Analyses

The ground and surface water samples were analyzed for NO_2^- and $NO_3^- + NO_2^- -$ at the Institute for Watershed Studies laboratory at Western Washington University, a laboratory certified by the Washington State Department of Ecology. Field duplicates (5% of all the samples collected) and lab duplicates (10% of the samples) were used for quality assurance. Dissolved oxygen was measured in a flow-through cell in the field with a Model 85 water analyzer (YSI, Yellow Springs, OH) with a detection limit of 0.1 mg L^{-1}. The water samples were filtered the day of the sampling with a 0.45-μm membrane filter. Laboratory NO_2^- tests were conducted within 48 h of sampling using a spectrophotometric method (USEPA 354.1) with a detection limit of 0.0009 mg N L^{-1}. Nitrate + nitrite samples were frozen and analyzed in the lab within 60 d of sampling using automated cadmium reduction (USEPA 353.2) with a detection limit of 0.006 mg N L^{-1}. Water samples were shipped to Coastal Science Laboratories (Austin, TX) for isotopic analysis. The method used by Coastal Science Laboratories for measuring the two stable isotopes of N (^{14}N and ^{15}N) in NO_3^- is based on methodology discussed by Velinsky et al. (1989). Coastal Science Labs estimated standard deviations for ground water N measurements to be 0.8 to 1.0% for samples of commonly encountered concentrations (0.5–5 mg N L^{-1}).

Data Analyses

The ground water NO_3^- concentrations, reported here as mg N L^{-1}, are categorized according to Tesoriero and Voss (1997). They used NO_3^- concentrations greater than 3 mg N L^{-1} as an indicator of contamination due to anthropogenic effects and to predict aquifer susceptibility and vulnerability in the Puget Sound region. The 10 mg N L^{-1} MCL was used as a second NO_3^- concentration category. The water quality data were not normally distributed and heteroskedastic; therefore, we examined the ground water NO_3^- concentrations using nonparametric graphical and descriptive statistics. These analyses include boxplots showing the minimum value, the 25th quartile, the median value, the 75th quartile, and the maximum value (Carlson and Thorne, 1997) and Kendall's τ correlation analysis (Helsel and Hirsch, 1992). The DBWT was used to separate NO_3^- concentrations measured from deep and shallow regions of the aquifer. Wells with DBWT levels less than 10 m were considered to be shallow, whereas wells with DBWT levels greater than 10 m were considered to be deep.

Stable isotope ratios were used to differentiate between inorganic, commercial fertilizers and animal waste as NO_3^- sources (Flipse and Bonner, 1985; Exner and Spalding, 1994; Wassenaar, 1995; Igbal et al., 1997). Stable isotope ratios are usually expressed in a δ format, which for N indicates the relative value of the ^{15}N to ^{14}N isotopic ratio as compared with the atmospheric (standard), and is expressed as:

$$\delta^{15}N(‰) = [(^{15}N/^{14}N_{sample} - {}^{15}N/^{14}N_{standard})/$$

$$({}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}})] \times 1000 \qquad [1]$$

where $\delta^{15}\text{N}$ has units of per mil (‰), ${}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}}$ is the stable isotopic ratio of the sample, and ${}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}}$ is the ratio of the atmospheric standard. Interpreting $\delta^{15}\text{N}$ data, however, can be difficult when the values are derived from ground water samples rather than from soil pore water beneath a source, because it is possible that the $\delta^{15}\text{N}$ values may have been enriched by denitrification or reflect a mixture of sources (Herbel and Spalding, 1993; Fogg et al., 1998). To maintain consistency, we compared our $\delta^{15}\text{N}$ results (Nanus, 2000) to those of Wassenaar (1995), who used three classes to categorize NO_3^- sources in the British Columbia study area from ground water–derived $\delta^{15}\text{N}$ values. Wassenaar's accepted range of $\delta^{15}\text{N}$ values for inorganic commercially derived NO_3^- in ground water was -1 to $+2$‰, whereas animal waste sources had $\delta^{15}\text{N}$ values greater than $+8$ to $+16$‰. Although human waste–derived NO_3^- is indistinguishable from animal waste, Cox and Kahle (1999) qualitatively estimated that septic tank effluent accounted for less than 4% of the total N entering the ground water as NO_3^- in the region. Values between $+2$ and $+8$‰ were considered indicative of a mix of animal and inorganic, commercial fertilizer sources or derived from natural soil nitrate.

RESULTS AND DISCUSSION

Nitrate Concentrations and Distributions

A total of 504 ground water samples from 26 wells were analyzed over the 22-month period. Except for some outliers, NO_2^- concentrations were usually below the detection limit of 0.0009 mg N L^{-1}. The minimum, maximum, and median NO_3^- concentration for each well is listed in Table 1. Most (63%) of all values and 17

well median values were greater than 3 mg N L^{-1} and indicate probable anthropogenic contamination (Tesoriero and Voss, 1997). In addition, 38% of all values and 12 of the median values were greater than the 10 mg N L^{-1} MCL. Of the 36 surface water samples analyzed, 34 had NO_3^- concentrations above 3 mg N L^{-1}, and seven samples were greater than 10 mg N L^{-1}.

To show the spatial distribution of NO_3^- concentrations, we plotted median values from each well location and two representative surface water sampling sites, along with the agricultural land use in the study area (Fig. 3). The distribution of elevated concentrations is characteristic of nonpoint agricultural sources and is consistent with the historical documentation of agricultural NO_3^- contamination in many parts of the Abbotsford–Sumas Aquifer area (Liebscher et al., 1992; Wassenaar, 1995; Erickson, 1998; Zebarth et al., 1998; Cox and Kahle, 1999; Hii et al., 1999). The concentrations in some wells remained high throughout the duration of the study. In the last month of sampling (January 1999), NO_3^- concentrations in 14 wells were greater than 3 mg N L^{-1}, and 9 wells yielded concentrations greater than the 10 mg N L^{-1} MCL.

Median NO_3^- concentrations for the wells are categorized by magnitude and by DBWT levels (Table 1; Fig. 4). Kendall's τ correlation analysis (Helsel and Hirsch, 1992) confirmed a statistically significant relationship between NO_3^- and DBWT, with higher NO_3^- concentrations at shallow depths and lower NO_3^- concentrations at deeper depths (Kendall's $\tau = -0.380$; $p < 0.001$). Despite the significant correlation, there was

Table 1. Well depth and values measured between April 1997 and January 1999 from wells in the northwestern Washington study area.†

Well number	Depth	CSWL	DBWT	NO₃⁻ Minimum	NO₃⁻ Median	NO₃⁻ Maximum	DO	δ¹⁵N
		m			mg N L⁻¹		mg L⁻¹	‰
				Shallow				
24	9.1	6.4	2.7	0.2	25.3	28.7	8.3	–
14	8.5	7.2	1.3	18.2	22.9	32.4	4.4	5.6
18	13.1	7.8	5.3	13.4	19.9	32.3	5.6	5.5
2	10.4	7.1	3.3	12.7	14.5	16.4	6.2	3.4
1	9.1	1.5	7.6	9.8	12.1	14.2	5.3	–
10	15.2	9.2	6.1	7.9	11.2	12.6	5.6	1.5
17	11.3	8.8	2.5	9.0	10.6	11.6	2.6	6.9
13	12.2	8.8	3.4	8.4	10.4	25.5	4.8	5.0
16	18.3	10.7	7.6	5.3	8.7	12.3	6.4	–
22	10.4	7.5	2.9	3.6	5.3	10.3		–
15	10.7	7.8	2.9	2.0	3.6	9.9	4.5	–
20	13.7	4.2	9.5	1.3	2.3	2.5	6.1	–
19	13.7	3.9	9.8	1.5	2.3	3.3	6.4	–
11	21.6	12.9	8.7	<0.006	2.1	5.4	3.9	–
4	9.1	7.1	2.1	0.04	1.8	6.6	3.3	–
8	18.3	9.3	9.0	0.4	1.2	13.0	2.2	–
12	22.9	13.1	9.7	<0.006	0.0	0.03	0.8	–
				Deep				
25	30.5	11.4	19.1	11.7	13.5	14.2	0.5	–
6	29.0	15.5	13.5	11.3	12.3	14.1	7.9	–
9	21.6	9.3	12.3	4.2	12.1	26.7	1.4	9.5
5	30.5	19.1	11.4	8.0	11.2	16.1	3.5	8.3
7	23.5	11.4	12.1	5.5	8.9	9.9	4.3	0.3
26	24.4	8.0	16.4	5.5	7.6	11.5	Na	–
23	22.9	3.8	19.1	0.1	0.8	2.4	8.3	–
21	17.4	5.8	11.6	0.002	0.0	0.04	0.54	–
3	28.0	7.4	20.7	<0.006	0.0	0.03	2.0	–

† Values include the median corrected static water level (CSWL); median well depth below the water table (DBWT); the minimum, median, and maximum nitrate concentration (NO₃⁻); median dissolved oxygen value (DO); and median nitrogen isotope ratio (δ¹⁵N) value. The wells are categorized into shallow DBWT levels (<10 m) and deep DBWT levels (>10 m) and by NO₃⁻ magnitude. Values that are below the detection limit are identified by <0.006.
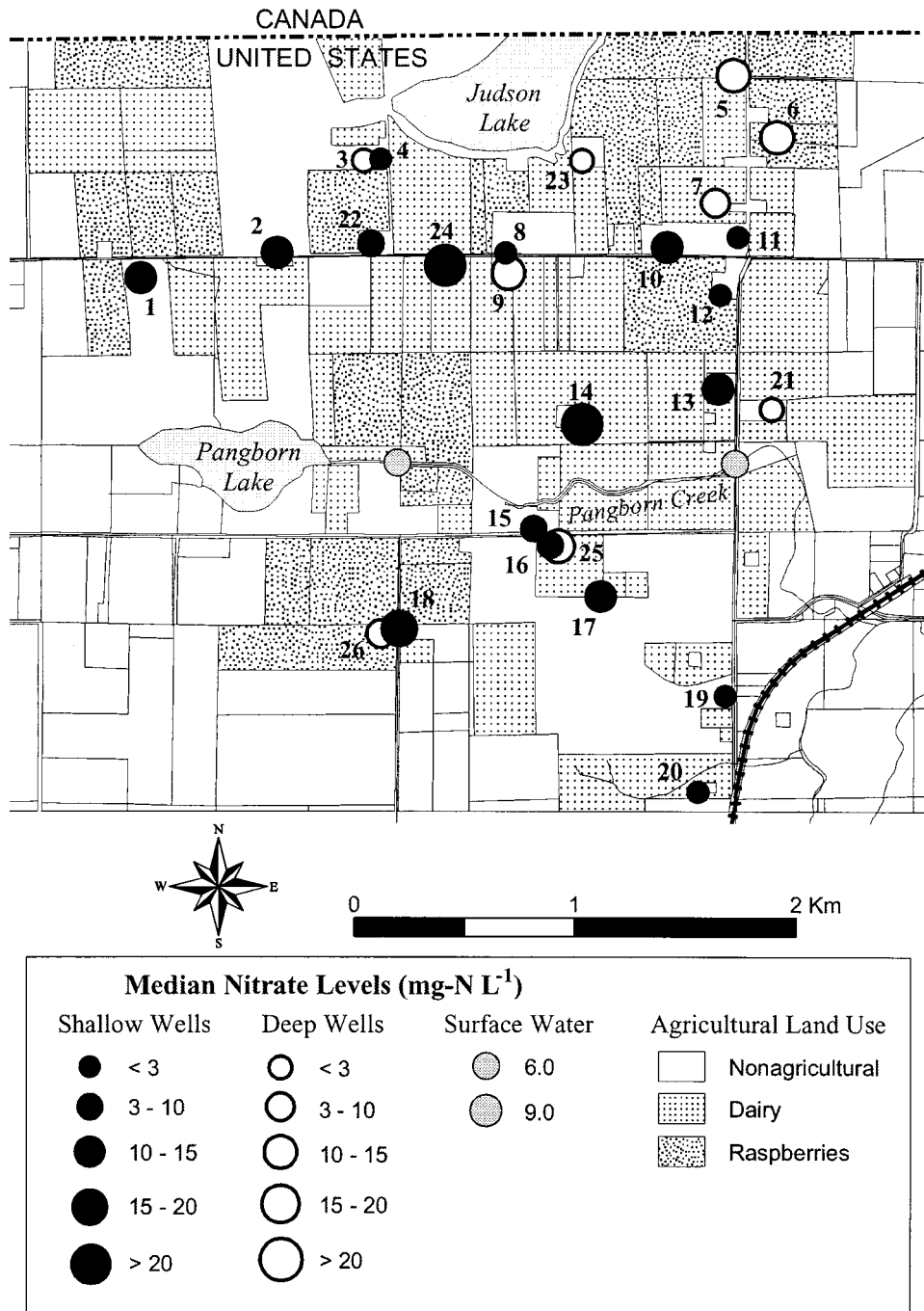
Fig. 3. Land use in the northwestern Washington study area and the associated median nitrate concentration values (mg N L⁻¹) at the domestic well sampling locations and two surface water sites. Nitrate concentrations are proportional to the size of the well symbol. Individual well numbers are shown by the well symbols.

considerable variability among wells (Fig. 4), indicating that the concentration of ground water NO_3^- was not just a simple bivariate correlation with DBWT. Gelinas (2000) used multivariate analyses (principal component analysis and metric and nonmetric clustering) to confirm the inverse relationship between NO_3^- and DBWT and reveal three distinct groups of wells. Deep wells with moderately high NO_3^- may represent an up-gradient NO_3^- source, and were distinct from shallow wells with very high NO_3^- concentrations (possibly from a local agricultural source), and both were distinct from low

NO_3^- "anomaly" wells, which were possibly influenced by denitrification.

Deep Aquifer Contamination

Deep Wells 5, 6, 7, and 9, located less than 1 km from the international boundary, have high NO_3^- concentrations (Table 1; Fig. 2), as do the more southerly deep wells (Wells 25 and 26). It is unlikely that the elevated NO_3^- concentrations at Wells 5, 6, 7, and 9 are related to northwestern Washington sources because it would
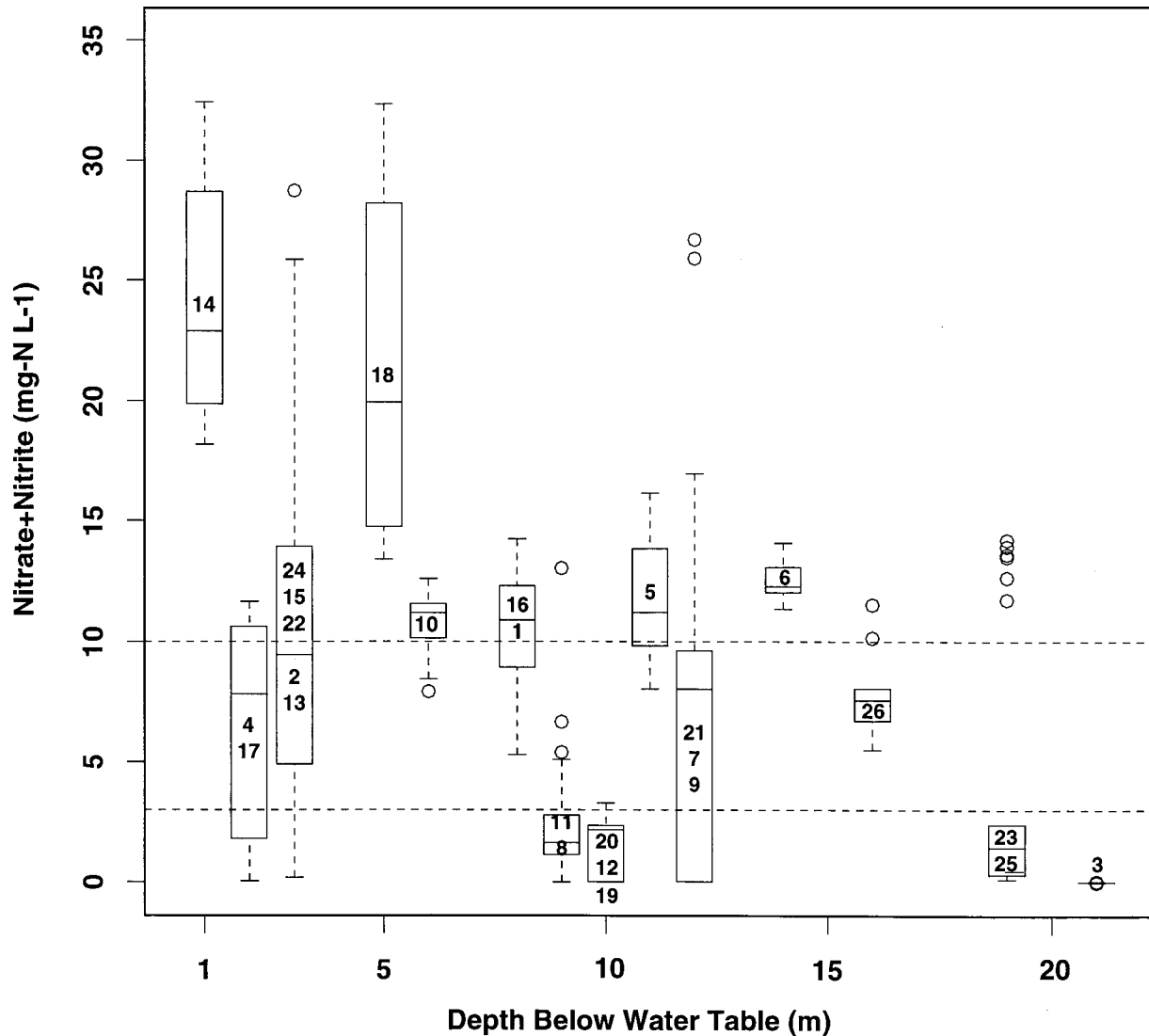
Fig. 4. Box plots of nitrate concentration (mg N L^{-1}) with depth below the water table (DBWT). Well numbers with equivalent DBWT magnitudes are listed in the boxes. Horizontal dashed lines represent probable anthropogenic contamination (3 mg N L^{-1}) and the 10 mg N L^{-1} maximum contaminant level (MCL).

require large vertical gradients to deliver NO_3^- to these well depths, and the vertical hydraulic gradients are minimal in the region (Zebarth et al., 1998). The unconfined aquifer in this region is a highly conductive mixture of gravel and sand where ground water flow is dominantly horizontal to the southeast (e.g., Cox and Kahle, 1999; Stasney, 2000). The elevated NO_3^- concentrations in these wells are probably the result of sources further north (up-gradient) in British Columbia. It is also likely that the elevated NO_3^- concentrations of 13.5 and 7.6 mg N L^{-1} at the more southerly Wells 25 and 26, respectively, are related to British Columbia sources because of their depth. We estimated a regional background concentration in the study area to be 10.7 mg N L^{-1}, which is the median concentration of the NO_3^- measurements from the contaminated deep wells in the study area (5, 6, 7, 9, 25, 26). This value is in the range predicted by Hii et al. (1999), who used hypothetical modeling to simulate a similar stratification and deep aquifer

contamination observed in the British Columbia study area (Hii et al., 1999; Zebarth et al., 1998). Using flow net analyses and a 20 mg N L^{-1} load to the water table, Hii et al. (1999) predicted NO_3^- concentrations averaging 10 mg N L^{-1} crossing the international boundary into some locations in northwestern Washington.

Nitrogen isotope ratios analyzed from water samples from three deep wells (Wells 5, 7, and 9) were used to test a British Columbia source hypothesis. Two of these wells, Wells 5 and 9, had the highest median $\delta^{15}N$ values of all the wells measured in the study area, 8.3 and 9.5‰, respectively (Table 1; Fig. 5). These values suggest an animal source, probably poultry manure (Wassenaar, 1995). Eighty percent of Wassenaar's ground water $\delta^{15}N$ values were between +7 and 16‰. The median $\delta^{15}N$ value from the other deep well, Well 7, was 0.3‰, which is surprisingly small, but consistent with the types of inorganic, commercial fertilizers used in the British Columbia study area. Although limited, when coupled with
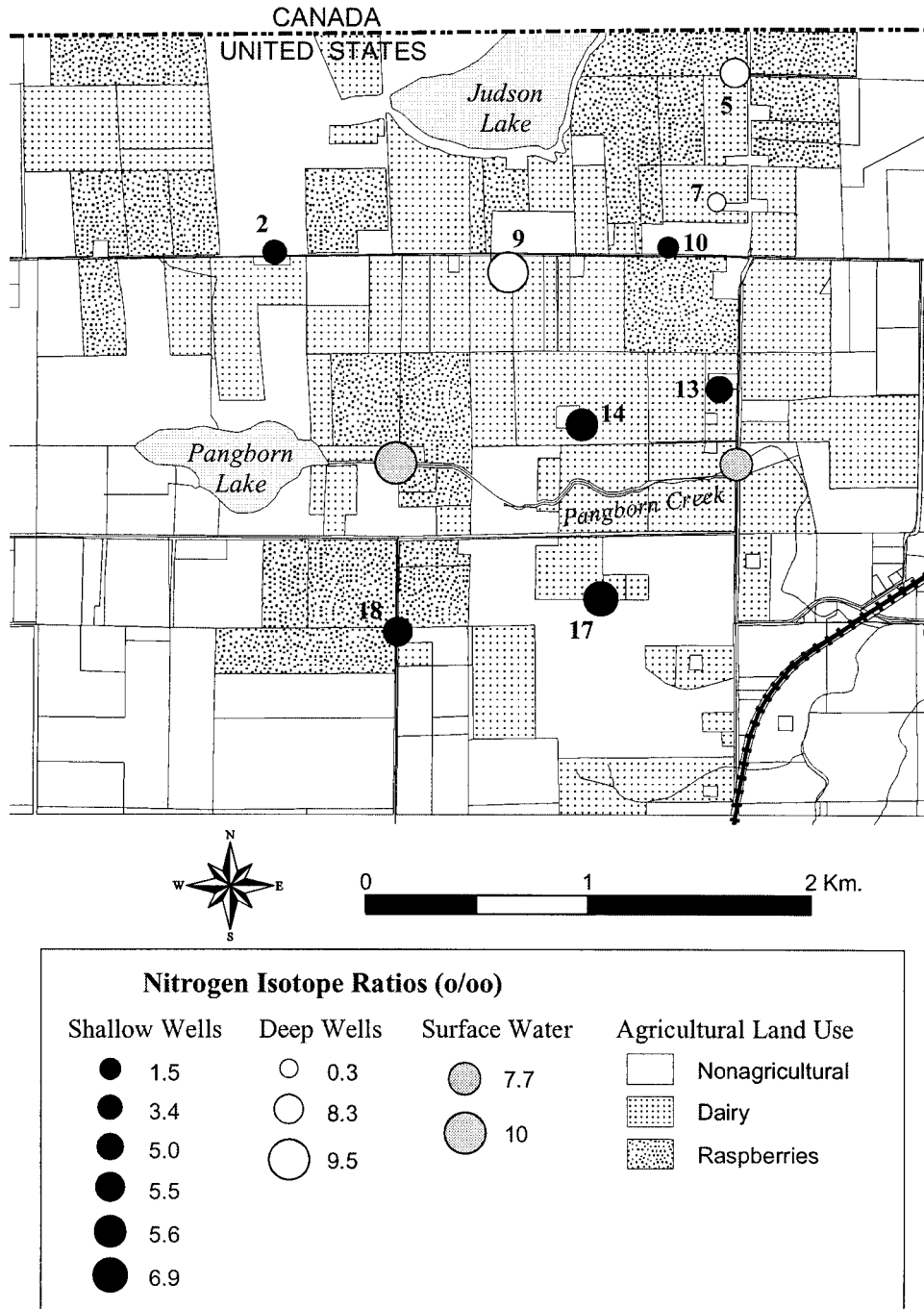
Fig. 5. Land use in the northwestern Washington study area and associated nitrogen isotope ratios ($\delta^{15}N$) at nine well locations and two surface water sites in the northwestern Washington study area. Nitrogen isotope ratios are proportional to the size of the well symbol. Individual well numbers are shown by the well symbols.

the proximity of the wells to the international border and depth, the $\delta^{15}N$ values suggest up-gradient sources.

Temporal variations in climate and land use in British Columbia can result in NO_3^- concentrations in excess of the 10 mg N L^{-1} MCL and add to the difficulty in managing localized sources. Nitrate concentrations from several shallow and deep piezometers, grouped west and east of Judson Lake in the British Columbia study area, showed pronounced fluctuation of NO_3^- concentrations beginning in 1995 and ending in 1997 (Hii et al., 1999). The increase was partly correlated to a rise

in water table that was observed during the same period. The rise in the water table can liberate accumulated NO_3^- from the vadose zone. Moreover, the higher water table corresponds to a larger recharge, which would increase the leaching of NO_3^- from the vadose zone to the water table. Although our well measurements started in April 1997, Well 9 had been intermittently measured, using comparable laboratory procedures, by the Washington State Department of Ecology between June 1993 and March 1997 (D. Garland, personal communication, 1997). The NO_3^- time series, combined with
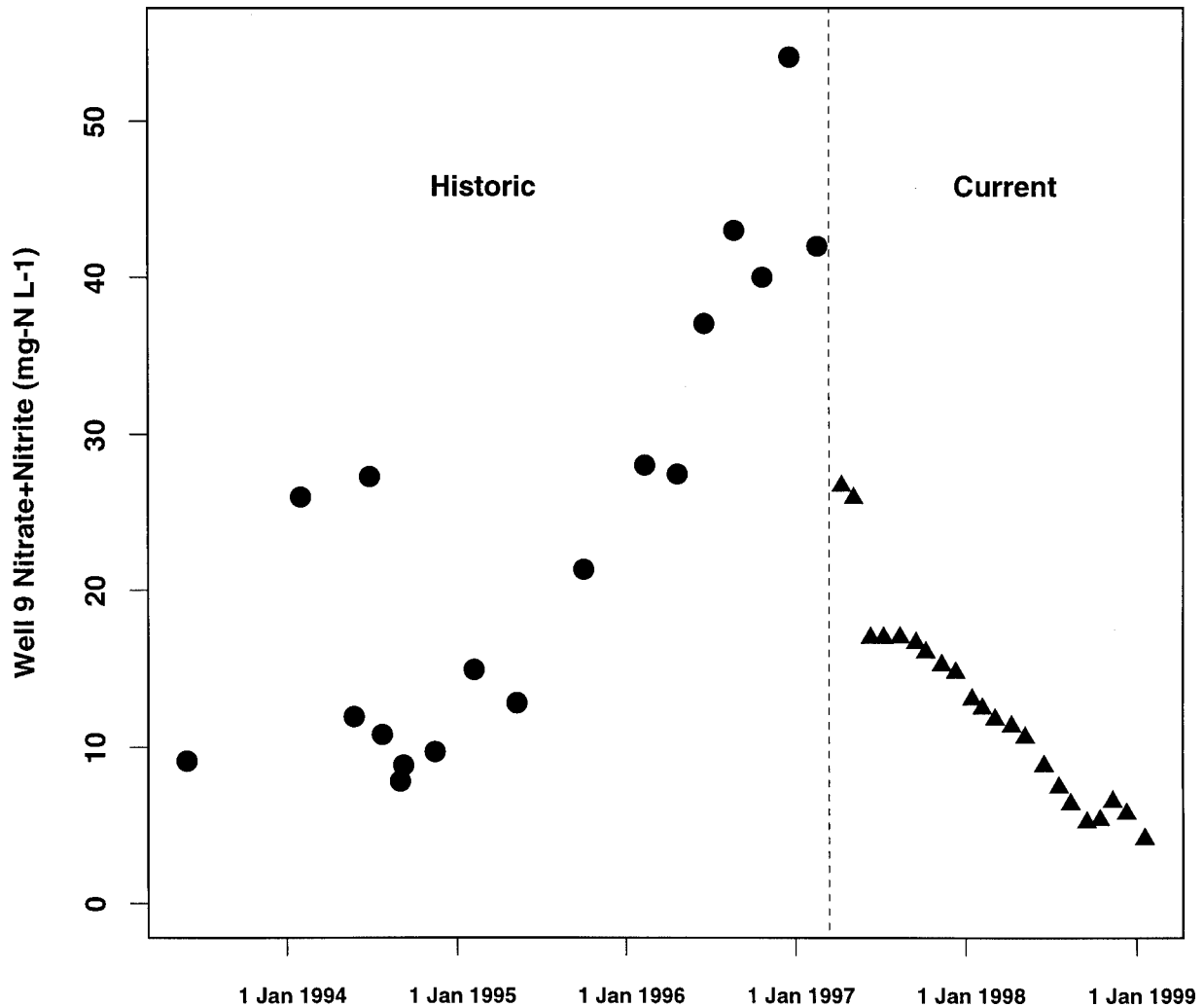
Fig. 6. Time series of nitrate concentrations (mg N L^{-1}) measured at Well 9. "Historic" values were measured by the Washington State Department of Ecology and "current" values are from this study.

our data between April 1997 and January 1999, clearly depicts a significant plume migrating past Well 9 between mid-1995 and mid-1997 that is similar in shape to those observed in the British Columbia study area (Fig. 6). The drop in concentration is probably due to a combination of lower recharge and a change in N loading. Unfortunately, we do not have a consistent time series before April 1997 at the other deeper wells in our study area to document a similar pattern, but we believe this plume could have migrated through the entire study area.

Shallow Aquifer Contamination

Bivariate and multivariate statistics support a stratified distribution of NO_3^- in the aquifer and suggest that land use in our study area contributed to ground water contamination. This was expected because the majority of the land use in the study area is agricultural (Fig. 3). If we assume a background NO_3^- concentration around 10 mg N L^{-1} in the aquifer due to up-gradient sources (using the contaminated deep-well median), then measured NO_3^- concentrations equal to or greater than the

MCL would suggest localized sources. Median values of eight shallow wells (1, 2, 10, 13, and 17) meet this criterion (Table 1), whereas Wells 14, 18, and 24 had median NO_3^- concentrations of 22.9, 19.9, and 25.3 mg N L^{-1}, respectively (Table 1). Measured NO_3^- concentrations in the wells also showed the most variation during the study (Fig. 3), suggesting that they are more responsive to land use changes because of their exceptionally shallow depth (<5 m).

Degraded surface water quality in Pangborn Creek also suggests contamination in the study area due to local contributions (Nanus, 2000). Median NO_3^- values in Pangborn Creek increased from about 6.0 mg N L^{-1} near Pangborn Lake to about 9.0 mg N L^{-1} at the eastern-most site (Fig. 2). The highest NO_3^- values measured in the creek were in May 1998 (median 8.8 mg N L^{-1}) and the lowest in November 1997 (median 5.9 mg N L^{-1}), and this range relates to seasonal rains and spring nutrient applications in the region. Median NO_3^- values for two representative sites along Pangborn Creek are shown in Fig. 3, and these data are consistent with the results of Wills (1998) and Butkus et al. (2000). Pang-

born Creek is a discharge zone for the aquifer, but also receives surface runoff from adjacent croplands via drainage ditches. The creek is listed as "impaired" and is subject to a total maximum daily load (TMDL) analysis in accordance with Section 303(d) of the Federal Clean Water Act (Butkus et al., 2000). The high NO_3^- concentrations that we measured are consistent with low dissolved oxygen and high fecal coliform counts, the impairments listed for the TMDL, which are linked to dairy waste sources. Median $\delta^{15}N$ values for the two sites along Pangborn Creek were 7.7 and 10.0, suggesting mixed and animal sources and reflecting the mixed fertilization practices that occur in the vicinity of Pangborn Creek (Fig. 5). Without piezometers along the creek, we were unable to distinguish ground water NO_3^- from runoff NO_3^-, but suspect that both are contributing to the degraded water quality of the creek.

Values of $\delta^{15}N$ varied from 1.5 to 6.9‰ during the study (Table 1). While these values do not support a single source of NO_3^-, there is a weak correlation of NO_3^- with dissolved oxygen (DO). The isotopic data measured from the shallow wells were not conclusive, but suggest local agricultural sources for the NO_3^- concentrations in the shallow portion of the aquifer in the study area. Qualitatively, the shallow wells with the highest median NO_3^- values (>10 mg N L^{-1}) were down-gradient of agricultural land use areas (Fig. 3). Whereas the British Columbia study area was dominated by poultry manure fertilization, croplands in our study area were fertilized by a mix of fertilizers. Regions identified as dairy in Fig. 3 and 5 represent lands applied with dairy manure (e.g., corn, grasses, and pasture); regions marked as raspberries are typically fertilized with inorganic, commercial fertilizers. It is difficult to ascertain the exact agricultural source associated with the elevated NO_3^- concentrations at a particular well from the $\delta^{15}N$ data because of potential isotopic enrichments of ^{15}N due to denitrification (Herbel and Spalding, 1993) and the mixing processes that are associated with non-point contamination in the unconfined aquifer. Although denitrification is probably occurring in isolated regions, we do not believe it is widespread in the aquifer. Wassenaar (1995), for example, determined from $\delta^{18}O$ of 117 ground water nitrate samples that no significant denitrification was occurring in the British Columbia study area. Vertical and lateral mixing can occur by the intermingling plumes along flow paths and by irrigation. About 0.30 to 0.45 m of water are added to sections of the study area each summer due to irrigation (J. Gillies, personal communication, 2001). Partial penetration of an unconfined aquifer by irrigation wells and screened domestic wells can cause localized lateral and vertical mixing of water and facilitate plume mixing. Moreover, irrigation can redistribute NO_3^- contaminated water on the ground surface, which can elevate ground water NO_3^- concentrations via recharge (Guimera, 1998) and combine sources. Because the $\delta^{15}N$ values were derived from ground water samples, it is probable that denitrification and mixing are in part responsible for the range of $\delta^{15}N$ results at of our shallow well locations (Table 1). The range of $\delta^{15}N$ values suggest naturally derived soil

nitrate or a mix of animal and inorganic fertilizers sources, an interpretation consistent with the fertilization practices in the study area (Fig. 5). Because poultry manure cannot be separated from dairy manure by $\delta^{15}N$ values, it is possible that NO_3^- from poultry manure sources in British Columbia may also be contributing to the mix in the shallower portions of the aquifer due to vertical mixing.

Low Nitrate Anomalies

A number of shallow wells (Wells 4, 8, 11, 12, 19, and 20) and deep wells (Wells 3, 21, and 23) in the study area produced NO_3^- concentrations below 3 mg N L^{-1} and in some cases, values near zero (Table 1). We also show a weak correlation between NO_3^- and dissolved oxygen, and this relationship suggests the effects of land use and/or fertilizer application. Our finding confirms a relationship found by Gelinas (2000) between low NO_3^- and low dissolved oxygen (Table 1) at some of these locations (Wells 3, 4, 8, 11, 12, and 21). Wells 19 and 20 are shallow wells down-gradient of a large gravel mining facility in the southern portion of the study area, which suggests that land use may have influenced some of these low NO_3^- concentrations (Fig. 3). The low NO_3^- values may also be the result of denitrification facilitated by organic carbon or iron, or both. Denitrification has been shown to be reducing NO_3^- concentrations near the water table in the aquifer, especially in areas where manure is applied (Paul and Zebarth, 1997a,b; Paul et al., 1997) and in riparian zones (Tesoriero et al., 2000). Although Wassenaar (1995) concluded that no significant denitrification was occurring deeper in the aquifer, it does occur in isolated zones having iron-containing minerals, where reduced forms of iron (e.g., pyrite) serve as electron donors in denitrification reactions (Tesoriero et al., 2000). We did not measure iron or byproducts associated with denitrification (i.e., N_2 gas).

CONCLUSIONS

For a period of 22 months, we measured NO_3^- concentrations in shallow and deep domestic wells in a study area in northwestern Washington and confirmed elevated NO_3^- concentrations, characteristic of nonpoint agricultural sources. The results suggest that NO_3^- concentrations are stratified in the unconfined aquifer due to sources up-gradient in British Columbia and local sources in the study area. The highest NO_3^- concentrations (>20 mg N L^{-1}) were found in the shallow region of the aquifer and were linked to northwestern Washington sources by using a combination of N isotope results, local agricultural land use relationships, and contaminated surface water in the study area. We also measured NO_3^- concentrations in excess of 10 mg N L^{-1} in deep wells in the study area and consider agricultural land use in British Columbia to be the NO_3^- source deeper in the aquifer based on $\delta^{15}N$ results and hydrogeology. Because of the low vertical gradients in the aquifer, long flow paths would be required to transport NO_3^- to the deep wells near the international boundary. In addition,

N isotope ratios from two of the three deep wells sampled near the international boundary suggest animal manure as the source, which is consistent with poultry manure fertilization practices in British Columbia.

The identification of two possible regional sources and a NO_3^- stratification in the aquifer adds to the difficulty in managing agricultural practices in northwestern Washington. Despite the implementation of best management practices for decades, elevated NO_3^- concentrations have persisted in ground water and surface water in the region. This has driven the development of the State of Washington's Dairy Nutrient Management Act (1998), which requires all dairy farms to develop and implement dairy nutrient management plans by 2003. To assess and refine these management plans, the magnitudes of the northwestern Washington contribution of NO_3^- to the aquifer must be quantified. Our results show that it will be difficult to determine these contributions because of the spatial and temporal variability of NO_3^- transported into the study area from up-gradient sources in British Columbia. In our analysis, we suggest a NO_3^- stratification in the aquifer based on a background NO_3^- concentration of about 10 mg N L^{-1}. However, the exact background level and spatial extent of background concentrations is not clear, nor is the degree of vertical and horizontal mixing of the two sources in the aquifer. Separating source contributions is complicated further by temporal changes in climate and up-gradient land use and aquifer heterogeneities that may cause ground water flow anomalies and localized denitrification. Our results suggest that using water measurements from domestic wells offers a cost-efficient approach in assessing NO_3^- concentrations and sources as well as identifying NO_3^- stratified regions in the aquifer. However, wide-spread implementation and monitoring of nested piezometers and soil lysimeters, coupled with nutrient loading information and extensive aquifer characterization and modeling, may be necessary to monitor NO_3^- accurately and manage N loading in northwestern Washington. Because of these difficulties, conservationists and farmers are faced with a problematic task and economic challenges when having to consider multiple sources and up-gradient contamination to refine management plans.

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