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Aquifer-scale controls on the distribution of nitrate and ammonium in ground water near La Pine, Oregon, USA ☆

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Summary Geochemical and isotopic tools were applied at aquifer, transect, and subtransect scales to provide a framework for understanding sources, transport, and fate of dissolved inorganic N in a sandy aquifer near La Pine, Oregon. NO_3 is a common contaminant in shallow ground water in this area, whereas high concentrations of NH_4–N (up to 39 mg/L) are present in deep ground water. N concentrations, N/Cl ratios, tracer-based apparent ground-water ages, N isotope data, and hydraulic gradients indicate that septic tank effluent is the primary source of NO_3. N isotope data, N/Cl and N/C relations, ^3H data, and hydraulic considerations point to a natural, sedimentary organic matter source for the high concentrations of NH_4, and are inconsistent with an origin as septic tank N. Low recharge rates and flow velocities have largely restricted anthropogenic NO_3 to isolated plumes within several meters of the water table. A variety of geochemical and isotopic data indicate that denitrification also affects NO_3 gradients in the aquifer. Ground water in the La Pine aquifer evolves from oxic to increasingly reduced conditions. Suboxic conditions are achieved after about 15–30 y of transport below the water table. NO_3 is

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denitrified near the oxic/suboxic boundary. Denitrification in the La Pine aquifer is characterized well at the aquifer scale with a redox boundary approach that inherently captures spatial variability in the distribution of electron donors.
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Introduction

Nitrate (NO_3) is the most common contaminant in ground water (Spalding and Exner, 1993). Identification of sources of NO_3, as well as other nitrogen (N) species, has received a tremendous amount of attention, due in part to health concerns regarding NO_3 ingestion (World Health Organization, 1996) and to potential ecosystem effects of N loading (Howarth and Marino, 2006). For example, the history and fate of NO_3 contamination have been carefully evaluated in multidisciplinary local transect studies in areas with agricultural sources (e.g. Böhlke and Denver, 1995; Tesoriero et al., 2000; Böhlke et al., 2002; Puckett et al., 2002) and septic tank sources (e.g. Robertson and Cherry, 1992; Wilhelm et al., 1996; Aravena and Robertson, 1998). However, resolution of N sources can be difficult in larger regional studies because of co-occurrence of multiple anthropogenic N sources and uncertainty in N transformation pathways. Furthermore, natural N may be an important but overlooked N source in some aquifers. Thus, identification of natural and anthropogenic N sources, as well as characterization of N geochemistry, remain challenging, particularly in aquifer-scale assessments.

In this paper, we present results of a multiscale study of N occurrence, loading, transport and fate for a sandy aquifer in Oregon, USA, in which the only significant anthropogenic N source (other than atmospheric loading) was septic tank effluent. The near absence of other anthropogenic N sources provided an opportunity to characterize the impact and point-source nature of septic tank N discharge to the aquifer. An important natural N source also was clearly identified and several approaches were used to distinguish between anthropogenic and natural N sources. Multiple lines of evidence point to a denitrification pathway for NO_3 removal from ground water, and a redox boundary approach is proposed for conceptualizing aquifer-scale NO_3 fate.

Study area and background

Rapid rural-residential development on lots as small as one-half acre (0.2 ha) has occurred in the vicinity of La Pine, Oregon, USA (Fig. 1) since the 1960s. A shallow, sandy aquifer serves as both source of drinking water and receptor of septic tank effluent for most residents. Most houses in this semiarid environment are surrounded by semidesert landscaping, and agricultural activities are almost nonexistent (Oregon Department of Environmental Quality, 1994; Hinkle et al., 2005). Fertilizer use is minimal, and septic tank effluent is the only important anthropogenic source of N to study area ground water (Century West Engineering Corporation, 1982). High concentrations of NO_3—N (>10 mg/L) became widespread in ground water beneath the town of La Pine by the early 1980s (Century West Engineering Corporation, 1982). Sewering of the core urban area of La Pine has reduced septic tank effluent loading there. However, most of the surrounding area is unlikely to support centralized sewer or water supply services in the foreseeable future. As of 1999, 5185 rural platted lots had been developed. Another 5010 developable lots remained in 1999. Hence, County and State resource managers are in need of an understanding of NO_3 source, transport and fate in the La Pine area. The work described in this paper arose in response to these needs, but the results have wider applicability.

The La Pine study area lies in Oregon's upper Deschutes Basin (Fig. 1). The area is underlain by as much as 300 m of Quaternary alluvial and lacustrine deposits in a structural basin of Quaternary and Tertiary basalt, andesite, vent deposits, and pyroclastic rocks (Lite and Gannett, 2002). Sand is common in the uppermost 37 m of the aquifer. Deeper sediment is dominantly fine grained, and includes extensive lacustrine deposits. Most ground-water use, and hence our emphasis, is focused in the uppermost 37 m of the aquifer.

Rain and snowmelt are the primary sources of recharge in the study area. Precipitation ranges from 40 to 50 cm/y over most of the area (Taylor, 1993), falling primarily from November through March. Regional ground-water fluxes from higher-elevation areas enter the study area from the west, and to lesser extents the south and east (Gannett et al., 2001). Ground water discharges to the Deschutes and Little Deschutes Rivers. The water table generally lies within 6 m of land surface, facilitating additional ground water loss via evapotranspiration.

Study design and methods

Well networks and other data

Chemical analyses of ground water from a network of 193 existing (primarily domestic) wells, sampled by Oregon Department of Environmental Quality (ODEQ) in June, 2000, provided an aquifer-scale (640 km^2 area of variable thickness) perspective of the distribution of dissolved oxygen (O_2) (188 sites), NO_3 (192 sites), ammonium (NH_4) (192 sites), and chloride (Cl) (191 sites). This network is referred to as the ODEQ synoptic network. (The raw data are provided as Supplemental data: supplemental_data_1.xls.)

Ground water from a group of 11 existing wells with elevated NH_4—N (>1 mg/L) was sampled by the US Geological Survey (USGS). These wells were primarily a subset of the ODEQ synoptic network. Samples were analyzed for field parameters; nutrients (N and phosphorus [P] species); non-purgable dissolved organic carbon (DOC); common ions; dissolved nitrogen (N_2), argon (Ar), and methane (CH_4); $\delta^{15}N$ in NH_4; and tritium (^3H). These data were used to determine the origin of elevated NH_4 concentrations in ground water. This network is referred to as the ''elevated-NH_4 network''.

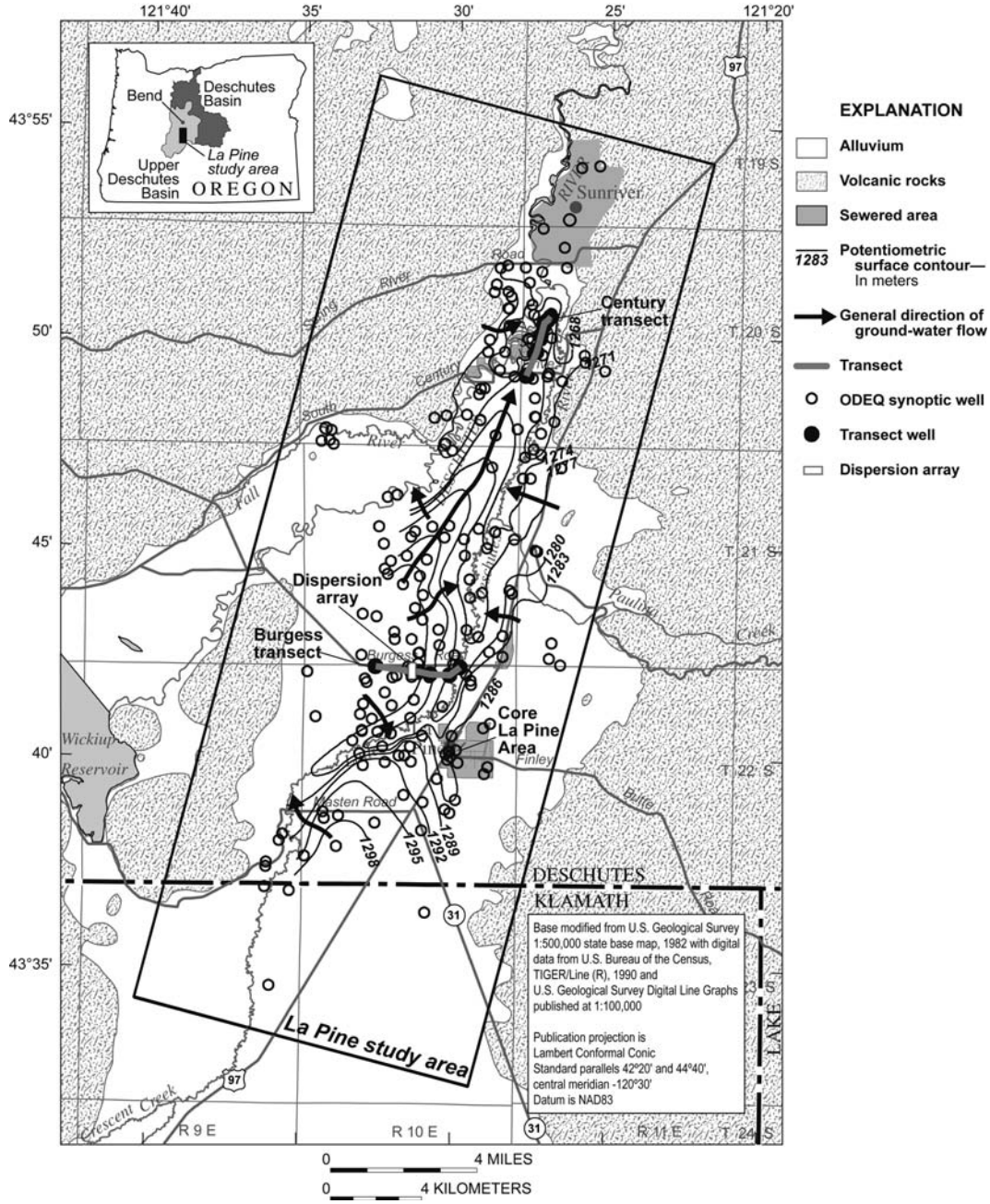

Figure 1 La Pine study area.

The USGS installed monitoring wells along two ground-water flowpaths (Burgess and Century transects, Fig. 1) and sampled the ground water for field parameters; nutrients; DOC; common ions; dissolved N_2, Ar, CH_4, and, at selected sites, neon (Ne); $\delta^{15}N$ in NO_3, NH_4, and/or N_2 (selected sites); and age-dating tracers (chlorofluorocarbons [CFCs] or ^3H; ^3H with ^3He and ^4He for $^3H/^3He$ age dating at selected sites). These data provided an understanding of the movement and geochemical evolution of ground water at the sub-aquifer scale. One to four wells were installed at each of six locations along transects, with a total of 17 wells along the Burgess transect and eight along the Century transect. Each site (containing one to four wells) was assigned a name, beginning with transect name (''Burgess'' or ''Century''), followed by a sequential number corresponding to location along the transect, with ''1'' being furthest upgradient and ''6'' furthest downgradient. Most sites contained nests of two to four wells; names for these wells included a decimal followed by a digit corresponding to position within the nest (''1'' for shallowest).

Transect wells were drilled with a hollow stem auger. Drilling fluids were not used, except at Burgess 2.4, where 68 L of tap water was added to prevent sand surging. Much of this water was immediately removed after placement of casing, and along with subsequent pumping, a total of 727 L was removed — a volume sufficient to ensure that contamination was unlikely. Wells were completed with 5.1-cm-diameter steam-cleaned PVC casing and 0.59-m-length screens. Native sediment usually caved around screens; otherwise, washed quartz sand was added. Well bores were

sealed with bentonite. Well development was done by surging and pumping.

ODEQ installed 33 temporary wells in an array near the Burgess transect (Fig. 1). This dense array, occupying a vertical plane 730 m long and 6.4 m deep, was oriented perpendicular to the Burgess transect at nest 2. These wells were installed by direct push of a 0.61-m-long stainless steel screen. Development of these wells was done with a peristaltic pump. These wells were sampled by ODEQ for NO_3, NH_4, and Cl (32 wells) and O_2 (33 wells) to provide information on solute dispersion normal to the direction of flow. This network of wells is referred to as the dispersion array. (The raw data are provided as Supplemental data: supplemental_data_2.xls.)

ODEQ used direct-push drilling to install one well near the center of each of three plumes of septic tank effluent. Plumes were identified by drilling and sampling from multiple exploratory wells on the downgradient side of septic tank drainfields; plume centers generally were characterized by NO_3—N >10 mg/L. Wells were developed by pumping with a peristaltic pump. The USGS sampled these wells for nutrients, $\delta^{15}N$—NO_3, and Cl. Water from one of these wells, DEQ1227, also was analyzed for DOC, common ions, and field parameters. These data supplemented ODEQ study area septic tank effluent data.

Atmospheric precipitation data were used to characterize potential background chemical fluxes. Precipitation-weighted mean N and Cl concentrations for calendar year 1999 (National Atmospheric Deposition Program, no date) for the Silver Lake Ranger Station (70 km SE of La Pine) were assumed typical of study area precipitation.

Sample collection and analysis

ODEQ samples

ODEQ samples (synoptic network and dispersion array) were collected following stabilization of field parameters. O_2 was measured electrochemically *in situ*, or by iodometric titration on-site. Samples for Cl were filtered on-site through 0.45-μm nominal-pore-size capsule filters. Samples for NO_3 and NH_4 from the ODEQ synoptic network were filtered in the laboratory (0.45-μm plate filters), whereas those from the dispersion array were filtered on-site through 0.45-μm capsule filters. Samples for NO_3 and NH_4 were preserved on-site with sulfuric acid to pH < 2. Analytical techniques are described by Clesceri et al. (1998). ODEQ analytical techniques were evaluated by the USGS interlaboratory analytical evaluation program. This blind sample program uses natural-matrix standard reference materials. Results are published semiannually (e.g. Farrar and Copen, 2000; Connor et al., 2001).

USGS samples

USGS sample collection and processing protocols are briefly described below. Greater detail is provided in US Geological Survey (1999).

Samples were generally collected after both purging of at least three bore volumes and stabilization of field parameters. O_2, pH, temperature, and specific conductance were measured electrochemically *in situ*. Alkalinity was measured on-site and in duplicate by titration.

Wells in the elevated-NH_4 network were primarily domestic wells, and had submersible pumps. Where possible, wells were sampled near the well head and upgradient from pressure tanks. If access upgradient from pressure tanks was unavailable, dissolved gases were not collected. Burgess and Century transect wells were sampled with a submersible pump; wetted pump parts were stainless steel and fluorocarbon polymer. Two types of tubing (copper and fluorocarbon polymer) were attached to the pump with a stainless steel union. CFC samples were collected from copper tubing. Other samples were collected from fluorocarbon polymer tubing. Monitoring wells in septic tank effluent plumes were sampled with a peristaltic pump.

Samples for nutrients, common ions, alkalinity, $\delta^{15}N$—NO_3, and $\delta^{15}N$—NH_4 were filtered through in-line 0.45-μm nominal-pore-size one-time-use capsule filters. Capsule filters were flushed with 1 L of deionized water and then flushed with sample water to remove deionized water prior to use. Cation samples (except NH_4) were preserved with ultrapure nitric acid (pH < 2). Samples for DOC were filtered through 0.45-μm nominal-pore-size silver plate filters. Samples for N_2, Ar, and CH_4 concentrations and for $\delta^{15}N$—N_2 were collected in a gas-free environment and preserved with potassium hydroxide. CFC samples were collected in flame-sealed borosilicate glass ampules under an atmosphere of purified N_2 following protocols of Busenberg and Plummer (1992). Samples for analysis of Ne, ^4He, and δ^3He were collected in-line in copper tubes that were crimped while under back-pressure. Samples for analysis of ^3H were collected in glass bottles or copper tubes.

Nutrients, common ions, and DOC were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado (Fishman and Friedman, 1989; Patton and Truitt, 1992; Brenton and Arnett, 1993; Fishman, 1993; Patton and Truitt, 2000). Dissolved N_2, Ar, and CH_4 were measured at the USGS Dissolved Gas Laboratory in Reston, Virginia, by gas chromatography (Busenberg et al., 1998). Isotopes of N were analyzed by mass spectrometry at the USGS Reston Stable Isotope Laboratory and are reported relative to N_2 in air (AIR; Coplen, 1993). Methods of freeze drying, combustion and analysis of $\delta^{15}N$—NO_3, and combustion and analysis of $\delta^{15}N$—N_2, were those of Böhlke and Denver (1995), with modification of the combustion reagents according to Böhlke et al. (1993). Methods of NH_4 extraction from water samples, combustion and analysis were those of Böhlke et al. (2006). Analyses of $\delta^{15}N$—NO_3 and $\delta^{15}N$—NH_4 were calibrated by analyzing laboratory solutions with known isotopic compositions, and the data were normalized against international reference materials according to Böhlke and Coplen (1995). Analyses of $\delta^{15}N$—N_2 were calibrated by analyzing air and air-equilibrated laboratory water samples. Samples for CFCs were analyzed in triplicate at the USGS Reston Chlorofluorocarbon Laboratory by purge-and-trap gas chromatography with an electron-capture detector (Busenberg and Plummer, 1992; Busenberg et al., 1998).

Tritium in ground-water samples from the elevated-NH_4 network, from Burgess 6.2, and from Century 1.2 and 6.2 were analyzed at the University of Miami Tritium Laboratory. Analysis was by electrolytic enrichment and gas counting (Östlund et al., 1974).

Analysis of Ne, ^4He, and δ^3He was done at Lamont-Doherty Earth Observatory of Columbia University (LDEO). Ne

was measured in a quadrupole mass spectrometer. Helium-4 and δ^3He were measured in a dedicated helium isotope mass spectrometer. Tritium for ^{3}H/^{3}He age dating also was measured at LDEO, using the ^{3}He ingrowth method. Analytical methods used at LDEO are described in Plummer and Mullin (1997a,b), and references therein.

Reporting and plotting conventions

Samples analyzed by USGS and ODEQ for NO_3 were analyzed for nitrite-plus-nitrate ($NO_2 + NO_3$). USGS samples analyzed for $NO_2 + NO_3$ were also analyzed for NO_2, and NO_2 concentrations were consistently negligible. We assume that NO_2 also was negligible in ODEQ-analyzed samples, and thus refer to $NO_2 + NO_3$ as NO_3.

For plotting purposes, USGS NO_3 and ODEQ NO_3 and Cl concentrations below the minimum reporting level (MRL) were plotted at one-half of the MRL. The USGS and ODEQ MRL for NO_3—N was 0.005 mg/L, and for ODEQ Cl, 0.5 mg/L.

Results and discussion

Aquifer scale distribution of NO_3 and NH_4

An aquifer-scale understanding of N distribution was provided by the ODEQ synoptic network. Ground-water samples containing >1 mg/L NO_3—N represented 22% of the sites, although samples from only two sites (1% of the sites) exceeded the US Environmental Protection Agency (USEPA) Maximum Contaminant Level of 10 mg/L NO_3—N. NO_3 currently occurs primarily near the water table. Well construction data were available for 89% of ODEQ synoptic network wells; of this group, ground water that contained >1 mg/L NO_3—N came from shallow wells in which the tops of the open intervals had median and maximum depths below water table of 3.3 m and 8.1 m, respectively.

Elevated concentrations of NH_4—N (>1 mg/L) were observed in 17% of the ground-water samples from the ODEQ synoptic network, and concentrations as high as 39 mg/L NH_4—N were documented. Well construction data were available for 171 of the 192 sites sampled for NH_4. Of these 171 sites, 30 yielded ground water with >1 mg/L NH_4—N. The 30 sites with elevated concentrations of NH_4 generally were deep or in the near-river environment, and the deeper samples among these tended to contain higher concentrations of NH_4 than did the shallower samples. Of the 30 sites with elevated concentrations of NH_4, 17 were wells in which the depth of the top of the open interval below the water table was >37 m (median NH_4—N 8.2 mg/L), and of the 13 shallow sites (median NH_4—N 3.2 mg/L), 10 were located within 600 m of rivers. Thus, in contrast to the distribution of NO_3 concentrations, NH_4 concentrations exceeding 1 mg/L NH_4—N generally were detected in deep ground water or in shallow ground water near rivers, the latter possibly representing deep ground water moving towards rivers, which serve as drains for regional ground water.

Ground-water age and temporal aspects of NO_3 and NH_4 occurrence

Age-dating techniques were used to estimate ground-water travel times along flowpaths. Age-dating information allowed us to determine whether ground water containing elevated concentrations of NO_3 and NH_4 was of recent origin (thus possibly related to anthropogenic activities), or if the ground water predated anthropogenic influences in the study area (thus implicating natural sources of NO_3 or NH_4). Physical, chemical and isotopic data from transects (Table 1) also helped define the distribution of NO_3 and NH_4 in the context of space and time.

Estimated recharge temperatures are needed for calculating apparent ground-water ages from CFC or ^{3}H/^{3}He data. Recharge temperature often is close to the mean annual air temperature (Andrews, 1992) or the mean annual soil temperature at the water table (about 1 °C greater than the mean annual air temperature; Stute and Schlosser, 2000). The mean annual air temperature in the study area is 7.2 °C (mean of mean annual air temperatures at the Wickiup Reservoir and Bend climate stations; Fig. 1) (National Climatic Data Center, 2005a,b). However, Ne and Ar concentrations plot along an excess air curve indicating a median recharge temperature of 5.2 °C (Fig. 2). Most study area recharge enters sediment between late fall and early spring as direct infiltration of precipitation and snowmelt. Much of this recharge occurs in a pulse during spring snowmelt and possibly takes little time to travel through the thin unsaturated zone. The difference between the mean annual air temperature (7.2 °C) and the recharge temperature estimated from Ne and Ar concentrations (5.2 °C) may reflect recharge primarily during colder months. Thus, a recharge temperature of 5.2 °C was used in calculations. A 2.0 °C increase in assumed recharge temperature would result in a median difference of 1 y in the CFC apparent ages calculated below and less than 0.1 y in the ^{3}H/^{3}He apparent ages.

All transect wells except Burgess 6.2, Century 1.2, and Century 6.2 were sampled for CFC-12, CFC-11, and CFC-113. A CFC-based apparent age represents the time of travel for water particles from their points of recharge at the water table to a well (Busenberg and Plummer, 1992; Cook and Solomon, 1997; Plummer and Busenberg, 2000). In general, CFC-12 concentrations provide the most reliable CFC apparent ages because CFC-12 does not tend to sorb and is resistant to microbial degradation until methanogenic conditions become well established, whereas CFC-11 and CFC-113 are more susceptible to microbial degradation and may sorb to organic carbon (Plummer and Busenberg, 2000). Thus, we generally used the median CFC-12 apparent age at most sites. However, samples from three sites (Century 1.1, Century 4, and Century 5) contained CFC-12 concentrations that were greater than could be accounted for by simple air—water solubility and that were highly variable among sequential samples (Table 2), thus indicating the presence of CFC-12 contamination. In instances where CFC-12 contamination was indicated, CFC-11 and CFC-113 apparent ages were evaluated. If the CFC-11 and CFC-113 apparent ages were similar (within 4 y, i.e. Century 1.1 and Century 4), the median of the six CFC-11 and CFC-113 apparent ages was used. On the other hand, if the CFC-12 concentrations indicated the presence of contamination, and the CFC-11 and CFC-113 apparent ages were not similar, the CFC-11 and CFC-113 may have been degraded, and the water was considered undatable by CFCs; this was the case for Century 5. Finally, the highly reducing conditions at Burgess 6.1 (1.07 mg/L CH_4, 12.3 mg/L iron [Fe], and no

Table 1 Geochemical and isotopic data from ground water transects, elevated-ammonium network, and plumes of septic tank effluent

Name	Sample date	Depth to top of open interval (m)	Depth to bottom of open interval (m)	Depth to water (m)	O_2 (mg/L)	pH	$NO_2^- + NO_3^-$ (mg N/L)	NH_4^+ (mg N/L)	Kjeldahl nitrogen (mg N/L)	NO_2^- (mg N/L)	P (mg/L)
Burgess 1.1	10/14/99	9.41	10.01	7.94	10.7	7.1	1.3	<0.02	<0.1	<0.01	0.12
Burgess 1.2	10/18/99	13.83	14.42	7.90	9.3	7.7	0.045	<0.02	E0.06	<0.01	0.16
Burgess 2.1	10/18/99	5.91	6.52	4.03	7.5	6.9	1.4	<0.02	E0.07	<0.01	0.25
Burgess 2.2	10/18/99	8.01	8.62	4.00	2.4	7.1	1.1	0.02	E0.07	0.01	0.20
Burgess 2.3	10/15/99	9.94	10.55	3.98	0.2	7.4	<0.005	0.02	<0.1	<0.01	0.34
Burgess 2.4	10/15/99	14.53	15.12	3.95	0.3	7.5	<0.005	<0.02	E0.05	<0.01	0.25
Burgess 3.1	10/16/99	5.74	6.33	2.74	3.9	7.0	1.5	<0.02	E0.09	<0.01	0.23
Burgess 3.2	10/16/99	7.72	8.31	2.72	5.1	7.2	1.2	<0.02	E0.07	<0.01	0.25
Burgess 3.3	10/16/99	10.64	11.23	2.58	0.2	7.3	<0.005	0.05	E0.08	<0.01	0.14
Burgess 4.1	10/17/99	6.50	7.09	3.67	0.4	7.1	0.031	<0.02	E0.07	<0.01	0.23
Burgess 4.2	10/17/99	9.02	9.61	3.58	0.2	7.1	0.013	0.03	0.1	<0.01	0.17
Burgess 4.3	10/17/99	13.90	14.50	3.52	0.3	7.4	<0.005	0.08	0.1	0.01	0.24
Burgess 5.1	10/19/99	5.71	6.31	4.07	0.7	7.1	<0.005	<0.02	E0.06	<0.01	0.17
Burgess 5.2	10/19/99	9.69	10.29	4.09	0.2	7.5	<0.005	0.08	0.1	<0.01	0.21
Burgess 5.3	10/19/99	13.84	14.43	3.79	0.3	8.2	<0.005	0.30	0.3	<0.01	0.50
Burgess 6.1	7/11/00	3.38	3.97	1.98	0.2	7.1	<0.005	0.08	0.2	<0.01	0.35
Burgess 6.2	7/11/00	12.14	12.73	1.97	<0.1	7.6	<0.005	4.5	5.0	<0.01	1.1
Century 1.1	7/14/00	2.65	3.23	1.85	4.1	6.8	3.6	<0.02	E0.09	0.03	0.05
Century 1.2	7/14/00	19.23	19.81	1.85	0.1	7.5	<0.005	5.5	6.2	<0.01	2.1
Century 2	7/12/00	2.29	2.86	1.05	<0.1	7.1	0.80	0.03	E0.1	0.01	0.04
Century 3	7/13/00	1.62	2.19	1.15	0.2	7.5	0.009	0.03	0.1	<0.01	0.08
Century 4	7/12/00	2.16	2.77	1.72	1.9	6.8	6.7	0.08	0.3	<0.01	0.06
Century 5	7/14/00	2.47	3.05	1.62	0.2	6.9	5.6	0.08	0.2	<0.01	0.04
Century 6.1	7/13/00	2.16	2.74	1.72	4.0	6.8	4.1	<0.02	E0.06	<0.01	0.10
Century 6.2	7/13/00	17.92	18.50	2.26	0.2	7.1	<0.005	2.3	2.7	<0.01	0.90
DEQ191	6/6/00	59	62	5.16	<0.1	7.0	<0.005	21	23	0.02	2.2
DEQ197	6/6/00	101	102	7.03	<0.1	7.6	<0.005	38	43	<0.01	1.6
DEQ204	6/6/00	98	98	3.01	0.2	7.7	<0.005	15	15	<0.01	2.2
DEQ142	6/7/00	134	140	15.45	<0.1	7.6	<0.005	15	16	<0.01	2.3
DEQ540	6/7/00	8	11	2.97[a]	<0.1	7.9	0.073	4.5	4.8	<0.01	0.96
DEQ108	6/8/00	104	113	2.47	<0.1	7.5	<0.005	8.1	9.3	<0.01	2.1
DEQ284	6/8/00	41	43	2.38	0.1	7.6	<0.005	5.8	5.9	<0.01	2.2
DEQ186	6/8/00	11	13	3.78	0.3	7.7	<0.005	1.3	1.4	<0.01	0.17
DEQ216	6/8/00	27	30	2.97	<0.1	7.3	<0.005	3.1	3.5	<0.01	1.2
DEQ214	6/9/00	37	40	3.08	<0.1	8.0	<0.005	1.5	1.6	<0.01	1.2
DEQ146	7/11/00	84	126	7[b]	<0.1	7.2	<0.005	32	35	<0.01	2.1
Plume 1 (DEQ1227)	5/15/00	4.45	5.30	3.48	8.3	6.7	26	0.09	0.4	<0.01	0.10
Plume 2 (DEQ2046)	11/30/00	1.19	3.05	2.10			38	<0.04	0.2	0.01	0.02
Plume 3 (DEQ2091)	5/14/01	2.44	3.05	2.13			49	<0.04	0.3	E0.003	0.08

(*continued on next page*)

Table 1 (*continued*)

Name	Cl^-	SO_4^{2-} (mg SO_4^{2-}/L)	HCO_3^- (mg HCO_3^-/L)	Fe (μg/L)	Mn (μg/L)	DOC (mg/L)	CH_4 (mg/L)	N_2 (mg/L)	Ar (mg/L)	Ne (μg/kg)	$\delta^{15}N$-NH_4^+ (‰) (AIR)	$\delta^{15}N$-NO_3^- (‰) (AIR)	$\delta^{15}N$—N_2 (‰) (AIR)
Burgess 1.1	2.7	3.9	59.5	17	E1	1.3	0.00	20.7	0.712			4.0	
Burgess 1.2	0.97	<0.3	61.0	18	E2	1.2	0.00	19.4	0.688				0.54
Burgess 2.1	3.0	3.3	41.4	350	6	0.8	0.00	18.2	0.658			6.2	0.51
Burgess 2.2	3.2	3.1	58.3	310	43	1.1	0.00	19.3	0.681			8.7	0.68
Burgess 2.3	1.2	1.4	55.1	510	12	1.3	0.13	19.3	0.684				
Burgess 2.4	1.1	0.5	54.9	1300	80	0.6	0.21	19.2	0.682				
Burgess 3.1	1.5	3.1	56.1	22	4	0.7	0.00	17.9	0.644			3.3	0.42
Burgess 3.2	2.4	2.6	40.3	65	4	0.8	0.00	18.4	0.660			5.7	0.60
Burgess 3.3	1.8	4.1	52.6	750	79	0.7	0.01	19.8	0.681				0.77
Burgess 4.1	2.9	9.3	78.1	24	<2	2.1	0.00	20.5	0.678				
Burgess 4.2	3.8	13	82.1	800	100	2.1	0.00	21.0	0.669				1.49
Burgess 4.3	4.2	7.0	57.3	1300	130	1.2	0.07	21.0	0.684				1.03
Burgess 5.1	1.3	1.6	56.1	E5	3	1.9	0.00	19.9	0.705				0.51
Burgess 5.2	1.1	5.4	70.2	230	120	1.6	0.01	20.6	0.705				0.91
Burgess 5.3	0.95	2.9	72.3	150	78	1.2	0.23	19.6	0.696	0.197			
Burgess 6.1	0.78	<0.3	83.4	12,300	250	2.8	1.07	18.1	0.670	0.179			
Burgess 6.2	1.3	<0.3	159	4600	360	3.6					2.6		
Century 1.1	8.1	2.1	56.7	E8	86	2.2	0.00	19.4	0.693	0.190		7.1	0.34
Century 1.2	2.0	2.0	204	220	87	6.1					2.5		
Century 2	13	5.7	122	91	130	3.0	0.00	22.5	0.723	0.192		11.5	1.20
Century 3	6.5	5.1	158	42	170	4.3	0.00	21.1	0.703	0.208			1.34
Century 4	7.4	9.0	116	12	260	2.3	0.00	20.5	0.712			9.5	0.31
Century 5	11	5.9	121	11	260	1.7	0.00	21.1	0.720			12.8	0.69
Century 6.1	7.5	3.5	122	E7	6	2.5	0.01	18.8	0.670	0.189		6.4	0.45
Century 6.2	3.0	0.6	104	950	390	2.2					3.8		
DEQ191	3.1	<0.3	410	10,600	360	6.2	90.0	11.4	0.431		3.2		
DEQ197	2.0	<0.3	858	5300	110	18	114	6.8	0.286		3.6		
DEQ204	3.2	1.6	293	1600	200	3.0	65.2	17.2	0.595		3.9		
DEQ142	2.2	2.2	227	1600	99	5.9	44.9	15.9	0.552		2.7		
DEQ540	1.6	1.0	102	370	56	1.5					3.2		
DEQ108	1.8	1.4	450	2700	160	9.9	82.5	14.2	0.508		3.3		
DEQ284	0.58	1.9	86.9	790	46	1.2					2.6		
DEQ186	2.0	3.1	295	410	330	0.8					3.2		
DEQ216	1.3	E0.2	112	3000	260	3.3	25.8	20.9	0.713		3.4		
DEQ214	2.1	0.8	152	890	240	1.3	23.7	16.9	0.610		3.9		
DEQ146	2.3	<0.3	752	5600	180	12	85.5	6.1	0.250		3.7		
Plume 1 (DEQ1227)	32	19	103	52	87	2.2						8.3	
Plume 2 (DEQ2046)	110											7.0	
Plume 3 (DEQ2091)	110											11.8	

These data are a subset of the complete analytical suite. The complete list of geochemical and isotopic data, along with location information, can be found in Supplemental data: supplemental_data_3.xls. ''E'' indicates estimated.

a Depth to water measured 6/6/00; no measurement with sample.

b Depth to water measured by driller 10/21/66; no measurement with sample.

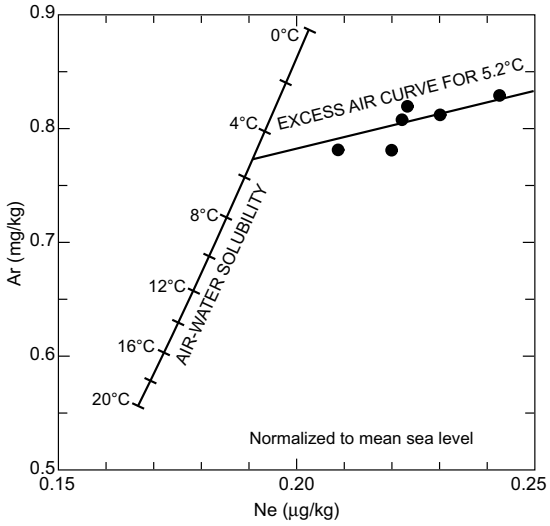

Figure 2 Ne and Ar concentrations in ground water (transect sites at which Ne was measured), with air—water solubility curve (Weiss, 1970, 1971) and excess air trend for water recharged at 5.2 °C. Data normalized to mean sea level (US Committee on Extension to the Standard Atmosphere, 1976) to remove variability associated with variable recharge elevations, where recharge elevation for a given sample was assumed to be the water table elevation at the sampling site.

detectable sulfate [SO_4]) could have led to microbial degradation of CFCs, and the CFC apparent age for this site was considered the maximum likely tracer-based apparent age. CFC apparent ages are presented in Table 2.

A subset of transect wells was sampled for $^3H/^3He$ ground-water dating (e.g. Schlosser et al., 1989; Cook and Solomon, 1997; Solomon and Cook, 2000). Calculated $^3H/^3He$ apparent ages are given in Table 2. Diffusive ^3He loss can occur in ground water with vertical flow velocities of less than about 0.25—0.50 m/y, leading to a young bias in $^3H/^3He$ apparent ages (Schlosser et al., 1989). Low recharge rates in the study area (discussed below) likely result in low vertical flow velocities and may cause a young bias in $^3H/^3He$ apparent ages. Thus, $^3H/^3He$ apparent ages are interpreted as minimum ages. Although $^3H/^3He$ apparent ages are qualified (presented as minimum apparent ages), they are consistent with the CFC apparent ages, and thus provide support for the reliability of the CFC dating method.

Ground water from three deep transect sites (Burgess 6.2, Century 1.2, and Century 6.2) was dated only with ^3H. In all three cases, ^3H concentrations were $\leqslant$0.2 TU (Table 2), clearly indicating pre-bomb (pre-1953) recharge. This apparent age of >47 y represents travel time through both the (thin) unsaturated zone and saturated zone.

Burgess transect hydrochronology (as well as O_2, NO_3, and Cl distributions) are shown in Fig. 3. There is good agreement between tracer-based apparent ground-water ages and position along the transect — ground-water apparent age increases with depth and in the downgradient direction. The relatively small apparent age (<34 y) at Burgess 6.1 (shallow well located adjacent to the Little Deschutes River) may reflect mixing of river and ground water.

In some types of simple aquifers, recharge rates may be estimated from individual tracer-based apparent ground-water ages by using the following equation (Vogel, 1967; Cook and Böhlke, 2000):

$$\boldsymbol{R} = (\boldsymbol{H}\varepsilon/\boldsymbol{T})\ln(\boldsymbol{H}/(\boldsymbol{H}-\boldsymbol{z})) \quad (1)$$

where $\boldsymbol{R}$ is the recharge rate, $\boldsymbol{H}$ the aquifer thickness, ε the porosity, $\boldsymbol{T}$ the time of travel, and $\boldsymbol{z}$ the depth below the water table. Eq. (1) holds for homogeneous, unconfined aquifers of constant thickness receiving uniform recharge. Eq. (1) was applied to the Burgess transect. (Shallow wells along the Century transect tap a 1- to 2-m sand layer underlain by about 10—20 m of clay; the 0.6-m screened intervals were sufficiently long relative to the sand layer thickness that the Century transect wells were not amenable to use in Eq. (1).) Sites with censored CFC apparent ages (associated with a ''>'' or ''<'') were not used. Assuming an aquifer thickness of 15 m (typical saturated thickness of sands overlying fine-grained materials along the Burgess transect) and a porosity of 0.3, Eq. (1) yields a median recharge rate of 5.4 cm/y, or about 12% of average annual precipitation. This recharge estimate is somewhat greater than the 3.6—3.8 cm/y estimated for the Burgess transect area by regional application of a water balance model (Bauer and Vaccaro, 1987) to the upper Deschutes Basin (Boyd, 1996; Gannett et al., 2001), but comparable to the 5.1—5.4 cm/y that provided the optimal fit during calibration of the aquifer-scale model accompanying the current study (Morgan et al., 2002). Note that a recharge rate of 5.4 cm/y and a porosity of 0.3 equates to vertical velocity near the water table of 0.18 m/y — sufficiently slow that incomplete ^3He confinement is possible, as described above.

The hydrochronology of ground water along the Century transect is consistent with the expectation that deeper ground water should generally be older than shallower ground water. The deep wells (Century 1.2 and 6.2, screened more than 15 m below the water table) contained pre-bomb water. The remaining wells were screened within 2 m of the water table, and yielded water with tracer-based apparent ground water ages of 9—23 y. Tracer-based apparent ages in the shallow Century transect wells do not vary in any obvious systematic manner along the transect. These shallow wells were installed along a narrow ridge in the potentiometric surface (Fig. 1), and ground water probably is shed laterally from this ridge with the result that shallow ground water collected along the length of the Century transect probably represents a collection of samples of locally recharged ground water and not a chronologic sequence of ground water.

Patterns of NO_3 and NH_4 distribution along the Burgess and Century transects (Fig. 3 and Table 1) are similar to those observed in the ODEQ synoptic network — NO_3 is found at shallow depth, whereas NH_4 is found in deeper ground water, or in downgradient ground water where regional ground water discharges towards rivers. NO_3 is found only in younger water that may have been affected by recent anthropogenic inputs, whereas NH_4 occurs primarily in older water that predates most anthropogenic activities in the area (Fig. 4).

Sources of NO_3 and NH_4

ODEQ synoptic network NO_3 and Cl data, along with potential endmember sources of N and Cl (atmospheric precipitation

Table 2 Tracer-based apparent ages for ground water from transect and elevated-ammonium-network wells

Site	Sample date	CFC concentration in solution (pg/kg)			CFC apparent recharge year[a]			^{3}H (TU)[b]	δ^3He (%)	^{4}He[c]	Apparent age (y)			Selected apparent age (y)
		CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113[d]				CFC	^{3}H	^{3}H/^{3}He	
Burgess 1.1	10/14/99	722.0	340.1	327.9	1985.5	1989.0	C				11			11
Burgess 1.2	10/18/99	279.7	125.6	41.9	1972.5	1972.5	1982.0				27			27
Burgess 2.1	10/18/99	570.2	268.1	146.7	1980.5	1984.0	C				16			16
Burgess 2.2	10/18/99	133.7	84.3	42.3	1967.5	1969.0	1982.0				31			31
Burgess 2.3	10/15/99	1.9	2.7	59.0	1950.0	1947.5	1984.5				52			52
Burgess 2.4	10/15/99	0.9	2.1	110.7	1948.5	1946.5	1990.5				53			53
Burgess 3.1	10/16/99	441.9	222.7	81.4	1976.5	1980.0	1987.0				20			20
Burgess 3.2	10/16/99	357.3	161.0	49.9	1974.5	1975.0	1983.5				25			25
Burgess 3.3	10/16/99	1.1	16.4	31.7	1949.0	1957.0	1979.5				43			43
Burgess 4.1	10/17/99	99.7	168.5	49.4	1965.5	1975.5	1983.0				24			24
Burgess 4.2	10/17/99	36.9	157.7	60.5	1960.5	1974.5	1985.0				25			25
Burgess 4.3	10/17/99	0.0	32.0	33.6	<1945.0	1962.0	1980.0				38			38
Burgess 5.1	10/19/99	80.9	64.3	253.5	1964.5	1967.0	C				33			33
Burgess 5.2	10/19/99	1.3	8.1	25.4	1949.0	1952.0	1978.0				48			48
Burgess 5.3	10/19/99	1.0	0.0	91.9	1948.5	<1940.0	1988.0	<0.05	4.20	4.86	>60		>62	>62
Burgess 6.1	7/11/00	0.0	63.6	0.0	<1945	1967.0	<1955.0	4.81	−0.33	4.35	<34		>1	$1 < X < 34$
Burgess 6.2	7/11/00							0.2				>47		>47
Century 1.1	7/14/00	743.3	350.8	93.2	1986.0	1990.0	1988.5	3.08	3.69	4.73	14		>7	14
	7/14/00	745.7	418.3	89.0	1986.5	C	1988.0							
	7/14/00	754.7	399.4	99.1	1986.5	C	1989.0							
Century 1.2	7/14/00							0.1				>47		>47
Century 2	7/12/00	87.0	196.9	0.0	1965.0	1978.0	<1955.0				23			23
Century 3	7/13/00	12.7	259.5	0.0	1955.0	1983.0	<1955.0	3.34	5.10	4.78	18		>8	18
Century 4	7/12/00	682.6	321.4	82.2	1984.5	1987.5	1987.0	3.14	0.67	5.23	14		>3	14
	7/12/00	655.9	398.6	84.5	1983.5	C	1987.5							
	7/12/00	651.4	482.5	78.3	1983.5	C	1987.0							
Century 5	7/14/00	637.8	470.6	82.9	1983.0	C	1987.5				(−)			(−)
	7/14/00	601.8	361.2	98.4	1982.0	1991.5	1989.0							
	7/14/00	591.1	420.8	99.9	1981.5	C	1989.0							
Century 6.1	7/13/00	744.8	361.7	86.4	1986.0	1991.5	1987.5	3.62	1.90	4.98	9		>4	9
Century 6.2	7/13/00							<0.1				>47		>47
DEQ191	6/6/00							<0.1				>47		>47
DEQ197	6/6/00							<0.1				>47		>47
DEQ204	6/6/00							<0.1				>47		>47
DEQ142	6/7/00							0.1				>47		>47
DEQ540	6/7/00							4.4				<47		<47
DEQ108	6/8/00							<0.1				>47		>47
DEQ284	6/8/00							<0.1				>47		>47
DEQ186	6/8/00							2.9				<47		<47
DEQ216	6/8/00							<0.1				>47		>47
DEQ214	6/9/00							<0.1				>47		>47
DEQ146	7/11/00							<0.1				>47		>47

CFC samples collected and analyzed in triplicate. For most sites, CFC-based apparent age was based upon median CFC-12 apparent age, and that one sample is listed. Some samples at each of three sites — Century 1.1, 4, and 5 — contained CFC-12 concentrations greater than could be accounted for by simple air—water solubility; for these sites, all three samples are listed and interpretation is discussed in text.

[a] ''C'' indicates contamination — concentration exceeds that expected for water in contact with uncontaminated atmosphere for any date prior to sampling date.

[b] Tritium by electrolytic enrichment and gas counting given to tenths; by helium ingrowth, to hundredths.

[c] Units of cm^3 STP/1.0×10^8 g H_2O.

[d] The CFC-113 apparent ages for Burgess nests 1—5, which were drilled in 1999, are consistently younger than CFC-11 and CFC-12 apparent ages, or are at contaminant levels, whereas CFC-113 apparent ages for other transect sites, which were drilled in 2000, are reasonable. It is possible that well casing used in 1999 was contaminated with CFC-113.

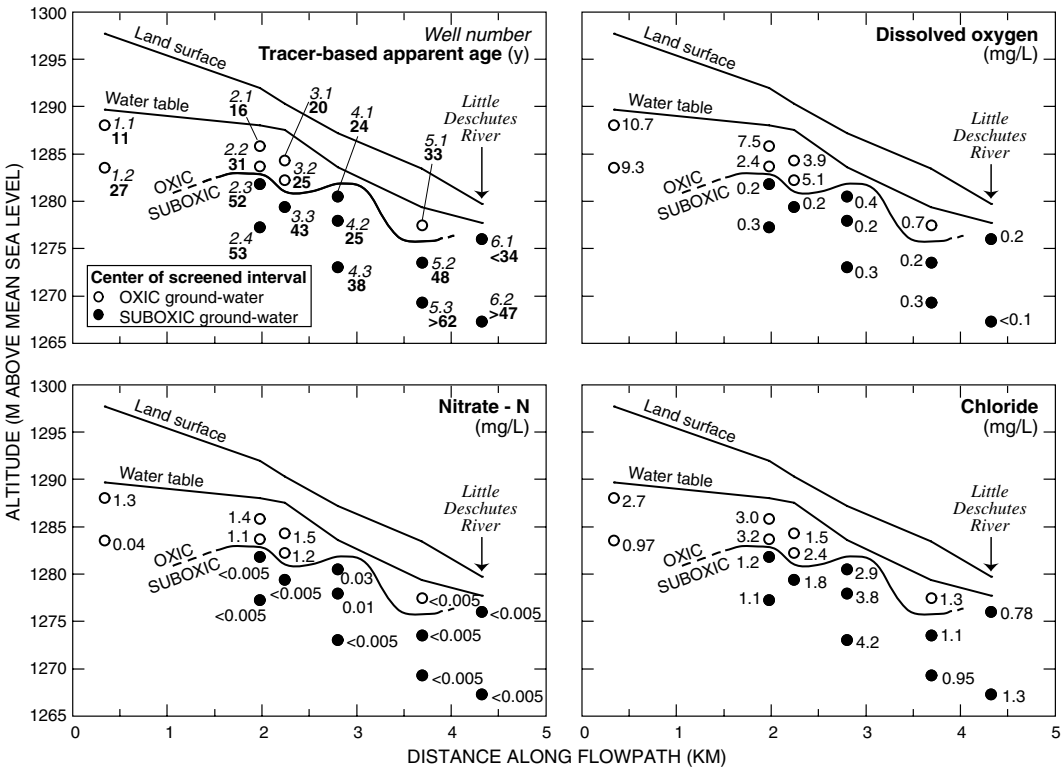

Figure 3 Tracer-based apparent ground-water ages, and O_2, NO_3, and Cl concentrations, along Burgess transect. Ground water moves down and towards the right, and discharges to the Little Deschutes River.

data and typical septic tank effluent values), are shown in Fig. 5. Atmospheric precipitation N and septic tank effluent N are shown in Fig. 5 as equivalent NO_3; that is, atmospheric NH_4 was combined with atmospheric NO_3 and plotted as equivalent NO_3, and septic tank N was plotted assuming all reduced N was oxidized to NO_3. Median N and Cl concentrations from study area septic tank effluent (55 N, 32 Cl samples; Rich, 2001) are plotted as a point in Fig. 5. Other data on typical septic tank effluent from the literature (US Environmental Protection Agency, 1978; Oregon Department of Environmental Quality, 1982; Alhajjar et al., 1989; Bushman, 1996; Bunnell et al., 1999; Bates, 2000) are included in the error bars in Fig. 5, which represent the ranges of medians (means if medians not provided) from these literature sources. The wider range in these literature values for Cl compared to N may reflect variations in Cl concentrations due to presence or absence of water softeners, and variations in Cl concentrations in sources of domestic water resulting from, for example, factors such as proximity to coastal environments, local use of road salt, or variations in evapotranspiration.

Concentrations of both N and Cl are higher in septic tank effluent than in ODEQ synoptic network ground-water NO_3 and Cl samples (Fig. 5). Septic tank effluent is likely the primary source of elevated Cl in La Pine ground water. Evaporites do not occur in the volcanic rocks and sediment of the study area, and agricultural sources of Cl are not important (''Study area and background'' section). Sodium chloride is not used on roads, and although compounds containing magnesium chloride are occasionally used, their use is limited and spatially restricted in the study area (Hinkle et al., 2005). For these reasons, and because Cl is nonreactive, Cl is a useful tracer of septic tank effluent in the La Pine area. Most of the ODEQ synoptic network data plot near a mixing line in Fig. 5 between the region representing precipitation (allowing for varying degrees of evapotranspiration and vegetative nutrient uptake) and a region of N- and Cl-rich septic tank effluent. Low-O_2 samples plotting primarily below the mixing region will be discussed in the next section. Thus, NO_3/Cl relations in Fig. 5 are consistent with a septic tank effluent source of elevated NO_3 concentrations. In addition, the observation that ODEQ synoptic network detections of NO_3 > 1 mg/L NO_3—N occur near the water table is consistent with, although not uniquely indicative of, septic tank effluent being the dominant anthropogenic source of NO_3 in the study area.

Geochemical data along the Burgess and Century transects also point to a septic tank effluent source of NO_3 (and Cl) to study area ground water (Fig. 3, and Tables 1 and 2). In general, concentrations of NO_3 and Cl are greater in ground water with apparent ages <40 y (NO_3—N up to 6.7 mg/L, Cl up to 13 mg/L) than in ground water with apparent ages >40 y (NO_3—N <0.01 mg/L, Cl $\leqslant$3.0 mg/L). These data indicate relatively recent loading of both NO_3 and Cl, consistent with the history of home construction along the transects.

Ground-water NO_3 concentrations from the dispersion array, a dense network of wells in a 730 × 6.4 m plane oriented perpendicular to the Burgess transect, are shown in Fig. 6. NO_3 and Cl (data not shown) are correlated

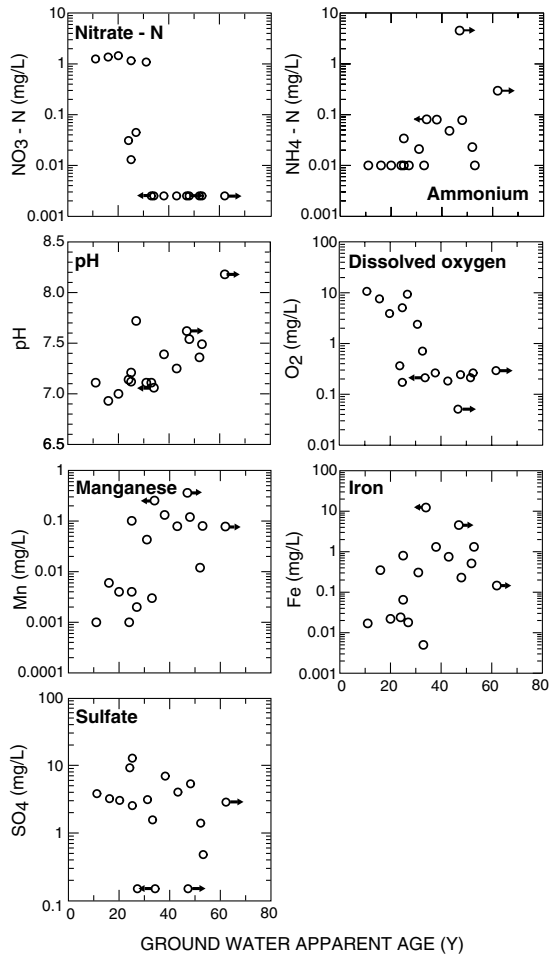

Figure 4 NO_3, NH_4, pH, O_2, Mn, Fe, and SO_4 concentrations along Burgess Transect, as function of tracer-based apparent ground-water age. Arrows indicate censored apparent ages, where a right arrow indicates that apparent age is greater than plotted age, and a left arrow indicates that apparent age is less than plotted age. Concentrations below detection limit plotted at half the detection limit.

($r^2 = 0.77$, $p < 0.0001$). NH_4—N concentrations (data not shown) for the 32 sites were low, with a median of 0.02 mg/L and a maximum of 0.07 mg/L. NO_3 occurs in discrete plumes, each of which could represent a plume from an individual septic tank drainfield, or the coalescing of plumes from several distinct drainfields. The heterogeneous distribution of NO_3 concentrations is consistent with a number of point sources of septic-tank-derived NO_3, rather than a uniform nonpoint source such as from agricultural sources, and provides additional support for a septic-tank source of NO_3 in the study area. The occurrence of low to modest NO_3 concentrations along the Burgess transect (Table 1) may be understood in the context of the dispersion array if upgradient Burgess transect wells tap ground water primarily from locations either between or below NO_3 plumes.

The elevated concentrations of NH_4 in many of the study area ground-water samples are unusual. Although N in septic tank effluent is predominantly in the form of NH_4, reduced forms of N in septic tank effluent are rapidly oxidized to NO_3 in the unsaturated zone in the drainfields

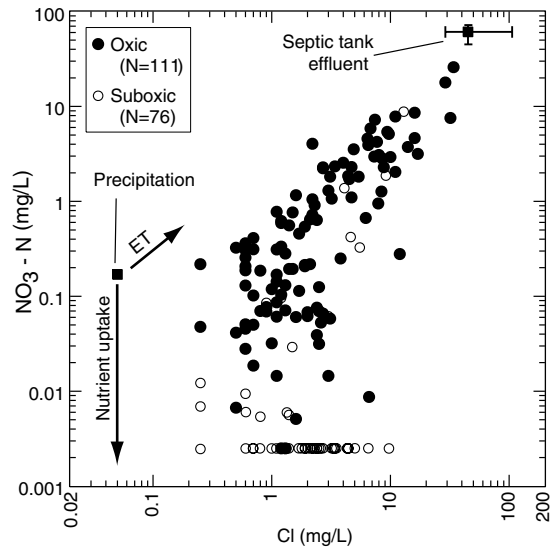

Figure 5 NO_3 and Cl concentrations from ODEQ aquifer-scale synoptic. End-member mixing components are septic tank effluent and atmospheric precipitation; see text for discussion of these components. ODEQ synoptic samples are interpreted to represent a mixture of precipitation and septic tank effluent, where precipitation may be subject to enrichment by evapotranspiration (ET) and to vegetative NO_3 uptake (arrows). Low NO_3 concentrations in most suboxic samples are interpreted to represent effects of denitrification in the saturated zone. Square symbols showing septic tank effluent and unevaporated precipitation represent total nitrogen (septic tank effluent) or $NO_3 + NH_4$ (atmospheric precipitation) plotted as equivalent NO_3. Concentrations below detection limit plotted at half the detection limit.

(Walker et al., 1973; Robertson and Cherry, 1992; MacQuarrie et al., 2001). Subsequent reduction of NO_3 in downgradient reducing regions of an aquifer could yield either NH_4 or N_2, but reduction to NH_4 is generally for assimilative pur-

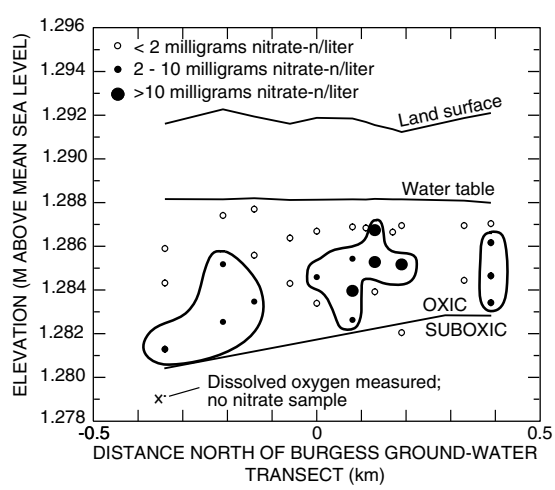

Figure 6 Dispersion array of ground-water samples. Array oriented perpendicular to Burgess transect at second nest (at flowpath distance of 2.0 km in Fig. 3). Ground water flow is out of page towards reader. NO_3 is present in isolated plumes.

poses (Brock and Madigan, 1988), and most NO_3 reduction in flowing ground water has been attributed to dissimilative reduction to N_2 (Freeze and Cherry, 1979). Elevated concentrations of NH_4 observed in the ODEQ synoptic network tended to be deep or (apparently) near the ends of ground-water flowpaths, consistent with either NO_3 reduction or a natural, possibly sedimentary organic matter source for the NH_4, perhaps associated with the lacustrine deposits that underlie the primary aquifer. However, the low Cl concentrations of NH_4-rich ODEQ synoptic ground water (Fig. 7) point to a source other than septic tank effluent for the elevated concentrations of NH_4. That is, the Cl data make it highly unlikely that the NH_4 could have originated directly from septic tank N, or by oxidation of septic tank N to NO_3 with subsequent, downgradient reduction to NH_4. A similar conclusion is indicated by data from the Burgess and Century transects, where elevated concentrations of NH_4 are associated with low-Cl ground water (Fig. 7), and are found in downgradient (Fig. 3 and Table 1), older (Fig. 4 and Table 2) ground water. The Cl data, therefore, are inconsistent with a septic tank source for the elevated NH_4. A more likely possibility is that NH_4 is derived from natural sedimentary organic matter.

Additional insight into the origin of the NH_4 is provided by detailed analyses of ground water from 11 sites with elevated concentrations of NH_4 (Tables 1 and 2). These samples contain high concentrations of Fe (median 1.6 mg/L) and CH_4 (median 74 mg/L for a subset of eight samples), reflecting highly reducing conditions that typically accompany organic matter degradation. These samples also contain elevated concentrations of P (median 2.1 mg/L), which might have been mobilized during organic matter degradation. Total carbon (C) and total N for the subset of these sites at which dissolved gases were analyzed are well correlated, with $r^2 = 0.85$ and C:N mass ratio of 6.0 (slope of ''line of organic correlation'', for functional relationships in which neither variable is the independent variable; Helsel and Hirsch, 1992). For this correlation, total C was defined to be inorganic carbon + DOC + CH_4, and total N was defined to be Kjeldahl N + NO_3 (N_2 excluded because largely of atmospheric origin). Because carbonate phases are not known to be present in the aquifer, the observed correlation is consistent with an organic matter source of N (C:N of photosynthetic organic matter is typically 106:16 on a molar basis, or about 5.7:1 on a mass ratio basis). Finally, ^3H concentrations mostly are $\leqslant$0.1 TU (Table 2), reflecting dominantly pre-bomb ground water that is less likely to have received inputs of anthropogenic N than would more recently recharged ground water.

N isotopes can be useful locally in identifying N sources. For example, $\delta^{15}N$ values of NO_3 derived from wastewater sources typically are >5‰, but <5‰ for NO_3 derived from natural soil organic matter (Fogg et al., 1998). The $\delta^{15}N$—NO_3 values from shallow ground water along transects are, for the most part, both similar to $\delta^{15}N$—NO_3 values from septic tank effluent plumes, and distinct from $\delta^{15}N$—NH_4 values for elevated-NH_4 network sites and transect sites with elevated NH_4 concentrations (Fig. 8). Two samples did have $\delta^{15}N$—NO_3 values <5‰. NO_3 in these samples could represent NO_3 that is, at least in part, of natural origin. Alternatively, fractionation of septic-tank-derived N during NH_4 nitrification in the unsaturated zone beneath drainfields upgradient from these two sites, in combination with sorption of a portion of the NH_4, could result in isotopically depleted aqueous NO_3 (Hübner, 1986). These two samples notwithstanding, the overall similarity between the $\delta^{15}N$—NO_3 values from shallow ground water along transects and those representing septic tank effluent further support the concept of septic tank effluent being the predominant NO_3 source in study area ground water. Furthermore, differences between $\delta^{15}N$—NO_3 values of transect and septic tank effluent plume samples on the one hand, and $\delta^{15}N$—NH_4 values of high-NH_4 ground-water samples on the other, indicate that the source of elevated concentrations of NH_4 is distinct from that of most of the NO_3. The isotopic data are inconsistent with transport and subsequent reduction of septic-tank-derived NO_3 to NH_4 because reduction of all of the NO_3 to NH_4 would yield $\delta^{15}N$—NH_4 values greater than those observed. Reduction of only a portion of the NO_3 to

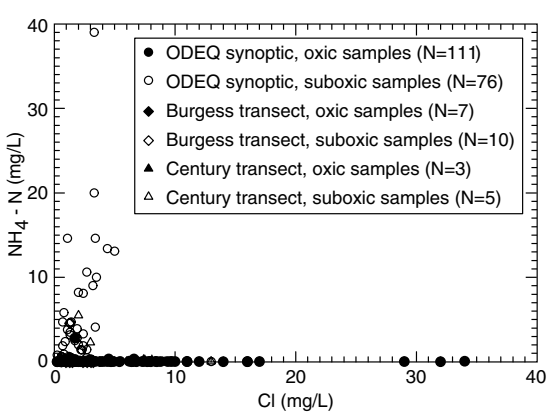

Figure 7 NH_4 and Cl concentrations from transects and ODEQ aquifer-scale synoptic. Elevated concentrations of NH_4 are associated with low Cl concentrations, indicative of a natural, presumably sedimentary source of NH_4. Elevated concentrations of NH_4 also tend to be suboxic.

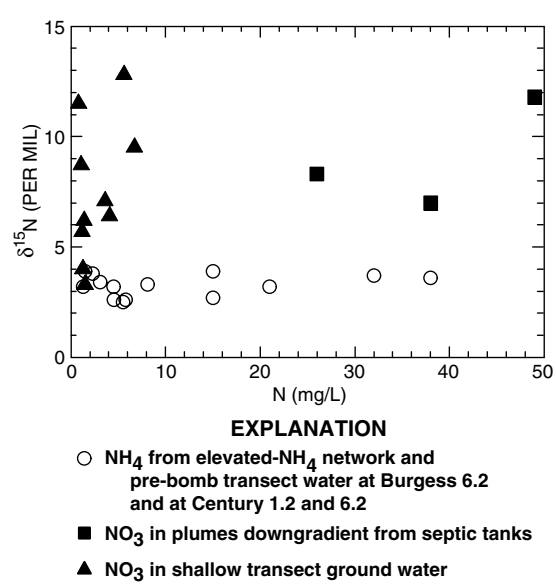

Figure 8 Nitrogen concentrations and $\delta^{15}N$ values for study area ground water.

NH_4, with kinetic fractionation, could yield smaller $\delta^{15}N$–NH_4 values, but would be unlikely to yield consistently such a small range of $\delta^{15}N$–NH_4 values (2.5–3.9‰) across a large range of NH_4–N concentrations (1.3–38 mg/L). It also would be difficult to reconcile the highest concentrations of NH_4–N (up to 38 mg/L) with only partial reduction of NO_3 to NH_4. On the other hand, $\delta^{15}N$–NH_4 values are similar to those of aquifer sediments from the study area, which decrease with increasing N content and level off asymptotically at about 2–3‰ at higher N concentrations (provided as Supplemental data: supplemental_data_4.doc). Thus, the isotopic data are interpreted as additional evidence for a natural, sedimentary source of elevated aqueous NH_4 concentrations as mineralization of organic N may be accompanied by relatively little isotopic fractionation (Högberg, 1997; Kendall and Aravena, 2000).

Evidence for denitrification

Denitrification is the dominant NO_3 sink in most groundwater systems (Kinzelbach et al., 1991; Postma et al., 1991). Denitrification is inhibited by the presence of O_2 (Brock and Madigan, 1988), but once O_2 is consumed, denitrification is thermodynamically favored. Denitrification in aquifers commonly is coupled to oxidation of organic carbon:

$$1.25CH_2O + NO_3^- = 0.5N_2 + 1.25HCO_3^- + 0.25H^+ + 0.5H_2O \quad (2)$$

where CH_2O represents organic carbon. NO_3 can also be denitrified by other electron donors, notably Fe sulfide (FeS_2) and other ferrous Fe phases (Kölle et al., 1985; Postma et al., 1991; Robertson et al., 1996; Straub et al., 1996; McMahon et al., 1999; Böhlke et al., 2002).

N_2 and Ar concentrations were used to assess the distribution of denitrification in the ground water. Concentrations of N_2 and Ar from the Burgess and Century transects (Fig. 9, top) plot near or to the right of the curve representing 5.2 °C recharge with varying amounts of excess air (Heaton and Vogel, 1981). Offset to the right (high N_2) side of the excess air curve may reflect recharge at temperatures >5.2 °C for some samples. However, N_2 concentrations in several samples cannot be accounted for simply by warmer recharge temperatures, as the offsets in Fig. 9 are too great for an area with a mean annual air temperature of 7.2 °C or a mean annual soil temperature of around 8.2 °C, even if we disregard the fact that recharge occurs mainly from late fall through early spring. Furthermore, the presence of isotopically enriched N_2 ($\delta^{15}N$–N_2 > 1.0‰) in four samples provides evidence that some of this N_2 was nonatmospheric in origin. Dissolved N_2 in equilibrium with air will be enriched in ^{15}N relative to AIR by about 0.8‰ at a recharge temperature of 5.2 °C (Klots and Benson, 1963), whereas N_2 from excess air will be close to 0.0‰. N is fractionated isotopically during denitrification, with product N_2 having lower $\delta^{15}N$ than reactant NO_3. However, when denitrification goes to completion (complete conversion from NO_3 to N_2) in a closed system, the $\delta^{15}N$ value of the N_2 produced by denitrification will be equal to that of the original NO_3 reactant. Given the range of $\delta^{15}N$ values observed in study area NO_3, 3.3–12.8‰ (Fig. 8), $\delta^{15}N$–N_2 values >1.0‰ in samples with little or no remaining NO_3 constitute evidence for denitrification, and

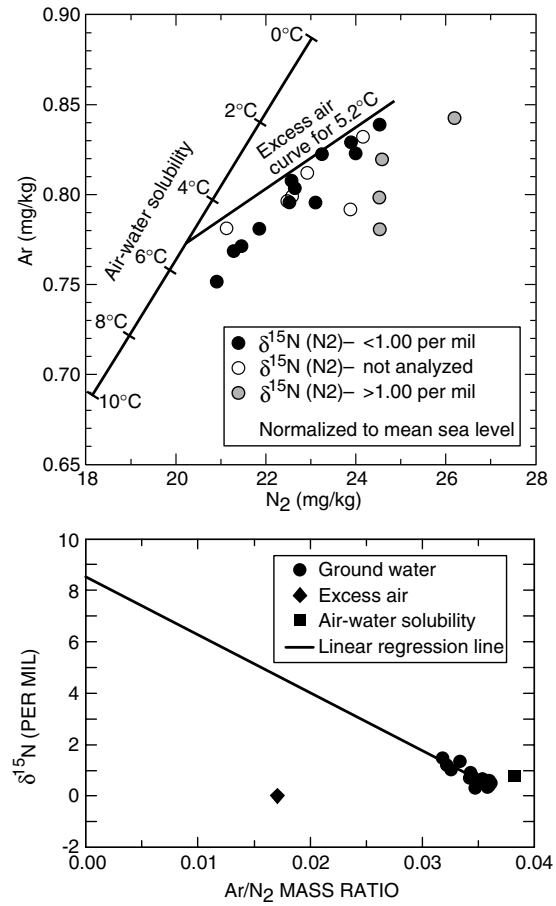

Figure 9 Top, N_2 and Ar concentrations in ground water, with air–water solubility curve (Weiss, 1970) and excess air trend. Data normalized to mean sea level (US Committee on Extension to the Standard Atmosphere, 1976). Isotopically enriched N_2 is interpreted to contain a component of NO_3 that has been quantitatively denitrified. Bottom, Ar/N_2 ratios and $\delta^{15}N$ values for ground water and two recharge components consisting of air–water solubility (5.2 °C) and excess air ($\delta^{15}N$ values for these components discussed in text). N_2 in ground water appears to be composed of a mixture of N_2 derived from air–water solubility and excess air, with some samples containing additional, isotopically enriched N_2. A linear regression line through the ground-water samples can be extrapolated to an N_2 end-member with $\delta^{15}N$ about 8.5‰, consistent with a source as denitrified NO_3 of septic-tank origin.

represent denitrification of a few mg/L NO_3–N. Generally increasing $\delta^{15}N$–N_2 values with decreasing Ar/N_2 ratios, with a trend towards an N_2 end-member with $\delta^{15}N$ of about 8.5‰, also supports denitrification of septic-tank-derived NO_3 (Fig. 9, bottom).

The relation between NO_3 and Cl from the ODEQ synoptic network (Fig. 5) is interpreted to indicate mixing of NO_3 and Cl from two sources, with departure from this mixing zone explained by NO_3 loss in suboxic (O_2 < 0.5 mg/L) ground water. Although vegetative uptake of NO_3 might occur locally where the water table is near land surface, this process cannot explain the widespread NO_3 loss implied by Fig. 5. Similarly, although reduction of NO_3 to NH_4 could

occur locally, spatial, temporal, and isotopic data are inconsistent with reduction of NO_3 to NH_4 (''Sources of NO_3 and NH_4'' section). Denitrification is considered to be the major mechanism for NO_3 loss in the suboxic ODEQ synoptic network samples.

Progressive geochemical evolution is evident in the Burgess transect data (Figs. 3 and 4). Increases in pH with increases in tracer-based apparent age reflect progression of kinetically slow hydrolysis reactions. Younger, upgradient ground water typically is oxic, with suboxic conditions developing after about 30 y of transport below the water table. NO_3 tends to be found in younger, upgradient ground water, whereas older water is essentially O_2 and NO_3 free. In general, concentrations of manganese (Mn) and Fe are higher in older ground water than in younger ground water, whereas SO_4 concentrations tend to be lower in older ground water than in younger ground water. These data reflect progression to increasingly reducing conditions as ground-water residence time increases. It appears that denitrification goes essentially to completion in the vicinity of the oxic/suboxic boundary. Similar patterns are evident in the Century transect data, with suboxic conditions developing after about 15 y of transport below the water table (Tables 1 and 2). As was observed in ODEQ synoptic network samples, NO_3 along the Burgess and Century transects generally is not present at concentrations >1 mg/L NO_3—N in suboxic ground water. Of the suboxic transect sites, only Century 5 (screened between 0.85 and 1.43 m of the water table) contained >1 mg/L NO_3—N. Thus, older ground water along these transects is largely NO_3-free because of a combination of (1) smaller N loadings at earlier time and (2) denitrification during geochemical evolution.

The dominant electron donor for study area denitrification reactions has not been identified. DOC is not likely to be an important electron donor for these reactions. DOC concentrations along the Burgess transect do not change systematically with ground-water evolution (Table 1), indicating little DOC consumption. Other studies also have noted that aqueous reductants generally play a minor role in denitrification reactions compared to the role played by solid phases (Kinzelbach et al., 1991; Postma et al., 1991; Böhlke and Denver, 1995; Aravena and Robertson, 1998; Böhlke et al., 2002). Even portions of aquifers directly receiving septic tank effluent generally do not receive sufficient DOC to balance denitrification, as organic carbon from septic tank effluent is efficiently oxidized in the unsaturated zone (Wilhelm et al., 1994; MacQuarrie et al., 2001; also, one of the samples from septic tank effluent plumes was analyzed for DOC, and at 2.2 mg/L (Table 1), suggests low DOC loading to the aquifer). Sedimentary organic carbon (SOC), on the other hand, could be a potential electron donor for denitrification as well as for other redox reactions. SOC is a common component of alluvial sediment. Furthermore, a sediment core penetrating the boundary between oxic and suboxic ground water exhibited an increase in SOC beneath the oxic/suboxic boundary 6.0 m below land surface (Hinkle et al., 2005). Excluding the uppermost layer of the core, which contains soil with plant detritus and thus is not representative of the organic carbon content of the aquifer, the core-layer-thickness-weighted organic carbon concentration of the sediment in the oxic zone was <0.07%, whereas that of the suboxic zone was 0.13%, indicating that the SOC was an electron donor at this redox boundary. Alternatively, ferrous Fe in volcanic sediment could be an electron donor in some study-area redox reactions, and other electron donors cannot be ruled out. Our solid-phase data do not allow definitive identification of electron donors.

A redox boundary approach for representing denitrification

Data from the ODEQ synoptic network demonstrate that NO_3 reactivity closely parallels O_2 reactivity and indicate that denitrification proceeds quickly once O_2 is consumed (Fig. 5). Of 76 suboxic ODEQ synoptic network samples, only three contained >1 mg/L NO_3—N. These samples were from shallow wells (screened within 7 m of the water table), and probably represent conditions in which O_2 already had been reduced and in which denitrification was the dominant redox reaction. With only three of the suboxic samples representing the denitrification zone and the remaining 73 representing more reduced conditions, it would appear that the denitrification zone is narrow, and that the redox gradient near the oxic/suboxic boundary is sharp. It is also worth noting that the three suboxic sites with >1 mg/L NO_3—N did not yield consistent results when sampled by ODEQ on three other occasions during 1999—2001. NO_3—N concentrations were variable at these sites, and at times dropped below 1 mg/L at two sites. These data may indicate varying contributions of undenitrified and denitrified water from above and below a sharp redox boundary at or near the depth of the well screen.

An abrupt redox transition also is evident in the Burgess transect data (Fig. 3). There, the boundary between oxic and suboxic ground water is constrained by well placement to somewhere within a zone of about 2—3 m, and, within the resolution of the scale of well placement, NO_3 occurs essentially only on the oxic side of that boundary. Also, the apparent absence of ^{15}N-depleted N in N_2 (Fig. 9) indicates a relative paucity of intermediate-stage denitrification that would be expected to accompany slowly denitrifying NO_3, further supporting a hypothesis of fast denitrification relative to the scales of observation.

These patterns of O_2 and NO_3 occurrence indicate that aquifer-scale NO_3 reactivity in the La Pine aquifer can be conceptualized with a redox boundary mapped on the basis of presence or absence of redox indicator species such as O_2. An oxic/suboxic boundary for the La Pine aquifer was delineated (Fig. 10) by constraining the elevation of the oxic/suboxic boundary at each project well and then contouring these elevations in a manner similar to that required to map a subsurface lithologic contact from well logs. Such a redox boundary could be used for conceptualizing NO_3 reactivity for regional vulnerability assessments or could be used as a reaction boundary for an aquifer-scale NO_3 transport model.

The use of a redox boundary to conceptualize or represent NO_3 reactivity has limitations. Denitrification at microsites of anoxia within the oxic zone of the aquifer will not be accounted for with such a conceptualization; in transport simulations, this could lead to a positive bias in NO_3 concentrations in the oxic zone. Also, a redox boundary approach

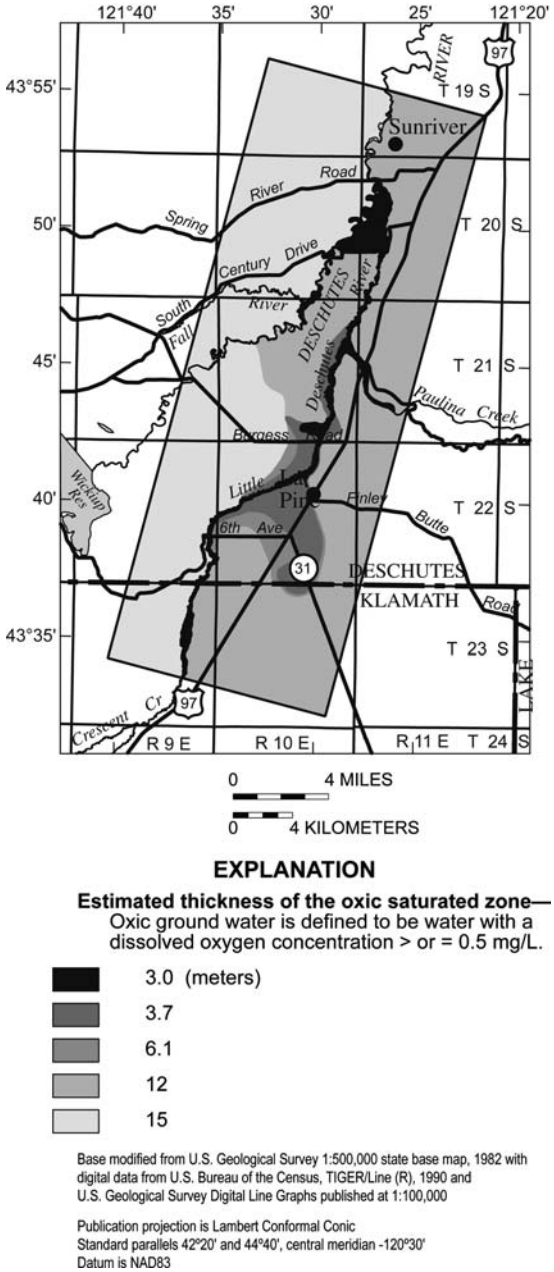

Figure 10 Map showing the estimated oxic saturated zone thickness (depth from top of water table to oxic/suboxic boundary), derived from contouring data from 256 wells.

will not account for NO_3 that remains after O_2 has been consumed — usually NO_3 will continue to be advected for some discrete distance beyond the oxic/suboxic boundary. The combined effect of these two limitations in a redox-boundary transport simulation will be to misrepresent what may be a gradational NO_3 front as a sharp (presence/absence) front. Another limitation of a redox boundary conceptualization is that such a boundary will migrate as solid-phase electron donors are consumed by O_2 and NO_3 reduction. Nevertheless, the effectiveness of a redox boundary for characterizing zones of current NO_3 stability and instability in the La Pine aquifer is supported by analysis of ODEQ synoptic data. Of the ODEQ synoptic wells for which well construction data were available and for which NO_3 concentrations were >1 mg/L NO_3—N (37 wells), 35 were screened at least in part in the mapped (Fig. 10) oxic zone. Thus, the field data indicate that, on the temporal and spatial scales of ground-water flow in the La Pine aquifer, the redox boundary may give a better representation of NO_3 transport than a uniform kinetic reaction model because the redox boundary appears to be controlled by a heterogeneous distribution of electron donors.

Summary

Septic tank effluent is the primary anthropogenic source of NO_3 to the La Pine aquifer. In contrast, elevated concentrations of NH_4 in the aquifer appear to originate from a natural source, probably sedimentary organic matter. A septic tank source of NO_3 and Cl is evident in NO_3/Cl relations, demonstrating mixing of septic-tank-derived NO_3 and Cl with a dilute precipitation end-member. Association of NH_4 with low-Cl ground water and correlation between total dissolved N and C in ground water are consistent with an organic matter source for the NH_4. δ^{15}N values in NO_3 were generally higher than δ^{15}N values in the NH_4, supporting a septic tank source for the NO_3 and a natural source for the NH_4. NO_3 was found in modern (<40 y), shallow ground water as isolated or coalescing plumes within several meters of the water table. NH_4 generally occurred in old (pre-bomb) ground water, either in deep portions of the aquifer or in shallow ground water near discharge zones where regional ground water discharges to rivers. Thus, although septic tank N itself occurs as reduced N, primarily as NH_4, this reduced N is readily oxidized once it leaves the septic tank environment, and it does not represent an important source of NH_4 in this aquifer system.

Denitrification in portions of the La Pine aquifer is indicated by decreases in NO_3/Cl ratios in suboxic water relative to oxic water, the timing of NO_3 loss relative to the progressive geochemical evolution towards increasingly reduced conditions, and the presence of elevated N_2/Ar ratios and δ^{15}N—N_2 values in some samples. An aquifer-scale oxic/suboxic redox boundary successfully represents most instances of NO_3 stability and instability, and thus serves as an effective means of conceptualizing the occurrence of denitrification at the aquifer scale.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhydrol.2006.09.013.

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