

Prepared in cooperation with Deschutes County

## Ground Water Redox Zonation near La Pine, Oregon: Relation to River Position within the Aquifer–Riparian Zone Continuum



Scientific Investigations Report 2007–5239

**Cover:** Photograph showing process of installing a transect of wells in the Deschutes River at River Mile 206.4.  
(Photograph taken by Stephen R. Hinkle, U.S. Geological Survey, March 2006.)

# **Ground Water Redox Zonation near La Pine, Oregon: Relation to River Position within the Aquifer-Riparian Zone Continuum**

By Stephen R. Hinkle, David S. Morgan, Leonard L. Orzol, and Danial J. Polette

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## Conversion Factors, Datums, Abbreviations, and Acronyms

### Conversion Factors

Multiply	By	To obtain
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second (m <sup>3</sup> /s)
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
gram (g)	0.03527	ounce, avoirdupois (oz)
liter (L)	33.82	ounce, fluid (fl. oz)
mile (mi)	1.609	kilometer (km)
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32.$$

River edges are referred to as “left edge” or “right edge” from a frame of reference of looking downstream.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μg/L).

### Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27) and North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

## Conversion Factors, Datums, Abbreviations, and Acronyms—Continued

### Abbreviations and Acronyms

Abbreviation or Acronym	Meaning
$\delta^{15}\text{N-NO}_3^-$	delta- <sup>15</sup> N (ratio of <sup>15</sup> N to <sup>14</sup> N, relative to the standard AIR, in units of per mil) of nitrate
$\delta^{18}\text{O-NO}_3^-$	delta- <sup>18</sup> O (ratio of <sup>18</sup> O to <sup>16</sup> O, relative to the standard VSMOW, in units of per mil) of nitrate
CH <sub>4</sub>	methane
Cl <sup>-</sup>	chloride
Fe	iron
FeS <sub>2</sub>	pyrite
H <sub>2</sub> S	hydrogen sulfide
mg N/L	milligram of nitrogen per liter
Mn	manganese
MRL	method reporting level
N	nitrogen
<sup>15</sup> N	nitrogen-15
NH <sub>4</sub> <sup>+</sup>	ammonium
NO <sub>2</sub> <sup>-</sup>	nitrite
NO <sub>3</sub> <sup>-</sup>	nitrate
O <sub>2</sub>	dissolved oxygen
oxic	oxygen-reducing; containing > 0.5 milligrams per liter of dissolved oxygen
‰	per mil
redox	reduction/oxidation
SO <sub>4</sub> <sup>2-</sup>	sulfate
TMDL	total maximum daily load
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water

# Ground Water Redox Zonation near La Pine, Oregon: Relation to River Position within the Aquifer–Riparian Zone Continuum

By Stephen R. Hinkle, David S. Morgan, Leonard L. Orzol, and Danial J. Polette

## Abstract

Increasing residential development since in the 1960s has led to increases in nitrate concentrations in shallow ground water in parts of the 247-square-mile study area near La Pine, Oregon. Denitrification is the dominant nitrate-removal process that occurs in suboxic ground water, and suboxic ground water serves as a barrier to transport of most nitrate in the aquifer. Oxidic ground water, on the other hand, represents a potential pathway for nitrate transport from terrestrial recharge areas to the Deschutes and Little Deschutes Rivers. The effects of present and potential future discharge of ground-water nitrate into the nitrogen-limited Deschutes and Little Deschutes Rivers are not known. However, additions of nitrogen to nitrogen-limited rivers can lead to increases in primary productivity which, in turn, can increase the magnitudes of dissolved oxygen and pH swings in river water. An understanding of the distribution of oxidic ground water in the near-river environment could facilitate understanding the vulnerability of these rivers and could be a useful tool for management of these rivers.

In this study, transects of temporary wells were installed in sub-river sediments beneath the Deschutes and Little Deschutes Rivers near La Pine to characterize near-river reduction/oxidation (redox) conditions near the ends of ground-water flow paths. Samples from transects installed near the center of the riparian zone or flood plain were consistently suboxic. Where transects were near edges of riparian zones, most ground-water samples also were suboxic. Oxidic ground water (other than hyporheic water) was uncommon, and was only detected near the outside edge of some meander bends. This pattern of occurrence likely reflects geochemical controls throughout the aquifer as well as geochemical processes in the microbiologically active riparian zone near the end of ground-water flow paths. Younger, typically less reduced ground water generally enters near-river environments through peripheral zones, whereas older, typically more reduced ground water tends to discharge closer to the center of the river corridor. Such distributions of redox state reflect ground-water movement and geochemical

evolution at the aquifer-scale. Redox state of ground water undergoes additional modification as ground water nears discharge points in or adjacent to rivers, where riparian zone processes can be important. Lateral erosion of river systems away from the center of the flood plain can decrease or even eliminate interactions between ground water and reducing riparian zone sediments. Thus, ground water redox patterns in near-river sediments appear to reflect the position of a river within the riparian zone/aquifer continuum.

Spatial heterogeneity of redox conditions near the river/aquifer boundary (that is, near the riverbed) makes it difficult to extrapolate transect-scale findings to a precise delineation of the oxidic-suboxic boundary in the near-river environment of the entire study area. However, the understanding of relations between near-river redox state and proximity to riparian zone edges provides a basis for applying these results to the study-area scale, and could help guide management efforts such as nitrogen-reduction actions or establishment of Total Maximum Daily Load criteria. Coupling the ground-water redox-based understanding of river vulnerability with ground-water particle-tracking-based characterization of connections between upgradient recharge areas and receiving rivers demonstrates one means of linking effects of potential nitrate loads at the beginning of ground-water flow paths with river vulnerability.

## Introduction

Nitrate ( $\text{NO}_3^-$ ) ingestion may adversely affect human health (World Health Organization, 1996), and discharge of ground-water  $\text{NO}_3^-$  into surface-water bodies can have detrimental effects on ecosystem health (U.S. Environmental Protection Agency, 1998; Howarth and Marino, 2006). Shallow aquifers are particularly susceptible to  $\text{NO}_3^-$  contamination because aquifers often receive nitrogen (N) inputs from anthropogenic activities at or near land surface. Shallow aquifers frequently have a direct connection to rivers, and hence represent a pathway for widely dispersed chemical constituents to enter rivers.

## 2 Ground Water Redox Zonation near LaPine, Oregon: Relation to River Position within the Aquifer-Riparian Zone Continuum

Ground water near La Pine, Oregon (fig. 1) is vulnerable to  $\text{NO}_3^-$  contamination as a result of residential development using conventional (non-nitrogen-reducing) onsite wastewater treatment systems (septic tanks). In ground water near La Pine,  $\text{NO}_3^-$  is derived primarily from septic tank effluent and occurs in the shallow part of the aquifer (approximately the uppermost 20 ft of saturated sediments). Evidence for a septic tank effluent source includes (1) similarity between  $\delta^{15}\text{N}$  values (nitrogen isotopic content) of  $\text{NO}_3^-$  in shallow ground water and those in septic tank effluent, (2) relations between  $\text{NO}_3^-$  and chloride ( $\text{Cl}^-$ ), (3) relations between  $\text{NO}_3^-$  and tracer-based ground-water ages, (4) hydraulic gradients, and (5) occurrence of  $\text{NO}_3^-$  in discrete plumes (Hinkle and others, 2007). In coming years,  $\text{NO}_3^-$  concentrations in ground water will increase in many parts of the aquifer as historically loaded  $\text{NO}_3^-$  is transported farther along flow paths and as additional  $\text{NO}_3^-$  from existing and new homes is added to the aquifer (Morgan and others, 2007).

Ammonium ( $\text{NH}_4^+$ ), as well as  $\text{NO}_3^-$ , occurs in the aquifer. However, the distribution of  $\text{NH}_4^+$  differs from that of  $\text{NO}_3^-$ . Ammonium at elevated concentrations (concentrations greater than 1 milligram nitrogen per liter [mg N/L]) occurs in deep ground water (100–400 ft below the water table), or in shallow ground water near rivers where deep,  $\text{NH}_4^+$ -rich ground water discharges to rivers. This  $\text{NH}_4^+$  is derived from decomposition of sedimentary organic matter (not from reduction of  $\text{NO}_3^-$ ), as indicated by (1)  $\delta^{15}\text{N}$  values of  $\text{NH}_4^+$ , (2) relations between  $\text{NH}_4^+$  and  $\text{Cl}^-$ , (3) relations between  $\text{NH}_4^+$  and carbon, (4) occurrence of  $\text{NH}_4^+$  in old ground water, and (5) location of  $\text{NH}_4^+$  in deep and downgradient regions of the aquifer (Hinkle and others, 2007).

Ground water reduction/oxidation (redox) conditions in the aquifer near La Pine evolve from oxygen-reducing (oxic) conditions near the water table in recharge areas to increasingly reducing (suboxic, or post-oxygen-reducing) conditions farther downgradient. (A dissolved oxygen [ $\text{O}_2$ ] concentration of 0.5 mg/L was used by Hinkle and others [2007] as a threshold between oxic and suboxic conditions; this threshold value is used in this report.) N is a redox-sensitive element that usually occurs as  $\text{NO}_3^-$  under oxic conditions. In redox processes,  $\text{NO}_3^-$  becomes reduced (typically, in ground water, through denitrification, with an end product of nitrogen gas [ $\text{N}_2$ ]) once most  $\text{O}_2$  is reduced. Denitrification is the dominant  $\text{NO}_3^-$  sink in ground water in the aquifer near La Pine (Hinkle and others, 2007). Following denitrification, manganese (Mn) and iron (Fe) reduction occur, followed by sulfate ( $\text{SO}_4^{2-}$ ) reduction and later by methanogenesis. Mn and Fe reduction usually involves reduction of solid-phase (sediment) Mn and Fe to aqueous-phase Mn and Fe.  $\text{SO}_4^{2-}$  reduction results in formation of hydrogen sulfide ( $\text{H}_2\text{S}$ ), and methane ( $\text{CH}_4$ ) is formed during methanogenesis.

The typical redox progression in ground-water evolution is:

1. Aqueous  $\text{O}_2$  concentrations decrease as a result of  $\text{O}_2$  consumption;
2.  $\text{NO}_3^-$  concentrations decrease (if present in recharge water) due to denitrification;
3. Mn and Fe concentrations increase;
4.  $\text{SO}_4^{2-}$  concentrations decrease and are accompanied by increased  $\text{H}_2\text{S}$  concentrations; and then
5.  $\text{CH}_4$  occurs.

Complications to this redox sequence can occur. Redox conditions can evolve beyond Fe reduction without large increases in aqueous Fe concentrations if iron sulfide solid phases such as pyrite ( $\text{FeS}_2$ ) precipitate from solution, or if aquifer materials do not contain sufficient solid-phase Fe for Fe reduction. Nevertheless, this progression of redox state as inferred by the relative abundances of these redox-indicator species generally is observed during the evolution of ground water along flow paths through aquifers. An understanding of redox state inferred by the occurrence of redox-sensitive species in ground water can be used to infer zones of chemical (for example,  $\text{NO}_3^-$ ) stability and instability in aquifers. Generally,  $\text{NO}_3^-$  is not reduced to  $\text{NH}_4^+$  in ground water, but patterns of  $\text{NH}_4^+$  occurrence in ground water near La Pine largely correspond with redox conditions, with elevated concentrations of  $\text{NH}_4^+$  in suboxic ground water, and negligible concentrations in oxic ground water (Hinkle and others, 2007).

Previous studies of ground water in the La Pine region focused on the overall aquifer and emphasized the effects of septic tank effluent on the ground-water resource (Morgan and others, 2007; Hinkle and others, 2007). In these previous works, a flow model was developed to evaluate alternatives for management of  $\text{NO}_3^-$  loads from septic tanks to the aquifer system. The model simulated the three-dimensional ground-water velocity distribution in the upper 120 ft of alluvial sediments (Morgan and others, 2007). Redox zonation was used to conceptualize the occurrence and fate of  $\text{NO}_3^-$  in the aquifer and to represent a reaction boundary for  $\text{NO}_3^-$  in the flow model. These geochemical and modeling investigations, including aquifer redox zonation efforts, were not specifically designed to address questions about  $\text{NO}_3^-$  transport to rivers such as the Deschutes and Little Deschutes Rivers. An understanding of  $\text{NO}_3^-$  transport to rivers has been hampered by uncertainty in redox zonation near the rivers. Redox zonation near these rivers was poorly constrained in this previous work because (1) few data were available on redox conditions near rivers, and (2) redox conditions tend to exhibit tremendous spatial variability in the near-river environment (Hill, 1996). The thickness of the oxic zone in the aquifer

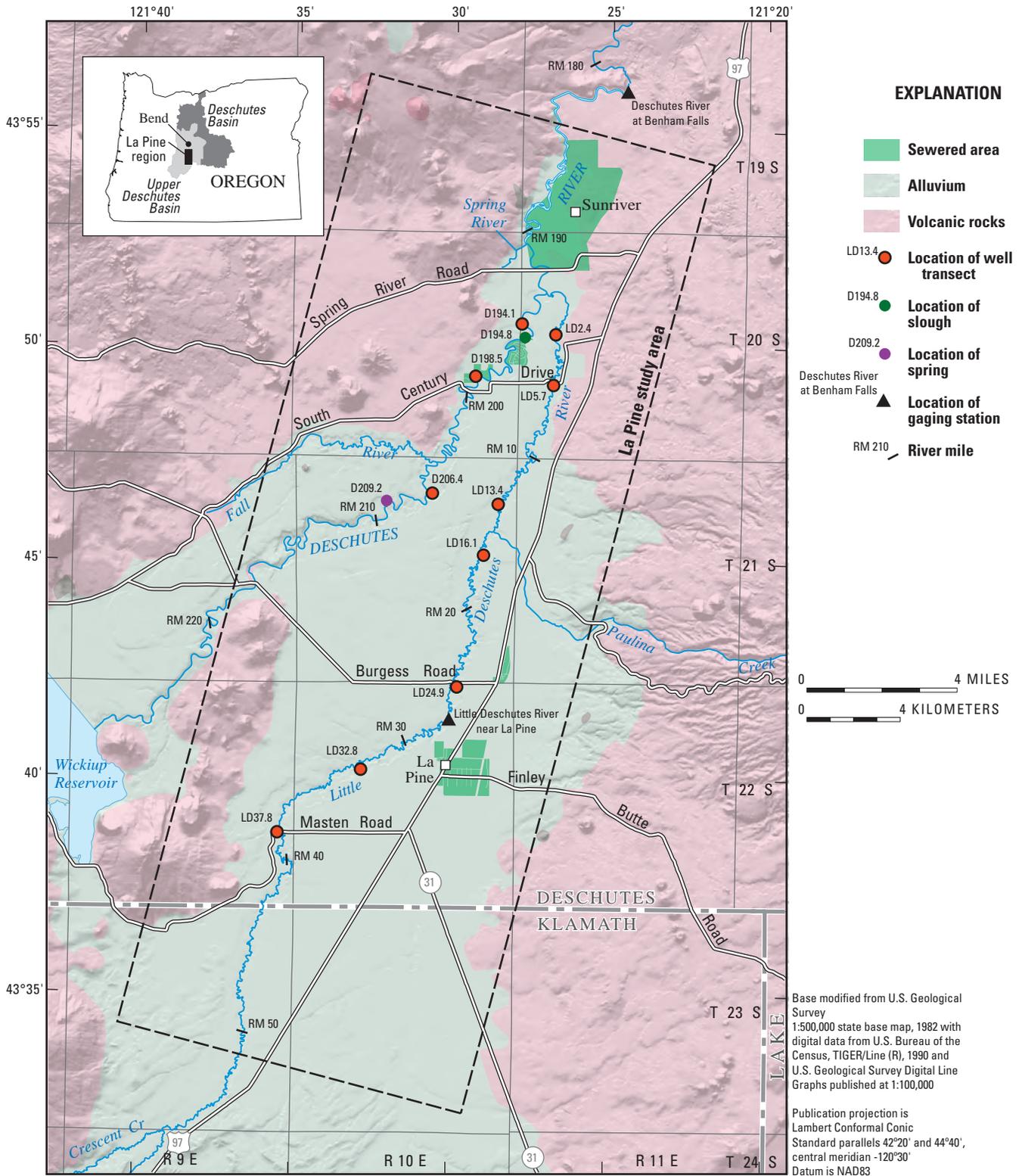


Figure 1. Location of study area near La Pine, Oregon.

in the near-river environment was estimated to be 10 ft by Morgan and others (2007), based on available but limited data from domestic and monitoring wells (Hinkle and others, 2007). This estimate allowed for the possibility of shallow, oxic ground-water discharge to rivers, with the realization that the oxic zone in the near-river environment likely was thinner or nonexistent in some zones.

A refined understanding of redox conditions near rivers in the study area is needed before the link between ground-water and river-water conditions can be more fully addressed. This work was initiated by a cooperative study by the Deschutes County Community Development Department and the U.S. Geological Survey (USGS). The resulting understanding could be used to help guide management decisions for river protection. For example, if  $\text{NO}_3^-$  is loaded to ground water in the zone of contribution (beginning of ground-water flow paths) during the recharge process, that  $\text{NO}_3^-$  can be carried into rivers where oxic ground water enters rivers. Removal of that  $\text{NO}_3^-$  could be accomplished by reducing  $\text{NO}_3^-$  loads in the zones of contribution. Alternatively, reduction of  $\text{NO}_3^-$  loads to rivers could be accomplished by altering geochemical conditions at the end of ground-water flow paths through, for example, the creation of  $\text{NO}_3^-$ -removing artificial wetlands in vulnerable discharge areas (Martin and others, 1999).

## Purpose and Scope

The purpose of this report is to provide a conceptual framework describing the distribution of redox conditions in aquifer sediments near the Deschutes and Little Deschutes Rivers. Suboxic ground water in the aquifer near La Pine, Oregon, represents a zone of  $\text{NO}_3^-$  instability in which denitrification generally can be expected (Hinkle and others, 2007). This framework will provide resource managers with a refined understanding of the  $\text{NO}_3^-$  attenuation capacity of part of the aquifer that was poorly constrained in previous assessments of the overall aquifer. The improved understanding of redox state in the near-river ground-water environment may assist in evaluating river vulnerability to  $\text{NO}_3^-$  from ground water or in identifying steps that can be taken to reduce that vulnerability.

This report characterizes redox conditions in the near-river environment by presenting data from ground-water samples collected from sub-river sediments at various points along transects in the Deschutes and Little Deschutes Rivers and analyzed for redox indicator species (primarily  $\text{O}_2$ ). Multiple measurements were made at each of 10 transects, with sampling designed to characterize spatial variability in redox conditions along transects oriented perpendicular to the rivers. These data were used to relate ground water

redox state to geomorphologic and landscape variables and features that can be used to extrapolate the results to the near-river ground-water environments of the Deschutes and Little Deschutes Rivers near La Pine. Particle tracking with an existing ground-water flow model demonstrated one way to relate potentially vulnerable river reaches to upgradient recharge areas.

The redox characterization work described in this report is limited to the near-river environment. Although study results were consistent with basic principles of ground-water geochemical evolution and ground-water/surface-water interactions, they were restricted by the limited number of transects installed for the study. Therefore, conclusions drawn from this work were inherently general and the patterns observed hold for many, but not all river segments.

## Description of Study Area

The La Pine study area, as defined in previous investigations by Morgan and others (2007) and Hinkle and others (2005 and 2007), encompasses 247 mi<sup>2</sup> of the upper Deschutes Basin in central Oregon (fig. 1). About 30 river miles of the Deschutes River and 50 river miles of the Little Deschutes River are represented in the study area. The area is underlain by Quaternary alluvial and lacustrine deposits in a structural basin of Quaternary and Tertiary basalt, andesite, vent deposits, and pyroclastic rocks (Lite and Gannett, 2002). These sediments contain an aquifer that provides the primary source of drinking water to most local residents, numbering about 18,000 in 2005 and expected to number 26,000 by approximately 2019 (Rich and others, 2005; Morgan and others, 2007).

Rain and snowmelt are the primary sources of recharge. Precipitation ranges from 15 to 20 in/yr over most of the area (Taylor, 1993), falling primarily from November through March. In addition to recharge from rain and snow, ground water also flows into the study area from neighboring high-elevation areas (Gannett and others, 2001). Ground water discharges to the Deschutes and Little Deschutes Rivers, which meander across a flood-plain-and-wetland complex as much as one-quarter-mile or more wide.

The Deschutes and Little Deschutes Rivers are N limited (Jones, 2003), and are susceptible to increases in N loads. Increased N concentrations can increase primary productivity, which can increase the magnitudes of  $\text{O}_2$  and pH swings in river water. Parts of the Deschutes River do not meet State of Oregon water-quality standards for  $\text{O}_2$  and are included in the state 303(d) list of water-quality-impaired streams. Data currently are insufficient to determine the status of  $\text{O}_2$  conditions in the Little Deschutes River (Anderson, 2000).

## Study Design and Methods

Ground water was sampled to characterize the geochemistry of water discharging to the Deschutes and Little Deschutes Rivers. Where ground water discharges to rivers, that shallow ground water represents the ends of flow paths converging at and discharging into rivers. Ground-water samples were analyzed for  $O_2$ , Fe,  $NO_3^-$ ,  $NH_4^+$ , Cl<sup>-</sup>, as well as specific conductance and temperature. Dissolved oxygen was the primary redox indicator species of interest because previous work demonstrated that redox gradients in the study area are sharp and that most  $NO_3^-$  is removed by denitrification near the oxic/suboxic boundary (Hinkle and others, 2007). Thus, the presence of suboxic ground water in sediment under a river could be used to indicate the presence of a barrier that would prevent most ground-water  $NO_3^-$  from discharging to the river at that point. Note, however, that ground water at a point beneath the riverbed may not flow directly up into the river at that point. A point measurement beneath a river to determine the redox state of ground water entering the river above the measurement point is an approximation. Iron also was used as a redox indicator species. Nitrate and  $NH_4^+$  can be used as redox indicator species. Alternatively, other redox indicator species (here  $O_2$  and Fe) can serve as predictor variables for the presence of conditions favorable for  $NO_3^-$  and  $NH_4^+$  occurrence. Chloride is useful as a tracer of septic tank effluent (Hinkle and others, 2007).

### Temporal and Spatial Considerations for Sampling Network

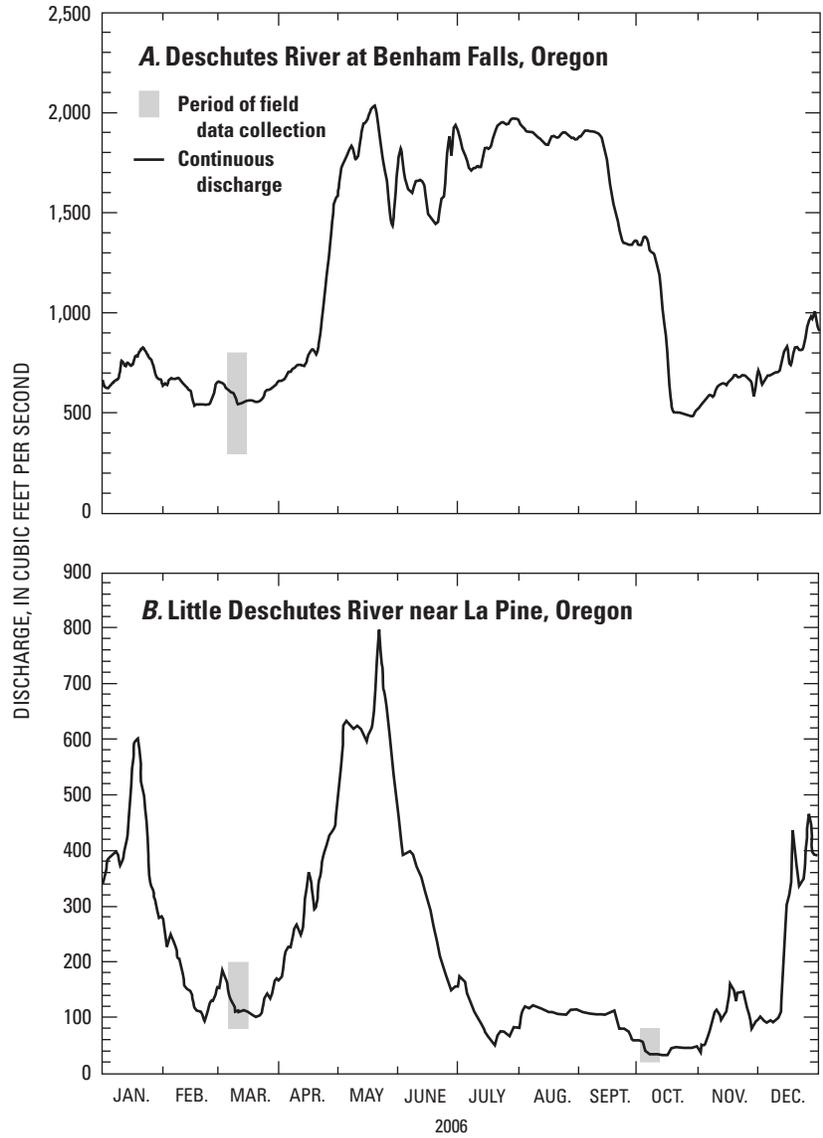
Exchanges between ground water and surface water are complex as a result of spatial and temporal variations in hydraulic gradients, spatial heterogeneities in aquifer hydraulic properties, and convergence of multiple ground-water flow paths at rivers (rivers commonly serving as regional drains for ground-water discharge). A network design that accounts for these complexities was used in this study. The network consisted of temporary wells installed directly in the riverbeds. Transects of wells were installed at 10 locations: 3 along the Deschutes River and 7 along the Little Deschutes River (fig. 1). At each transect, 2–9 wells (40 wells total among the 10 transects) were installed to allow characterization of redox state at different points. Wells were installed with the center of the screen generally at a depth of 1.0 ft, but several were screened at 2.0 ft, and one at 3.0 ft. Shallow ground-water samples collected where ground water discharged to rivers represent the ends of flow paths converging at and discharging into rivers.

Aquifers may alternately discharge to rivers and receive recharge from rivers at different times, or at the same time but at different places. Given the need to characterize the

geochemical nature of ground water discharging to rivers, water samples were collected during periods of low river flow. Previous field measurements of hydraulic gradients between ground water and the Deschutes and Little Deschutes Rivers in the study area indicated that at almost all measurement sites, vertical hydraulic gradients were upward (toward the rivers) during low flow (Morgan and others, 2007). Thus, in the present study, ground-water sampling occurred during periods of low river flow in March and October 2006 (fig. 2). This sampling structure minimized the potential for sampling ground water that originated in the river.

Within a single cross section of a river, ground water often consists of multiple flow paths of varying ages that can vary from days to millennia (Winter and others, 1998). Characterization of ground-water inputs to a river requires attention to this spatial variability. According to one conceptual model that describes the nature of ground-water discharge to a gaining river, the oldest ground water (generally the most geochemically evolved) enters in the center of the river channel. The age of ground water decreases as the point of entry into the river moves from the center to the edges of the river (Modica and others, 1998). “Geochemically evolved” is a relative term that refers to ground water that has changed to a relatively great extent due to chemical reactions with geologic materials. Geochemically evolved ground water may be more reduced, may contain higher concentrations of dissolved solids, and (or) may be older than ground water that has had less interaction with geologic materials.

Browne and Guldan (2005) suggest an alternative conceptual model in which a river meanders across a relatively flat valley floor and ground water discharges to this valley-floor system rather than solely into the river. In this conceptual model, the river intercepts relatively young ground water where the river bends toward the edge of the valley floor, and intercepts relatively old ground water where the river course lies near the center of the valley. The oldest ground water within a given transect might enter the river at the inside edge of a meander bend (edge closest to the center of the valley floor), and the youngest ground water might enter the river at the outside edge (edge closest to the margin of the valley floor) (Brown and Gulden, 2005). Therefore, in any given river transect, younger ground water may tend to enter a river by flow paths near one edge of the river (Browne and Guldan, 2005) or near both edges (Modica and others, 1998). In either conceptual model, though, ground water entering a river near the edges may be particularly young, and river edges may be particularly vulnerable to discharge of young ground water. To account for such spatial variability in ground-water age, and implicitly, geochemical character, the sampling regime used in this study incorporated multiple samples across river transects.



**Figure 2.** Discharge in Deschutes and Little Deschutes Rivers at selected sites near La Pine, Oregon, during calendar year 2006. (Source: U.S. Bureau of Reclamation, 2007).

Ten transects were installed to represent some of the spatial variability of ground water redox state along the axes of the rivers. The geochemical character of ground water flowing into a river may vary along the length of the river in response to a spatially variable geologic and hydrologic framework and to spatially varying qualities of the riparian environment. The riparian zone has been broadly defined as the zone at which terrestrial and aquatic ecosystems overlap (Gregory and others, 1991; Martin and others, 1999). Riparian zone sediment tends to be a zone of enhanced geochemical cycling; therefore, riparian zones can be particularly effective zones of denitrification (Hill, 1996). In riparian zones,  $\text{NO}_3^-$  loss primarily is due to denitrification; plant and microbial uptake generally is less important than denitrification (Martin and others, 1999). Denitrification in riparian zones is due, in large part, to the abundance of labile (reactive) organic carbon derived from wetland plants and other riparian zone plants, as well as that available in sediment deposited by rivers. This organic carbon serves as an electron donor for redox reactions including denitrification. Therefore, riparian zone processing of ground-water  $\text{NO}_3^-$  potentially represents a useful explanatory variable for ground water redox conditions along rivers. Published literature on N cycling in riparian environments has tended to focus on individual sites rather than on larger spatial scales (Vidon and Hill, 2004), and elucidation and characterization of N dynamics at larger spatial scales (for example, river scales) currently is in its infancy (Boyer and others, 2006). For an effective river-scale assessment, identification of differences among transect sites is needed to understand the processes governing redox state along rivers.

## Site Selection

The sampling framework calls for installation of multiple wells along multiple transects. Site selection within this framework was designed to provide broad coverage within the study area (fig. 1). Site selection also was designed to emphasize the identification of oxic ground water. This emphasis was introduced into the sampling design because it was assumed that most ground water discharging to the Deschutes and Little Deschutes Rivers in the study area would be suboxic. Although identifying suboxic ground water is highly useful for constraining the redox character of ground water discharging to rivers, oxic ground water presents the dominant vulnerability for  $\text{NO}_3^-$  transport into the rivers; these factors that accommodate retention of  $\text{O}_2$  in ground water need elucidation.

The site selection focus on identifying oxic ground water lead to emphasizing coarse-grained sediments (sand, gravel) and avoiding macrophyte beds. Oxic ground water more commonly is detected in coarse-grained sediments

than in fine-grained sediments (silt and clay) because of greater concentrations of organic carbon in and slower water movement through fine-grained sediments (Vidon and Hill, 2004; Pinay and others, 2007). Macrophyte beds were avoided because macrophytes can trap fine-grained sediments, and exudates from macrophyte roots could create local conditions of anoxia (Martin and others, 1999).

Transect site names begin with a “D” (Deschutes River) or “LD” (Little Deschutes River), followed by the location in river miles (as indicated on USGS topographic maps). For example, “D194.1” is a site on the Deschutes River at river mile 194.1. Individual wells are assigned a name beginning with the transect site name, followed by a decimal and a number to represent the well. For example, “D194.1.1” is one well in the transect “D194.1”.

## Sample Collection and Analytical Methods

Ground-water samples were collected by installing temporary stainless steel wells in riverbed sediment. Screen lengths were 0.25 ft (36 wells) and 0.05 ft (4 wells). Wells were developed and then sampled by pumping with a peristaltic pump.

Field parameters ( $\text{O}_2$ , specific conductance, and temperature) were measured on-site in flow-through cells. The flow-through cell for  $\text{O}_2$  measurements was created from a capped, high-density polyethylene beaker fitted with a fluorocarbon polymer inlet tube to which the pump tubing was attached and with an outlet hole to allow sample water to exit the flow-through cell. The inlet tube allowed sample water to enter the bottom of the flow-through cell, where the tip of the  $\text{O}_2$  probe was located. The outlet hole was located at the top of the flow-through cell. The flow-through cell was large enough to accommodate the  $\text{O}_2$  probe, but sized sufficiently small as to allow operation with low pumping rates. The flow-through cell allowed  $\text{O}_2$  measurements on ground water that was not exposed to atmospheric gasses during measurement. A similar flow-through cell was used for specific conductance and temperature measurements.

Following well purging (more than three well bore volumes) and stabilization of field parameters, wells were sampled for nitrite-plus-nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ),  $\text{NH}_4^+$ , Fe, and  $\text{Cl}^-$  (U.S. Geological Survey, 1999). In this report,  $\text{NO}_2^- + \text{NO}_3^-$  is assumed to contain negligible  $\text{NO}_2^-$ ; this assumption is based on previous experience in this basin (Hinkle and others, 2007) and in other aquifers. Thus,  $\text{NO}_2^- + \text{NO}_3^-$  is referred to as  $\text{NO}_3^-$ . Four wells also were sampled for isotopes of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$ ) (isotopic content of N and O in  $\text{NO}_3^-$ ).

Samples were filtered through in-line 0.45- $\mu\text{m}$  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.

Samples for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were preserved by chilling to near-freezing. Fe samples were preserved with ultrapure nitric acid ( $\text{pH} < 2$ ).

Samples for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , Fe, and  $\text{Cl}^-$  were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado. Methods are described in Fishman and Friedman (1989) and Fishman (1993).

Samples for  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  were analyzed at the USGS Reston Stable Isotope Laboratory (<http://isotopes.usgs.gov>). Analyses were done by bacterial conversion of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$  and subsequent measurement on a continuous flow isotope-ratio mass spectrometer (Sigman and others, 2001; Casciotti and others, 2002; Coplen and others, 2004), with values of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  reported relative to  $\text{N}_2$  in air (AIR) and Vienna Standard Mean Ocean Water (VSMOW), respectively. Analyses of  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  were calibrated by analyzing laboratory solutions with known isotopic compositions, and data were normalized against internationally distributed reference materials (Böhlke and Coplen, 1995; Böhlke and others, 2003) for:  $\delta^{15}\text{N}-\text{NO}_3^-$ , IAEA-N3 = +4.7 per mil (‰) and USGS32 = +180 ‰, and for  $\delta^{18}\text{O}-\text{NO}_3^-$ , IAEA-N3 = +25.6 ‰ and USGS34 = -27.9 ‰. Average reproducibility of normalized values for samples analyzed more than once was about  $\pm 0.2$  ‰ for  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\pm 0.4$  ‰ for  $\delta^{18}\text{O}-\text{NO}_3^-$ .

For plotting purposes,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations less than the method reporting level (MRL) were plotted at one-half of the MRL. The MRL for  $\text{NO}_3^-$  was 0.016 mg N/L, and for  $\text{NH}_4^+$ , 0.04 mg N/L.

Project quality-control data are presented in [table A1 \(appendix A\)](#). These data demonstrate contamination-free sampling and analysis, tight analytical precision, and negligible analytical bias.

## Particle Tracking

Potential ground-water flow paths for advection of  $\text{NO}_3^-$  from septic tank sources to near-river environments were delineated using a numerical ground-water flow model (Morgan and others, 2007) in conjunction with the MODPATH particle tracking program (Pollock, 1994). For these simulations, four particles were placed at the water table in each water-table cell in the model and tracked to the river location where they were simulated to discharge. Aquifer-scale denitrification was represented in the flow model using the redox-boundary approach in which  $\text{NO}_3^-$  transported across the redox boundary (from oxic to suboxic conditions) was assumed to be instantaneously denitrified. Pathlines for particles that were transported into the suboxic part of the system were removed from the ensemble of oxic and suboxic pathlines. In these simulations, aquifer-scale denitrification processes were the only chemical reactions represented in the model; additional near-river reactions were not represented.

Although flow-model boundary conditions accounted for and allowed evapotranspiration and discharge to wells, particles in the particle-tracking simulations were not allowed to leave the system by evapotranspiration or discharge to wells and particles did not represent volumes of ground-water discharge. Therefore, greater densities of pathlines should not be interpreted as greater volumes of ground-water discharge to rivers.

## Previous Near-River Redox Work in Study Area

Hydraulic gradients between ground water and surface water at 32 sites in the study area were measured with a minipiezometer during autumn 2000 (Morgan and others, 2007). One or more measurements of hydraulic gradient were made at each site, at depths of 1.0, 2.0, and (or) 3.0 ft. In conjunction with that work, reconnaissance-level geochemical data were collected at seven sites along the Little Deschutes River ([table A2, appendix A](#)). One sample was collected at the center of the river at each site. Additional samples were collected at one of the seven sites: one sample half-way between the center of the river and the edge of the river in each direction. Thus, six sites were represented by single samples, and one site (at river mile 24.9) was represented by three samples.

Samples were analyzed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .  $\text{O}_2$  was not measured, but the presence or absence of  $\text{H}_2\text{S}$  odor was noted (the presence of  $\text{H}_2\text{S}$  odor indicates highly reducing water). Samples were analyzed by Oregon Department of Environmental Quality, by methods described in Hinkle and others (2007). Collection and processing protocols were the same as those used in the current study.

Samples collected at each of the six single-sample sites contained  $\text{H}_2\text{S}$ , indicating the presence of highly reducing water; these samples were considered to be suboxic. These six samples contained  $\text{NH}_4^+$  at concentrations ranging from 0.34 to 2.6 mg N/L and  $\text{NO}_3^-$  at concentrations less than 0.1 mg N/L, reflecting the suboxic conditions. The presence of suboxic ground water is consistent with concepts that describe mechanisms by which ground water may evolve to suboxic conditions in the aquifer prior to reaching the near-river environment, or may become reduced in the near-river environment.

Samples collected at the multi-sample site (Little Deschutes River at river mile 24.9) indicated spatially variable redox conditions. The sample near the left edge of water (defined from a position facing downstream) contained  $\text{H}_2\text{S}$ ,  $\text{NH}_4^+$  at a concentration of 0.31 mg N/L, and  $\text{NO}_3^-$  at a concentration of only 0.011 mg N/L, consistent with reduced conditions. The other two samples contained no detectable

H<sub>2</sub>S, contained NH<sub>4</sub><sup>+</sup> at concentrations less than the Oregon Department of Environmental Quality MRL of 0.02 mg N/L, and contained NO<sub>3</sub><sup>-</sup> at elevated concentrations (1.29 and 2.73 mg N/L). These data indicate that less reduced (apparently either O<sub>2</sub>- or NO<sub>3</sub><sup>-</sup>-reducing) ground water was present in these two samples. The samples were collected from the center of the river and from a point near the right edge of water. The site was where the Little Deschutes River bends toward the eastern edge of the riparian zone. Less reduced ground water entering the river in the center and right edge where the right edge of the river cuts toward the edge of the riparian zone also is consistent with concepts presented earlier in this report.

Of these seven sites, the site on the Little Deschutes River at river mile 24.9 was particularly valuable because (1) NO<sub>3</sub><sup>-</sup> was detected in some ground water under the river, and (2) the boundary between NO<sub>3</sub><sup>-</sup>-bearing (either O<sub>2</sub>- or NO<sub>3</sub><sup>-</sup>-reducing) and more reduced ground water was identified. This site was resampled in greater detail as part of this study.

## Results

The locations of the 10 ground-water transect sites are shown in [figure 1](#). Well locations and screen depths are listed in [table 1](#). Geochemical data are listed in [table 2](#).

### Transect Configurations

Transects generally consisted of a well installed in the center of the river, and one or more wells toward each edge of the river (lateral wells) ([fig. 3](#)). Lateral wells generally were installed near the river edge in coarse sediments and not in sloughed bank material. These wells tapped sediments likely to have a relatively direct connection to aquifer sediments, rather than collapsed-bank sediments that may behave more as a barrier than a conduit for aquifer discharge to the river. Most wells were screened at 1.0 ft below the riverbed. Transect configurations that deviated from these guidelines are discussed below.

### Ground-Water Transects on Deschutes River

Site D194.1 consisted of two wells ([table 1](#)). River depth prevented installation of a well in the center.

Site D198.5 consisted of four wells: one in the center, one at each bank, and one toward the left edge of water. In attempting to install a well near (but not at) the left edge of water to complement the well at the left edge, multiple

attempts at increasingly greater distances away from the left edge failed to yield a well that would produce water, until a well installed 18.8 ft from the left edge produced water. Sediment on the riverbed at this point was silt with macrophytes—conditions that generally were avoided but were accepted in this instance due to difficulty in finding a suitable location closer to the left edge of water. Sub-riverbed sediments between this well and the left edge of water probably are heterogeneous and have little correlation to lithologies on the riverbed itself.

### Ground-Water Transects on Little Deschutes River

Site LD16.1 consisted of five wells. One nest of two wells (depths of 1.0 and 2.0 ft) was installed in the center of the river, another nest (depths of 1.0 and 2.0 ft) toward the left edge, and a single well toward the right edge. The shallow (1.0 ft) ground water in the center and near the left edge contained oxic, dilute ground water. Values of specific conductance (related to dissolved-ion content) were 53 and 58 μS/cm at 25°C, respectively ([table 2](#)), similar to the value of 54 μS/cm at 25°C measured in the river water during well installation. The presence of oxic ground water with specific conductance values similar to the specific conductance of river water suggested the presence of hyporheic water. The hyporheic zone is a place of interaction between river and ground water, commonly occurring in near-river sediments. Physical processes occurring at small spatial scales can promote hyporheic exchanges against a backdrop of unidirectional hydraulic gradients at larger spatial scales. For example, hyporheic exchanges can occur in response to localized hydraulic gradients arising from pool-and-riffle sequences in rivers (Harvey and Bencala, 1993). The apparent presence of hyporheic water prompted the decision to install deeper wells because the presence of oxic, hyporheic water in sediments under a river does not provide information about the redox state of ground water moving from terrestrial recharge areas to the river. The deeper (2.0 ft) ground water in the center and near the left edge contained suboxic ground water with slightly greater values of specific conductance (63 and 71 μS/cm at 25°C, respectively). The deeper ground water was more geochemically evolved than the shallower ground water, indicating that either hyporheic water had undergone a longer geochemical evolution, or ground water had entered the sediments from recharge areas away from the river. Regardless of the origin of the deeper ground water, the presence of suboxic ground water at a depth of 2.0 ft at these two points represents a NO<sub>3</sub><sup>-</sup>-reducing zone between the river at these locations and terrestrial recharge areas.

10 Ground Water Redox Zonation near LaPine, Oregon: Relation to River Position within the Aquifer-Riparian Zone Continuum

**Table 1.** Ground-water transect site wells and miscellaneous sites near La Pine, Oregon, March and October 2006.

[Well and site locations are shown in [figure 1](#). **Depth**, depth of center of screen below riverbed. **Latitude and longitude of center of transect:** in degrees, minutes, seconds; North American Datum of 1927 (NAD 27). **Abbreviations:** LEW, left edge of water looking downstream; RM, river mile; –, not collected]

Well or site No.	Distance from LEW (feet)	Depth (feet)	Width (feet)	Station No.	Latitude	Longitude
Ground-water transect site wells near Deschutes River						
D194.1.1	3.0	1.0	88	435033121275501	43°50'33.0"	121°27'54.8"
D194.1.2	85.0	1.0	88	435033121275502	43°50'33.0"	121°27'54.8"
D198.5.1	37.5	1.0	75	434920121292201	43°49'19.7"	121°29'22.5"
D198.5.2	.0	1.0	75	434920121292202	43°49'19.7"	121°29'22.5"
D198.5.3	75.0	1.0	75	434920121292203	43°49'19.7"	121°29'22.5"
D198.5.4	18.8	1.0	75	434920121292204	43°49'19.7"	121°29'22.5"
D206.4.1	30.5	1.0	61	434638121304301	43°46'38.0"	121°30'42.8"
D206.4.2	3.0	1.0	61	434638121304302	43°46'38.0"	121°30'42.8"
D206.4.3	58.0	1.0	61	434638121304303	43°46'38.0"	121°30'42.8"
Ground-water transect site wells near Little Deschutes River						
LD2.4.1	29.0	1.0	58	435018121265001	43°50'18.1"	121°26'50.0"
LD2.4.2	3.0	1.0	58	435018121265002	43°50'18.1"	121°26'50.0"
LD2.4.3	55.0	1.0	58	435018121265003	43°50'18.1"	121°26'50.0"
LD5.7.1	19.0	1.0	38	434908121265401	43°49'07.9"	121°26'54.1"
LD5.7.2	9.0	1.0	38	434908121265402	43°49'07.9"	121°26'54.1"
LD5.7.3	29.0	1.0	38	434908121265403	43°49'07.9"	121°26'54.1"
LD13.4.1	19.0	1.0	38	434623121283601	43°46'23.1"	121°28'36.3"
LD13.4.2	6.0	1.0	38	434623121283602	43°46'23.1"	121°28'36.3"
LD13.4.3	30.0	1.0	38	434623121283603	43°46'23.1"	121°28'36.3"
LD16.1.1	27.0	1.0	54	434512121290301	43°45'12.3"	121°29'02.6"
LD16.1.2	5.5	1.0	54	434512121290302	43°45'12.3"	121°29'02.6"
LD16.1.3	52.5	1.0	54	434512121290303	43°45'12.3"	121°29'02.6"
LD16.1.4	5.5	2.0	54	434512121290304	43°45'12.3"	121°29' 02.6"
LD16.1.5	27.0	2.0	54	434512121290305	43°45'12.3"	121°29' 02.6"
LD24.9.1	26.5	1.0	53	434212121295201	43°42'12.4"	121°29' 52.4"
LD24.9.2	.0	1.0	53	434212121295202	43°42'12.4"	121°29'52.4"
LD24.9.3	40.0	1.0	53	434212121295203	43°42'12.4"	121°29'52.4"
LD24.9.4	26.5	2.0	53	434212121295204	43°42'12.4"	121°29'52.4"
<sup>1</sup> LD24.9.5	40.5	1.0	54	434212121295205	43°42'12.4"	121°29'52.4"
<sup>2</sup> LD24.9.6	25.6	1.0	35	434212121295206	43°42'12.4"	121°29'52.4"
LD24.9.7	53.0	1.0	53	434212121295207	43°42'12.4"	121°29'52.4"
LD24.9.8	53.0	2.0	53	434212121295208	43°42'12.4"	121°29'52.4"
LD24.9.9	53.0	3.0	53	434212121295209	43°42'12.4"	121°29'52.4"
LD32.8.1	25.0	2.0	41	434016121325301	43°40'16.4"	121°32'52.7"
LD32.8.2	3.0	1.0	41	434016121325302	43°40'16.4"	121°32'52.7"
LD32.8.3	38.0	2.0	41	434016121325303	43°40'16.4"	121°32'52.7"
LD32.8.4	31.5	2.0	41	434016121325304	43°40'16.4"	121°32'52.7"
LD37.8.1	16.5	2.0	33	433848121352901	43°38'48.5"	121°35'29.2"
LD37.8.2	1.0	2.0	33	433848121352902	43°38'48.5"	121°35'29.2"
LD37.8.3	29.0	2.0	33	433848121352903	43°38'48.5"	121°35'29.2"
LD37.8.4	6.0	2.0	33	433848121352904	43°38'48.5"	121°35'29.2"
Miscellaneous sites near Deschutes River						
Slough at RM 194.8	–	–	–	435014121274900	43°50'13.7"	121°27'49.0"
Spring at RM 209.2	–	–	–	434627121321001	43°46'27.2"	121°32'09.6"

<sup>1</sup> At thalweg (deepest point in the river cross section), 16 feet downstream of primary transect.

<sup>2</sup> At thalweg, 69 feet downstream of primary transect.

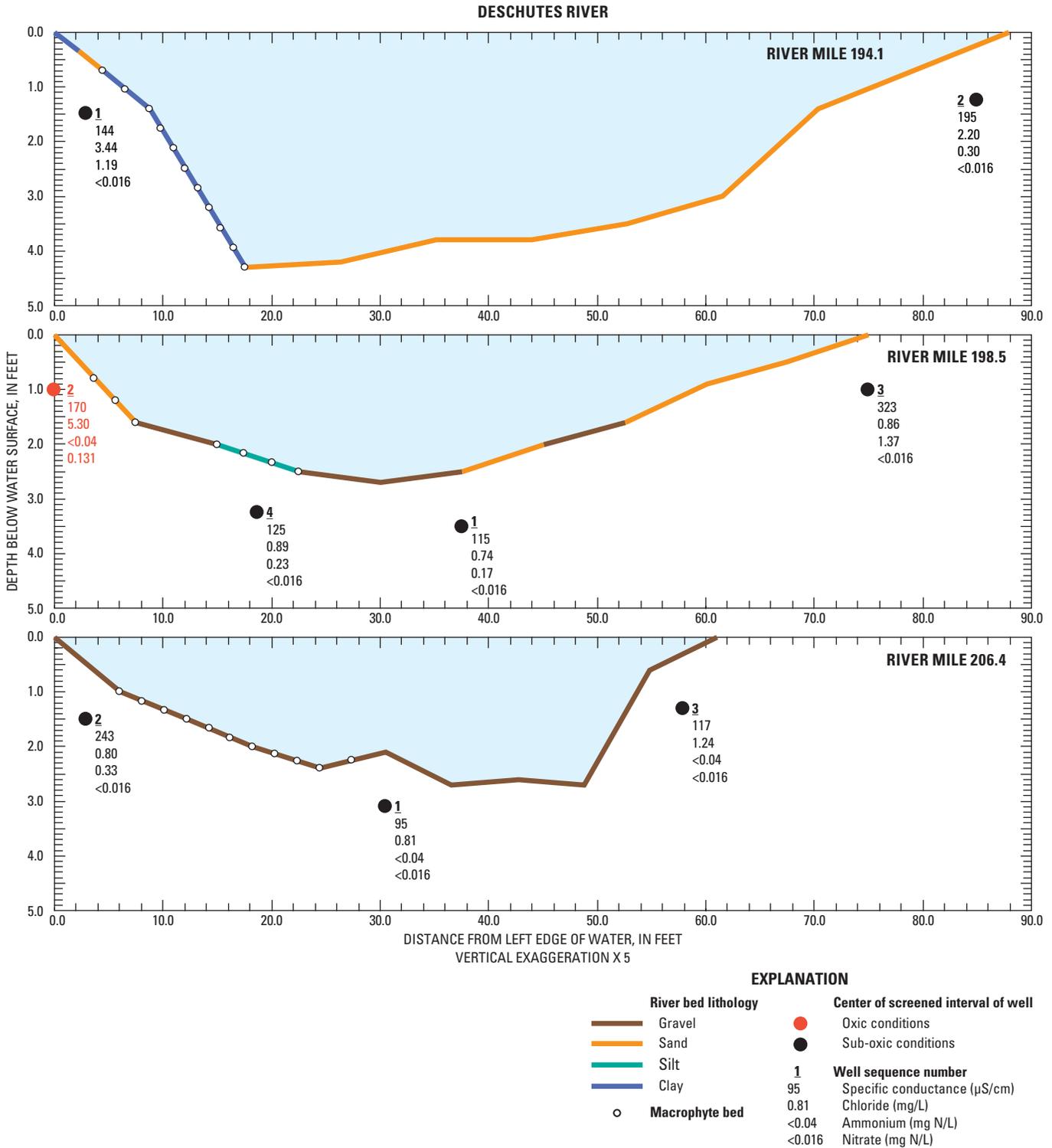
**Table 2.** Chemical and isotopic data for ground-water transect site wells and miscellaneous sites near La Pine, Oregon, March and October 2006.

[Well locations are shown in [figure 1](#). **Depth**, depth of center of screen below riverbed. **Abbreviations:** mg/L, milligram per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25°C; °C, degrees Celsius; mg N/L, milligram of nitrogen per liter;  $\mu\text{g}/\text{L}$ , microgram per liter; RM, river mile; ‰, per mil; <, less than; –, not collected]

Well or site No.	Date	Time	Depth (feet)	Dissolved oxygen (mg/L)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Temperature (°C)	Chloride (mg/L)	Ammonium (mg N/L)	Nitrite-plus-nitrate (mg N/L)	Iron ( $\mu\text{g}/\text{L}$ )	$\delta^{15}\text{N}-\text{NO}_3^-$ (‰)	$\delta^{18}\text{O}-\text{NO}_3^-$ (‰)
Ground-water transect site wells near Deschutes River												
D194.1.1	03-07-06	1300	1.0	0.3	144	3.9	3.44	1.19	<0.016	7,360	–	–
D194.1.2	03-07-06	1400	1.0	.5	195	3.6	2.20	.30	<.016	12,700	–	–
D198.5.1	03-06-06	1800	1.0	.1	115	4.4	.74	.17	<.016	609	–	–
D198.5.2	03-06-06	1700	1.0	5.1	170	5.1	5.30	<.04	.131	<6	–	–
D198.5.3	03-08-06	1000	1.0	.1	323	2.3	.86	1.37	<.016	12,000	–	–
D198.5.4	03-08-06	1300	1.0	.2	125	4.0	.89	.23	<.016	4,790	–	–
D206.4.1	03-09-06	1100	1.0	.3	95	2.2	.81	<.04	<.016	25	–	–
D206.4.2	03-09-06	1300	1.0	.3	243	2.0	.80	.33	<.016	9,040	–	–
D206.4.3	03-08-06	1700	1.0	.4	117	3.9	1.24	<.04	<.016	2,580	–	–
Ground-water transect site wells near Little Deschutes River												
LD2.4.1	03-14-06	1200	1.0	0.2	108	1.4	1.95	<0.04	<0.016	38	–	–
LD2.4.2	03-14-06	1400	1.0	.2	184	2.1	2.58	.52	<.016	12,000	–	–
LD2.4.3	03-14-06	1500	1.0	.3	209	3.2	1.49	.69	<.016	14,400	–	–
LD5.7.1	03-15-06	1500	1.0	.4	118	2.8	2.56	.51	<.016	11,000	–	–
LD5.7.2	03-15-06	1400	1.0	.3	106	2.9	2.22	<.04	<.016	350	–	–
LD5.7.3	03-15-06	1300	1.0	.3	138	4.3	4.35	.60	<.016	10,400	–	–
LD13.4.1	10-11-06	1300	1.0	.4	73	10.8	.96	.21	<.016	218	–	–
LD13.4.2	10-11-06	1400	1.0	.4	228	11.9	.84	1.59	<.016	16,700	–	–
LD13.4.3	10-11-06	1600	1.0	.4	125	12.1	.38	.24	<.016	186	–	–
LD16.1.1	03-16-06	1200	1.0	4.6	53	3.1	1.21	<.04	.048	751	–	–
LD16.1.2	03-16-06	1000	1.0	3.5	58	2.2	1.20	<.04	.088	15	–	–
LD16.1.3	03-13-06	1600	1.0	.2	206	2.9	3.24	.99	.021	14,600	–	–
LD16.1.4	03-16-06	1100	2.0	.2	71	2.7	1.15	<.04	<.016	1,710	–	–
LD16.1.5	03-16-06	1400	2.0	.2	63	2.9	1.09	.07	<.016	2,680	–	–
LD24.9.1	10-02-06	1600	1.0	1.0	52	13.5	.66	<.04	.098	35	–	–
LD24.9.2	10-03-06	1000	1.0	.1	62	11.5	.58	.11	<.016	2,060	–	–
LD24.9.3	10-02-06	1800	1.0	.1	173	12.6	6.14	<.04	1.57	296	9.7	-4.0
LD24.9.4	10-02-06	1700	2.0	.2	94	13.3	1.49	.05	.068	35	–	–
<sup>1</sup> LD24.9.5	10-03-06	1100	1.0	.2	105	12.1	1.80	.22	<.016	4,570	–	–
<sup>2</sup> LD24.9.6	10-03-06	1300	1.0	.2	254	12.9	9.44	.50	<.016	10,700	–	–
LD24.9.7	10-12-06	1700	1.0	.7	184	10.2	6.74	<.04	.701	45	14.3	-.5
LD24.9.8	10-12-06	1730	2.0	.7	181	9.1	6.71	<.04	1.24	17	10.5	-3.0
LD24.9.9	10-12-06	1800	3.0	1.1	178	8.7	6.39	<.04	1.30	20	9.1	-4.4
LD32.8.1	10-05-06	1500	2.0	.1	90	11.7	.73	1.83	.080	169	–	–
LD32.8.2	10-05-06	1400	1.0	.1	67	12.2	.66	1.17	<.016	2,150	–	–
LD32.8.3	10-05-06	1300	2.0	.2	213	9.2	1.03	7.73	<.016	3,900	–	–
LD32.8.4	10-05-06	1600	2.0	.1	153	11.4	.91	4.17	<.016	1,100	–	–
LD37.8.1	10-04-06	1200	2.0	.2	50	11.9	.48	<.04	<.016	77	–	–
LD37.8.2	10-04-06	1400	2.0	2.8	46	12.4	.59	<.04	.118	57	–	–
LD37.8.3	10-04-06	1430	2.0	.1	95	10.4	.58	.12	<.016	6,790	–	–
LD37.8.4	10-04-06	1500	2.0	2.4	42	12.6	.57	<.04	.156	76	–	–
Miscellaneous sites near Deschutes River												
Slough at RM 194.8	03-07-06	1000	–	5.2	171	0.9	13.2	0.63	0.278	1,650	11.9	-1.0
Spring at RM 209.2	03-09-06	1500	–	.2	131	6.3	.75	.15	<.016	3,460	–	–

<sup>1</sup> At thalweg (deepest point in the river cross section), 16 feet downstream of primary transect.

<sup>2</sup> At thalweg, 69 feet downstream of primary transect.



**Figure 3.** Configurations of ground-water transects at Deschutes and Little Deschutes Rivers near La Pine, Oregon. (Two wells at river mile 24.9 on the Little Deschutes River were installed downstream of the cross section and are not shown.)

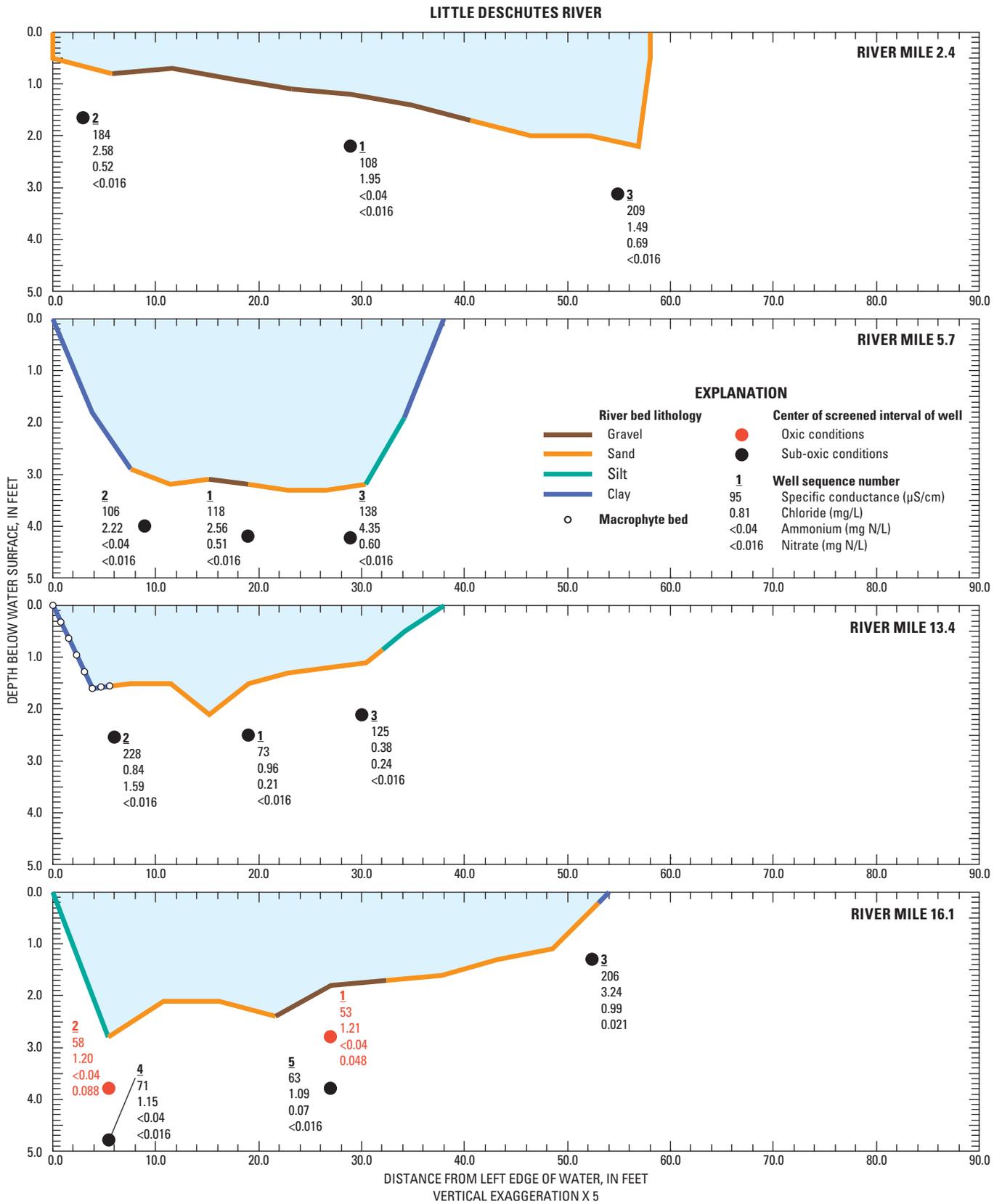


Figure 3.—Continued

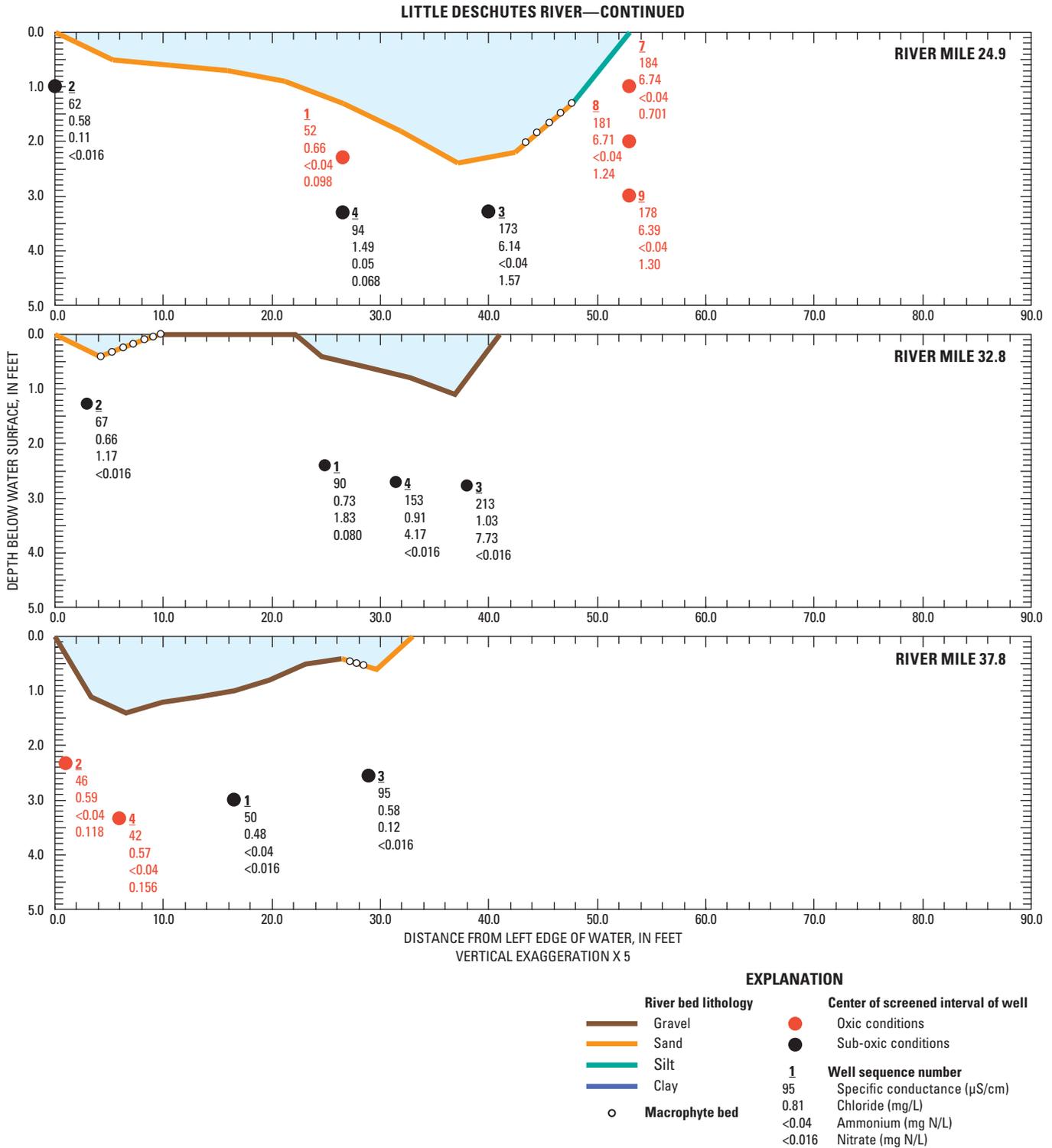


Figure 3.—Continued

Site LD24.9, with nine wells, was more densely instrumented than the other sites in an attempt to provide a more detailed characterization of the nature and geometry of the oxic/suboxic boundary in the near-river environment (table 1). Seven of the nine wells were installed along one transect, and the other two wells were installed in the river thalweg (deepest part of the channel) 16 and 69 ft downstream of the primary transect. One nest of two wells (depths of 1.0 and 2.0 ft) was installed in the center of the river. One well was installed at the left edge of water, another well between the center of the river and the right edge of the river, and a nest of three wells at the right (east) edge of water (depths of 1.0, 2.0, and 3.0 ft).

The shallow well in the center of the river (LD24.9.1) yielded oxic water with a specific conductance of 52  $\mu\text{S}/\text{cm}$  at 25°C, similar to the specific conductance of the river water during well installation (46  $\mu\text{S}/\text{cm}$  at 25°C). The deeper well in the center (LD24.9.4) was suboxic, with a specific conductance of 94  $\mu\text{S}/\text{cm}$  at 25°C. As was observed at site LD16.1, a layer of oxic hyporheic water appears to overlie a deeper layer of suboxic ground water in part of the transect at LD24.9.

The nest of three wells at the right edge of water at site LD24.9 (fig. 3) was installed to provide increased definition of the geochemical nature of ground water entering the river from the east—the presumed source area for  $\text{NO}_3^-$  previously measured in ground water near this site (table A2, appendix A). The nest of wells was installed at the transect edge where the riverbed was composed of silt. However, there was no obvious bank slough, and the river reach at this site was primarily sand and gravel, indicating an overall coarse-textured sedimentary geologic framework.

The two off-transect wells at site LD24.9 were installed to provide information about the longitudinal scale of the  $\text{NO}_3^-$ -bearing ground-water plume at this site. These wells also helped characterize the spatial heterogeneity of oxic and suboxic ground water occurrence in near-river ground water.

At site LD32.8, an island caused most water to flow in a right channel, and a small amount of water to flow in a left channel. Site LD32.8 consisted of three wells in the right channel, including one in the center of that channel, plus one well near the left edge of the left channel. The three wells in the right channel were installed at a depth of 2.0 ft because of concern that the well-sorted, coarse gravel in the bed of the right channel at this site could promote hyporheic flow. The left channel, however, was sandy, and the well depth there was set at 1.0 ft.

Site LD37.8 consisted of four wells. The riverbed at site LD37.8 consisted primarily of well-sorted, coarse gravel (some gravely sand near the right edge), so the wells were installed at depths of 2.0 ft in an attempt to sample below possible hyporheic water.

## Redox Conditions, Nitrogen, and Chloride in Ground Water from Transects

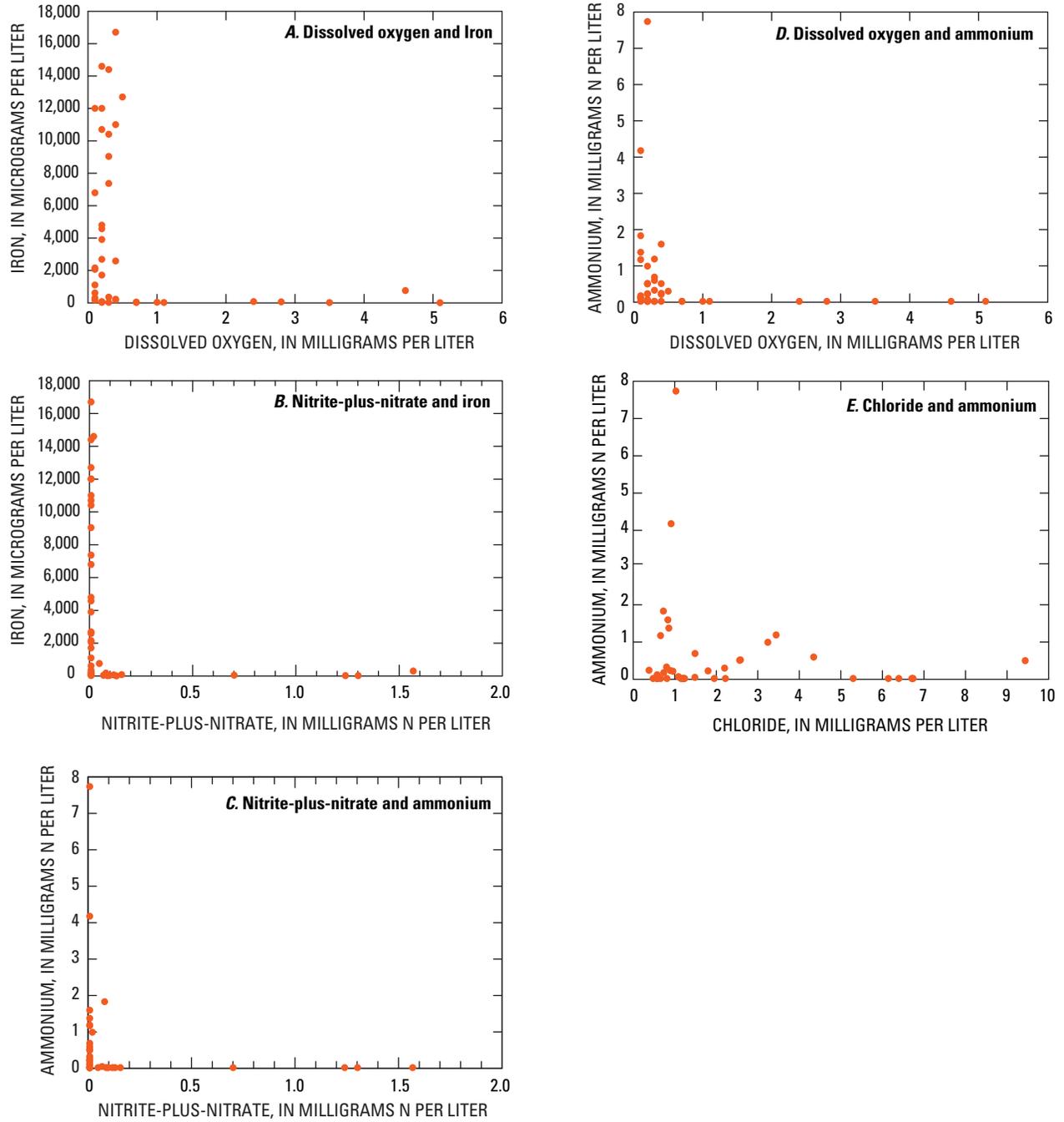
The previous section described well nests at transects LD16.1 (two nests) and LD24.9 (one nest) that yielded oxic ground water in shallower wells and suboxic ground water in deeper wells. Other wells yielding oxic ground water were (1) the well at the left edge of water at D198.5, (2) all three wells in the nest at the right edge of water at LD24.9, and (3) the two wells near the left edge of water at LD37.8. (The  $\text{O}_2$  concentration in ground water near the right edge of water at D194.1.2, 0.5 mg/L was borderline oxic/suboxic. This ground water had a  $\text{H}_2\text{S}$  odor and an Fe concentration of 12,700  $\mu\text{g}/\text{L}$ —one of the highest Fe concentrations measured in this study. These data indicate strongly reducing conditions. Thus, this sample is considered to be suboxic.)

Origin of water and solutes, availability of nutrients, and additional characterization of redox conditions can be inferred by evaluating concentrations of and relations between  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , Fe, and  $\text{Cl}^-$ . Relations between Fe and  $\text{O}_2$  concentrations (fig. 4A) reflect the suppression of Fe dissolution in the presence of  $\text{O}_2$  and in the absence of strongly acidic (for example, acid-mine drainage) conditions. This pattern is consistent with basic principles of redox progression in aquifers.

Relations between Fe and  $\text{NO}_3^-$  concentrations (fig. 4B) also are consistent with the expected sequence of redox progression in aquifers. Concentrations of  $\text{NO}_3^-$  are low or less than the MRL in Fe-rich ground water.

Nitrate and  $\text{NH}_4^+$  appear to be mutually exclusive (fig. 4C).  $\text{NH}_4^+$  is a reduced form of N, but reduction from  $\text{NO}_3^-$  to  $\text{NH}_4^+$  generally is for assimilation (Brock and Madigan, 1988), and most  $\text{NO}_3^-$  reduction in ground water is by denitrification, usually to  $\text{N}_2$  (Freeze and Cherry, 1979). However,  $\text{NO}_3^-$  or  $\text{NH}_4^+$  occurrence does reflect environmental redox state— $\text{NO}_3^-$  is stable and mobile in oxic ground water, whereas elevated concentrations of  $\text{NH}_4^+$  tend to occur in suboxic ground water (fig. 4D).

Patterns of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in ground water near La Pine also reflect different sources of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Concentrations of  $\text{Cl}^-$  also reflect  $\text{NO}_3^-$  and  $\text{NH}_4^+$  origin;  $\text{Cl}^-$  is a particularly useful tracer because it is nonreactive in most ground water systems. Septic tank effluent contains several tens of milligrams of N and  $\text{Cl}^-$  per liter, and  $\text{NO}_3^-$  and  $\text{Cl}^-$  co-occur in ground water receiving septic tank effluent. Other potential  $\text{Cl}^-$  sources, such as road salt applications, agricultural fertilizers, and dissolution of evaporites, generally are negligible in the study area (Hinkle and others, 2007). Ground water in the La Pine study area with background concentrations of  $\text{Cl}^-$  (on the order of a few milligrams per liter or less) indicate that ground water is unimpacted or minimally impacted by septic tank effluent, whereas concentrations of more than several milligrams per liter frequently indicate a septic tank effect.



**Figure 4.** Relation between chemical constituents in samples from wells at all ground water transects in the Deschutes and Little Deschutes Rivers near La Pine, Oregon, March and October 2006.

Mineralization of sedimentary organic matter, however, yields ground water characterized by elevated concentrations of  $\text{NH}_4^+$  but low concentrations of  $\text{Cl}^-$ . Patterns of  $\text{NH}_4^+$  and  $\text{Cl}^-$  (fig. 4E) reflect this source of  $\text{NH}_4^+$ .

Redox data presented in figure 4 demonstrate understandable patterns of solute occurrence within a redox framework. Such a framework can be used to infer the sources of some solutes and to predict the occurrence of redox-sensitive solutes within a given redox zone.

## Spring and Slough Samples

Ground water enters rivers through sediments beneath the rivers; this part of the resource was the component intercepted by transect wells. Ground water also enters rivers by discharge from springs and seeps. Data collection activities often relied on canoe access, an activity that, along with additional scouting from roads and trails, provided opportunities for identification of springs and seeps. Numerous seeps and minor springs were observed, but only one flowing spring was found (river mile 209.2 on the Deschutes River) that yielded sufficient water volume for meaningful measurement of  $\text{O}_2$  and for collection of water samples with a peristaltic pump (fig. 1, tables 1 and 2). The spring water was suboxic.

Samples were collected from one slough, a cut-off meander bend of the Deschutes River at river mile 194.8 (fig. 1, tables 1 and 2). At the time of sampling, the water elevation in the slough was greater than the elevation of the Deschutes River, and drainage occurred through a narrow, flowing stream connecting the slough to the river. The slough water was oxic, as would be expected for such a surface-water body. However, other data from the slough indicated the presence of complex geochemistry.

## Discussion

### Distribution of Dissolved Oxygen and Nitrate in Ground Water in the Near-River Environment

Oxic ground water was uncommon in transect samples, in spite of a sampling design that emphasized identification of oxic ground water. Some well nests at transects LD16.1 and LD24.9 yielded oxic ground water in shallower wells and suboxic ground water in deeper wells. In these well nests, shallow, oxic ground water was attributed to hyporheic processes, whereas deeper, suboxic ground water represented a  $\text{NO}_3^-$ -reducing zone between the river and terrestrial recharge areas. Other occurrences of oxic ground water are discussed in the following three paragraphs.

Oxic ground water from the well at the left edge of water at D198.5.2 appears to have originated in terrestrial recharge areas. The specific conductance, 170  $\mu\text{S}/\text{cm}$  at 25°C, and  $\text{Cl}^-$  concentration, 5.30 mg/L, suggest such an origin. The concentration of  $\text{Cl}^-$  could indicate a possible septic tank influence on the ground water. However, the  $\text{NO}_3^-$  concentration, 0.131 mg N/L, does not support such a link. Furthermore, the region upgradient from this transect is one of the few sewerred neighborhoods in the La Pine study area (fig. 1). Wastewater is treated nearby; wastewater lagoons are within 0.25 mi of the transect, and land-based wastewater disposal occurs adjacent to the lagoons. Such wastewater would be expected to be low in N but still retain wastewater  $\text{Cl}^-$ . This could be a source of the slightly elevated  $\text{Cl}^-$  concentration for water from the well at the left edge of the transect. Although specific conductance and  $\text{Cl}^-$  data indicate that this oxic sample has a terrestrial recharge origin, the sample possibly represents a mixture of (1) ground water that is relatively enriched in solutes but is suboxic, and (2) river water that is relatively dilute but is oxic. However, the  $\text{Cl}^-$  concentration, 5.30 mg/L, is typical of wastewater-impacted ground water in the study area (Hinkle and others, 2007), indicating minimal dilution, whereas the  $\text{O}_2$  concentration, 5.1 mg/L, would require a considerable component of river water.

Oxic ground water in two wells near the left edge of water at LD37.8 (LD37.8.2 and LD37.8.4) could have originated as terrestrial recharge or as hyporheic water. The wells were screened at 2.0 ft, and deeper wells were not installed. The dilute nature of the water from these wells—specific conductance 46 and 42  $\mu\text{S}/\text{cm}$  at 25°C and  $\text{Cl}^-$  concentrations 0.59 and 0.57 mg/L, respectively—would be consistent with water originating as hyporheic water. Alternatively, such dilute ground water could have been recharged locally, such as ground water originating from near-river flood plains that receive recharge from precipitation or dilute river water during floods. The dilute nature of this ground water indicates that distal terrestrial recharge areas are a less likely source of this water than local or hyporheic recharge areas. The presence of oxic but dilute ground water at these locations, without additional data from deeper wells, leaves delineation of the oxic/suboxic boundary for the left side of the transect at LD37.8 ill-defined because the redox state of ground water upgradient (earlier in the flow paths) from the dilute, oxic ground water is not known.

Oxic ground water in samples collected from all three wells (LD24.9.7, LD24.9.8, and LD24.9.9) in the nest at the right edge of water at LD24.9 probably originated in terrestrial recharge areas. Specific conductance values for water from these three wells, 178–184  $\mu\text{S}/\text{cm}$  at 25°C, and  $\text{Cl}^-$  concentrations, 6.39–6.74 mg/L, were similar. Dissolved

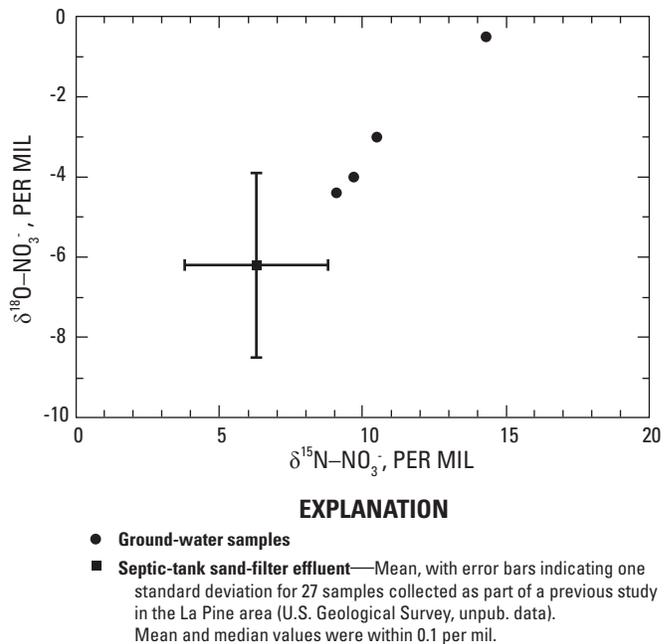
oxygen (and  $\text{NO}_3^-$ ) concentrations were lower at the 1.0-ft zone than at the 3.0-ft zone (table 2). This redox sequence is inverted from the sequence typically observed in recharge areas, where ground-water flow has a downward component and redox conditions tend to progress from less reduced at shallow depths to more reduced at greater depths. The physically inverted redox sequence at this well nest is consistent with the typical mechanism of discharge through a riverbed, in which ground water moves through the near-river environment toward the river with an upward component of flow, and in which redox conditions evolve from less reduced toward more reduced conditions along the flow path. In this case, redox conditions in some ground water sampled from this transect remained oxic to the end of the flow path at the river, or at least to within 1 vertical foot of the river edge.

Four transect wells at LD24.9 yielded ground water with  $\text{NO}_3^-$  concentrations greater than 0.2 mg N/L. All four wells were at LD24.9, a transect near the outskirts of the city of La Pine where residential development has been in place for several decades. These four wells included the nest of three at the right edge of water (LD24.9.7, LD24.9.8, and LD24.9.9), and the well 13 ft from the right edge of water (LD24.9.3). Concentrations of  $\text{NO}_3^-$  ranged from 0.701 to 1.57 mg N/L (table 2). The three wells at the right edge of water were oxic, but well LD24.9.3 was suboxic.

In the redox boundary approach developed to represent the occurrence of denitrification in the La Pine study area, Hinkle and others (2007) observed that the oxic/suboxic boundary closely matched the denitrification boundary, and as such, was a useful representation of denitrification at the aquifer scale. However, a redox boundary that appears relatively sharp at the aquifer scale may appear more gradational at smaller spatial scales. Some  $\text{NO}_3^-$  may be denitrified on the oxic side of the boundary in response to denitrification in reduced microenvironments, and some  $\text{NO}_3^-$  may be advected beyond the oxic/suboxic boundary as microbial systems adjust from  $\text{O}_2$ -reducing to  $\text{NO}_3^-$ -reducing conditions. Thus, the occurrence of  $\text{NO}_3^-$  in suboxic ground water in one well is reasonable, especially in light of the geochemical structure at this site, where oxic,  $\text{NO}_3^-$ -bearing ground water apparently migrated to the right edge of the river without evolving to suboxic conditions. The redox sequence at the right edge of water, in which both  $\text{O}_2$  and  $\text{NO}_3^-$  concentrations decreased with increasing proximity to the riverbed, also is consistent with redox boundary concepts in that some  $\text{NO}_3^-$  may undergo denitrification at microsites of anoxia within the oxic zone prior to arrival at the redox boundary.

Samples collected from the four wells at and near the right edge of water at LD24.9 were analyzed for stable isotopes of  $\text{NO}_3^-$  (fig. 5). The mean and standard deviation

of a set of 27 samples of septic tank effluent collected after percolation through unsaturated volcanic sand in the study area, approximating the isotopic character of septic tank  $\text{NO}_3^-$  loaded to the aquifer, also are shown in figure 5. The enrichment in both  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  in the transect samples is indicative of fractionation during denitrification (Groffman and others, 2006), and indicates that  $\text{NO}_3^-$  in these sediments had been partially denitrified. Thus, the oxic/suboxic boundary can be seen as an imperfect representation of the denitrification boundary, insofar as denitrification actually can begin before  $\text{NO}_3^-$  reaches the boundary (as evidenced by the isotopes of  $\text{NO}_3^-$ ) and can continue to occur downgradient from the boundary (as evidenced by the presence of  $\text{NO}_3^-$  in ground water beyond the oxic/suboxic boundary). In locations where the oxic/suboxic boundary is near the river, some  $\text{NO}_3^-$  can migrate beyond the boundary and potentially discharge to the river. On the other hand, as  $\text{NO}_3^-$  approaches the oxic/suboxic boundary, some denitrification can occur prior to arriving at the oxic/suboxic boundary, lessening the mass of  $\text{NO}_3^-$  available for discharge to the river.



**Figure 5.** Relation between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate in samples from wells at ground-water transect LD24.9 (wells containing nitrite-plus-nitrate concentrations greater than 0.5 mg N/L) and sand-filter effluent from septic tanks near La Pine, Oregon.

## Integration of Ground-Water Flow Paths at a Cut-Off Slough

The slough that enters the Deschutes River at river mile 194.8 (fig. 1) provided an opportunity to characterize surface water that likely received sizable contributions from multiple ground-water flow paths. Slough water may have contained a component of river water that entered the slough during a period of high river stage and (or) a component of surface runoff from snowmelt. However, slough water contained 1,650  $\mu\text{g/L}$  of Fe, indicating a component of suboxic ground water. (Oxic ground water may also discharge to the slough.) The balance between the kinetically controlled nature of Fe oxidation and precipitation, and the relatively short residence times of most surface water relative to most ground water, accounts for the presence of both  $\text{O}_2$  and Fe in the slough water. Slough water contained 0.278 mg N/L of  $\text{NO}_3^-$  and 0.63 mg N/L of  $\text{NH}_4^+$ , also indicating non-equilibrium redox conditions (table 2).

Nitrate in slough water could have been present in ground water that discharged to the slough (the area near the slough was developed earlier and more densely than most other locations in the study area). Alternatively,  $\text{NO}_3^-$  in the slough could have been produced by nitrification of  $\text{NH}_4^+$  in the presence of  $\text{O}_2$  in the slough. The  $\delta^{15}\text{N}-\text{NO}_3^-$  value, 11.9 ‰ (table 2), suggests that  $\text{NO}_3^-$  in the slough water primarily was from ground water (with possible denitrification of some  $\text{NO}_3^-$ ). The  $\text{Cl}^-$  concentration (13.2 mg/L) also is consistent with a ground-water source for the  $\text{NO}_3^-$ . Although slough water was not analyzed for  $\delta^{15}\text{N}-\text{NH}_4^+$ , other ground-water  $\delta^{15}\text{N}-\text{NH}_4^+$  values measured in the La Pine area ranged from 2.5 to 3.9 ‰ (Hinkle and others, 2007), and  $\text{NO}_3^-$  derived from nitrification of  $\text{NH}_4^+$  would be isotopically depleted (lighter) than source  $\text{NH}_4^+$  (Hübner, 1986). The  $\delta^{15}\text{N}-\text{NO}_3^-$  value for the slough water indicates that nitrification of  $\text{NH}_4^+$  was not a dominant source of  $\text{NO}_3^-$  in the slough at the time of sampling. The occurrence of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the slough water reflects distinct contributions of N from various sources:  $\text{NO}_3^-$  apparently from septic tank effluent (based on  $\text{Cl}^-$  and stable isotopes of  $\text{NO}_3^-$ ) and  $\text{NH}_4^+$  apparently from natural sources (based on the presence of Fe).

## Redox Controls at the Scale of River Reaches

The widespread occurrence of suboxic ground water beneath the Deschutes and Little Deschutes Rivers represents an extensive denitrifying zone between rivers and upgradient recharge areas that appears to remove much of the  $\text{NO}_3^-$  being transported from upgradient recharge areas. However, oxic

ground water does occur in sediments directly beneath these rivers in places, and these oxic zones are potential pathways for  $\text{NO}_3^-$  transport from terrestrial recharge areas to rivers.

Oxic ground water, where detected, tended to be present near the outside edge (edge closest to the margin of the valley floor) of a river meander bend (pl. 1). The three transects where oxic ground water was detected (excluding sites where oxic hyporheic water was underlain by suboxic water) were: (1) D198.5 (left or western edge), (2) LD24.9 (right or eastern edge), and (3) LD37.8 (left or western edge; oxic, but possibly hyporheic or otherwise of local origin). The pattern of oxic ground water occurrence relative to river meander bends is apparent on plate 1: oxic ground water was detected at the western edge of D198.5, where the river bends toward the west, in the eastern part of LD24.9, where the river bends towards the east, and in the western part of LD37.8, where the river hugs the western edge of the flood plain. Oxic water, when detected, was near the outside edge of meander bends, but not all ground water near the outside edge of meander bends was oxic.

Occurrence of oxic ground water also was related to riparian zone extent. Oxic ground water was detected in zones where the width of the riparian environment adjacent to a site on the outside edge was narrow relative to the overall width of the riparian zone in the valley at the site (pl. 1). Plate 1 shows the riparian zone extent using a geographical information system (GIS) representation the cryaquoll soils (Natural Resources Conservation Service, 2006). GIS coverage is available for 9 of the 10 transect sites. Relations between ground water redox state and riparian zone size are hampered because transect D198.5 is not represented by GIS coverage. However, field observations indicated that the west bank (but not the east bank) at this site had essentially no riparian zone; the west bank consisted of a beach of eroded aquifer gravel and a near absence of vegetation. Some transects with a relatively narrow riparian zone extent between the river and the outside edge (for example, LD2.4), or even, in the case of D194.1, essentially lacking a riparian zone, were largely free of oxic ground water (no oxic ground water was detected). As a consequence, establishing quantitative estimates of riparian zone width associated with suboxic (or, alternatively, oxic) ground water in the near-river environment is difficult. The inability to draw quantitative conclusions reflects the limited number of transects available for making such an analysis. However, it also reflects the facts that the near-river geochemical environment is highly heterogeneous, and that ground water redox conditions in the near-river environment are controlled not only by near-river redox processes, but also by redox processes occurring in parts of the aquifer upgradient from the near-river environment.

Although oxic ground water appears to be relatively uncommon in sub-river sediments, the redox state of ground water discharging to rivers through springs and seeps in the study area has received little attention. Seeps usually were located near the outside bends of river meanders (near the edge of the flood plain, which closely corresponds to the edge of the riparian zone). Although seeps were not represented in this analysis, they tended to be located in the same types of sites (outside bends of river meanders) as sites where oxic sub-river ground water was detected.

Particle tracking analysis can be used in combination with an understanding of occurrence patterns of near-river ground water redox conditions to infer relative degrees of river reach vulnerability to ground-water  $\text{NO}_3^-$ . Particle tracking results delineate areas where  $\text{NO}_3^-$  reaching the water table from septic tanks could be transported to the near-river environment, subject to the aquifer-scale redox controls discussed earlier. In this analysis, pathlines for particles transported into the suboxic part of the system (most pathlines) were removed. Only pathlines for particles that remain in the oxic part of the ground-water system were retained, providing a delineation of oxic ground-water contributing zones to rivers as represented by the aquifer-scale model (pl. 1). (Pathlines for particles that travel through suboxic zones, although not shown on plate 1, generally lie beneath pathlines for particles in oxic zones.) Because the thickness of the oxic zone in the near-river environment was represented in the aquifer-scale model by a 10-ft minimum thickness, the suite of particle pathlines shown on plate 1 should be considered to represent the maximum number of pathways for  $\text{NO}_3^-$  transport into rivers.

Particle tracking results provide insights at scales ranging from the scale of transects to the scale of the aquifer. At the aquifer scale, oxic pathlines primarily occur near the rivers (pl. 1). Oxic ground-water pathlines extend farther from the river in the northern part of the study area, where (primarily forested) volcanic uplands contain thick oxic zones. These results indicate that rivers generally are less vulnerable to residential development farther from rivers than development closer to rivers.

Particle tracking results at the scale of transects are consistent with study results. For example, simulated oxic pathlines on the west at D198.5, east at LD24.9, and west at LD37.8 (pl. 1) are consistent with the measurement of oxic ground water at the same sites, as well as the detection of  $\text{NO}_3^-$  at wells near the east edge of LD24.9. Simulated oxic pathlines near the slough that enters the Deschutes River at river mile 194.8 (pl. 1), together with the observation that the area near the slough contains residential development, are consistent with the detection of  $\text{NO}_3^-$  in the slough (table 2). At other transect sites, ground water simulated to remain oxic in the aquifer scale model appears to be suboxic based on field

measurements. For example, oxic pathlines were simulated for D194.1 and D206.4, but field measurements identified only suboxic ground water. These results also are consistent with study results, insofar as near-river redox processes not represented in the aquifer-scale model still are expected to occur in some areas.

The combination of particle tracking analysis with near-river redox characterization has potential application in a variety of hydrologic or environmental assessments. For example, resource managers attempting to reduce potential N loads to rivers could prioritize N-reduction efforts in recharge areas or could prioritize locations for riparian zone protection or establishment in discharge areas by focusing on oxic pathlines that link unsewered neighborhoods with river reaches that occur near the edges of riparian zones. Residential neighborhoods are approximately represented on plate 1 by the networks of roads. Alternatively, strategies for establishing river Total Maximum Daily Load (TMDL) guidelines could use an analysis in which a range of scenarios for pathline redox state, based on a range of riparian zone widths, is used to bracket likely  $\text{NO}_3^-$  loads to river reaches. Actual identification of pathlines that would likely remain oxic along their entire lengths (including during transport through near-river sediments) was not depicted on plate 1 because (1) uncertainty remains regarding the potential for ground water to remain oxic along the near-river parts of the pathlines, and (2) different potential applications of this analysis preclude the presentation of a single subset of pathlines. However, the absence of a more quantitative assessment does not prevent useful applications. For example, at LD5.7, oxic pathlines essentially do not extend beyond the riparian zone extent, suggesting a relatively small degree of vulnerability to  $\text{NO}_3^-$ . Near LD13.4, oxic pathlines do extend beyond the riparian zone, but do not appear to extend to residential areas, again suggesting a relatively small degree of vulnerability. However, large areas of the Deschutes River between river miles 190 and 200 contain residential development and large numbers of oxic pathlines, indicating a potentially large degree of vulnerability.

## Effects of Ground-Water Discharge to Rivers

Ground water is a potential source of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to rivers in the study area. The cut-off slough adjacent to the Deschutes River at river mile 194.8 demonstrates this potential, with 0.278 mg N/L of  $\text{NO}_3^-$  and 0.63 mg N/L of  $\text{NH}_4^+$  at the time of sampling. The magnitude of the  $\text{NO}_3^-$  concentration and the ratio of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  in the slough sample indicate the existence of a considerable contribution of oxic ground water to the slough, consistent with the extension of the slough 0.6 mi away from the riparian zone (pl. 1).

Most river reaches, however, likely would be less vulnerable to  $\text{NO}_3^-$  from sub-river ground water sources because of the widespread occurrence of suboxic ground water in sub-river sediments and large amounts of water for dilution.

Contributions of oxic ground water, and therefore, potential contributions of  $\text{NO}_3^-$  to rivers in the study area probably are limited primarily to areas where rivers bend toward the outside of the riparian environment. Thus, contributions of  $\text{NO}_3^-$  to rivers likely are restricted to relatively small areas of river reaches. However, the potential effects of such N loads to rivers might not be negligible because rivers can be highly sensitive to changes in nutrient fluxes (nutrient over-enrichment represents the single greatest source of impairment to rivers in the United States; U.S. Environmental Protection Agency, 1998). A seepage run (series of river discharge measurements along a section of river) with water sampling was done on the Little Deschutes River during a period of stable low flow in October 2006 (table A3, appendix A). Total N concentrations were less than 0.10 mg N/L in all samples, whereas dissolved orthophosphate concentrations were about 0.04 mg/L, indicating N-limited conditions. Generally increasing discharge, specific conductance, and  $\text{Cl}^-$  downstream (figure A1, appendix A) indicate a river receiving ground-water discharge. Concentrations of N were variable and may have been depressed by plant uptake; rivers in the study area contain extensive algae and macrophytes. Concentrations of  $\text{NO}_3^-$  in study area ground water likely will increase over time as  $\text{NO}_3^-$  currently in the aquifer is transported farther along ground-water flow paths and as continued residential development leads to increasing  $\text{NO}_3^-$  loads to the water table (Morgan and others, 2007), but potential effects of future increased ground-water  $\text{NO}_3^-$  contributions to rivers in the study area have not been investigated.

## Summary

The redox state of ground water exerts a strong control on nitrate ( $\text{NO}_3^-$ ) stability, and therefore on  $\text{NO}_3^-$  discharge from aquifers to rivers. Oxic ground water was uncommon in sub-river ground-water samples in the La Pine area. Ground-water samples from transects of temporary wells installed near the center of the riparian zone were always suboxic. Where transects were located near edges of riparian zones, ground-water samples from transect centers were always suboxic, as were ground-water samples from points on the inside part of each transect (toward the center of the river/riparian zone system). Oxic ground water (other than hyporheic water), if detected, was detected only near the outside edge of transects at meander bends. However, zones in which oxic ground water discharges to rivers represent locations of potential river vulnerability to  $\text{NO}_3^-$ .

The redox state of ground water in near-river sediment is controlled by geochemical processes occurring throughout the aquifer and also by geochemical processes occurring near the intersection of riparian zones and ground-water discharge zones. Younger, less geochemically evolved ground water generally enters the near-river environment near the edges of the river corridor, whereas older, more geochemically evolved ground water (water that generally has traversed more of the aquifer) tends to be in more regional flow systems that discharge to locations closer to the center of the river corridor. Riparian zone processes that occur in many near-river sediments become important as ground water nears discharge points in or adjacent to rivers; lateral erosion of river systems away from the center of the flood plain can decrease interactions between ground water and reducing riparian zone sediments. Thus, ground water redox patterns in near-river sediments reflect the position of a river within the river/riparian zone/aquifer continuum. Spatial heterogeneity of redox conditions in the near-river environment reflects the interplay of these (aquifer and riparian zone) processes, and makes it difficult to quantitatively define conditions under which oxic ground water might be expected in near-river sediments. Nevertheless, this general understanding of factors controlling near-river redox state, particularly if coupled to a ground-water-flow-path-based understanding of linkages between upgradient recharge areas and rivers, may be useful for managing river water quality.

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## Appendix A. Project Quality-Control Data, Historical Near-River Ground-Water Data Collected near the Little Deschutes River Near La Pine, Oregon, and Project Discharge and Chemical Data from the Little Deschutes River near La Pine, Oregon, 2006

Project quality-control data are shown in [table A1](#). Geochemical data collected from sediments beneath the Little Deschutes River during October 2000 (Morgan and others, 2007) are shown in [table A2](#).

River discharge was measured, and chemistry data were collected, at five sites along the Little Deschutes River during low-flow conditions October 9–10, 2006 and are listed in [table A3](#) and shown in [figure A1](#). For these discharge

measurements, tributary inflows along the studied reaches accounted for less than 0.2 ft<sup>3</sup>/s. Water samples were collected using isokinetic, depth-integrated, equal-width-increment sampling methods. Collection and processing methods were those described by U.S. Geological Survey (1999). Analytical techniques used were those described by Fishman (1993) and Patton and Kryskalla (2003).

**Table A1.** Project quality-control data, March and October 2006.

[Standard reference samples prepared by M.C. Doyle, U.S. Geological Survey. **Abbreviations:** mg/L, milligram per liter; mg N/L, milligram of nitrogen per liter; µg/L, microgram per liter; ‰, per mil; NWQL, National Water Quality Laboratory; –, not collected]

Sample type	Station No.	Date	Time	Chloride (mg/L)	Ammonium (mg N/L)	Nitrite + nitrate (mg N/L)	Iron (µg/L)	$\delta^{15}\text{N-NO}_3^-$ (‰)	$\delta^{18}\text{O-NO}_3^-$ (‰)
Replicate	434212121295203	10-02-06	1800	6.14	<0.04	1.57	296	–	–
Replicate	434212121295203	10-02-06	1801	6.18	<.04	1.56	287	–	–
Replicate	434212121295203	10-02-06	1802	6.15	<.04	1.55	302	–	–
Standard deviation of replicates				.02	–	.01	8	–	–
Replicate	435014121274900	03-07-06	1000	–	–	–	–	11.9	-1.0
Replicate	435014121274900	03-07-06	1001	–	–	–	–	11.9	-.7
Standard deviation of replicates				–	–	–	–	.0	.2
Equipment blank	–	03-01-06	1508	<.20	<.04	<.016	<6	–	–
Standard reference sample 1									
Standard concentration	–	03-01-06	1603	5.20	.53	1.00	–	–	–
Reported by NWQL	–	03-01-06	1603	5.14	.54	.99	–	–	–
Reported concentration, as percentage of standard				98.8	102	99	–	–	–
Standard reference sample 2									
Standard concentration	–	03-01-06	1613	11.9	.91	2.78	–	–	–
Reported by NWQL	–	03-01-06	1613	11.0	.93	2.68	–	–	–
Reported concentration, as percentage of standard				92.4	102	96.4	–	–	–
Standard reference sample 3									
Standard concentration	–	03-01-06	1623	15.4	1.93	3.06	–	–	–
Reported by NWQL	–	03-01-06	1623	14.5	1.86	2.97	–	–	–
Reported concentration, as percentage of standard				94.2	96.4	97.1	–	–	–

**Table A2.** Historical ground-water data for samples collected from sediments beneath the Little Deschutes River, Oregon.

[Historical data from Morgan and others, 2007. Nitrogen samples analyzed by Oregon Department of Environmental Quality, using methods described in Hinkle and others, 2007. **River mile**, as indicated on U.S. Geological Survey topographic maps. **Depth**, depth of center of screen below riverbed. **Latitude and longitude**: North American Datum of 1927 (NAD 27). **Abbreviations**: LEW, left edge of water looking downstream; mg N/L, milligram of nitrogen per liter; <, less than]

River mile	Sample location	Depth (feet)	Latitude	Longitude	Date	Dominant river bed lithology	Nitrite+ nitrate (mg N/L)	Ammonium (mg N/L)	Hydrogen sulfide odor
7.8	Center of river	1.0	43° 48' 6.2"	121° 27' 10.7"	10-27-00	Sand	<0.005	0.34	Present
9.8	Center of river	3.0	43° 47' 30.2"	121° 27' 29.1"	10-27-00	Sand	<.005	1.6	Present
12.5	Center of river	3.0	43° 46' 41.5"	121° 28' 12.0"	10-27-00	Sand	.006	.44	Present
16.7	Center of river	1.0	43° 44' 58.2"	121° 29' 15.8"	10-26-00	Sand	<.005	1.3	Present
19.1	Center of river	2.0	43° 44' 15.8"	121° 29' 21.4"	10-26-00	Sand	.071	2.3	Present
21.2	Center of river	2.0	43° 43' 32.5"	121° 29' 26.8"	10-26-00	Sand	.006	2.6	Present
24.9	One-fourth of distance across from LEW	3.0	43° 42' 12.3"	121° 29' 52.4"	10-23-00	Gravel	.011	.31	Present
24.9	Center of river	3.0	43° 42' 12.3"	121° 29' 52.4"	10-23-00	Gravel	1.29	<.02	Absent
24.9	Three-fourths of distance across from LEW	3.0	43° 42' 12.3"	121° 29' 52.4"	10-23-00	Gravel	2.73	<.02	Absent

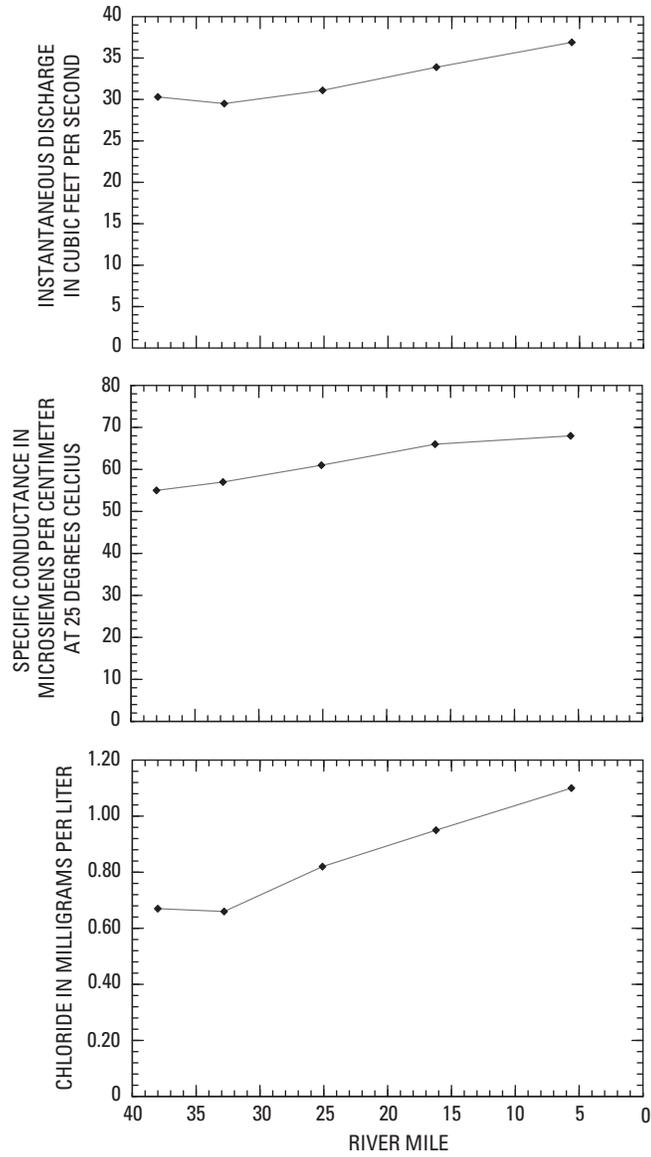
**Table A3.** Discharge measurements and chemical samples collected from Little Deschutes River near La Pine, Oregon, October 2006.

[Total nitrogen and field parameters on unfiltered samples; other analyses on filtered samples. **Latitude and longitude**: North American Datum of 1927 (NAD 27). **Abbreviations**: NAVD 88, North American Vertical Datum of 1988; RM, river mile, as indicated on U.S. Geological Survey topographic maps. ft<sup>3</sup>/s, cubic foot per second; mg/L, milligram per liter; µS/cm, microsiemens per centimeter at 25°C; °C, degrees Celsius; mg N/L, milligram of nitrogen per liter; mg P/L, milligram of phosphorus per liter; <, less than]

Site	Station No.	Date	Time	Latitude	Longitude	Altitude (feet above NAVD 88)	Instantaneous discharge (ft <sup>3</sup> /s)	Dissolved oxygen (mg/L)	Specific conductance (µS/cm)
RM 37.8	433846121352800	10-09-06	1610	43° 38' 45.7"	121° 35' 28.1"	4,235	30.3	10.2	55
RM 32.6	434022121324600	10-10-06	1110	43° 40' 22.2"	121° 32' 46.5"	4,205	29.5	9.8	57
RM 24.9	434212121295700	10-10-06	1340	43° 42' 12.4"	121° 29' 52.4"	4,195	31.1	10.4	61
RM 16.0	434515121290200	10-10-06	1510	43° 45' 14.7"	121° 29' 02.0"	4,170	33.9	10.6	66
RM 5.4	434917121270000	10-10-06	1720	43° 49' 16.8"	121° 26' 59.8"	4,165	36.9	10.3	68

Site	Station No.	Temperature (°C)	Chloride (mg/L)	Ammonium (mg N/L)	Nitrite+ nitrate (mg N/L)	Nitrite (mg N/L)	Total nitrogen (mg N/L)	Orthophosphate (mg P/L)
RM 37.8	433846121352800	11.5	0.67	<0.02	<0.06	<0.002	0.08	0.039
RM 32.6	434022121324600	7.1	.66	<.02	<.06	<.002	.09	.040
RM 24.9	434212121295700	8.9	.82	<.02	<.06	<.002	.08	.041
RM 16.0	434515121290200	9.7	.95	<.02	<.06	<.002	<.06	.053
RM 5.4	434917121270000	10.3	1.10	<.02	<.06	<.002	.06	.041



**Figure A1.** Spatial patterns of instantaneous discharge, specific conductance, and chloride, Little Deschutes River near La Pine, Oregon, October 9–10, 2006.

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