SURFACE-SUBSURFACE HYDROLOGIC EXCHANGE AND NITROGEN DYNAMICS IN THE HYPORHEIC ZONE OF THE TANANA RIVER

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A

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ABSTRACT

The aquatic-terrestrial interface is an active site of biogeochemical transformation, regulating the flux of nutrients between ecosystems. I addressed the hydrologic controls on nitrogen biogeochemistry in the hyporheic zone of a glacially fed river. I measured hyporheic concentrations of solutes and gases along subsurface flowpaths on two islands. Denitrification was quantified using an *in situ* $\delta^{15}NO_3^-$ push-pull technique. Nitrate concentration was consistently greater in river than in hyporheic water. Denitrification ranged from 1.9 – 29.4 mgN kg sediment^{-1} day^{-1}. Hotspots of methane partial pressure, averaging 50,000 ppmv, were found in densely vegetated areas with low oxygen concentration (< 0.5 mgO_2 L^{-1}). Hyporheic flow was an important source of nitrogen to microbes and vegetation, transporting on average 0.41 gNO_3^--N m^{-2} day^{-1} through surface sediments. Results suggest that denitrification is a major sink for river nitrate in boreal forest floodplain soils, particularly at the river-sediment interface. The stability of the river hydrograph is a key factor regulating anaerobic metabolism in the hyporheic zone.

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PREFACE

This thesis is in manuscript format. Chapter 1 is an introduction of the biogeochemical processes that occur in the hyporheic zone. Chapter 2 is formatted for submission to the peer-reviewed journal *Biogeochemistry.*

I would like to gratefully acknowledge my advisor, Jay Jones, for his assistance throughout this research. Thanks also to my committee members, Knut Kielland and Richard Boone, who provided valuable comments on the research and manuscript. Thanks to Larry Hinzman for help at the beginning of this project. I'd like to thank Nicolas Lisuzzo, Karl Olson, and Jessica Eichmiller for their assistance in the field and laboratory. Thanks to Kelly Balcarczyk, Emma Betts and Jon O'Donnell for help with laboratory analyses. Thanks to Jamie Hollingsworth and Brian Carlson for lifts down the river. I would also like to thank Dayton Dove for his endless support.

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CHAPTER 1: INTRODUCTION

The hyporheic zone

The hyporheic zone is the saturated sediments beneath and adjacent to rivers and streams, and functions as an ecotone between aquatic and terrestrial environments (Triska et al. 1993a, Boulton et al. 1998). Unlike ground water, hyporheic water exchanges with surface water, linking biological and chemical processes occurring in the subsurface with surface waters (Jones and Holmes 1996). The flow of surface water into the hyporheic zone serves as a vector for oxygen, organic matter and nutrient transport to microbes. Relatively rapid supply of nutrients to microbes in sediments at the aquatic-terrestrial interface enhances microbially-mediated chemical reactions compared with in-stream or groundwater environments (Findlay 1995, Hedin et al. 1998, Morrice et al. 2000).

The extent of surface-subsurface hydrologic exchange varies greatly among rivers, and is a function of river morphology, discharge, and sediment porosity (Boulton et al. 1998, Dahm et al. 1998). The degree of mixing between surface and subsurface water has been investigated using conservative tracers. Using such techniques, Triska et al. (1989) defined the hyporheic zone as the saturated sediment with 10 – 98 % advected surface water (Fig. 1). In contrast, Stanford and Ward (1993) delineated the hyporheic zone in a biological context, as a saturated zone hydrologically connected with channel, and accessed by lotic-dwelling macroinvertebrates. Spatial and temporal heterogeneity of the hyporheic zone, in part due to discharge variability, requires that definitions are based on specific research questions. Therefore, for this study, I defined the hyporheic zone as the saturated sediments hydrologically linked to the river channel, characterized by physical and chemical gradients (e.g., in dissolved oxygen, ammonium, dissolved organic carbon (DOC), nitrate, methane, carbon dioxide, pH and temperature).

Biogeochemical transformations along hyporheic flowpaths

Hyporheic sediments are heterotrophic components of river ecosystems and therefore are strongly influenced by the supply of oxygen and organic matter (Champ et al. 1979, Rysgaard et al. 1994, Findlay 1995, Hedin et al. 1998, Morrice et al. 2000). The slow rate of oxygen diffusion in water means that delivery of oxygen to hyporheic sediments is primarily mediated by the rate of flow, which is a function of pore size, hydraulic conductivity, and the hydraulic gradient. Microbial oxidation-reduction reactions occur according to the yield of free energy, where microbes that can extract higher energy yields gain a competitive advantage for electron acceptors (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO^{4-}, CO_2) and donors (DOC, CH_4, HS^-, Fe^{2+}, Mn^{2+}, NH_4^+, H_2). As the residence time of water increases along subsurface flowpaths and biotic (heterotrophic respiration) and chemical (e.g., Fe^{2+} and CH_4 oxidation) demand for oxygen exceeds the influx of oxygen, then anaerobic processes such as denitrification, sulphate reduction, and methanogenesis can become energetically favorable (Champ et al. 1979, Duff and Triska 1990, Holmes et al. 1996, Morrice et al. 2000).

Chemolithotrophic nitrifying bacteria (*Nitrosomonas sp.* and *Nitrobactor sp.)* need oxic conditions to oxidize ammonium to nitrite and nitrate (Table 1); in near-stream/river environments, where sediments are well oxygenated, ammonium concentration is often depleted and nitrate is elevated (Jones and Holmes 1996, Hedin et al. 1998, Morrice et al. 2000; Fig. 2). As hydrologic exchange decreases and oxygen is consumed along hyporheic flowpaths, ammonium concentration increases in the absence of nitrifying bacteria (Fig. 2; Triska et al. 1993b). Aerobic respiration and nitrate reduction generate similar energy yields per mole of CH_2O oxidized (-501 and -476 kJ free energy, respectively; Table 1); when anoxia develops (< 1 molO_2 L^{-1}; Fig. 3) denitrification is generally the first anaerobic metabolic pathway to occur. Denitrification can cause nitrate concentration to decrease along subsurface flowpaths as nitrate is reduced to nitrous oxide and dintrogen gases (Fig. 2; Hedin et al. 1998, Hill 2000).

As redox conditions become increasingly reduced along flowpaths, alternative anaerobic processes can occur. Obligate anaerobic bacteria reduce sulfate concentrations via sulfate reduction and produce methane via methanogenesis. These processes produce approximately five times less free energy (-102 and -66 kJ, respectively; Table 1) than denitrification and therefore are restricted to sediments in which higher energy yielding electron acceptors have been depleted (Champ et al. 1979, Hedin et al. 1998).

Nitrogen transformations in near-river environments are of particular note as nitrogen is an essential nutrient for primary productivity, and hyporheic sediments can control the supply of nitrogen from aquatic to terrestrial ecosystems (Lowrance et al. 1984, Hedin et al. 1998, Hill 2000, Schade et al. 2002, Vidon and Hill 2004). Several processes retain or remove nitrogen as hyporheic water flows through sediment. Assimilatory pathways include nitrogen uptake by plants and microbes. Dissimilatory pathways include dissimilatory nitrate reduction to ammonium (DNRA), and denitrification (the permanent removal of nitrate via conversion to nitrous oxide and dinitrogen gases). A large range in redox potential exists between the reduced (ammonium = valance of -3) and oxidized (nitrate = valance of +5) state of nitrogen. As a result, reactions that transform ammonium to nitrate produce energy used by chemolithotrophic bacteria. In contrast, reactions that transform nitrogen from an oxidized to reduced state (i.e., denitrification) require energy from organic matter (Duff and Triska 2000). Denitrifying bacteria are facultative anaerobes and can therefore switch between aerobic and anaerobic respiration as environmental conditions change. As a consequence, denitrification can be a substantial sink for nitrogen in anoxic regions at the river-sediment interface where supply of nitrate and DOC is great (Triska et al. 1989, Dahm et al. 1998, Hedin et al. 1998, Pinay et al. 1998, Baker and Vervier 2004). In nitrogen-limited riparian zones, denitrifying bacteria have to contend with competition for nitrate with plants and other bacteria (Murray et al. 1989, Zak et al. 1990) and leaching of nitrate through the soil profile (Brady and Weil 2002).

Dissolved organic carbon is the dominant electron donor in many environments and can be more important than oxygen status in determining the rate of denitrification (Vervier et al. 1993, Holmes et al. 1996, Hedin et al. 1998, Hill et al. 2000). In addition to the quantity of DOC available for heterotrophs, quality of DOC is also recognized as a rate controlling factor (Bernhardt and Likens 2001, Sobczak et al. 2002, Baker et al. 2004). The primary sources of DOC to heterotrophs in the hyporheic zone are the decomposition of organic matter and supply through river water intrusion (Vervier et al. 1993).

Nitrogen supply in riparian zones

Nitrogen is an essential element whose availability can limit primary production in terrestrial and aquatic ecosystems (Vitousek 1994). Consequently, as hyporheic water exchanges between aquatic and terrestrial environments, plant assimilation and denitrification constitute effective sinks for nitrogen (Hill 1996, Lowrance et al. 1997). In terrestrial ecosystems, nitrogen occurs most commonly in organic forms, and in infertile soils mineralization rate of organic matter to plant available nitrogen is a critical determinant of nitrogen nutrition in plants. Recent research has revealed that plants can also tap into pools of organic nitrogen, assimilating nitrogen in the form of amino acids (Kielland 1994, McFarland et al. 2002, Neff et al. 2003, Kielland et al. 2006). Hyporheic flow represents an additional source of nitrogen to the rooting zone of riparian vegetation (Schade et al. 2002, Adair et al. 2004). The rate of nitrogen acquisition is generally controlled by diffusion to the root surfaces of plants (Lambers et al. 1998). In riparian zones, advective flow of hyporheic water through the rooting zone can substantially accelerate the transport of nutrients to plant roots.

The efficiency at which nitrate is removed from hyporheic water varies temporally as well as spatially. Seasonal variation in the extent and duration of saturation in riparian soils affects the demand for oxygen and consequently the redox potential (Duff and Triska 2000), which in turn regulates nitrogen loss via denitrification. During periods of peak river flow, denitrification and uptake of nitrogen by vegetation can be substantial sinks for nitrogen (Schade et al. 2002, Baker and Vervier 2004). High river stage and associated flooding lead to enhanced river water intrusion in the hyporheic zone, supplying DOC and nitrate to plant roots and subsurface microbes, and thus increasing metabolism (Meyer 1988, Findley 1995, Jones et al. 1995, Bartley and Croome 1999, Adair et al. 2004). In contrast, during low river stage when hyporheic flow may be directed away from the floodplain and toward the river, riparian zones can be a source of nutrients to the river. If low river stage occurs during the winter, nitrogen released from plant senescence and root turnover (Groffman et al. 2001, Ruess et al. 1998) may be a source of nitrate to the river.

Hydrology and biogeochemistry of the Tanana River at Bonanza Creek LTER.

The Tanana River in interior Alaska is nearly 1000 km in length and is a major tributary to the Yukon River (Anderson 1970). The Tanana River flows northwest from glacial headwaters in the Alaska Range (85% of total annual discharge of the Tanana River), draining a basin of about 113,920 km^2 (Anderson 1970). The Tanana Valley consists of glaciofluvial sediments and alluvial fans, deposited from Tanana River glacial waters and groundwater fed streams that drain from the Yukon-Tanana Uplands that bound the river to the north (Anderson 1970). Sedimentary deposits on the Tanana River floodplain can be over a 100 m thick (Péwé et al. 1976, Péwé and Reger 1983); as a consequence, geochemistry of floodplain soil is governed by weathering of exogenous sediments rather than the local parent material.

Dahm et al. (1998) addressed the importance of unconstrained, sinuous river channels for hydrologic exchange as a pathway for hyporheic nutrient retention. The diverse fluvial geomorphology of the Tanana River likely increases infiltration of river water into the hyporheic zone and provides greater contact of nutrients with microbes in the sediment. In addition, low hydraulic conductivity of Tanana River sediment increases the residence time of water in the hyporheic zone, thereby initiating regions of anoxia and resultant anaerobic microbial processes such as denitrification and methanogenesis. Collectively, these hydrologic features of the Tanana River may influence the capacity of adjacent floodplain sediment to function as a sink for nutrients.

Young terraces (< 10 years) on the Tanana River floodplain are characterized by nutrient poor alluvial sediments that flood periodically during high river stage (Fig. 4). Despite this, productive pioneer communities of willow, such as *Salix interior*, *Salix alaxensis*, *Salix brachycarpa Nutt.*, *Salix nova-anglaea* and *Salix lasiandra*, dominate this stage of succession (Viereck et al. 1993). The lack of a developed soil organic horizon results in low mineralization rate (Van Cleve et al. 1993) that cannot account for the nitrogen requirements of these riparian willow communities (Lisuzzo et al. in review). Advective flow of water, through the hyporheic zone to the roots of plants, may be particularly important for the development of riparian vegetation and could explain the discrepancies in the nitrogen budget of these plants. High river stage in the summer can result in saturation of early successional soils to less than a few centimeters below the soil surface (Viereck et al. 1993). Annual precipitation in this region is low (ca. 270 mm), and is exceeded by potential evapotranspiration (ca. 470 mm) (Viereck et al. 1993), thus vertical flux of hyporheic water to surface soils may also be an important vector of nitrogen transport to the roots of plants. Capillary rise on early successional soils is evident from thick salt crusts that develop over the summer. As hyporheic water is transported vertically from the water table and evaporates from the soil surface, calcium and magnesium (the dominant ions in solution) become unstable and precipitate. Spring snow melt and subsequent percolation of water through the soil profile may also represent a significant pulse of nitrate to floodplain soils (Kielland unpublished).

The hydrology of glacially-fed rivers is intimately linked with regional climate (Fig. 5). As a consequence, climatic warming, which is predicted to occur most rapidly at high latitudes, may directly impact the hydrologic regime of glacially-fed rivers like the Tanana. Presently, Alaskan glaciers are thinning at an average rate of $-0.52\ \mathrm{m\ y^{-1}}$ (Arendt et al. 2002), which raises questions about the effects of rising river levels on hyporheic biogeochemistry and floodplain ecology. Flow conditions control both physical and chemical factors that may work collectively to alter the biogeochemistry of the floodplain (Baker and Vervier 2004). Increased flood frequency and changes in the stability of river stage could alter the availability of hyporheic water and nutrients for early successional vegetation. Furthermore, increased saturation of floodplain sediment may be particularly important for the transformation and loss of nitrate as dinitrogen gas, as well as release of methane to the atmosphere via methanogenesis.

In this study, I compared hyporheic biogeochemistry at two early successional stage islands of the Tanana River. Hyporheic well transects were installed to determine the spatial and temporal controls of river hydrology on hyporheic anaerobiosis and nutrient supply to floodplain vegetation. Using an *in situ* push-pull $\delta^{15}NO_3^-$ technique, I measured denitrification rate during peak river stage in the summer. Using historical river discharge data from the USGS and the relationship between river stage and ground water elevation, I predicted the seasonal availability of hyporheic nitrate to early successional vegetation of the Tanana River floodplain. Lateral flux of nitrogen through the rooting zone as a mechanism for nitrate loss was modeled from measurements of subsurface flow rate, hyporheic nitrogen concentration, and hyporheic water height. I evaluated the fate of nitrogen in the hyporheic zone by addressing the relative importance of denitrification versus plant assimilation.

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Process	Reaction	Free Energy (kJ)
a) Decreasing pE		
1. Aerobic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-501
2. Denitrification	$CH_2O + ({}^4/_5)\,NO_3^- + ({}^4/_5)\,H^+ \rightarrow CO_2 + ({}^2/_5)N_2 + ({}^7/_5)H_2O$	-476
3. Sulfate reduction	$CH_2O + (\tfrac{1}{2})SO_4^{2-} + (\tfrac{1}{2})H^+ \rightarrow (\tfrac{1}{2})HS^- + H_2O + CO_2$	-102
4. Methanogenesis	a) $CH_2O \rightarrow (\tfrac{1}{2})CH_4 + (\tfrac{1}{2})CO_2$	-93
	b) $(\tfrac{1}{2})CO_2 + 2H_2 \rightarrow (\tfrac{1}{2})CH_4 + H_2O$	-66
b) Increasing pE		
5. Methane oxidation	$O_2 + (\tfrac{1}{2})CH_4 \rightarrow (\tfrac{1}{2})CO_2 + H_2O$	-408
6. Sulfide oxidation	$O_2 + (\tfrac{1}{2})HS^- \rightarrow (\tfrac{1}{2})SO_4^{2-} + (\tfrac{1}{2})H^+$	-399
7. Nitrification	$O_2 + (\tfrac{1}{2})NH_4^+ \rightarrow (\tfrac{1}{2})NO_3^- + H^+ + (\tfrac{1}{2})H_2O$	-181

TABLE. 1. Sequence of microbial redox reactions (from Hedin et al. 1998), arranged according to decreasing yield of free energy for conditions of decreasing versus increasing redox state pE of the environment at pH 7 (pE = -log{electron activity}). More negative values indicate a reducing environment. Energy yields are calculated per mole of organic matter for (a) reduction reactions and (b) per mole O_2 for oxidation reactions.

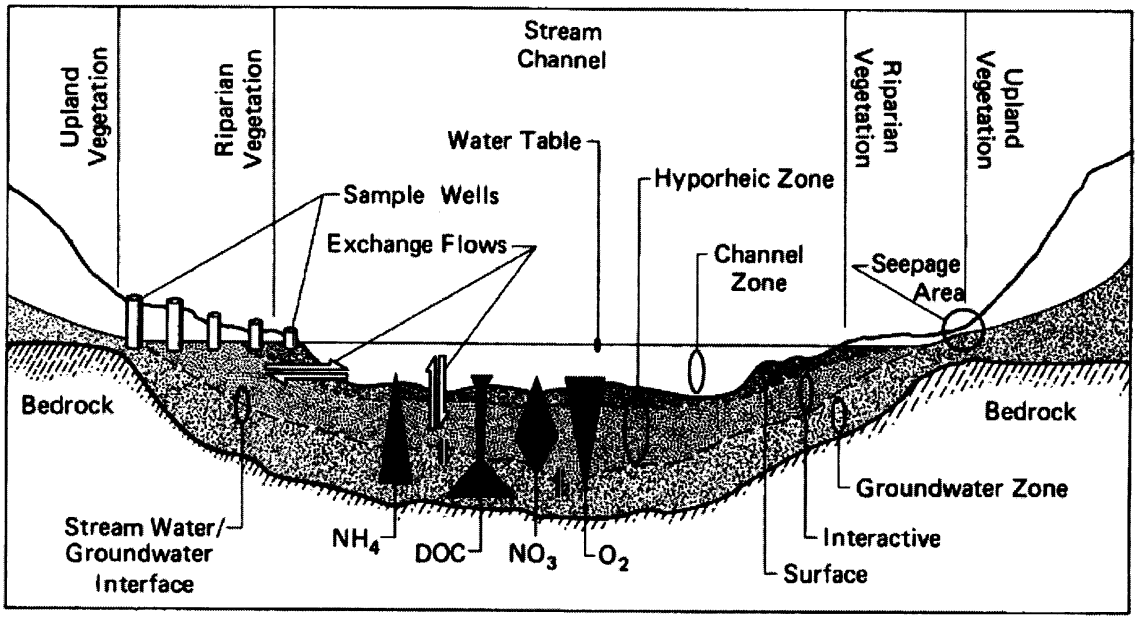

FIGURE. 1. Conceptual model of the groundwater-surface water interface from Triska et al. (1989). Waters are divided into three zones: a channel zone containing surface water, a hyporheic zone, and a groundwater zone. The hyporheic zone is characterized by chemical gradients in NH_4^+, O_2, DOC, NO_3^-.

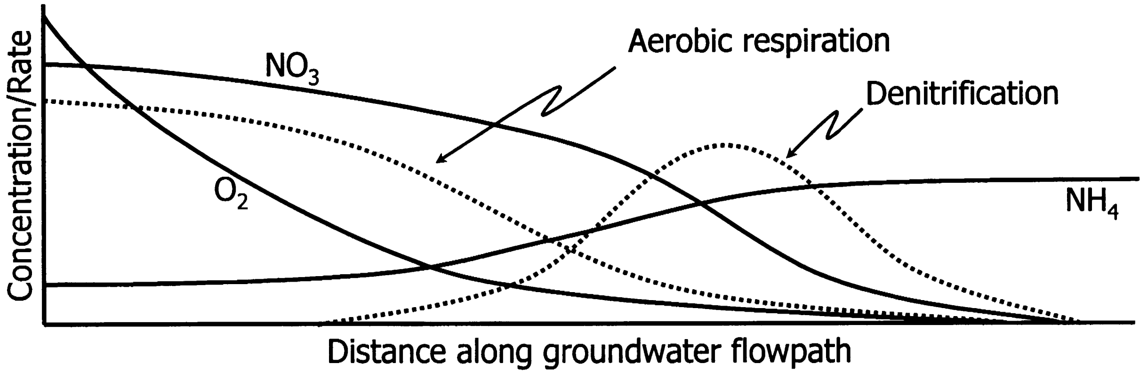

FIGURE. 2. Conceptual model of metabolic processes along subsurface flowpaths from Jones (1994).

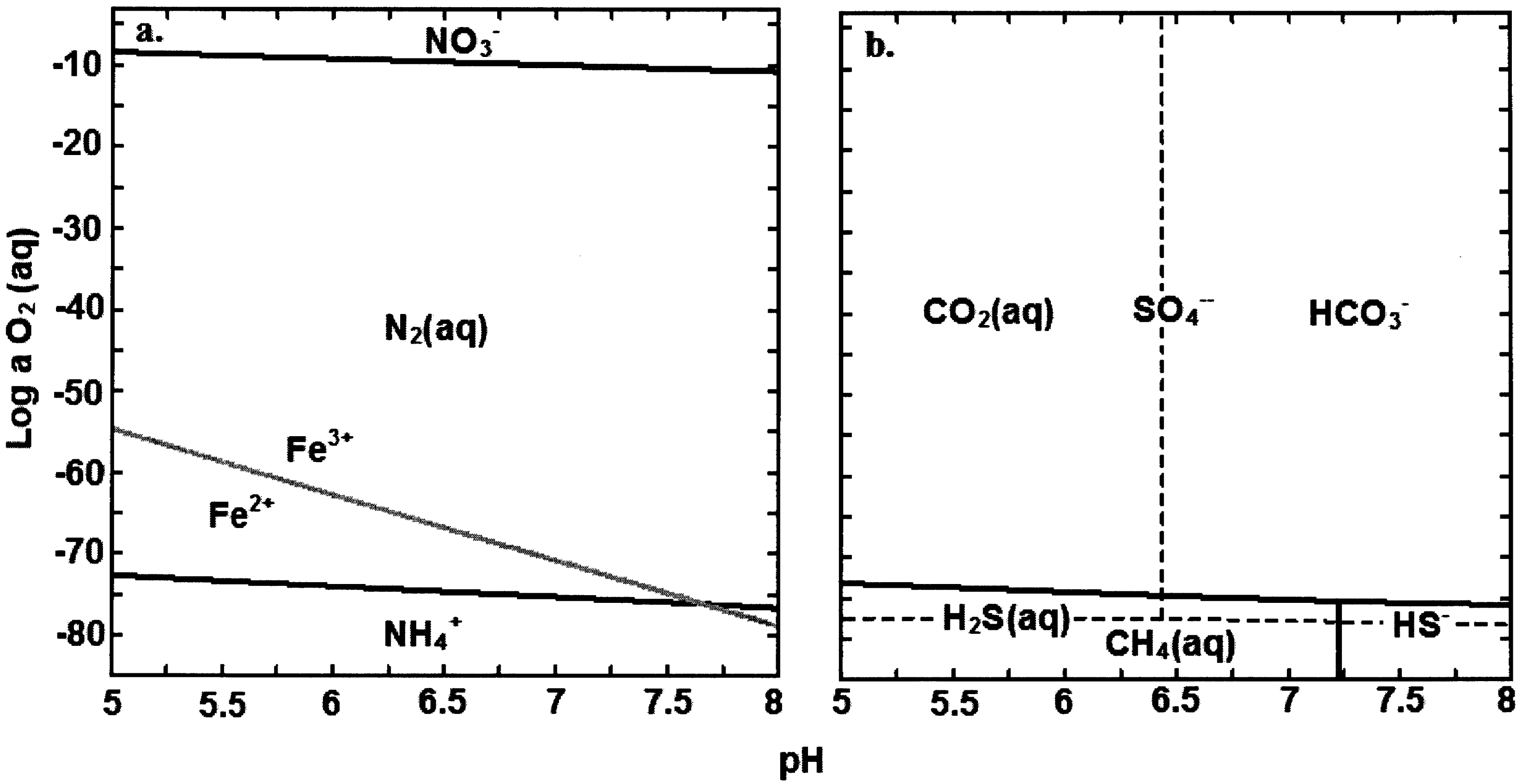

FIGURE. 3. Predicted thermodynamic equilibrium proportions of electron donors and acceptors as a function of the pH and oxygen activity (log a O_2) at 15°C, generated using Geochemist's Workbench 5.0. In deionized water, the activity of oxygen is equal to the concentration of oxygen (mol L^{-1}). Nitrogen is the black line and iron is the grey line (panel a). Sulfur is the black line and carbon is the dashed line (panel b).

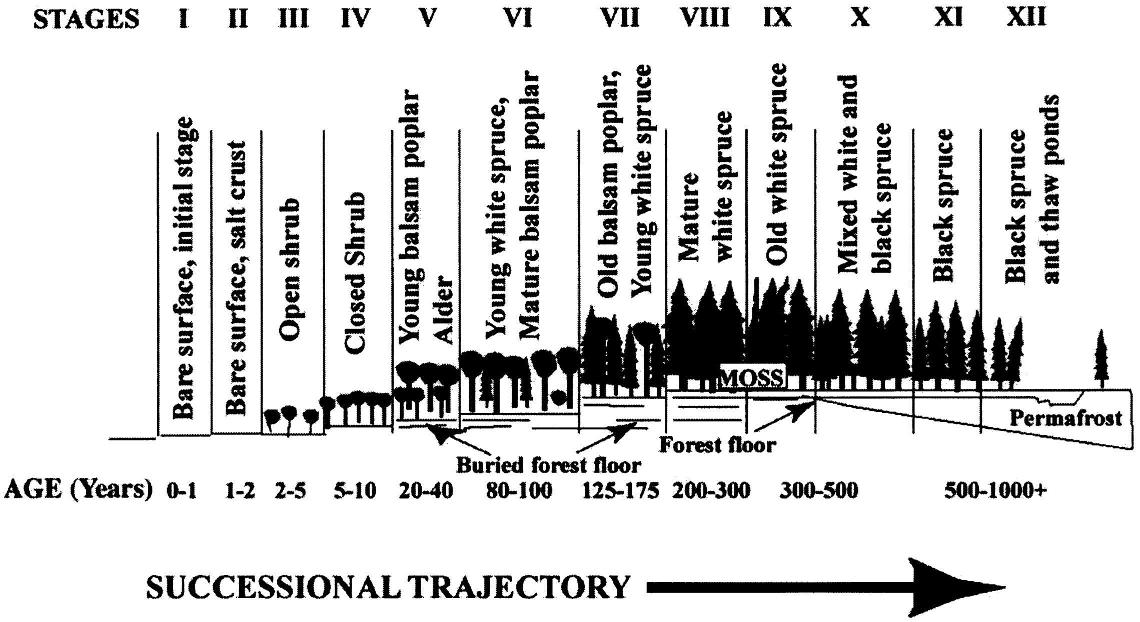

FIGURE. 4. Stages of primary succession on the Tanana River floodplain in interior Alaska (adapted from Viereck et al. 1993).

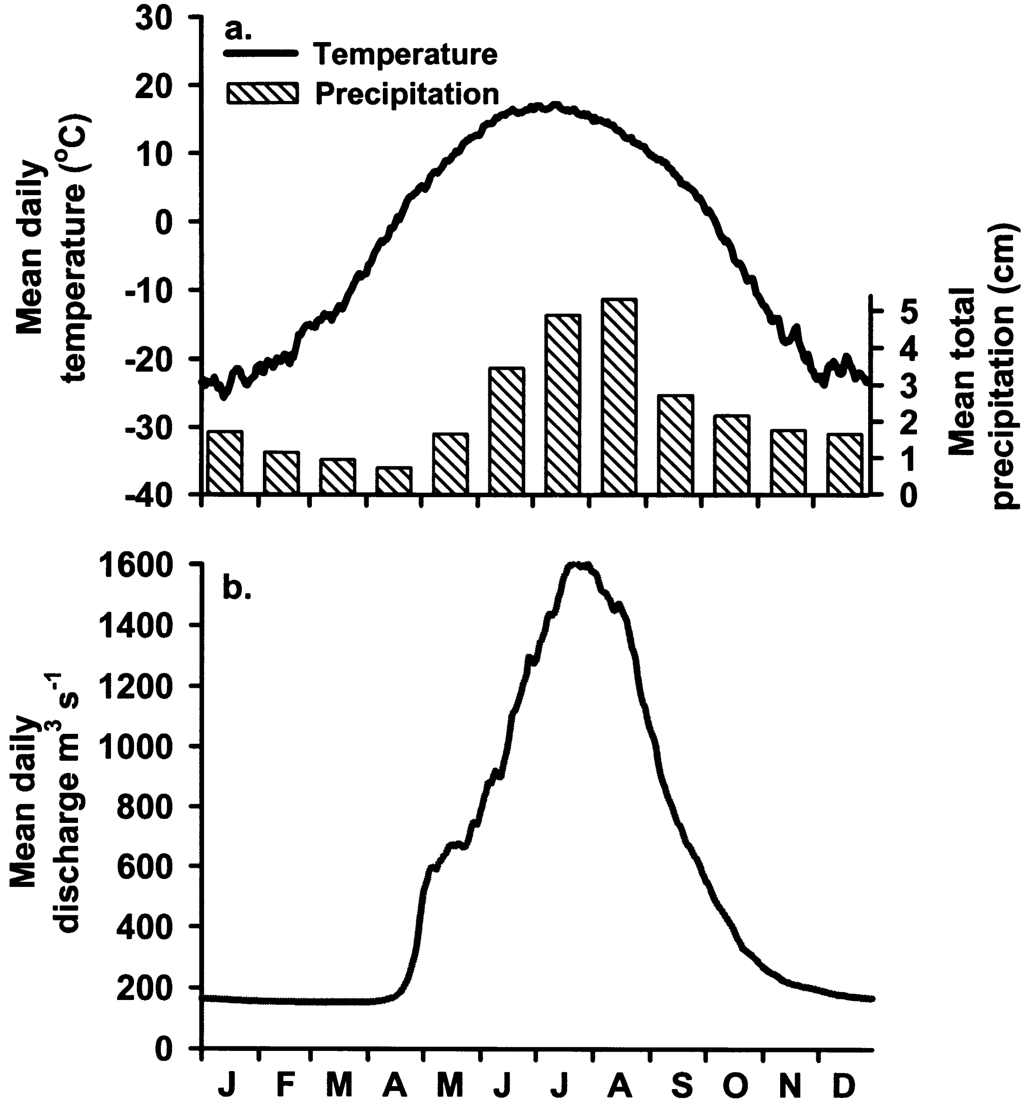

FIGURE. 5. Temporal variation in Fairbanks, Alaska mean temperature and precipitation from 1930 – 2005 (panel a) and Tanana River discharge for the long term mean 1973 – 2005 (panel b). Climate data are from the University of Alaska Fairbanks Climate Research Center and river discharge data are from the USGS gauging station at Fairbanks.

CHAPTER 2: SURFACE-SUBSURFACE HYDROLOGIC EXCHANGE AND NUTRIENT DYNAMICS IN THE HYPORHEIC ZONE OF THE TANANA RIVER IN INTERIOR ALASKA[1]

ABSTRACT

We examined the hydrologic controls on nitrogen biogeochemistry in the hyporheic zone of the Tanana River, a glacially-fed river, in interior Alaska. We measured hyporheic solute concentrations, gas partial pressures, water table height, and flow rates along subsurface flowpaths on two islands for three summers. Denitrification was quantified using an *in situ* $\delta^{15}NO_3^-$ push-pull technique. Hyporheic water level responded rapidly to change in river stage, with the sites flooding periodically in mid-July to early-August. Nitrate concentration was consistently greater in river (ca. 100 μgNO_3^--N L^{-1}) than hyporheic water (ca. 38 μgNO_3^--N L^{-1}), with approximately 60 – 80 % of river nitrate being removed during the first 50 m of hyporheic flowpath. Denitrification during high river stage ranged from 1.9 to 29.4 mgN kg $sediment^{-1}$ day^{-1}. Hotspots of methane partial pressure, averaging 50,000 ppmv, occurred in densely vegetated areas in conjunction with mean oxygen concentration below 0.5 mgO_2 L^{-1}. Hyporheic flow was an important mechanism of nitrogen supply to microbes and plant roots, transporting on average 0.41 gNO_3^--N m^{-2} day^{-1}, 0.22 gNH_4^+-N m^{-2} day^{-1}, and 3.6 gDON m^{-2} day^{-1} through surface sediment (top 2 m). Our results suggest that denitrification can be a major sink for river nitrate in boreal forest floodplain soils,

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[1] Clilverd, H. M., J. B. Jones Jr., and K. Kielland. Surface-subsurface hydrologic exchange and nutrient dynamics in the hyporheic zone of the Tanana River in interior Alaska. Prepared for submission to Biogeochemistry.

particularly at the river-sediment interface. The stability of the river hydrograph and the resulting duration of soil saturation are key factors regulating the redox environment and anaerobic metabolism in the hyporheic zone.

INTRODUCTION

The aquatic-terrestrial interface is an active site of biogeochemical transformations, regulating the flux of nutrients between ecosystems (Triska et al. 1989, Jones et al. 1995a, Hedin et al. 1998, Dahm et al. 1998, Baker and Vervier 2004). A strong redox gradient largely driven by hydrological transmissivity and the residence time of hyporheic water can occur at the interface within a short distance (e.g., < 1 m) of surface water entering the hyporheic zone (Hedin et al. 1998). The supply of electron donors and acceptors to hyporheic sediments drives microbially-mediated, redox-sensitive reactions such as aerobic respiration, nitrification, denitrification, sulfate reduction, methanogenesis, and methane oxidation (Grimm and Fisher 1984, Holmes et al. 1996; Duff and Triska 2000, Hill 2000, Morrice et al. 2000, Ostrom et al. 2002).

Nitrate retention, in particular, is of interest in near-river environments as hyporheic sediments can mediate the supply of nitrogen from aquatic to terrestrial environments (Lowrance et al. 1984, Jones and Holmes 1996, Hedin et al. 1998, Hill 2000, Schade et al. 2002, Sabater et al. 2003, Vidon and Hill 2004). Nitrate assimilation by plants and removal via denitrification can be influenced by periods of flooding that saturate the rooting zone and alter the local redox environment. In glacially fed rivers, river hydrology, and its subsequent effect on hyporheic biogeochemistry, is largely controlled by regional climate and rate of glacial melt. Increased thinning of glaciers in interior Alaska (Arendt et al. 2002) due to climatic warming is predicted to lead to increased frequency and magnitude of flooding (Hinzman et al. 2000). Rising river level can lead to enhanced river water intrusion into the hyporheic zone, prolonging anoxia, and increased supply of dissolved organic carbon and nitrate to subsurface biota, thus increasing floodplain metabolism (Meyer 1988, Findley 1995).

In our research, we examined the effects of river stage on hyporheic zone biogeochemistry in a glacially-fed river in interior Alaska. We addressed the following research questions at two early successional stage floodplain islands: 1) how does the biogeochemistry of hyporheic water change along subsurface flowpaths, and 2) how does temporal variation in river discharge regulate floodplain anaerobiosis and the supply of nutrients to floodplain vegetation? We predicted that microbially mediated reduction of hyporheic nitrate would be greatest at the river-sediment interface. Second, we predicted that prolonged saturation of the sediment profile during summer peaks in glacial melt and river discharge would lead to increased anoxia of floodplain sediment, and greater anaerobiosis.

METHODS

Study site

The study was conducted on two islands of the Tanana River located approximately 20 km southwest of Fairbanks, Alaska (64° 51'N, 147° 43'W; elevation ca. 120 m) within the Bonanza Creek Long Term Ecological Research site. The climate is continental with temperature extremes that range from -50 °C to +30 °C. Average daily temperature ranges from -24.9 °C in January to +16.4 °C in July, with an average annual temperature of -3.3 °C (Viereck et al. 1993a). Annual precipitation in the region is low (ca. 270 mm), and is exceeded by potential evapotranspiration (ca. 470 mm). As a consequence, salt precipitates on exposed floodplain soil surfaces in the summer (Viereck et al. 1993a). The Tanana River is a major tributary to the Yukon River. The Tanana River is nearly 1000 km in length, flowing northwest from glacial headwaters in the Alaska Range, and draining a basin of about 113,920 km^2 (Anderson 1970). Floodplain soil is a mixture of alluvial deposits that vary from sand to silt-loam across primary successional stages (Viereck et al. 1993b). Newly deposited silt is first colonized by communities of willow (*Salix spp.)* and horsetail (*Equisetum spp.*). Alder (*Alnus tenuifolia*)/willow stands develop with increasing distance from the river, followed by balsam poplar (*Populus balsamifera*), white spruce (*Picea glauca*) and finally black spruce (*P. mariana*). A more detailed description of the climate and vegetation on the Tanana River floodplain is given by Viereck et al. (1993a, 1993b).

The two study islands were approximately 1 km wide and 1 to 2 km in length. We focused our research on recently deposited alluvium (< 10 years old), where vegetation is dominated by willow. An organic soil horizon was absent and, as a consequence, soil organic carbon and nitrogen standing stocks were very low (Viereck et al. 1993b, Kielland et al. 2006). Permafrost is generally absent under the riverbed and the adjacent alluvium, but develops in later successional stages as vegetative cover increases (Yarie et al. 1998). The soil water chemistry is dominated by calcium and magnesium, and is moderately basic (pH 7 – 8). Atmospheric N deposition is low with a mean wet N deposition < 0.09 gN m^{-2} yr^{-1} (National Atmospheric Deposition Program, 2003 - 2005).

Study design

We examined spatial variation in subsurface biogeochemistry by 1) installing well transects to determine water table height and flow velocity, 2) measuring hyporheic solute and gas concentrations, 3) measuring *in situ* denitrification, and 4) calculating nitrogen flux along hyporheic flowpaths. We installed hyporheic well transects (one transect per island) approximately 1 km in length across the two islands. Seven to nine wells per island were aligned parallel to the hyporheic flow direction, extending all the way across the islands at intervals of 70 m at Island I and 100 m at Island II. Additional wells were installed lateral to each well transect to determine the slope and direction of hyporheic water flow from hydraulic head measurements. Wells were 3 m long (3.8 cm diameter) and the bottom of the wells was approximately 1 m below the average annual minimum water table height. The wells were made from PVC pipe wrapped in geotextile cloth to prevent blockage with fine silts, and the tops were covered with PVC caps between sampling dates.

Sampling and analytical techniques

We sampled wells every two weeks over the growing season (June – September) for three years (2003 – 2005). Before sampling, wells were purged to introduce fresh hyporheic water. At the time of sampling the water height in each well was measured. Water and gas samples were collected using a peristaltic pump and Tygon tubing (6.4

mm ID), and stored in 100 mL polyethylene bottles and 30 mL syringes, respectively. Sample bottles and syringes were acid-washed and rinsed with deionized water prior to use. Samples were stored in a cooler until return to the laboratory, refrigerated, and then filtered within 24 hours. Water samples that could not be analyzed within a week of collection were frozen.

We analyzed cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) and anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, Br^-) on a Dionex DX-320 ion chromatograph. Total dissolved nitrogen (TDN), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were determined using a Shimadzu TOC-5000 analyzer plumbed to an Antek 7050 nitric oxide chemoluminescent detector. We calculated dissolved organic nitrogen (DON) as the difference between TDN and dissolved inorganic nitrogen (DIN). Gases (CH_4, CO_2, N_2O) were extracted from syringe samples by headspace equilibration with helium and measured using a Varian CP-3800 gas chromatograph the day after collection. Electrical conductance was measured using an Accument portable ASPSO conductivity meter, pH was measured using a Beckman-390 pH meter, and dissolved oxygen was quantified *in situ* using a YSI-55 meter. We calculated bicarbonate concentration using the USGS aqueous geochemical model PHREEQC using measured ion concentrations, DIC, and pH.

Subsurface flow rate was measured using dilution gauging of a conservative tracer (15 gNaCl L^{-1}) injected into hyporheic wells (n = 10 wells total). After adding salt, wells were mixed using a miniature gear pump to continuously circulate water. We measured the decrease in electrical conductance of the well water every five minutes for a minimum of one hour. We calculated subsurface flow rate (υ ; m day^{-1}) from the decline in electrical conductance over the sample time as

$$\upsilon = \frac{V_{\mathrm{well}}\, r}{A_{\mathrm{well}}} \tag{1}$$

where V_{well} is the volume of the well (m^3), r is the decay constant (day^{-1}), and A_{well} is the cross-sectional area of the well exposed to flow (water depth × well diameter; m^2). The decay constant r was solved by fitting a regression line to the following equation

$$r = \ln \frac{\left(\frac{C_i}{C_0}\right)}{t} \tag{2}$$

where C_i is the electrical conductance at time i, C_0 is the intial electrical conductance, and t is time (day). We calculated hydraulic conductivity assuming Darcian flow as

$$K = \frac{(\upsilon\, \eta)}{\left(\frac{\Delta h}{\Delta l}\right)} \tag{3}$$

where K is hydraulic conductivity (m min^{-1}), η is effective porosity. We calculated η from the difference in the mass of saturated and dry sediment collected from 0 – 20 cm depths, $\Delta h/\Delta l$ is the water table slope, and υ is flow rate in (m day^{-1}; Freeze and Cherry 1979).

In situ denitrification

Hyporheic denitrification rate was measured at both island sites using an *in situ* push-pull δ^{15}N-NO_3^- technique (Addy et al. 2002, Baker and Vervier 2004). This method uses a conservative tracer (NaBr) and enriched $\delta^{15}NO_3^-$ dosing solution to measure denitrification rate in wells without disturbing sediments. We measured denitrification rates every two weeks from June to September in 2005. First, we inserted suspended bladders, spaced 0.2 m apart, into wells to isolate a section that was 1.8 m below the sediment surface (volume of isolated section = 0.23 L; Fig. 1). Then, we used a peristaltic pump to extract (pull) 20 L of hyporheic water into a collapsible cubitainer. This volume of sample pulled water from a sediment volume of approximately 38 L. The pulled water was amended with a $\delta^{15}NO_3^-$ and NaBr solution. The nitrate concentration in the cubitainer was elevated approximately 20% above background (background = 33 $\mu g\ L^{-1}\ \delta^{14}NO_3^-$-N; amendment = 6.6 $\mu g\ L^{-1}\ \delta^{15}NO_3^-$-N) and the bromide concentration was elevated from a mean of 0.05 mgBr L^{-1} to a mean of 0.75mgBr L^{-1}. Following the amendment, the solution was injected (pushed) back into the same section of the well. Prior to amendments, we collected background water and gas samples.

During the incubation we collected 30 mL gas and 25 mL water samples every 30 minutes for a minimum of three hours. Prior to each sampling we purged wells for four minutes (pumping rate = 1 L min^{-1}) to remove water from the tubing and the well, and to draw water from the interstitial space of sediments. After return to the lab, gas samples were extracted from the water by headspace equilibration with helium and transferred to evacuated vials. Water samples were filtered and analyzed for nitrate and bromide using the methods previously described. The concentrations and isotopic composition of N_2 and N_2O gases were determined on an isotope ratio mass spectrometer at the University of California Davis Stable Isotope Facility. The ^{15}N:^{14}N ratio was expressed in units of atom % ^{15}N.

Push-pull calculations

To calculate denitrification rate from the push-pull method it is necessary to account for both the dilution of substrate ($^{15}NO_3^-$) and dilution of the end products ($^{15}N_2O$ and $^{15}N_2$). Thus, denitrification rate is calculated from the increase in groundwater dilution corrected $^{15}N_2O$ and $^{15}N_2$ over time (Fig. 2). We used Bunsen solubility coefficients (N_2O = 0.607 L gas L^{-1} H_2O, N_2 = 0.015 L gas L^{-1} H_2O) from Wanninkhof (1992) and Weiss and Price (1980) to calculate the concentrations of N_2O and N_2 in solution. The concentrations of $^{15}N_2O$ and $^{15}N_2$ were calculated by multiplying the concentrations of N_2O and N_2 by the respective atom % ^{15}N. During each sampling interval, the production of $^{15}N_2O$ and $^{15}N_2$ and concentration of $^{15}NO_3^-$ were corrected for dilution using the geometric mean of the decline in bromide concentration. Denitrification rate (R; µg L^{-1} min^{-1}) is the slope of the increase in groundwater dilution corrected $^{15}N_2O$ and $^{15}N_2$ over time, computed as

$$R = \frac{\left(\dfrac{{}^{15}N_{gas_t} - \beta\,{}^{15}N_{gas_0}}{{}^{15}NO_3^-(\%)\ \beta}\right)}{t} \tag{4}$$

where ${}^{15}N_{gas_t}$ is the concentration of ^{15}N ($N_2O + N_2$; µg L^{-1}) at time t, ${}^{15}N_{gas_0}$ is the concentration of gaseous ^{15}N (µg L^{-1}) at the beginning of each assay, $^{15}NO_3^-$ (%) is the percent $^{15}NO_3^-$ added to the well at the start, β is the geometric mean of dilution (D), and t is the incubation time (min).

The dilution of $^{15}NO_3^-$, $^{15}N_2O$, and $^{15}N_2$ in the well from subsurface water flow was calculated from the decline in the conservative tracer as

$$D = \frac{Br_t}{Br_0} \tag{5}$$

where Br_t is the bromide concentration ($\mu g\ L^{-1}$) at time t, and Br_0 is the initial bromide concentration ($\mu g\ L^{-1}$). Denitrification rate was expressed per mass of sediment and on an areal basis using bulk density and sample depth values of 1.15 g cm^{-3} and 0.2 m (spacing of bladders), respectively. For the areal expression of denitrification, using the spacing of bladders provided a conservative estimate of the overall rate.

The large concentration of $^{14}N_2$ in the atmosphere is a potential source of interference in $^{15}N_2$ studies. To ensure that our sample vials were gas-tight and that measured $^{15}N_2$ concentration was not diluted due to $^{14}N_2$ contamination from the atmosphere, we calculated the expected mass of N_2 if there was no air contamination (assuming that the water samples were at equilibrium N_2 levels with the atmosphere) and then used the expected and measured N_2 concentrations to calculate the percent of N_2 in the samples gained from the atmosphere. We did not use samples that contained greater than 1 % N_2 contamination.

Data analysis

Simple linear regression was used to analyze relationships between mean river stage and mean water table height. Change in hyporheic chemistry along well transects was tested using one-way Analysis of Variance (ANOVA). If a significant difference was found ($p < 0.05$), we used Tukey's test to determine which wells were significantly different ($p < 0.05$). One-way ANOVA was used to test for significant differences in denitrification rate between the islands. Two-way ANOVA was used to determine temporal variations in hyporheic solute or gas concentrations along each well transect.

Analysis of subsurface hydrology and capillary rise

We evaluated the fate of nitrogen in the hyporheic zone by addressing the relative importance of denitrification versus plant uptake. Saturation of the rooting zone as a mechanism for nitrate loss was modeled from measurements of subsurface flow rate and hyporheic water height. To characterize fluctuations in water table height two wells at each island were instrumented with Campbell Scientific CR10X dataloggers and pressure transducers that recorded water table height every 15 minutes in 2003 and 2005. Water table height measured by the dataloggers was calibrated with biweekly measurements of well water height. The direction of subsurface water flow was then mapped using the height of hyporheic water among the wells. The response of water table height relative to river stage was determined from mean daily river stage data from the USGS Tanana River gauging station at Fairbanks, AK. To determine the temporal variation in sediment saturation, we modeled mean hyporheic water height from 1990 – 2005 using the linear relationship between floodplain water table height and river stage.

The height of capillary rise above the water table was calculated as a function of soil pore size, with fine soil particles exerting the most control over capillary rise. Using soil sieves we measured the effective particle size (D_{10}), which is the diameter (mm) of the smallest size fraction that accounts for less than 10% of total soil mass. We then used Hazen's formula (Henry 1995, Das 2002) of capillary rise

$$h_c = \frac{m}{D_{10}} \tag{6}$$

where the mean height of capillary rise is h_c (mm), and m is a constant of 30 mm^2. The rate of capillary rise for sandy soils is approximately 0.5 m day^{-1} (Lu and Likos 2004; assuming capillary rise and vertical hydraulic conductivity values of 0.85 m and 0.1 m day^{-1}, respectively). Accordingly, we use a conservative lag period of two days for the capillary fringe to respond to changes in water table height.

In order to compare the lateral flux of nitrogen in hyporheic flow with areal measurements of soil nitrogen mineralization (Kielland et al. 2006) we calculated area specific hyporheic nitrogen turnover. Nitrogen turnover was calculated assuming a water depth of 2 m (depth of wells). Nitrogen turnover (F; gN m^{-2} day^{-1}) was calculated as

$$F = (T\,N\,z)\eta \tag{7}$$

where T is the hydrologic turnover time (well volume (m^3) / water flux into well (m^3 day^{-1}), N is the mean nitrogen concentration in hyporheic water (gN m^{-3}) , z is water depth (2 m), and η is the mean porosity (0.54).

Long term patterns in climate and river hydrology

To address the importance of local climate on river discharge and the subsequent effects on hyporheic biogeochemistry, we analyzed 30 years of river discharge data and 70 years of climate data. Daily air temperature data for Fairbanks were obtained from the University of Alaska Fairbanks Climate Center. Tanana River discharge was measured daily at the U.S Geological Survey (USGS) gauging station (#15485500) on the Tanana

River at Fairbanks, AK. These data were used to evaluate seasonal and interannual patterns in river and hyporheic nitrate concentration and methane partial pressure.

RESULTS

Climate and river hydrology

Discharge of the Tanana River was closely correlated with daily maximum air temperature (Fig. 3). Maximum river discharge occurred in mid to late July (ca. 1500 m^3 s^{-1}; Fig. 3) during the time of high solar radiation and glacial melt. Over the three study years, flooding (> 1500 m^3 s^{-1}) of the floodplain occurred in July of 2003 and in late June to early July of 2005. However, river discharge was elevated (> 1300 m^3 s^{-1}) from June-August in 2004 and 2005 (Fig. 3).

Spatial patterns in hyporheic chemistry

Dissolved oxygen concentration was low in all wells, but was significantly greater in Island I, averaging 2.3 mgO_2 L^{-1}, compared with 0.9 mgO_2 L^{-1} at Island II ($p < 0.05$; Fig. 4). Oxygen concentration did not significantly change along the well transect across Island I ($p = 0.53$), whereas across Island II, oxygen concentration was higher in the well closest to the river ($p < 0.05$), and tended to decline with distance from the river (Fig. 4).

Similar to oxygen, hyporheic nitrate concentration was greater ($p < 0.05$) at Island I (29.1 ± 1.7 μgNO_3^--N L^{-1}) than Island II (24.0 ± 2.0 μgNO_3^--N L^{-1}). Substantial change in nitrate concentration occurred as river water entered the hyporheic zone. The concentration of nitrate in river water was on average three-fold greater than the concentration in hyporheic water ($p < 0.05$; Fig. 4). Approximately 60 – 80 % of river water nitrate was removed during the first 50 m of the flowpaths; however, following this initial decline at the river-sediment interface, nitrate concentration was fairly stable along the remaining flowpaths ($p > 0.05$; Fig. 4). DON was approximately two-fold greater in river water than hyporheic water, and did not change significantly along the well transects or between islands ($p > 0.05$). In contrast to nitrate, DON, ammonium and DOC concentrations did not vary significantly between the two islands ($p > 0.05$; Table 1). In river and hyporheic water, cation concentrations followed the pattern of Ca>Mg>Na>K. However, base cation, bicarbonate, and hydrogen ion concentrations increased significantly as river water entered the subsurface ($p < 0.05$; Table 2).

Hyporheic water was always supersaturated in carbon dioxide, with carbon dioxide averaging 53-fold greater than atmospheric equilibrium (Fig. 5), and ranging from 5,197 – 45,768 ppmv at Island I and 1,510 – 55,149 ppmv at Island II. The partial pressure of carbon dioxide increased along the well flowpaths at both islands ($p < 0.05$; Fig. 5). In contrast to carbon dioxide, the partial pressure of methane did not increase along the flowpaths ($p > 0.05$), but instead was elevated in hotspots with supersaturation ranging from 100 – 2000 times greater than atmospheric equilibrium (Fig. 5). The partial pressure of methane was on average an order of magnitude greater at Island II (1450 ± 372 ppmv) than Island I (364 ± 134 ppmv).

Hyporheic chemistry at the transitional boundary between willow and alder stands at Island II was markedly different than hyporheic chemistry in the wells located on younger terraces, which were colonized primarily with willow (Table 1). Of particular interest was the high methane partial pressure (73,344 ± 14,856 ppmv) measured at

Island II transitional wells (Table 1). This area of the floodplain was inundated with water for much of the summer, resulting in prolonged soil saturation and consistently low oxygen concentration (0.5 ± 0.1 mgO_2 L^{-1}; Fig. 6). Methane concentration at the transitional boundary between willow and alder stands at Island II averaged 1.3 mgC L^{-1}, a sizable concentration compared with DOC (4.0 mgC L^{-1}; Fig. 6, Table 2). Using the ratio of CH_4 (mg C L^{-1}) to CO_2 (mgC L^{-1}) as an index of anaerobic metabolism (Dahm et al. 1991, Jones and Mulholland 1998), anaerobic metabolism in transition wells was, on average, 60 times higher (CH_4:CO_2 = 0.15) than in the open willow stands (CH_4:CO_2 = 0.0024) on Island II, and on average 145 times higher than open willow stands on Island I (CH_4:CO_2 = 0.0010; $p < 0.05$; Fig. 6).

Subsurface hydrology and nitrogen losses

The direction of hyporheic water flow closely aligned with the orientation of the hyporheic well transects (Fig. 7). At Island I and Island II, respectively, hydraulic conductivity averaged 6.2 and 4.1 m day^{-1} (Table 2), and hydraulic gradient averaged 3.5 % and 4.0 % (Table 2). Hyporheic flow rates were not statistically different through the two islands, averaging 0.3 m day^{-1} ($p = 0.85$; Table 2). Despite low horizontal flow rate, change in water table height was rapid (Fig. 8). We found a strong positive linear relationship between mean river stage and mean water table height ($r^2 = 0.93$, $p < 0.05$), with an average 1 m change in river height resulting in an average water table height increase of 0.82 m with little lag time (< 1 day; Fig. 8). The mean water table height (1990-2005) was above the mean rooting depth for floodplain willow (0.75 m; Lisuzzo et al. in review) for approximately two months (mid-June to August). In addition, modelled capillary rise was an additional 0.72 ± 0.26 m, which increased saturation of the rooting zone by approximately 90 days (Fig. 8).

Loss of nitrate via denitrification was highly variable among wells, ranging from 2 – 30 mgN Kg $sediment^{-1}$ day^{-1} at Island I and 3 – 25 mgN Kg $sediment^{-1}$ day^{-1} at Island II. We found no significant differences in denitrification rates between the islands ($p = 0.57$; Fig. 9). Subsurface flux of nitrogen through the top 2 m of sediment averaged 0.41 ± 0.05 gNO_3^--N m^{-2} day^{-1}, 0.22 ± 0.03 gNH_4^+-N m^{-2} day^{-1} and 3.6 ± 1.5 gDON m^{-2} day^{-1}.

Temporal variation in hyporheic chemistry

The influence of river stage on hyporheic chemistry was examined by analyzing temporal variations in hyporheic nitrate concentration, DOC concentration, and methane partial pressure relative to change in river flow. During peak river stage (July – early August), mean hyporheic nitrate concentration at Island II decreased two-fold compared with early summer (June) concentration ($p < 0.05$; Fig. 10). In addition, methane partial pressure was one to two orders of magnitude greater during peak flow in 2004 and 2005 than during base flow ($p < 0.05$; Fig. 10). The saturation of surface sediment was prolonged throughout the summer in the 2004 and 2005 study years (warm and dry summers), whereas in 2003 (cooler and wetter summer) the floodplain was relatively dry, except for brief flooding in July (Fig. 3; Fig.11). Associated with this increased saturation in 2004 and 2005, mean methane partial pressure was three-fold greater in 2004 and 2005 than in 2003 ($p < 0.05$; Fig. 10).

DISCUSSION

Hyporheic zone hydrology and nitrogen transformation

The height of the water table on the Tanana River floodplain was closely coupled to river stage, which in turn was controlled by rate of glacial melt due to increased ambient air temperature. Horizontal subsurface flow was restricted by the low hydraulic conductivity (ca. 5 – 7 m day^{-1}) of fine alluvial sediments, suggesting that movement of river water and nutrients through the subsurface was more likely dominated by rapid (< 1 day) vertical changes in water table height in response to river stage.

Hydrologic exchange between well oxygenated, nutrient rich surface water and metabolically active alluvial sediment is important for nutrient retention (Jones et al. 1995b, Pinay et al. 1995) and floodplain productivity (Schade et al. 2002). Surface water of the Tanana River is richer in nitrate and DOC relative to the hyporheic zone and thus represents a potential source of nutrients. Spatial differences in subsurface nitrogen chemistry were most pronounced at the river-sediment interface, with rapid removal of nitrate (60 – 80 % reduction) during the first 50 m of hyporheic flowpaths. Strong removal of nitrate at the river-sediment interface was most likely attributable to denitrification rather than plant uptake as this region of the floodplain was sparsely vegetated. This rapid loss is similar to previous findings that have shown that the aquatic-terrestrial interface is an important control point for nitrogen retention (Holmes et al. 1996, Hedin et al. 1998, Devito et al. 2000). Rapid denitrification at the river-sediment interface is likely driven by the supply of electron acceptors and donors from surface water, and the sharp oxygen gradient as surface water enters the hyporheic zone

(Duff and Triska 1990, Vervier et al. 1993, Baker et al. 1999, Baker and Vervier 2004). Apart from the initial decline in nitrate concentration between the river and the first hyporheic wells, hyporheic nitrate concentration was relatively constant along the remaining flowpaths and was a stable pool of nitrogen. This consistency indicates that the rates of processes that govern the concentration of hyporheic nitrate, such as mineralization, denitrification and plant uptake, were balanced overall throughout the top 2 m of sediment.

Denitrification rates measured in our study were similar to those in a nitrogen-limited Sonoran desert stream (Holmes et al. 1996), and studies that also used an *in situ* push-pull method on the Garonne River (Baker and Vervier 2004) and in riparian zones in Rhode Island (Addy et al. 2002). Our denitrification data suggest that in the boreal forest, floodplain sediments have a large capacity for denitrification during peak river stage in the summer. Moreover, denitrification rate (1.98 ± 0.46 gN m^{-2} day^{-1}) in hyporheic water beneath early succession willow stands of the Tanana River is approximately two orders of magnitude greater than plant uptake (0.013 gN m^{-2} day^{-1}; Lizzuso et al. in press), and appears to be the dominant pathway of nitrogen removal.

Hyporheic flow appears to be an important mechanism of nitrogen supply to willow stands on the Tanana River floodplain. Horizontal fluxes of dissolved nitrogen (averaging 0.6 gDIN m^{-2} day^{-1} and 3.6 gDON m^{-2} day^{-1}) through the top 2 m of sediment far exceed nitrogen inputs from soil organic matter turnover (0.0028 gN m^{-2} day^{-1}; Kielland et al. 2006), nitrogen fixation (0.00027 gN m^{-2} day^{-1}; Klingensmith and Van Cleve, 1993) and atmospheric deposition (0.00025 mgN m^{-2} day^{-1}; National Atmospheric

Deposition Program). Vertical fluctuations in water table height dominate the movement of water in the hyporheic zone, and represent a large pool of nitrate (sediments on the Tanana River floodplain can be > 100 m thick; Péwé and Reger 1983) that could supply nitrogen to microbes and vegetation. The capillary fringe is within the rooting zone for early successional floodplain vegetation and may further enhance hydrologic connectivity between hyporheic water and the rooting zone of vegetation. Our results are comparable to capillary rise measurements of 1.0 – 1.5 m for weakly compacted alluvial sandy loams (Chubarova 1972), and reports of capillary rise to 0.1 – 0.5 m below the soil surface in open willow stands on the Tanana River floodplain (Viereck et al. 1993b).

Subsurface methane and carbon dioxide

Although at both islands carbon dioxide was the dominant gas in solution, methane comprised a significant proportion of respiratory gases at Island II. Hotspots of methane production at Island II occurred where mean oxygen concentration had fallen below 0.5 $mgO_2\ L^{-1}$. The partial pressure of methane was greatest in hyporheic water at the transitional boundary between willow and alder stands at Island II, where subsurface flow through dense vegetation converged with sediment that was covered with standing water for prolonged periods. At this boundary, methanogenesis was a sizable component of subsurface metabolism based on CH_4:CO_2 and composed one-third of the dissolved carbon pool in the sediment when summed with DOC. To test whether upwelling of deeper groundwater could account for the high methane partial pressure at Island II transitional wells, we compared base cation concentrations among the wells. The concentration of calcium and magnesium did not differ significantly between the well transects and transitional wells (Fig. 12) indicating that spatial differences in hyporheic biogeochemistry were not driven by source waters other than the river. Alternatively, differences in hyporheic biogeochemistry in the transitional wells may result from hydrologic flow through later successional stands, such as alder, and balsam poplar. In comparison to open willow stands, soils in these stands have a developed organic horizon and higher nitrate concentration (Viereck et al. 1993b, Kielland et al. 2006), which may serve as a source of DOC and nitrate for hyporheic metabolism and warrants further research.

Climate, river hydrology and hyporheic chemistry

Hydrology of glacially fed rivers is largely governed by regional climate. During high river stage in the summer, the net flow of water is from the surface channel to the hyporheic zone which functions as a sink for nitrogen. Hyporheic chemistry was coupled to periods of flooding that saturated the sediment profile and altered the oxidation state of hyporheic water. Denitrification was an important sink for nitrogen in the hyporheic zone and was most pronounced at the river-stream interface. Methane partial pressure was particularly high during years with prolonged soil saturation throughout the summer, suggesting that a high and stable river stage promotes lower redox potential of floodplain sediment and increases the rate of anaerobiosis. Similarly, the supply of hyporheic nutrients to floodplain vegetation will be greatest during summers with highest river discharge. Indeed, as interior Alaska continues to warm (Hinzman et al. 2006), associated changes in the hydrologic regime of the Tanana River have the potential to increase the productivity of early successional floodplain vegetation, and enhance anaerobic metabolism in the hyporheic zone.

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TABLE. 1. Ion concentrations and partial pressure of gases for the Tanana River, hyporheic well transects (Island I and II) and the willow-alder transitional wells (Mean ± SE; n.d. = no data).

	Site				
	River	Island I transect wells	Island II transect wells	Island I transitional well	Island II transitional wells
pH	7.9 ± 0.04	7.7 ± 0.03	7.8 ± 0.03	7.7 ± 0.4	7.77 ± 0.07
Conductivity (μs cm^{-1})	246 ± 7	779 ± 16	651 ± 11	671 ± 18	649 ± 11
Na^+ (mg L^{-1})	4.0 ± 0.1	7.7 ± 0.4	7.48 ± 0.5	5.9 ± 0.4	6.0 ± 0.1
Mg^{2+} (mg L^{-1})	8.6 ± 0.3	29.6 ± 1.1	23.0 ± 0.6	23.8 ± 1.3	23.8 ± 0.7
K^+ (mg L^{-1})	1.7 ± 0.1	4.6 ± 0.4	4.0 ± 0.2	3.2 ± 0.3	4.1 ± 0.2
Ca^{2+} (mg L^{-1})	37.0 ± 1.3	135 ± 6	83.3 ± 3.3	104 ± 10	77.4 ± 4.2
NH_4^+ (μgN L^{-1})	12.4 ± 2.6	14.6 ± 1.6	15.3 ± 1.7	20.2 ± 10.7	32.0 ± 4.3
HCO_3^- (mg L^{-1})	91.1 ± 8.6	328 ± 25	349 ± 15	304 ± 23	369 ± 18
SO_4^- (mg L^{-1})	16.2 ± 1.8	53.6 ± 2.6	22.8 ± 1.7	35.7 ± 2.3	11.4 ± 2.6
NO_3^- (μgN L^{-1})	86.5 ± 6.3	29.1 ± 1.7	24.3 ± 2.0	37.4 ± 7.5	14.2 ± 4.6
DON (μgN L^{-1})	362 ± 42	228 ± 10	240 ± 8	239 ± 33	309 ± 30
DOC (mgC L^{-1})	4.0 ± 0.9	3.8 ± 0.7	2.7 ± 0.08	2.7 ± 0.4	4.0 ± 0.3
SUVA (L mg^{-1} m^{-1})	3.8 ± 0.6	1.8 ± 0.2	1.8 ± 0.1	1.7 ± 0.4	2.2 ± 0.13
DO (mgO_2 L^{-1})	n.d.	2.3 ± 0.2	1.5 ± 0.2	2.0 ± 0.4	0.53 ± 0.05
N_2O (ppmv)	n.d	0.51 ± 0.1	1.2 ± 0.6	0.5 ± 0.1	2.6 ± 2.0
CO_2 (ppmv)	1876 ± 175	19752 ± 536	20585 ± 859	15871 ± 1547	22080 ± 1572
CH_4 (ppmv)	128 ± 19	364 ± 134	1450 ± 371	85 ± 26	73344 ± 14856

TABLE. 2. Hydraulic gradient, hydraulic conductivity, and subsurface flow rate (mean ± SE) for Islands I and II.

Site	Hydraulic gradient ($\Delta h/\Delta l$)	Hydraulic conductivity (m day^{-1})	Subsurface flow rate (m day^{-1})
Island I	0.036 ± 0.007	6.2 ± 1.0	0.33 ± 0.05
Island II	0.040 ± 0.010	4.1 ± 0.7	0.32 ± 0.06

FIGURE. 1. Diagram of the *in situ* push-pull $\delta^{15}NO_3^-$ technique. A conservative tracer (NaBr) and $\delta^{15}NO_3^-$ was injected (pushed) into a sealed 20 cm section of the well. During the extraction (pull) phase, gas samples for $\delta^{15}N_2O$ and $\delta^{15}N_2$ and water samples for NaBr and $\delta^{15}NO_3^-$ analysis were collected.

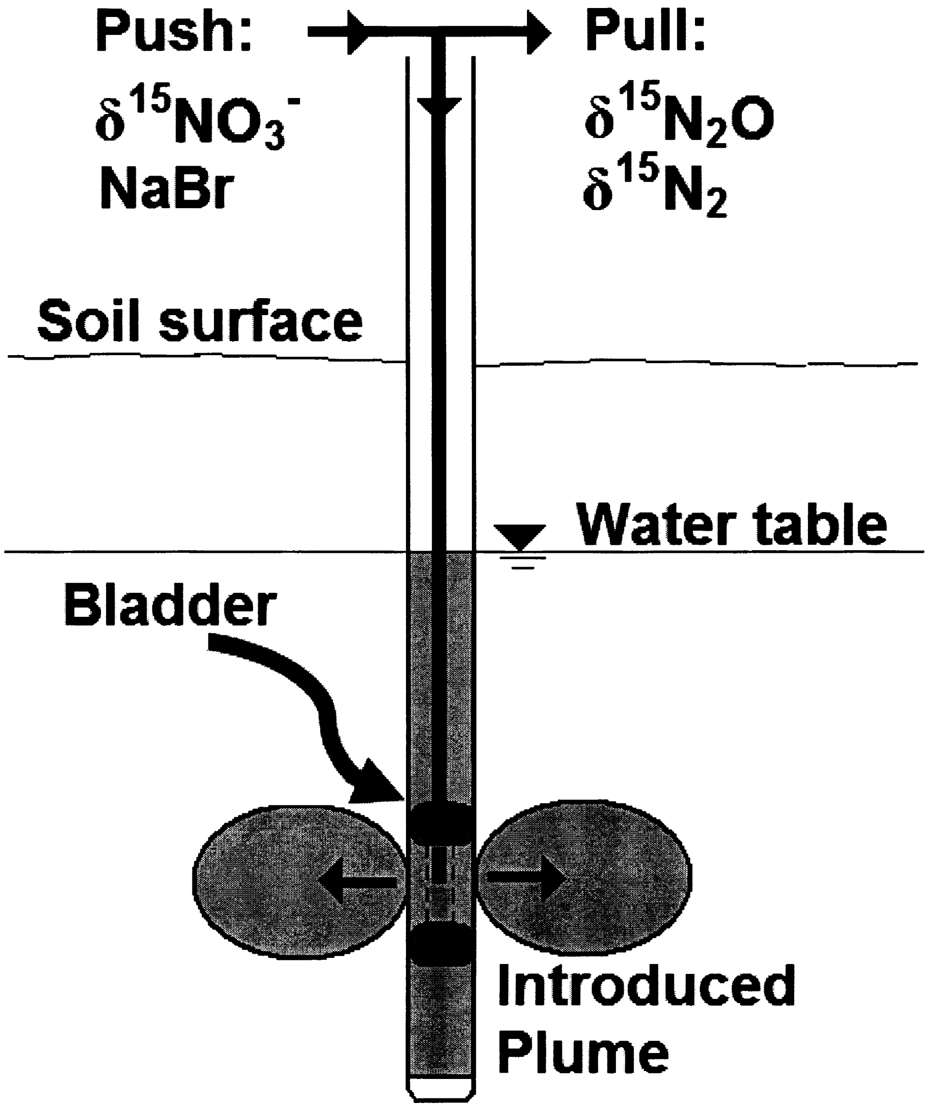


FIGURE. 2. Example data of the production of groundwater dilution corrected $^{15}N_2O$ and $^{15}N_2$ during the incubation period using the *in situ* push-pull technique.

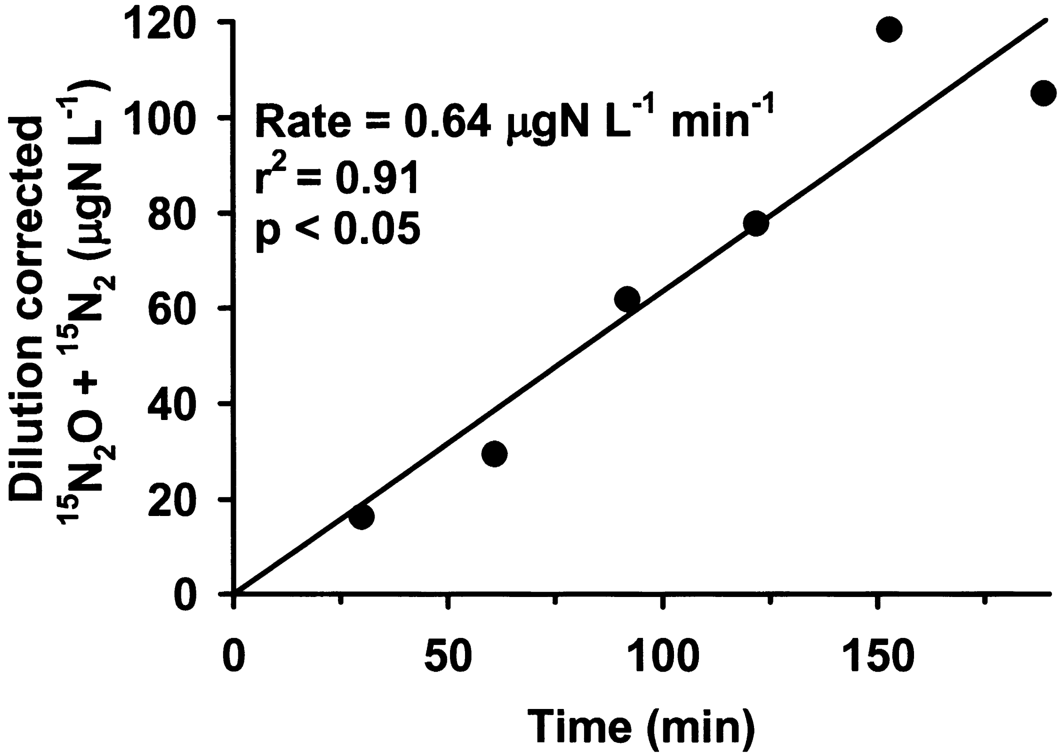


FIGURE. 3. Cubic regression between mean daily air temperature and mean daily river discharge from 1973 – 2005 (panel a). Trends in river discharge: with increasing air temperature from January to mid-July ($y = 234.79 + 24.45 * x + 1.95 * x^2 + 0.046 * x^3$; $r^2 = 0.95$; $p = < 0.05$), and decreasing air temperature from mid-July to December ($y = 456.43 + 36.18 * x + 2.10 * x^2 + 0.045 * x^3$; $r^2 = 0.99$; $p = < 0.05$). Temporal variation in river discharge for the long term mean 1973-2005, and three study years (panel b). Discharge data are from the USGS gauging station (#15485500) located at Fairbanks, Alaska.

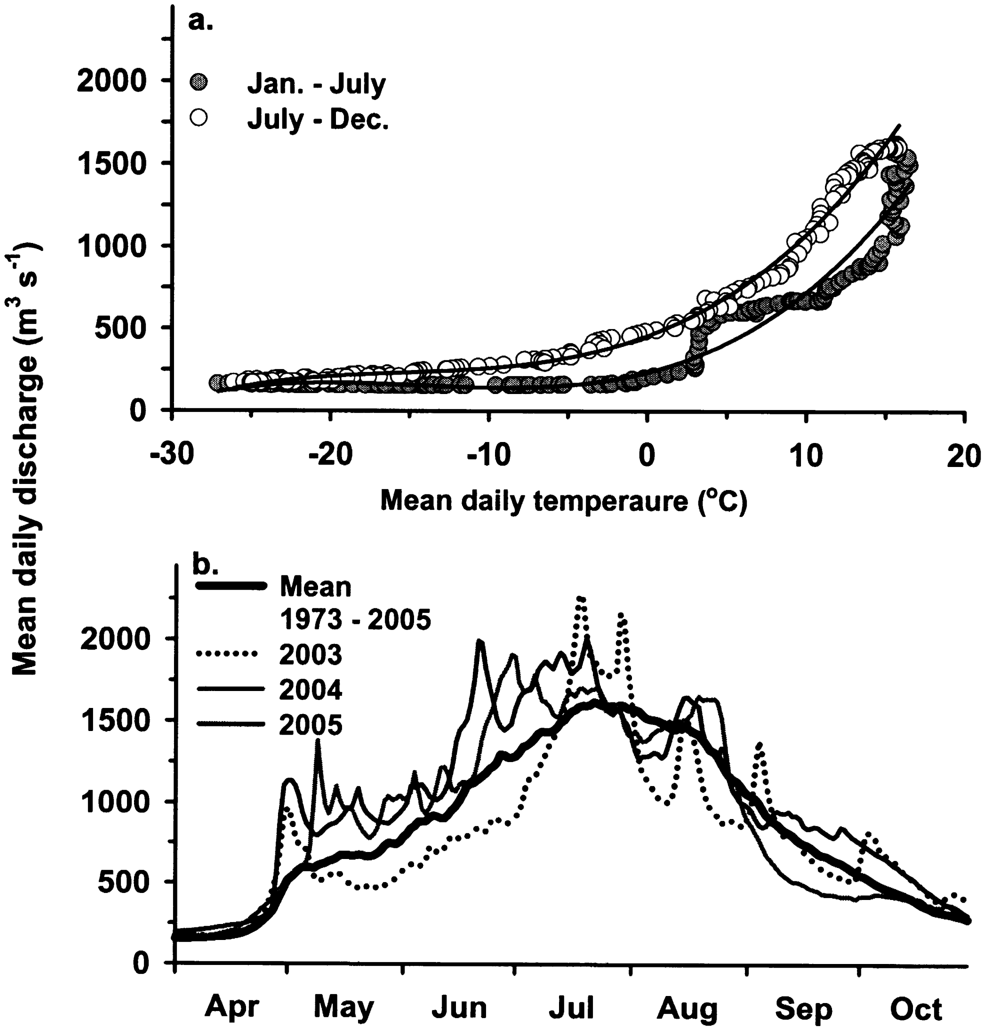


FIGURE. 4. Longitudinal patterns of oxygen (panel a) and nitrate (panels b and c) concentrations at Island I and Island II. The solid center line, broken line, box extent and error bars circles denote the median, mean, 25th and 75th, 10th and 90th percentiles, respectively.

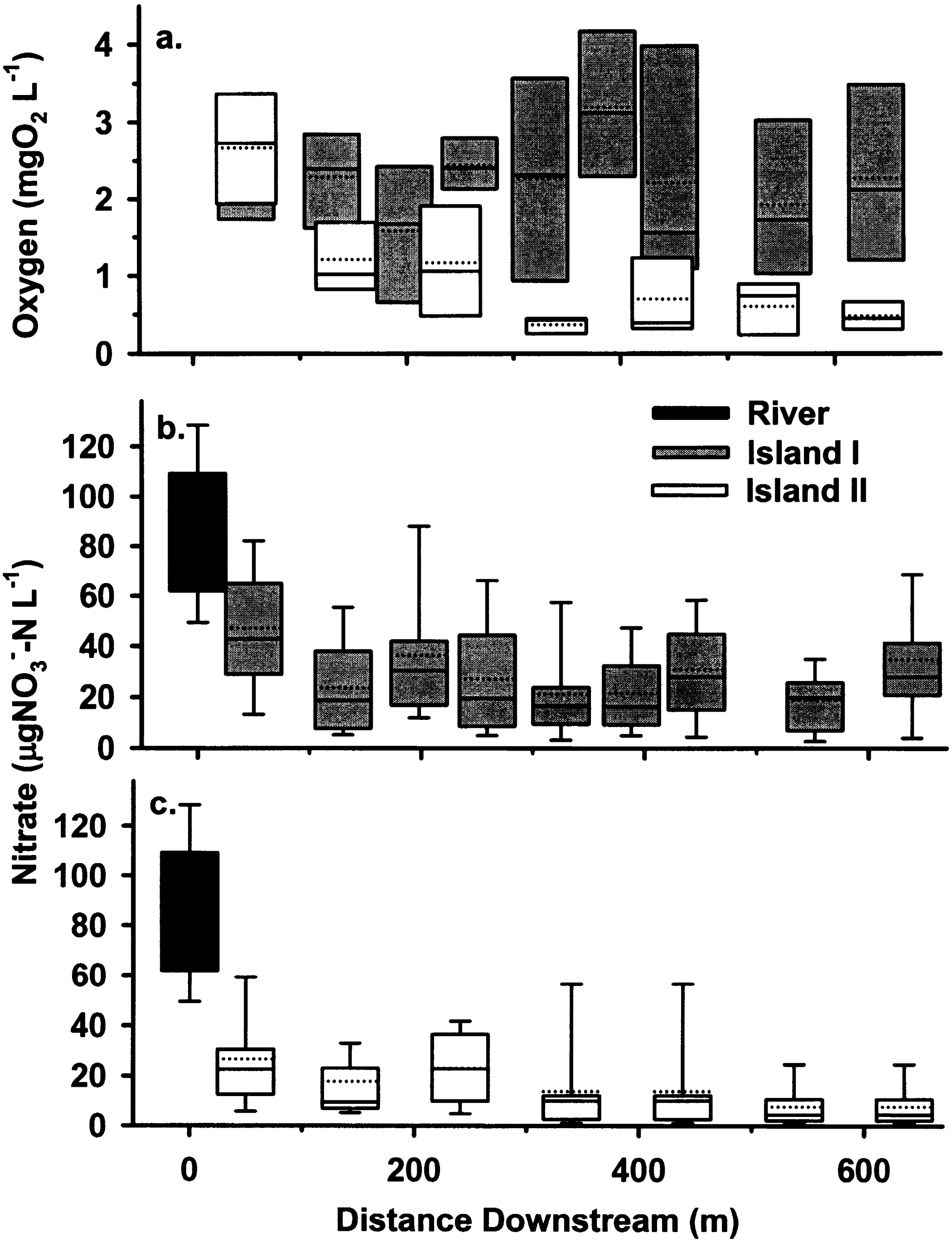


FIGURE. 5. Longitudinal patterns in the partial pressure of carbon dioxide (panel a) and methane (panel b) at Island I and Island II. The river is 0 m downstream.

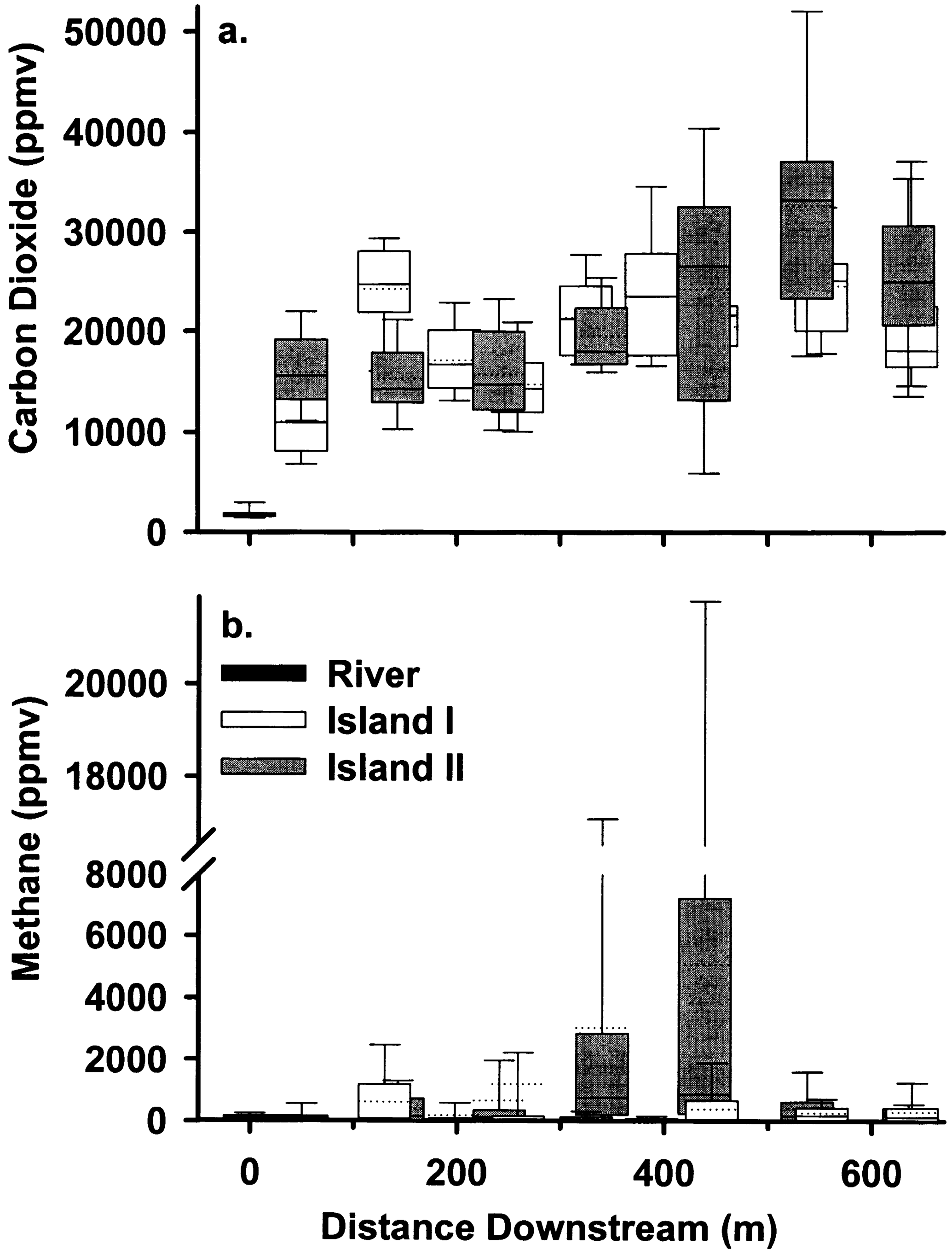


FIGURE. 6. Concentrations of hyporheic oxygen and dissolved organic carbon (mean ± SE; panel a), and indices of hyporheic anaerobiosis (CH_4:CO_2; mean ± SE) for the well transects (Island I and II) and wells at the willow-alder transitional wells (Island I T and Island II T; panel b).

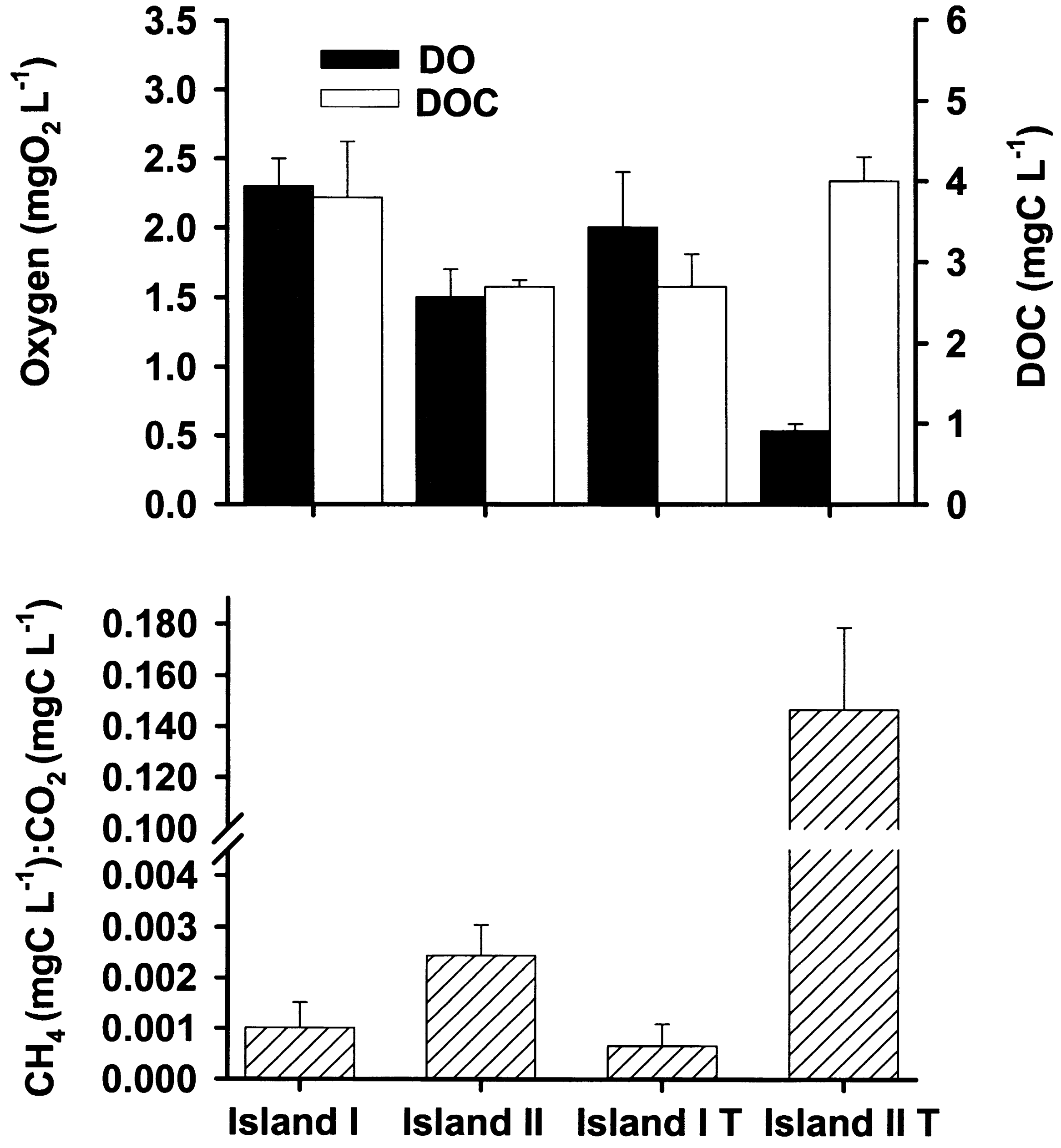


FIGURE. 7. Location of hyporheic wells (●) at Island II on the Tanana River. Arrows represent dominant flow vectors along subsurface flowpaths calculated from the change is hydraulic head in wells.

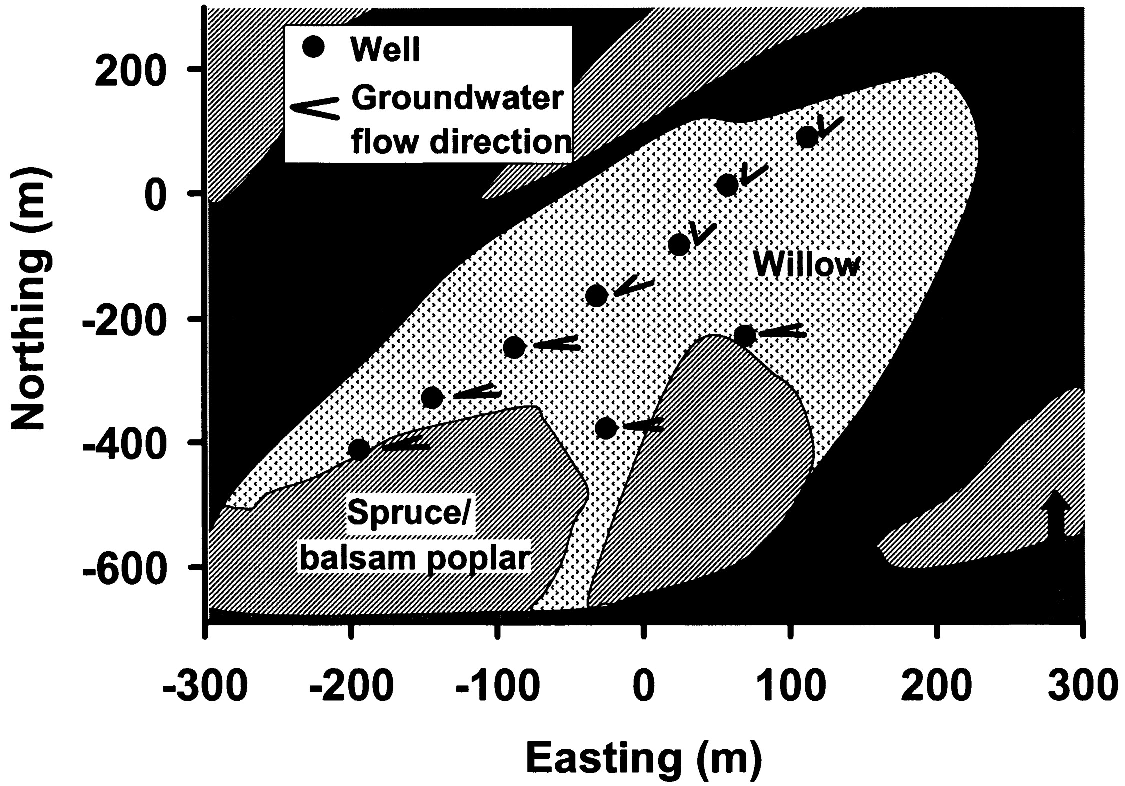


FIGURE. 8. Relationship between mean water table height and mean daily river stage (panel a) for both islands. Line indicates statistically significant regression at $p < 0.05$ and $r^2 = 0.93$, Slope = 0.82 and $y = 0.8227x + -6.2044$. Predicted mean water table height using the regression relationship in panel a and river stage data (mean river stage from 1990 - 2005) from Fairbanks USGS gauging station (panel b). Dashed horizontal line denotes mean willow rooting depth.

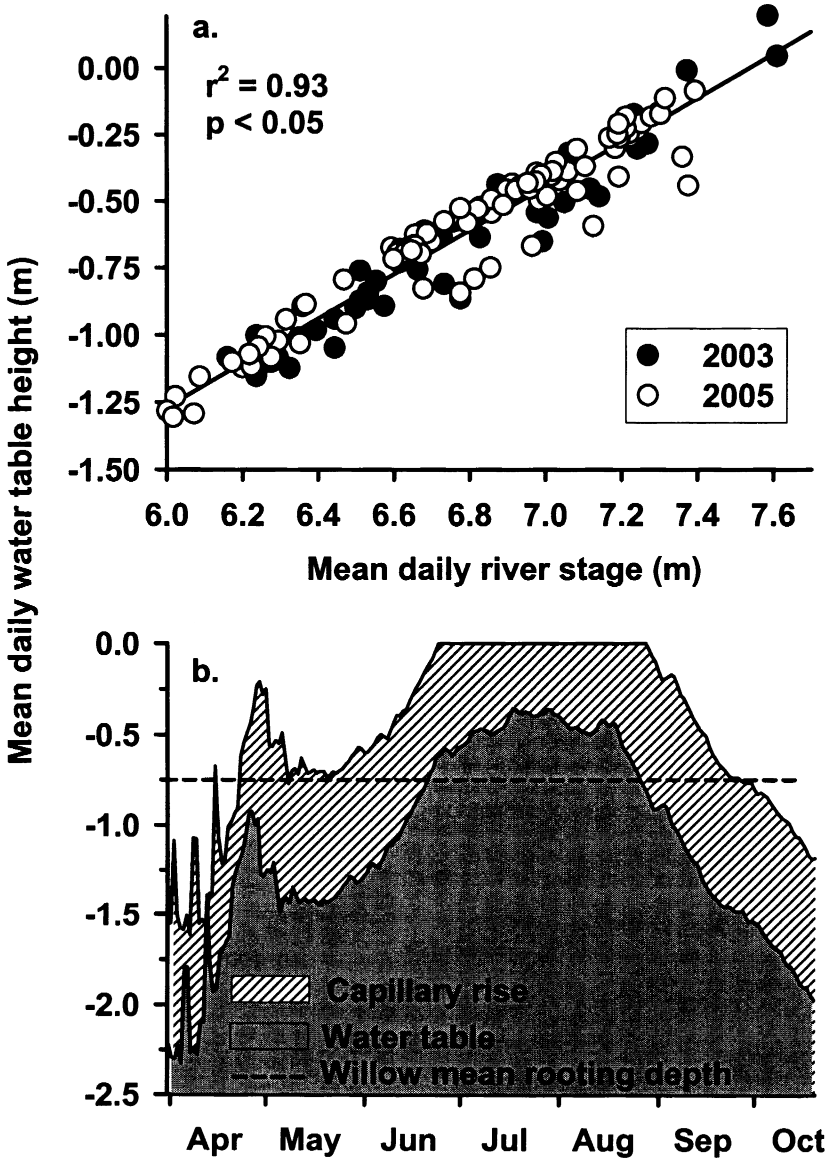


FIGURE. 9. Denitrification rates in hyporheic sediment (mean ± SE) for Island I and II from July to September in 2005.

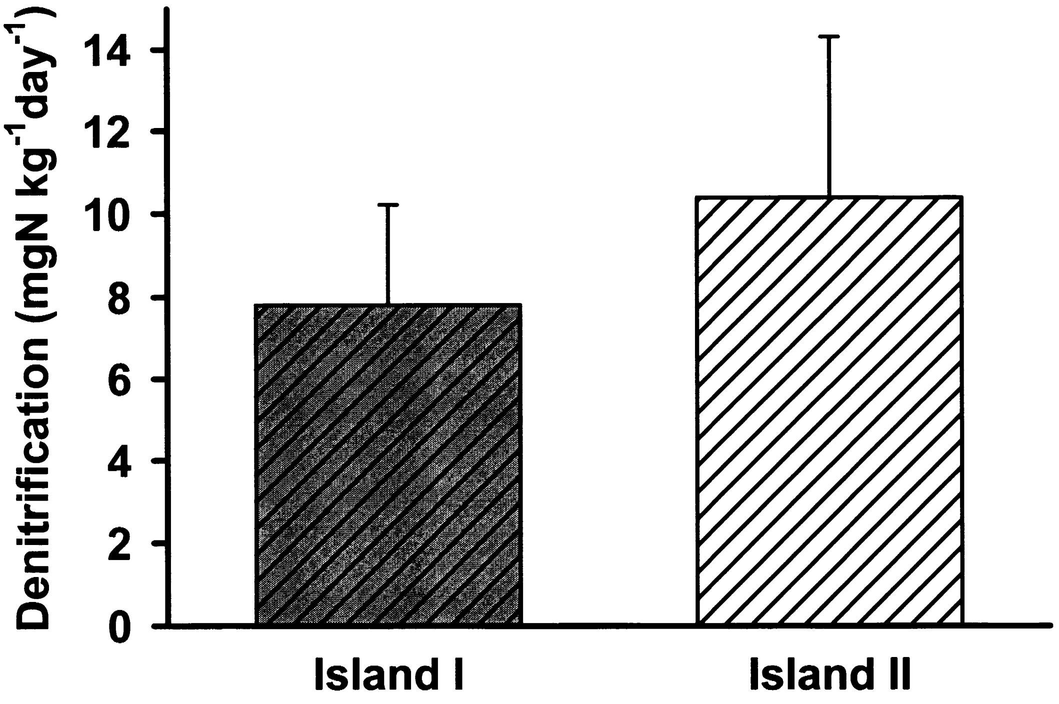


FIGURE. 10. Temporal variations in hyporheic nitrate concentration (mean ± SE; panel a) and methane partial pressure (mean ± SE; panel b) at Island II over the three study years.

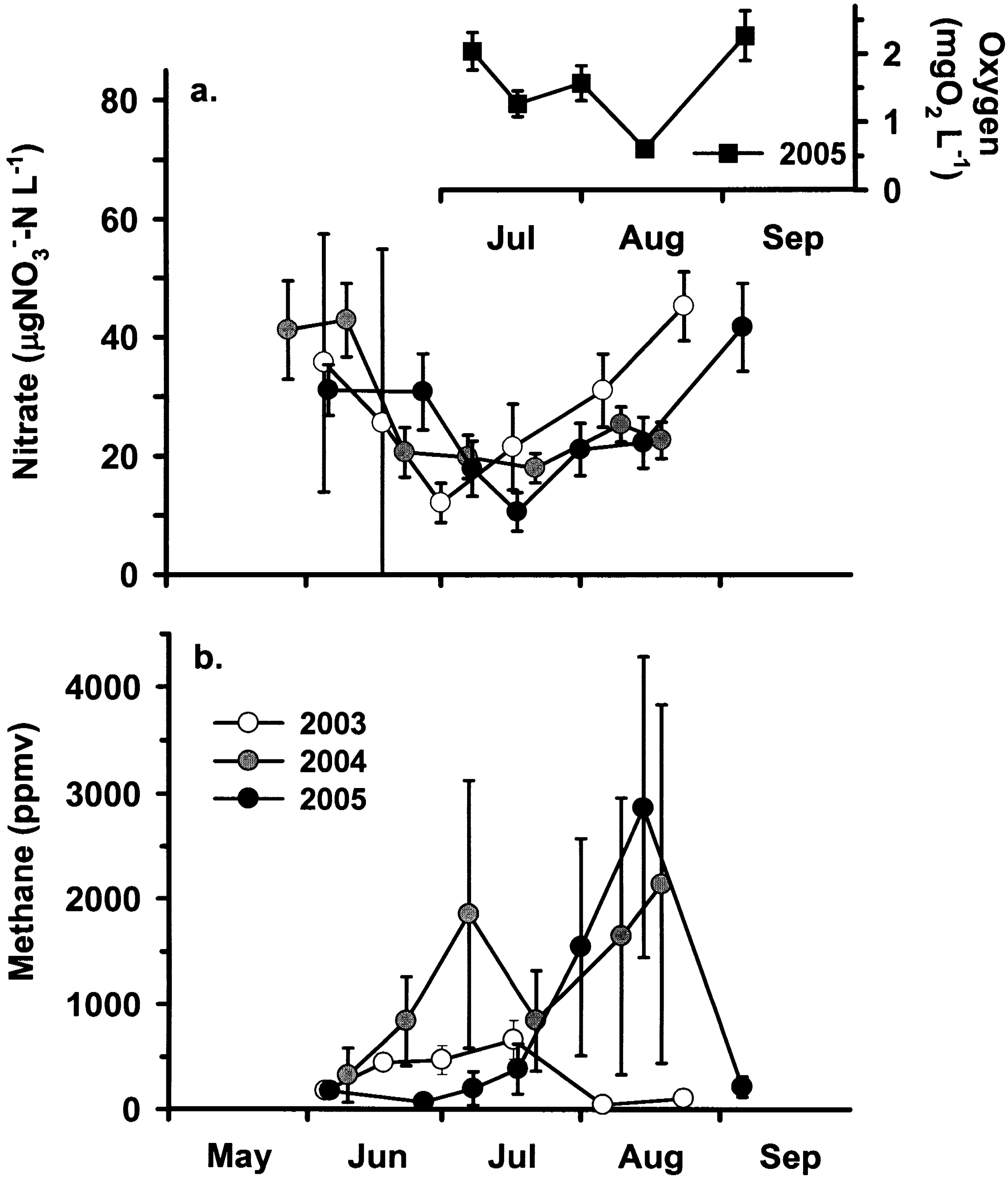


FIGURE. 11. Predicted mean number of days from 1993 – 2005 that the water table was above the mean rooting zone (0.75m depth) for willow on the Tanana River floodplain. River stage data was taken from the USGS gauging station located at Fairbanks, and water table height was calculated from the relationship between river and measured water table height for 2003 and 2005 in FIGURE. 8a.

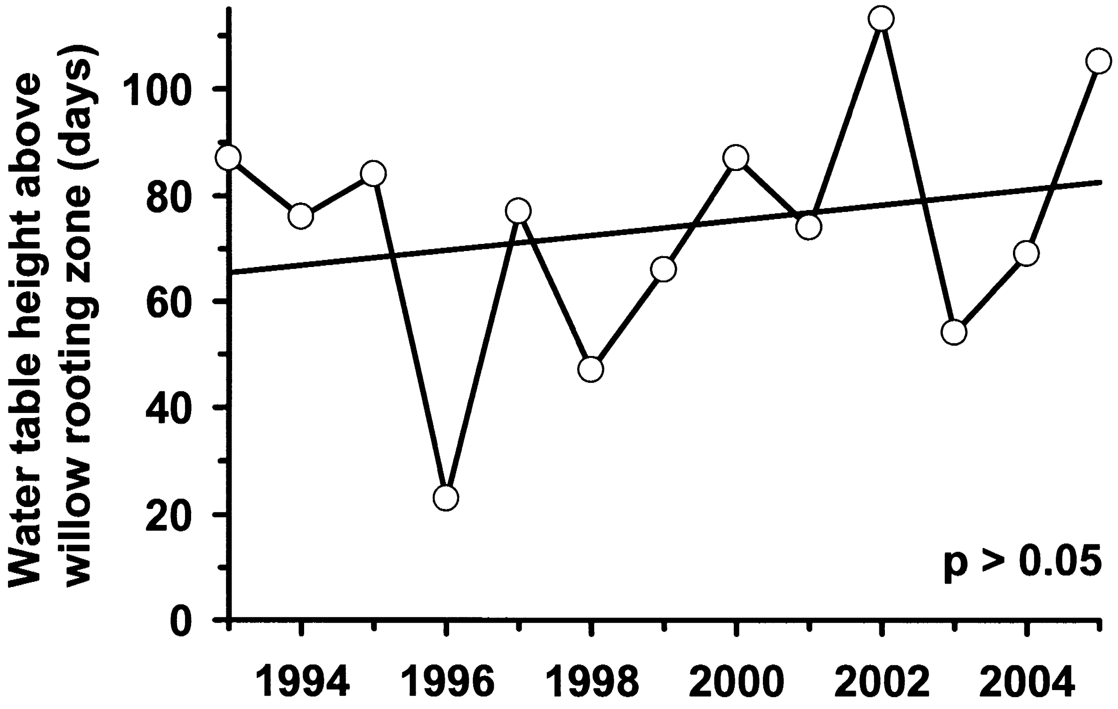
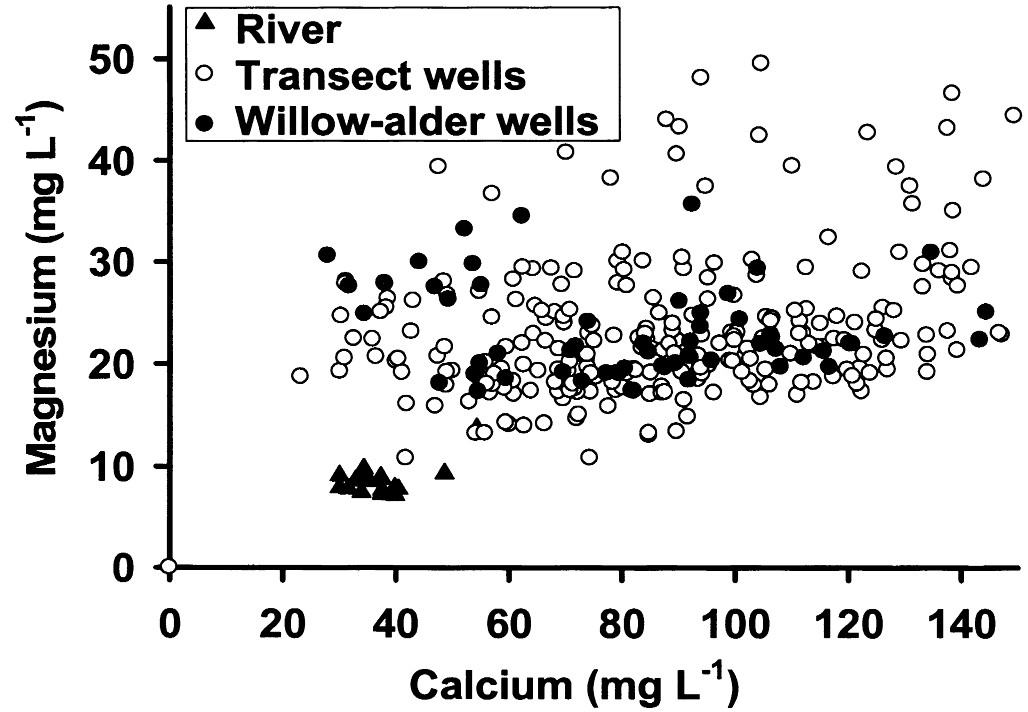


FIGURE. 12. Comparison of the calcium and magnesium concentrations in river water, hyporheic water along the well transects, and hyporheic water in the willow-alder transitional wells.



CHAPTER 3: CONCLUSIONS

The river-sediment interface is an important control point for nutrient flux between aquatic and terrestrial ecosystems (Hedin et al. 1998, Dahm 1998). This research examined the effects of river stage on supply of hyporheic nutrients to subsurface microbes and floodplain vegetation. Hyporheic water level responded rapidly to change in river stage, with the sites flooding periodically in mid-July to early-August. Vertical hydrologic exchange dominated the movement of water in the hyporheic zone, influencing redox potential of surface sediment and transporting nutrients through the soil profile.

Hyporheic biogeochemistry differed most at ecological boundaries. Methane partial pressure was greatest at the transition zone between willow and alder successional stages, and removal of nitrate was greatest at the river-sediment interface. Hyporheic flow was an important mechanism of nitrogen supply to microbes and plant roots. Relative to mineralization, denitrification was the dominant mechanism for nitrogen removal. Results suggest that denitrification can be a major sink for river nitrate in boreal forest floodplain soils, particularly at the river-sediment interface. The stability of the river hydrograph and the resulting duration of soil saturation were key factors regulating the redox environment and anaerobic metabolism in the hyporheic zone.

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