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Article

Dissolved inorganic nitrogen dynamics in the hyporheic zone of reference and human-altered southwestern U. S. streams

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With 8 figures and 3 tables

Abstract: Canalization and incision are common morphological alterations associated with human land use that reduce hydrological/hydrodynamic linkages between surface and ground waters in stream ecosystems. To explore the impacts of these anthropogenic changes on nutrient spiraling in streams, we measured the linkage between hyporheic and surface zones of reference and human-altered streams using ^{15}N-nitrate ($^{15}NO_3^-$) and bromide (Br^-) tracer injection experiments. Experiments were conducted in 7 streams (3 reference, 3 agricultural and 1 urban) in Arizona and New Mexico, USA, over a 3 yr period during the Lotic Intersite Nitrogen eXperiment (LINX II). Groundwater wells (6–9 in each stream) were inserted to 30 cm depth and multilevel samplers (MLS) were installed downstream from injection sites to measure inorganic nitrogen (N) and Br^- concentrations in hyporheic water. There was measurable surface water-ground water (SW-GW) connectivity, as indicated by Br^- concentrations in shallow alluvial ground water (0–30 cm depth) at all sites. SW-GW connectivity was higher in reference than in human-altered streams. Concentrations of NO_3^- and NH_4^+ in MLS cells (0–10, 10–20, and 20–30 cm below streambed) were inversely correlated, and ^{15}N-enrichment of both N species was measurable in groundwater wells. Hyporheic zones with lower surface-water infiltration had higher quantities of $^{15}NH_4^+$ than of $^{15}NO_3^-$. Whole stream uptake (k_{tot}; calculated during the LINX II experiments) was correlated with $\delta^{15}NH_4^+$ in wells; i.e., high $\delta^{15}NH_4^+$ in wells was associated with high stream uptake, and both whole stream NO_3^- uptake and $\delta^{15}NH_4^+$ were highest in the human-altered streams. The presence of enriched $^{15}NH_4^+$ in many of the wells within 24 h of injection suggested that dissimilatory nitrate reduction to ammonium (DNRA) was occurring in the hyporheic zone.

Key words: canalization, incision, human land use, surface waters, ground waters, stream ecosystem.

Introduction

The hyporheic zone, the region beneath and lateral to streambeds and riverbeds where surface water and ground water mix (Orghidan 1959, Dahm et al. 2006), is an important subsurface habitat. It has been defined by biological, chemical, and hydrological characteristics. For example, Triska et al. (1989) empirically categorized the hyporheic zone into two regions with the use of chemical tracers: a surface hyporheic zone, where > 98 % of the water is recently transported into the alluvial ground water from surface water in the

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channel, and an interactive hyporheic zone, where there is > 10 % but < 98 % surface water mixed with older ground water.

The hyporheic zone plays a critical role in nutrient input, transformation and retention in stream ecosystems. For example, oxygen-poor, nutrient-rich ground water can enter a stream at upwelling locations or oxygen-rich, nutrient-poor surface-stream water may enter ground water at downwelling locations, transporting nutrients to and from nutrient-limited habitats (Stanford & Ward 1988, Grimm et al. 2005, 2007). These exchanges between surface and subsurface water promote nutrient cycling and metabolism by moving electron donors and acceptors across redox boundaries (Hall et al. 2002, Sheibley et al. 2003, Thomas et al. 2003). At the ecosystem scale, hyporheic zones play a critical role in nutrient retention (Valett et al. 1996, Marti et al. 1997, Fellows et al. 2006).

Anthropogenic nitrogen (N) additions have had dramatic and sometimes devastating effects on many aquatic ecosystems. For example, the growing hypoxic zone in the Gulf of Mexico is caused by greater amounts of inorganic N delivered to the Gulf of Mexico by the Mississippi River (Turner & Rabalais 1994). This concern about increased nutrient runoff has spawned intensive efforts to evaluate sources of N pollution throughout the catchment of the Mississippi. A recent regional agreement calls for a 30 % reduction in N discharge from the river system to the Gulf of Mexico by 2015. On a catchment basis, small streams transform and retain N more efficiently than large rivers (Peterson et al. 2001). This suggests small streams substantively control N retention in catchments because they make up the majority of catchment river miles (Alexander et al. 2000). Within many small, "pristine" streams, hyporheic zones are often the major sites of N retention and removal (Valett et al. 1996, Morrice et al. 1997, Fellows et al. 2001), but the role of the hyporheic zone in streams that have been extensively modified by agriculture and urbanization is less clear.

Understanding N transformations in streams and rivers is a major focus for ongoing research, especially where high NO_3^- concentrations result from agricultural practices (Turner & Rabalais 1994) or urban runoff (Groffman & Crawford 2003). To measure NO_3^- transformation rates, $^{15}NO_3^-$ can be added to a stream and the partitioning of the isotopic label into various biomass pools and chemical species of N followed. For example, denitrification rates can be estimated by measuring $^{15}N_2O$ and $^{15}N_2$ gases that are produced after addition of $^{15}NO_3^-$ (Mulholland et al. 2004, 2008). The advantage of an isotopic tracer is that concentration is not increased significantly and thus baseline process rates can be measured (Peterson & Fry 1987, Peterson et al. 2001, Mulholland et al. 2008). To further resolve the role of hyporheic sediments in these N transformations, groundwater wells can be installed and sampled to provide a vertical dimension to the study of NO_3^- transformation and retention.

This research was a component of a larger collaboration called the second Lotic Intersite Nitrogen eXperiment (LINX II) project. The LINX II project compared NO_3^- dynamics in surface waters and surface sediments of 72 streams in 8 different biomes across the US, using a uniform set of protocols and procedures. Nine study streams in each of 8 biomes included 3 streams each in urban areas, agricultural areas, and areas with native vegetation. The fate of NO_3^- was evaluated with the use of 24 h instream injection experiments that add both a conservative solute (Br^-) and $^{15}NO_3^-$. We report here a component of the LINX II project that included installation and sampling of hyporheic wells, which extended the LINX II characterization of surface waters to the hyporheic zone. This additional hyporheic zone sampling was carried out only at some of the LINX II sites located in the desert Southwest biome (Arizona and New Mexico).

The objective of this study was to better understand the role in NO_3^- cycling of the hyporheic zone of streams influenced to varying degrees by changes in land use and human alteration of streams. We asked the question, what are the effects of land use and stream alteration on hyporheic zones? We hypothesized that streams with greater exchange between surface and shallow ground waters have greater NO_3^- retention. The extent of water and $^{15}NO_3^-$ exchange between surface waters and shallow ground waters was quantified in seven streams (3 reference, 1 urban, and 3 agricultural; we were unable to obtain permits to install wells in the other 2 urban streams) that varied in the magnitude of anthropogenic N inputs and the extent of their hyporheic zones. The study was designed to explore three issues. First, stream transient-storage zone parameters were estimated and compared with a directly measured hyporheic exchange parameter (percent surface water or % SW). Second, vertical and spatial % SW and nutrient heterogeneity were determined. The possible fates of the $^{15}NO_3^-$ were investigated within wells that received surface water as determined by the presence of conservative tracer and the measurement of $^{15}NO_3^-$, $^{15}NH_4^+$ and $^{15}N_2O$. We measured $^{15}NO_3^-$ transformation to $^{15}NH_4^+$ that can occur through dissimilatory nitrate reduction to ammonium (DNRA) or

through biological uptake, intercellular reduction, and release. The concentration of $^{15}N_2O$ was determined to examine trace gas formation through pathways such as denitrification and DNRA. $^{15}N_2$ gases were sampled and analyzed but the values were not different from atmospheric isotopic ratios and therefore are not presented. Lastly, whole-stream NO_3^- uptake was compared to hyporheic NH_4^+ concentration. We predicted that human-altered streams would have less SW-GW exchange and thus reduced hyporheic processing of NO_3^- compared to unaltered streams.

Methods

Study sites

Seven experiments were carried out over a 3 yr period in the southwestern region of the United States, specifically central New Mexico (NM) and central Arizona (AZ). Three of the streams are bordered by agricultural land, 1 is bordered by urban land and the reference streams are dominated by native vegetation (Mulholland et al. 2008). The human-altered streams are more confined and incised whereas the reference sites were wider and unconfined as is typical in southwestern US streams. The human-altered streams have higher silt content in the bed whereas the reference streams greater sand content (Hancock 2002, Boulton 2007). Stream names, types, locations, width (W), depth (D), study reach length, sediment characteristics and well locations are shown in Table 1. Aqua Fria River (AFR), Rio Salado (RS) and Sycamore Creek (SYC) are reference streams with predominantly native vegetation in the catchment (Fig. 1). These streams had open canopies and the majority of the channels received full sunlight. Riparian vegetation of AFR, an arid land stream north of Phoenix, was native cottonwood trees (*Populus fremontii*) and mesquite (*Prosopis velutina*) (Grimm et al. 2005), while upland vegetation was predominantly pinon-juniper (*Pinus edulis* and *Juniperus monosperma*) woodland. Located northeast of Phoenix, AZ, SYC has been described extensively by others (e.g., Grimm 1987, Martí et al. 1997, Heffernan 2008). The vegetation of the riparian corridor was dominated by cottonwood, sycamore (*Plantanus wrightii*) and various grasses, while the upland vegetation was Sonoran Desert scrub. RS is a spatially intermittent river fed by a perennial spring a few kilometers above the study reach, located on the Sevilleta National Wildlife Refuge, site of the Sevilleta Long-Term Ecological Research (LTER) program (http://sev.lternet.edu/) in central NM (Fig. 1). Upland vegetation was desert grassland, Great Basin shrubland, and Chihuahuan Desert shrubland. The riparian zone vegetation was native desert willow (*Salix exigua*) and grasses intermixed with non-native salt cedar (*Tamarix chinensis*) and Russian olive (*Elaeagnus angustifolia*).

The urban stream, the Rio Rancho Drain (RRD), is an artificial irrigation ditch downstream of the city of Rio Rancho, NM that runs parallel to the Rio Grande. The drain is used for irrigation and transportation of runoff from the surrounding neighborhood. Adjacent vegetation surrounding the ditch was dominated by riparian vegetation from the Rio Grande, mainly Rio Grande cottonwood (*Populus deltoides* var. *wislizeni*). The

Table 1. Stream characteristics for the 7 study sites in New Mexico and Arizona. The well locations are the distance downstream from the injection point.

Stream	Stream type	Lat./ Long	Q (l/s)	W (m)	D (m)	Velocity (m/min)	Reach length (m)	Sed. char.	Well location (m)
AFR	REF	34.35160 –112.10410	11	3.1	0.17	6.2	120	Silt/sand/ cobble	63 102 213
RS	REF	34.33580 –107.0392	6	3.7	0.014	4.3	160	Sand	30 90 120
SYC	REF	33.75330 –111.5060	21	3.7	0.026	15.1	230	Sand/cobble	30 55
RRD	URB	35.19790 –106.64450	18	4.7	0.12	2.2	240	Silt	30 60 100
BOD	AGR	35.32670 –106.54710	24	2.9	0.17	2.2	215	Silt	10 28 65
RP	AGR	34.40980 –106.85830	3	1.3	0.084	1.3	326	Silt	20 95
SPR	AGR	35.275330 –111.50600	4	2.0	0.016	N. A.	165	Silt/gravel	30 60 100

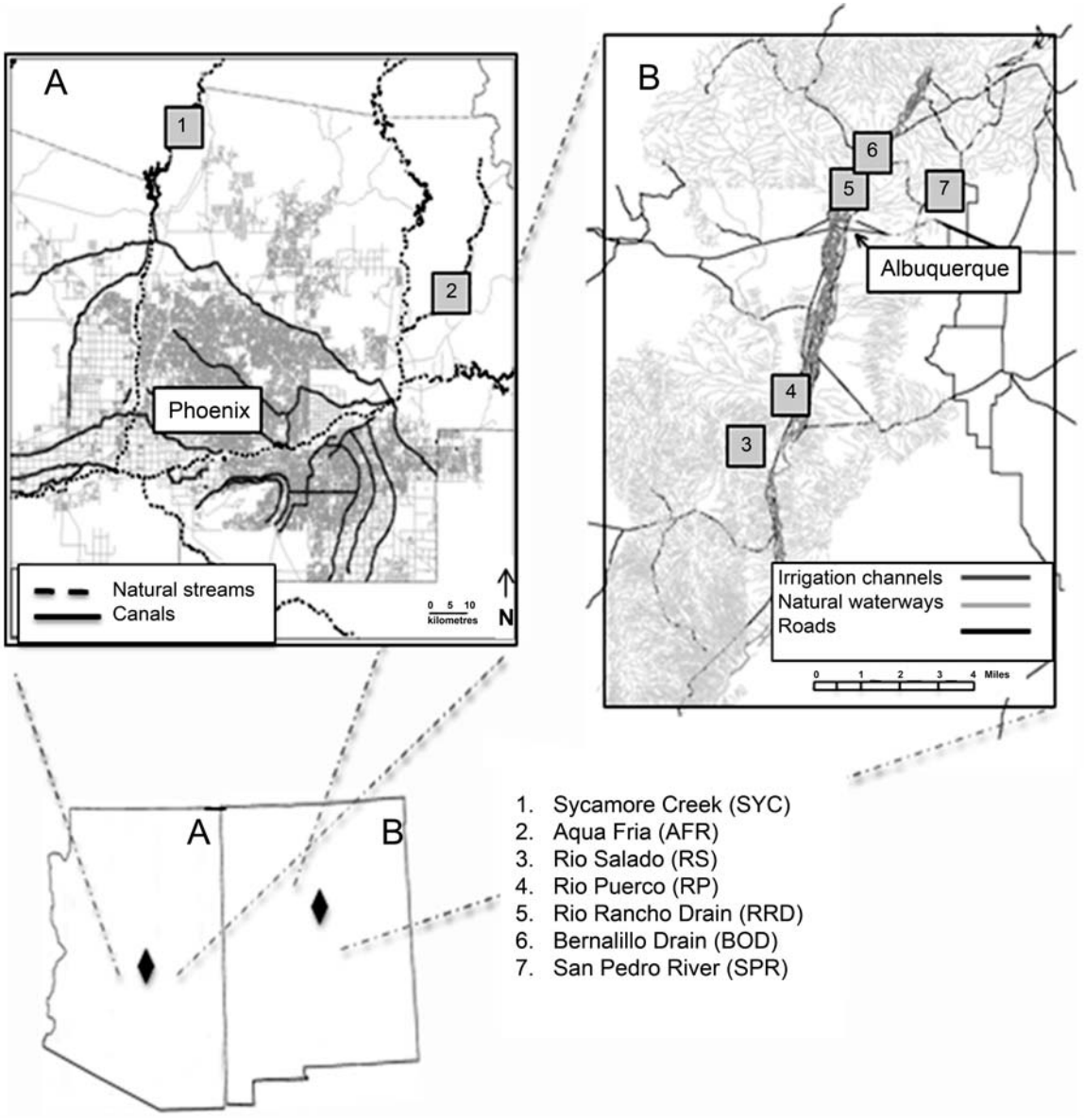

Fig. 1. Locations of study streams in Arizona **(A)** and New Mexico **(B)**. The boxes show the locations of the cities of Phoenix AZ (A) and Albuquerque NM (B).

riparian zone of the ditch was dominated by tumbleweeds (*Salsola kali*).

The three agricultural streams were Bernalillo Drain (BOD), Rio Puerco (RP), and the San Pedro River (SPR). BOD, located in Bernalillo, NM, north of Albuquerque, NM (Fig. 1), is an agricultural drain for irrigated farmland along the Rio Grande. Upland vegetation was rangeland for cattle grazing and alfalfa for horses and dairy cattle. The riparian vegetation was dominated by *Cryptantha* spp. The RP is a river draining a large catchment (> 1.5 million hectares) located on the northern border of the Sevilleta LTER (Fig. 1), with land use dominated by rangeland agriculture for beef production. Upland cover was a mixture of desert grassland, desert shrubland, juniper savannah, and pinon-juniper woodland. The riparian zone cover in the study reach was dominated by non-native salt cedar. SPR is in a cattle-grazed area near Tijeras, NM, northeast of Albuquerque, NM. The uplands within the catchment were predominantly pinon/juniper woodland and arid land grasses. The riparian cover was dominated by sedges (*Carex* spp.) and cottonwood.

Sediment characteristics

Sediments at the reference sites were dominated by sand-sized particles; the human-altered streams were dominated by silt-sized particles (Table 1). Two reference streams (AFR and SYC) did contain some cobbles, and one human-altered stream (SPR) had some gravel substrates. The reference sites were geomorphically unconfined reaches, while the human-altered streams were generally confined reaches, which were either human-produced (BOD, RRD) or due to cattle disturbance

(SPR, RP). The sites also were located within different geological settings. The catchment of RS is dominated by Mancos Shale and mudstone (Read et al. 2007, Cather & Baldridge 2008), RP, BOD and RRD drain through alluvial fans made up of a complex mix of geological types, SPR drains a catchment with a combination of limestone and shale, the SYC catchment is dominated by granitic alluvium, and AFR parent geology is weakly-consolidated conglomerate and sandstone. The parent geology of the seven catchments varied widely with sedimentary, igneous, and metamorphic units represented.

Isotope additions and calculations

Experimental tracer additions of $^{15}NO_3^-$ isotope were conducted as part of the LINX II project conducted throughout the US. A solution of $K^{15}NO_3^-$, along with a solution of a conservative salt (NaBr), was injected into each study stream at a steady rate (20 mL min^{-1}) for 24 h. The amount of $K^{15}NO_3^-$ added to the release solution was scaled for each study stream to produce a target $^{15}NO_3^-$ enrichment of ~20,000 ‰ for the NO_3^- in the stream water immediately below the injection location (Mulholland et al. 2008). Standardized methods of solute injections were used at the 72 research sites in the LINX II project (http://www.biol.vt.edu/faculty/webster/linx//).

Isotopic values are reported as $\delta^{15}N$ where $\delta^{15}N$ (‰) = $[(R_{samp}/R_{std}) - 1]*1000$. R_{samp} is the $^{15}N/^{14}N$ of the sample and R_{std} is the $^{15}N/^{14}N$ of the standard, atmospheric N_2. $\delta^{15}N$ was then converted to mole fraction (MF;$^{15}N/(^{14}N+^{15}N)$). Mole fraction excess of NO_3^- was calculated by subtracting out ambient MF of NO_3^- (~ 0.003663) as described in Mulholland et al. (2004, 2008) and Hall et al . (2009).

Whole stream uptake of $^{15}NO_3^-$ (K_{tot}) was calculated during each ^{15}N injection. K_{tot} is the distance-specific $^{15}NO_3^-$ uptake rate (m^{-1}) based on standard spiraling methods (Webster & Patten 1979, Newbold et al. 1981, Stream Solute Workshop 1990, Mulholland et al. 2008). Bromide was also sampled at a downstream location throughout the 24-h injection to allow modeling of transient storage, and periodic surface-water samples were collected at several stations along the reach to measure a suite of chemical constituents. Details of sampling and chemical analyses for these samples are given below.

Subsurface sampling

Five to nine wells were installed along the stream reach within each site. There were 2–3 transects within each site longitudinally downstream and 2–3 wells within each transect. There were only 2 transects at RP and SYC instead of 3 due to breakage of the wells during insertion or a poor seal at the sediment-water interface. Wells were constructed of 5-cm diameter polyvinyl chloride (PVC) with a screen length of 30 cm. Wells were inserted 35-cm into the streambed 24–48 h before the start of the injection experiment in a way that ensured no surface water could enter from the top of the wells by generating a tight seal around the top of the well. Multilevel samplers (MLS) designed by Margan MLS (Netanya, Israel) were installed within each well as the experiment began. The MLS was a solid polyvinyl chloride (PVC) rod fitted with 13-ml cylindrical diffusion cells capped with 0.2-µm nylon membranes. The cells were isolated in the well casing with neoprene seals at 10-cm depth intervals. The cells were filled with deionized water prior to the experiment so that they equilibrated with ambient shallow ground water during the injection experiment. Equilibration times determined previously with a conservative tracer were < 5 h. Recovered samples were transferred to acid-washed polyurethane bottles, placed on ice, and returned to the laboratory for analysis within 48 h of NO_3^-, NH_4^+ and Br^-. The MLS units were removed ~12 h after the ^{15}N injection began, and the wells were allowed to equilibrate with hyporheic water for multiple h (varied for different streams) before they were sampled for isotopic chemistry.

Water samples were collected from the stream and the wells at each well location 24 h after the injection began. Interstitial water (2 l) was slowly pumped from each well with a peristaltic pump (Geopump™; Geotech Environmental Equipment, Inc., Denver, Colorado) and filtered through a 47-mm Whatman GF/F glass fiber filter (0.7 µm) directly into the sampling bottle. Well samples were a composite sample of ground water from 5–35 cm depth because the volume of water required for stable-isotope analyses precluded the use of the low-volume MLS cells.

At 24 h after the injection began, dissolved $^{15}N_2O$ samples also were collected from wells using a 60-ml (2003) or 140 ml (2004, 2005) plastic syringe, fitted with a three-way stopcock. The syringe was attached to the end of the Geopump™ tubing and water was extracted slowly and carefully to avoid degassing of the water. Approximately 20 mL of high-purity helium (He) was added to the syringe while the syringe was submerged underwater. Syringes containing both He and well water were shaken for 5 min to allow equilibration of dissolved $^{15}N_2O$ gas into the He headspace. Water was expelled from the syringes under water and the He headspace was collected in evacuated 12-mL Exetainer® vials (Vial Type 3, Labco, High Wycombe, Buckinghamshire, UK). The sample vials were stored in water-filled centrifuge tubes to avoid atmospheric contamination and were analyzed for $^{15}N_2O$ by mass spectrometry (Mulholland et al. 2008).

Transient storage

Channel hydrologic parameters and transient storage-zone sizes for each stream were measured by injecting a hydrological conservative tracer (NaBr) into the stream (Webster & Ehrman 1996). Stream Br^- concentrations were measured throughout the 24 h ^{15}N injection at a pre-determined downstream station and ~10–20 m above the injection point. To ensure the streams were at steady-state, samples were periodically collected along the reach during the 24 h injection. The samples were returned to the laboratory and analyzed and the shape of the curve of Br^- concentration as a function of time at the downstream site was used to quantify transient storage zone parameters using the OTIS-P model (Stream Solute Workshop 1990, Runkel 1998).

Because each of the study reaches was relatively short, and there were no observable inflows, it was assumed that Q did not vary along the study reach. The upper boundary condition (UBC) was determined from a mass balance on Br^- between the downstream data at plateau and the injection flow rate and concentration to determine a step input for the model. Every injection occurred above a significant riffle section within these small streams, so mixing reaches of 10 m or less are very common. Periodic samples for Br^- concentration did not change significantly over time at downstream stations; therefore, we assumed the stream was well-mixed throughout the reach.

In order to obtain transient storage parameters for each stream, Br^- results were modeled using a one-dimensional solute transport model (Runkel 1998, 2002, McKnight et al. 2004).

Solute concentrations in the main channel (C) and transient storage (hyporheic) zone (C_s) are given by:

$$\frac{\delta C}{\delta t} = \frac{Q}{A}\frac{\delta C}{\delta x} + \frac{1}{A}\frac{\delta}{\delta x}\left(AD + \frac{\delta C}{\delta x}\right) + \frac{q_{LIN}}{A}\left(C_L - C\right) + \alpha\left(C_S - C\right) \quad \text{Eq. 1}$$

$$\frac{dC_S}{dt} = \alpha\frac{A}{As}\left(C - C_S\right)\left(C - C_S\right) \quad \text{Eq. 2}$$

where A is the main channel cross-sectional area (m^2), As is the storage zone cross-sectional area (m^2), C is the main channel solute concentration (mg/m^3), C_L is the lateral inflow solute concentration (mg/m^3), C_s is the storage zone solute concentration (mg/m^3), D is the dispersion coefficient (m/sec^2), Q is the volumetric flow rate (m^3/ sec), q_{LIN} is lateral inflow rate (m^3/ sec-m), t is time (sec), x is distance downstream of the injection point (m), and a is the storage zone exchange coefficient (/sec).

Estimates of A, As, D and α from the OTIS-P model can be used to determine other storage parameters. For example, As:A is a metric used to show the relative sizes of the transient storage zone relative to the cross sectional area of the stream (Harvey & Wagner 2000). $F_{MED}{}^{200}$ (Runkel 2002) is unitless and is defined as the fraction of the median travel time due to transient storage and is calculated as:

$$F_{MED}{}^{200} = \left(1 \cdot e^{\cdot L\alpha/u}\right)\frac{A}{As} \quad \text{Eq. 3}$$

where L is reach length and assigned a standard value of 200 m compared across reaches (Runkel 2002). In order to assess the reliability of the parameter estimates, and determine if adequate reach lengths were used, the unitless experimental Damköhler numbers (DaI) at each site were calculated as:

$$DaI = \alpha\frac{(1 + A/As)L}{u} \quad \text{Eq. 4}$$

where u is the average velocity of the reach. When DaI is > 1, the length of the study reach is too long so there is nearly complete solute transfer between the main channel and storage zone. When the DaI is < 1, very little solute enters the storage zone (Harvey & Wagner 2000). Ideal values of DaI should be ~ 1.0 but values between 0.5 and 5.0 are reasonable (Harvey & Wagner 2000). Average plateau and background Br^- concentrations in stream water and wells were used to calculate % surface water in the subsurface environment by dilution as described in Triska et al. (1989).

Laboratory methods

Surface and well-water samples were analyzed for some or all or the following parameters: NO_3^-, NH_4^+, $^{15}NO_3^-$, $^{15}NH_4^+$, $^{15}N_2O$, Br^-, soluble reactive phosphorus (SRP), and dissolved organic nitrogen (DON). Samples were collected for dissolved organic carbon (DOC) in surface samples only. Samples were analyzed for NH_4^+ concentration by using the indophenol method on a Technicon Auto-Analyzer (APHA 1995). Concentrations of NO_3^- and Br^- in samples were measured using a Dionex 500X ion chromatograph, and SRP in stream water was determined with the molybdate reduction method and analyzed on a Technicon Auto-Analyzer (APHA 1995). Surface DON and DOC concentrations were measured using a high-temperature catalytic oxidation method (Merriam et al. 1996) at the University of New Hampshire, Durham, New Hampshire.

The ^{15}N content of NO_3^- in surface waters was determined using a modified version of the method presented by Sigman et al. (1997). Surface water samples containing about 20 µg NO_3^- were concentrated by boiling with 3.0 g MgO and 5.0 g NaCl. Water samples collected during the isotope release were spiked with additional unlabeled NO_3^- to reduce $\delta^{15}N$ values to < 2,000 ‰. Samples were transferred to 250-mL media bottles to which an additional 0.5 g MgO, 0.5 g Devarda's Alloy (a strong reducing agent), and Teflon® filter packets were added. The Teflon® filter packet was constructed by sealing a 10-mm Whatman GF/D glass-fiber filter, acidified with 25 µL of 2.0 M $KHSO_4$ within a packet made of two Teflon filters. The seal around the GF/D glass fiber filter was formed using the rim of the scintillation vial. The $^{15}NO_3^-$ sample was reduced to $^{15}NH_4^+$ by reacting at 60 °C for 48 h with Devarda's alloy. Sealed media bottles were placed on a shaker for 7 d to allow for complete diffusion of the NH_3 into the acidified filter. The hydrophobic Teflon allowed for diffusion of NH_3 onto the acidified filter. The glass fiber filter was removed from the media bottle after the 7 d incubation, dried, and analyzed for ^{15}N on a dual-inlet Finnigan MAT "Delta S" (with a Heraeus elemental analyzer-cryogenic "trapping box" preparation system) at the Marine Biological Laboratory, Woods Hole, Massachusetts.

The $^{15}NH_4^+$ samples (2–4 L) were analyzed the same way as the $^{15}NO_3^-$ but without the boiling and reduction steps. The diffusion began in the field upon collection, followed by heating and shaking for 14 d. The GF/D glass fiber filter was processed as above and then sent to the Marine Biological Laboratory, Woods Hole, Massachusetts where the samples were analyzed using the same equipment.

Statistical analysis

A one-way analysis of variance (ANOVA) was used to compare differences among streams in % SW and nutrients. Exponential models were used to test for correlations between GW concentrations of NO_3^- and NH_4^+, and linear regression was used to examine correlations of % SW and $^{15}NH_4^+$ in the wells across the different streams. Statistica for Macintosh (Stat Soft, Tulsa, OK) was used to run these analyses.

Results

Stream physical characteristics

The three reference sites varied in W from 3.1 to 3.7 m, compared to a wider range of 1.3 to 4.7 m for the human-altered streams (Table 1). Ratios of W to D for the seven study streams ranged from 15 (RP) to 264 (RS). The reference streams all had W : D > 100, ranging from 142 to 264, whereas W : D for the impacted streams (15 to 125) was always less than in the reference streams.

Table 2. Transient storage zone (TSZ) parameters for the seven streams. As:A is the ratio of the cross sectional area of the stream to the cross sectional area of the TSZ. F_{MED}^{200} is the fraction of the median travel time due to transient storage. DaI is the Damköhler number. % SW is the percentage of surface water found in the hyporheic zone.

Stream	A	As	α	As:A	F_{MED}^{200}	DaI	% SW
AFR	0.13	0.053	$3.4e^{-4}$	0.401	0.14	1.36	81
RS	0.09	0.010	$9.6e^{-5}$	0.121	0.30	1.96	61
SYC	0.08	0.060	$1.4e^{-3}$	0.780	0.30	2.87	73
RRD	0.57	0.042	$1.0e^{-5}$	0.073	0.004	0.96	48
BOD	0.67	0.003	$6.4e^{-05}$	0.004	0.0012	98.0	37
SPR	N. A.	N. A.	N. A.	N. A.	N. A.	N. A	66
RP	0.11	0.004	$6.6e^{-06}$	0.040	0.0022	30.0	38

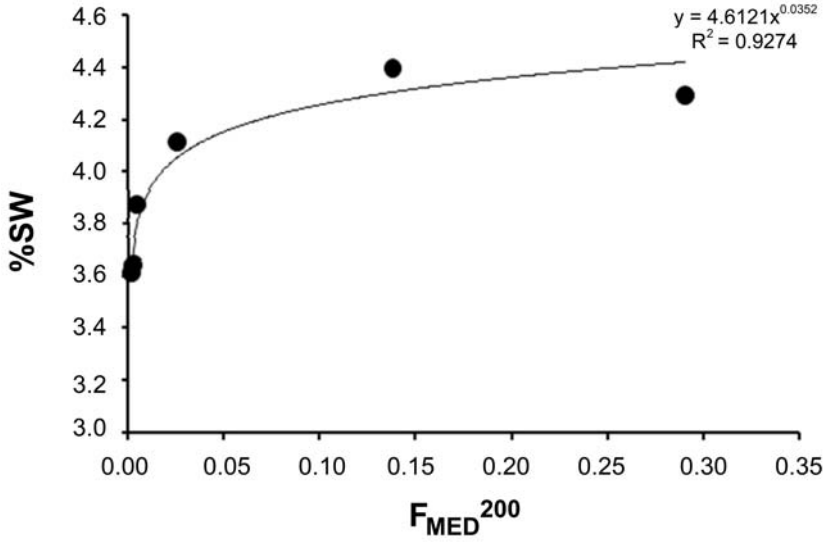

Fig. 2. The relationship between model-derived F_{MED}^{200} and % SW for the groundwater wells at the seven sites is shown. F_{MED}^{200} is calculated using transient storage modeling with OTIS-P and % SW is calculated from the wells using measurements of Br^-concentrations after 24 h of injection of the conservative tracer. No data for F_{MED}^{200} are available for SPR due to large fluctuations in discharge during the injection.

Transient storage parameters varied over more than two orders of magnitude among sites. As:A ranged from 0.004 (BOD) to 0.78 (SYC). Storage-zone exchange coefficients (α) were highly variable among sites and were not significantly different among stream types (Table 2). Average % SW in the well waters ranged from 37 % (BOD) to 81 % (AFR) for the seven streams. There was a strong correlation between F_{MED}^{200} values and % SW ($p < 0.05$, $R^2 = 0.93$; Fig. 2). Only 2 streams showed DaI values > 1.0, a range in which the OTIS-P modeling results probably do not represent transient storage processes accurately. For SPR, problems with the Br^- collection and analysis did not allow use of OTIS-P at this site.

Stream and hyporheic zone nutrient characteristics

Dissolved NO_3^- and NH_4^+ concentrations were low in the surface waters of the seven streams. Nitrate and NH_4^+ concentrations ranged from 1 to 297 µg/l and 2 to 65 µg/l, respectively (Table 3). The dominant dissolved N pool across most sites was DON, with concentrations ranging from 57 to 222 µg/l. One agricultural site (SPR), however, had higher NO_3^- (297 µg/l) than DON (44 µg/l). SRP concentration ranged from 3 to 56 µg/l, with all but one site (RP) having concentration > 10 µg/l. Concentration of DOC ranged from ~ 1 mg to 4 mg/l. In the hyporheic zone, NO_3^- concentration ranged from near the analytical detection limit (3 µg/l at RRD) to about 70 µg/l (RP), with large standard errors for NO_3^-concentration at many of the sites (Table 3). Average hyporheic zone NO_3^- concentration was higher than surface-stream concentration except at the RRD and SPR sites (Table 1). Average hyporheic zone NH_4^+ concentration was always higher than the NH_4^+ concentration of overlying surface waters.

Hyporheic zone connectivity and N variability

Connectivity between surface waters and ground waters ranged from 0–100 % SW (Fig. 3). The median % SW was greatest near the surface at one site (BOD), great-

Table 3. Average nutrient concentrations (NO_3^-, NH_4^+, DON, SRP, and DOC) measured for the seven study streams during the injection experiments. In addition, the average concentration for $^{15}NO_3^-$ ‰, $^{15}NH_4^+$ ‰ and $^{15}N_2O$ ‰ are reported for well waters from each site.

Stream	NO_3^- (µg/l)	NH_4^+ (µg/l)	DON (µg/l)	SRP (µg/l)	DOC (mg/l)	Hyporheic NO_3^- (µg/l)	Hyporheic NH_4^+ (µg/l)	Hyporheic $^{15}NO_3^-$ ‰	Hyporheic $^{15}NH_4^+$ ‰	Hyporheic $^{15}N_2O$ ‰
AFR	2 ± 2	2 ± 2	57 ± 4	56 ± 1	1 ± 0.03	26 ± 1	7 ± 4	26 ± 8	11 ± 2	28 ± 14
RS	3 ± 1	4 ± 0.3	88 ± 42	3 ± 3	1 ± 0.1	64 ± 26	7 ± 4	185 ± 90	–5 ± 2	N. A.
SYC	58 ± 13	2 ± 2	N. A.	32 ± 3	2.2 ± 0.01	66 ± 28	11 ± 8	4278 ± 1329	46 ± 23	57 ± 10
RRD	13 ± 3	4 ± 6	98 ± 20	50 ± 6	2.5 ± 0.1	3 ± 1	7 ± 2	35 ± 17	N. A.	130 ± 78
BOD	1 ± 0	2 ± 2	98 ± 7	37 ± 1	2 ± 0.04	15 ± 5	3 ± 2	121 ± 39	79 ± 26	191 ± 55
RP	3 ± 1	4 ± 0.5	222 ± 35	14 ± 0.3	3.9 ± 0.3	70 ± 64	37 ± 12	914 ± 103	110 ± 41	N. A.
SPR	297 ± 11	4 ± 1	44 ± 10	19 ± 0.3	0.9 ± 0.2	39 ± 15	26 ± 11	307 ± 35	18 ± 6	787 ± 225

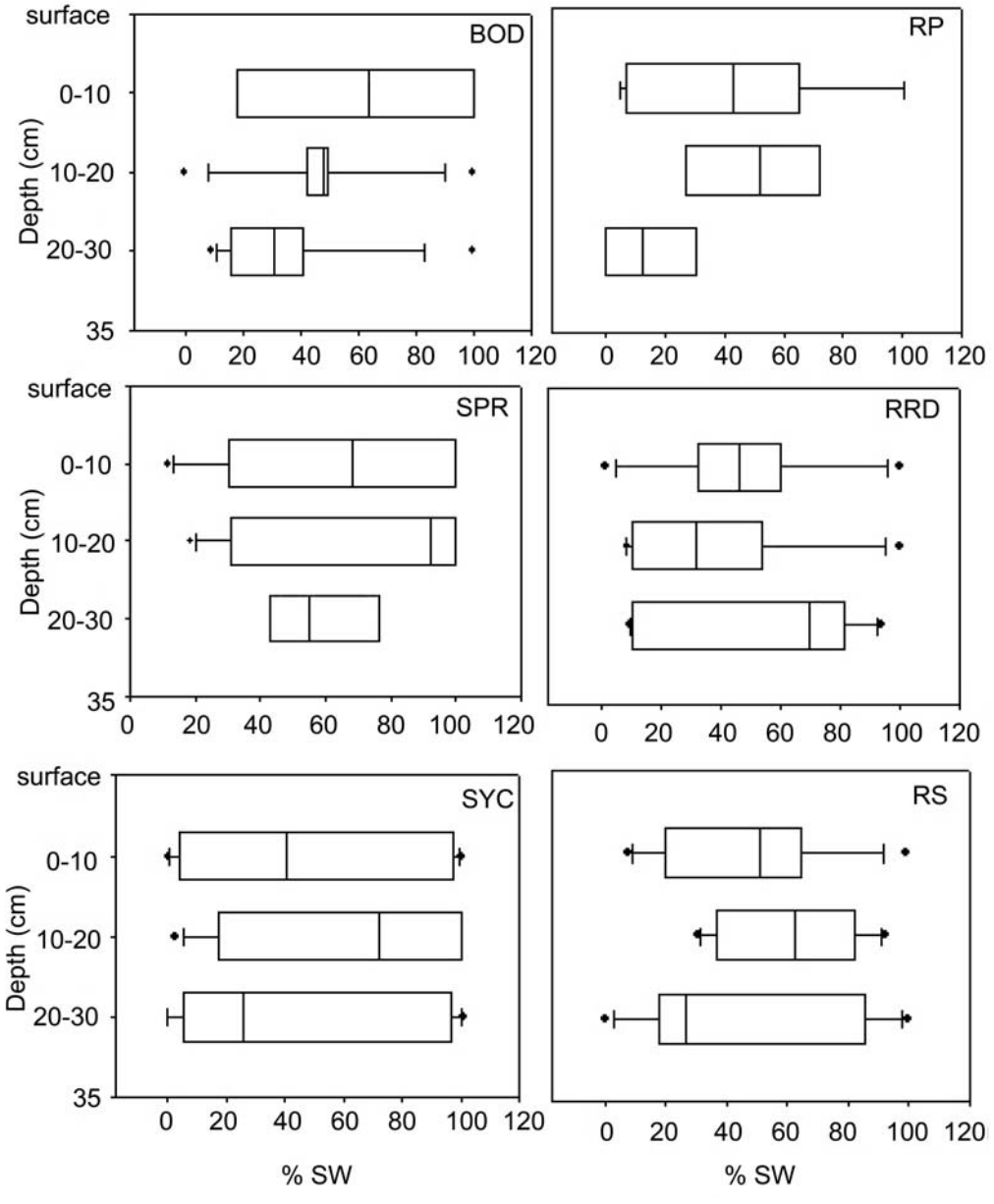

Fig. 3. Box plots of average % SW in the hyporheic zone of the study streams at different depths are shown. No samples are available for AFR. Box plots depict the smallest observation, lower quartile (Q1), median, upper quartile (Q3), and largest observation; in addition, the boxplot indicates which observations, if any, are considered unusual, or outliers.

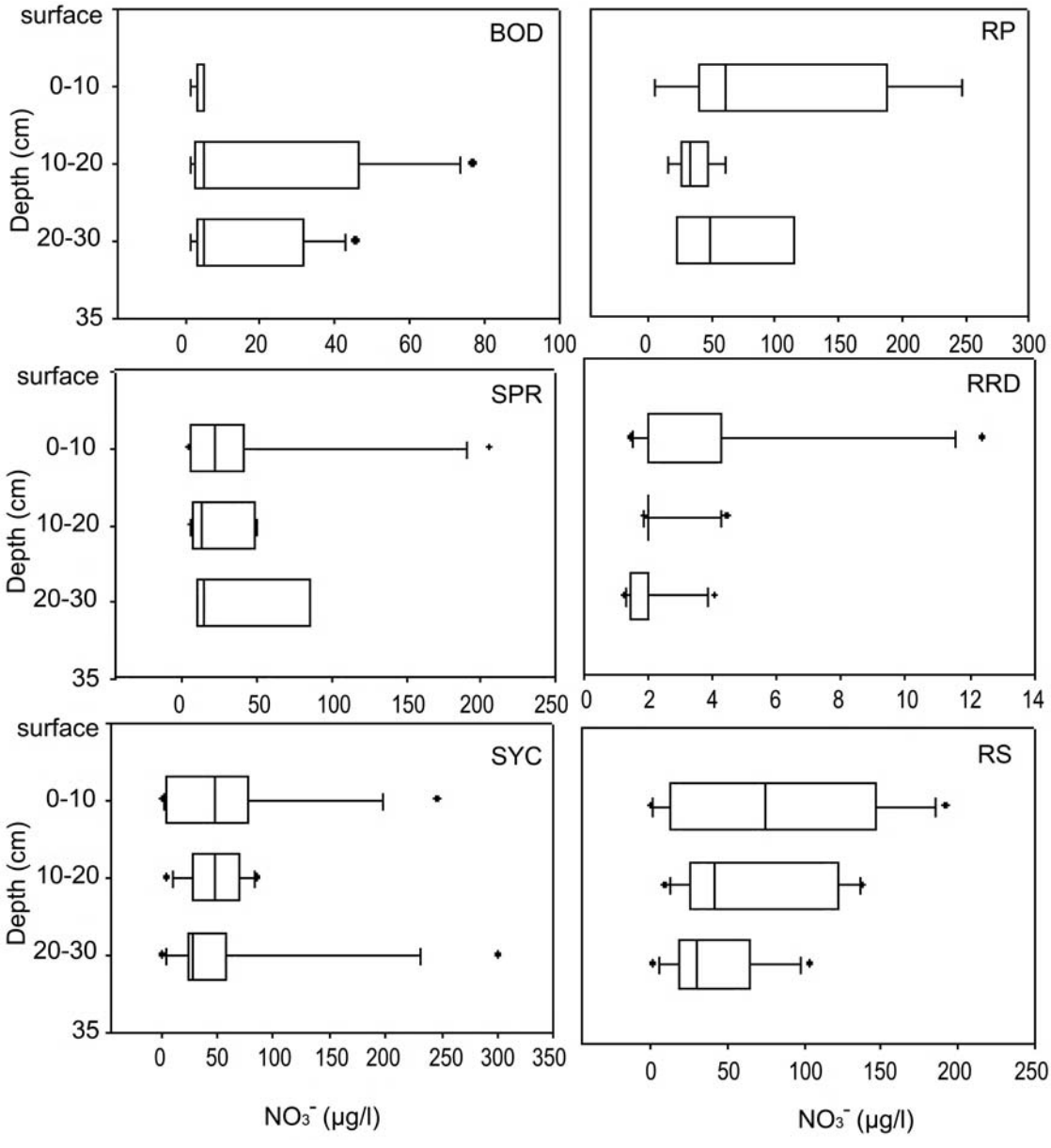

Fig. 4. Box plots of average NO_3^- at different depths in the six study streams are presented. No samples are available for AFR. Box plots depict the smallest observation, lower quartile (Q1), median, upper quartile (Q3), and largest observation; in addition, the boxplot indicates which observations, if any, are considered unusual, or outliers.

est at 10–20 cm depth at four sites (RP, SPR, SYC, and RS), and greatest at 20–30 cm depth at one site (RRD). The % SW in wells placed longitudinally across the active channel at the same distance from the injection point also commonly ranged from 0–100 % SW.

Nitrate concentration in the MLS cells varied from below the detection limit < 2 µg/l to > 300 µg/l. Patterns of NO_3^- concentration with depth also varied strongly among sites (Fig. 4). For example, BOD had low median NO_3^- concentration at all depths but with occasional higher values at depth, while RP had the lowest median concentration at 10–20 cm compared to 0–10 cm or 20–30 cm depth ($p > 0.05$). Concentration of NH_4^+ within the MLS cells also varied at each site (data not shown), but no significant differences were found among streams types or between different depths into the sediment ($p = 0.5$). Nitrate and NH_4^+ concentrations measured in the MLS cells across all depths correlated inversely with each other ($p = 0.03$, $R^2 = 0.18$; Fig. 5). High NO_3^- concentration was more commonly found when NH_4^+ concentration was low and vice versa.

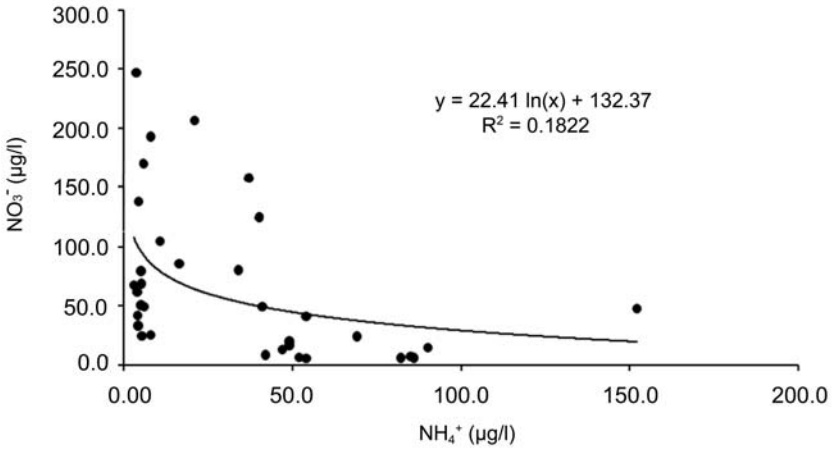

Fig. 5. A comparison of NO_3^- and NH_4^+ concentrations is shown from the MLS cells at all sites and all depths for the six study sites. The MLS samples taken at AFR were not analyzed due to a storage problem.

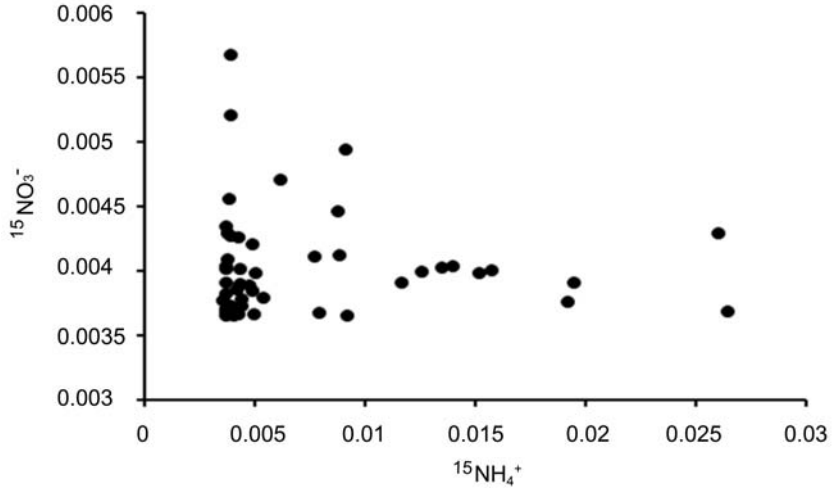

Fig. 6. The $^{15}NO_3^-$ and $^{15}NH_4^+$ molar fractions (mf) from each well at the six study sites are compared. High mf of $^{15}NO_3^-$ occurs at SYC and high mf of $^{15}NH_4^+$ occurs at RP.

Stable isotope results

Both the NO_3^- and NH_4^+ pools were measurably enriched with ^{15}N in all wells. Many of the streams had relatively low levels of $^{15}NO_3^-$ and $^{15}NH_4^+$ enrichment (Table 3). However, certain streams had distinct responses with higher levels of $^{15}NO_3^-$ than $^{15}NH_4^+$ and vice versa (Fig. 6). For example, SYC had high $^{15}NO_3^-$ enrichment in the wells, but little enrichment of $^{15}NH_4^+$, while RP had low levels of $^{15}NO_3^-$ enrichment but had high levels of $^{15}NH_4^+$ in comparison to the other streams. The $^{15}NH_4^+$ mole fraction (mf) was negatively correlated with well % SW among all wells and sites ($p = 0.03$, $R^2 = 0.16$, Fig. 7).

There was measurable enriched $^{15}N_2O$ in the wells at every site ranging from 0.0035 to 0.0083 mf. There was enrichment in the $^{15}N_2O$ pool in the human-altered streams (0.0048 ± 0.0012 mf) and reference streams (0.0041 ± 0.0005 mf). SPR had the greatest amount of $^{15}N_2O$ in the wells (0.006 mf) and SYC had the lowest (0.004 mf).

Hyporheic $\delta\ ^{15}NH_4^+$ and stream uptake

Whole stream uptake (K_{tot}) was calculated from surface-water injections and compared to hyporheic $\delta^{15}NH_4^+$ (Fig. 8). Streams with higher uptake tended to have high $\delta^{15}NH_4^+$ in the subsurface. For example, two altered streams (BOD and RP; 0.0132 m^{-1}, and 0.02035 m^{-1}, respectively) had the fastest whole-stream uptake rates and had more $^{15}NH_4^+$ (79 and 110 $^{o}/_{oo}$, respectively). In contrast, reference sites (RS and SYC) had lower K_{tot} values (0.0044 and 0.0054, respectively) and less $^{15}NH_4^+$. Samples for the measurement of $^{15}NH_4^+$ from RRD were lost.

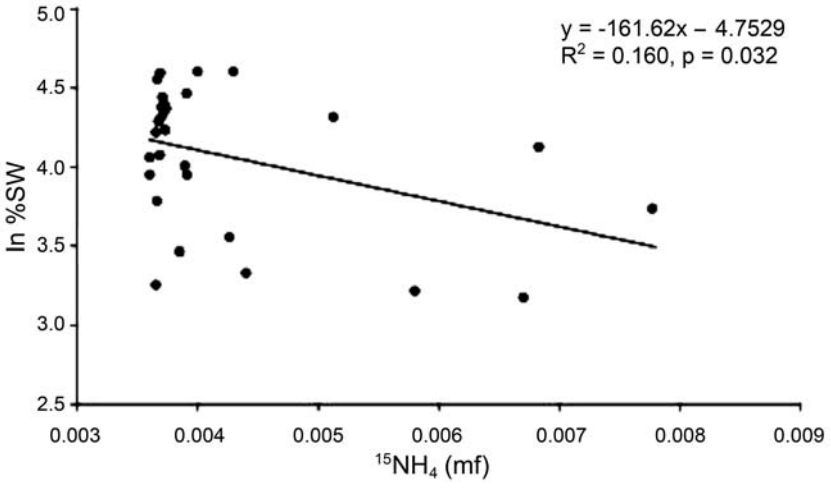

Fig. 7. Natural log (ln) transformed % SW data and $^{15}NH_4^+$ molar fraction (mf) data from each well at the six study streams are compared.

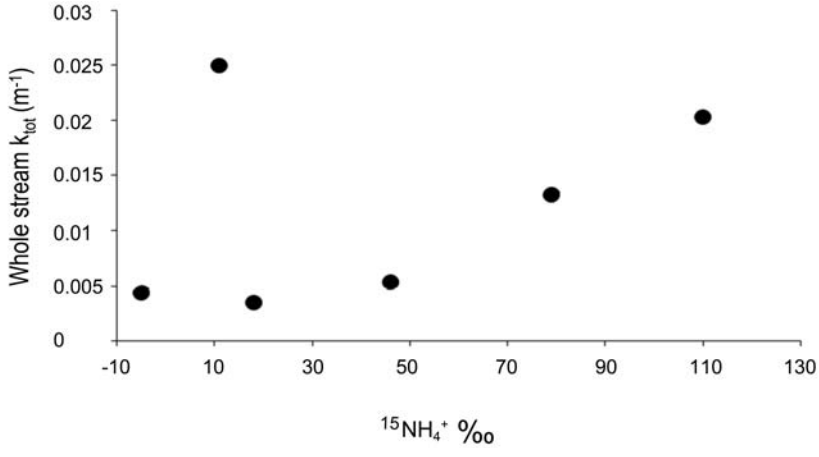

Fig. 8. Whole stream uptake (K_{tot}) versus average $\delta^{15}NH_4^+$ from wells from 6 of the 7 streams. RRD was not analyzed for $^{15}NH_4^+$ due to analytical problems.

Discussion

Surface-subsurface water exchange

Transient storage is a process by which water is stored either in stream channel dead zones or through exchange into the hyporheic zone. Transient storage increases the residence time of stream solutes and contact time with biological communities (Harvey & Bencala 1993, Kasahara & Wondzell 2003, Gooseff et al. 2006). As:A is a unitless ratio of the cross sectional area of the storage zone and the cross sectional area of the surface stream (Runkel et al. 1998, Harvey & Bencala 1993, Valett et al. 2002). As:A values were generally larger in the reference streams than the human-altered streams (Table 2). The same trend is evident with F_{MED}^{200}, another unitless model-derived parameter, defined as the fraction of the median travel time due to transient storage. This is consistent with previous studies that showed that relatively undisturbed streams have larger transient storage areas and greater connectivity with the hyporheic zone (Harvey & Bencala 1993, Kasahara & Wondzell 2003, Gooseff et al. 2006, Gooseff et al. 2007, Malcolm et al. 2010).

By combining modeling results from transient storage models with empirical data from hyporheic zone wells, we can better understand and resolve model predictions in relation to actual hyporheic zone dynamics. The results from these seven sites show that F_{MED}^{200} calculated from the OTIS-P model are linked to groundwater well %SW (Fig. 2). When combined with the As:A data (Table 2), the clear trend is that our reference sites have greater SW-GW connectivity than our human-altered streams. These results support other studies that show SW-GW interactions are de-

creased in human-altered streams. For example, Gooseff et al. (2007) found that reference streams were more geomorphologically complex when compared to agricultural and urban streams. The agricultural streams were intermediate between the reference and urban streams in geomorphic complexity in this comparison of stream ecosystems near Jackson Hole, WY. Transient storage increased as channel complexity increased in this study, similar to the results reported in this paper.

Streambed form and substrate type can directly influence both in-channel and hyporheic zone transient storage (Harvey & Bencala 1993, Valett et al. 1994, Gooseff et al. 2006, Gooseff 2007). The data from these studies show that surface water enters the hyporheic zone and is distributed heterogeneously across multiple depths along the study reaches of these streams. In general, there was greater % SW at depth in reference streams than in the human-altered streams (Table 2), but the vertical distribution of surface water in the multilevel wells was highly variable. For example, there were some wells where %SW was 100 % at 20–30 cm and < 20 %SW at 10–20 cm (Fig. 3). We interpret the overall decrease in %SW in the human-altered sediments of the agricultural and urban streams on bulk sediment type. This is reflected in the reference sites being dominated by sand and cobble and the altered streams dominated by silt (Table 1). There was, however, considerable heterogeneity in the vertical structure of the sediments along the stream channels where the wells were placed. This complex pattern of SW-GW connectivity between sites, longitudinally along the study reaches, and vertically into the sediments impacts nutrient cycling within these ecosystems and specifically affects the uptake and biogeochemistry of $^{15}NO_3^-$ linked to interactions with hyporheic sediments (Fig. 4).

We attribute the differences in sediment types to land use characteristics in the catchments. Another interpretation might focus on the parent geology of the catchments (e.g. Valett et al. 1996). The parent geologies of the study sites do vary from predominantly sedimentary to predominantly igneous, but most sites are either associated with the alluvial deposits of large catchments with highly variable geological substrata or are human-excavated channels in the alluvium along large rivers. The smaller catchments studied by Valett et al. (1996) were located in basins with differing parent lithology, but the study sites in this paper constitute a much larger and more heterogeneous geological template. We argue that land use rather than geology influences sediment type in these sites.

Hyporheic connectivity and inorganic N dynamics

Hyporheic zone sediments and waters are metabolically active with complex patterns of nutrient cycling that vary both spatially and temporally (Grimm & Fisher 1984, McDowell et al. 1992, Baker et al. 1999). Our data showed considerable variability in inorganic N in the hyporheic zone both spatially and temporally and among streams (Table 3 and Fig. 4). At all sites NH_4^+ concentrations were higher in subsurface than surface waters, while NO_3^- concentrations were higher in the subsurface in five of seven sites (Table 3). The degree of connectivity between surface waters and subsurface waters in the hyporheic zone plays a key role in stream inorganic N dynamics. While the importance of SW-GW connectivity has been nicely shown in previous studies (e.g. Jones 1995, Pusch 1996, Valett et al. 1996, Naegeli & Uehlinger 1997, Dahm et al. 1998, Hedin et al. 1998, Dent et al. 2001, Fellows et al. 2001 Thomas et al. 2003, Sheibley et al. 2003, Dahm et al. 2006), this study combines both a cross-system perspective with sampling that provides some insights into the vertical structure of these processes. Vertical sampling in the hyporheic zone has rarely been done (however, see Groffman & Crossey 1999), and the use of multilevel samplers provided the opportunity to take a first-level look at the vertical distribution of inorganic N concentrations.

Hyporheic zone inorganic N retention

The increasing use of stable isotopes and the growing need to mechanistically study NO_3^- removal has yielded a growing body of literature for alternative, microbially-mediated processes. These include dissimilatory (the reduction of N into other inorganic compounds) reduction of nitrate to ammonium (DNRA), chemoautotrophic denitrification, as well as abiotic nitrate removal processes. Because of the rapid appearance of $^{15}NH_4^+$ in solution in the hyporheic wells of many of the study sites, this study focuses on DNRA.

The conversion of NO_3^- to NH_4^+ can occur by two different pathways, assimilatory or dissimilatory (the reduction of N into other inorganic compounds) NO_3^- reduction to NH_4^+ (DNRA) (Tiedje 1988, Burgin & Hamilton 2007). While we have enrichment in the $^{15}NH_4^+$ pool in the wells, we do not know which pathway dominated. Because the $^{15}NH_4^+$ pool accumulated rapidly – within the 24-h sampling period – high rates of intercellular N turnover are necessary to implicate assimilatory reduction. Ammonium enrichment from DNRA activity can be detected hours after nitrate amendment (Koike & Hattori 1978), while benthic

N remineralization rates have been estimated on the order of weeks (e.g. Ashkenas et al. 2004). Most of our streams have enrichment in the $^{15}NH_4^+$ pool and therefore DNRA may play an important role in the hyporheic zone at some of our sites.

While DNRA is not commonly studied in hyporheic zones, significant activity has been documented in other streams (e.g. Kelso et al. 1997, Storey et al. 2004). In fact, DNRA rates were roughly five times greater than assimilation or denitrification rates in a small stream draining Canadian farmland (Storey et al. 2004). An overabundance of electron donors, such as labile organic carbon or reduced sulfur compounds, promotes the DNRA pathway over denitrification (Tiedje et al. 1982, Burgin & Hamilton 2007). The streams in which we measured the highest amount of enriched $^{15}NH_4^+$, RP and BOD, also had the highest surface water DOC : NO_3^- ratios (Table 3).

Streams that had strong SW-GW connectivity tended to have more $^{15}NO_3^-$ (SYC and AFR) present in the subsurface and very little $^{15}NH_4^+$ (Table 2, Fig. 6). Streams that had measurable but less connected hyporheic sediments had higher amounts of $^{15}NH_4^+$ in the subsurface (Fig. 6). This is one of the first studies we are aware of that shows evidence of DNRA in the shallow groundwater environment among multiple sites. The effects from human land use activities that alter stream beds can be large on overall N cycling (Baker et al. 1999, Fellows et al. 2001, Thomas et al. 2003, Grimm et al. 2005). By keeping NH_4^+ in the system instead of having the NO_3^- released through denitrification to N_2 (Burgin & Hamilton 2007), overall effectiveness of nitrate removal may be decreased. This difference in the final product from the uptake and processing of NO_3^- may play a critical role in managing human-altered streams and using N cycling to reduce overall NO_3^- loads.

The accumulation of gaseous byproducts enriched in ^{15}N in the study wells is further evidence of active hyporheic zone NO_3^- processing. Nitrate can be converted to N_2O and N_2 through denitrification (Tiedjie 1988, Burgin & Hamilton 2007). Also, significant N_2O production has been associated with DNRA activity (Welsh et al. 2001, Brunet & Garcia-Gil 1996). This study found $^{15}N_2O$ enrichment in many of our streams with larger levels of enrichment of $^{15}N_2O$ in the subsurface than in the surface water in most of our streams. The sediments of hyporheic zones of these desert streams were actively converting $^{15}NO_3^-$ to $^{15}N_2O$ with higher enrichment levels found in the human-altered stream sediments than in the reference sites (Table 3). The degree to which specific processes such as DNRA and denitrification contribute to the enrichment in $^{15}N_2O$ is not known.

The hyporheic zones of these desert streams are active sites for processing stream NO_3^-. The use of enriched stable isotopes of $^{15}NO_3^-$ allowed inferences to be made about the role of human land use practices on the uptake and processing of this solute. This study showed increasing concentrations of NH_4^+ with decreasing concentrations of NO_3^- in hyporheic zone wells across seven sites and a tendency for increased $^{15}NH_4^+$ mf with lower $^{15}NO_3^-$ mf in the same wells. The rapid appearance of $^{15}NH_4^+$ in some wells over a 24-h injection study was suggestive of active DNRA in the sediments of some sites. Enrichment in $^{15}NH_4^+$ was generally higher overall at the human-altered sites with finer-grained sediments usually showing greater enrichment. The possibility of changing human land use shifting hyporheic zone patterns of NO_3^- uptake and retention by favoring DNRA over denitrification deserves further study.

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