Stream-Aquifer and In-Stream Processes Affecting Nitrogen along a Major River and Contributing Tributary

Abstract

This study assesses the spatio-temporal patterns of water and nutrient mass exchange in a stream-riparian system of a major river and a contributing tributary in an irrigated semi-arid region. Field monitoring is performed along reaches of the Arkansas River (4.7 km) and Timpas Creek (2.0 km) in southeastern Colorado during the 2014 growing season, with water quantity and water quality data collected using a network of in-stream sampling sites and groundwater monitoring wells. Mass balance approaches were used to identify temporal and spatial trends in flow, nitrogen (N), and salinity in stream-aquifer exchange. In the Arkansas River, percent decrease of N concentration along the study reach averaged 36% over the period, with results from a stochastic mass balance simulation indicating a 90% probability that 44% to 50% of $\text{NO}_3\text{-N}$ mass in the study reach (109-124 kg/day/km) was removed by in-stream processes between 1 September and 8 November. Results suggest that contact with organic-rich river bed sediments has a strong impact on N removal. A greater decrease in concentrations of $\text{NO}_3\text{-N}$ along the reach during the low flow period suggests the effect of both in-stream processes and dilution by inflowing groundwater that undergoes denitrification as it flows through the riparian and hyporheic zones into the river. In contrast, N concentration decreases in the smaller Timpas Creek were negligible. Results for the Arkansas River also are in contrast with other large agriculturally-influenced rivers, which have not exhibited capacity to remove N at significant rates. Results provide important insights across spatial and temporal scales and point to the need for investigating nutrient dynamics in large streams draining agriculturally-dominated watersheds.

Keywords: Groundwater-surface water interaction; Nitrate; River Mass Balance; Solute Transport

1. Introduction

Nitrogen (N) often is a primary limiting nutrient in marine and aquatic environments and a requirement in plant and animal nutrition (Novotny 2002, Mueller et al. 1992). Excess amounts of these nutrients from agricultural and urban diffuse pollution cause eutrophication in rivers, lakes, estuaries, and coastal ocean waters leading to toxic algal blooms, oxygen depletion, and loss of aquatic life (Mueller et al. 1992). The primary diffuse agricultural sources of N and P are over-application of industrial fertilizers and manure (Novotny 2002). Nutrients are of particular concern in irrigated agriculture due to fertilizer use increase as the demand for food increases (Monteagudo et al. 2012). For example, irrigated agriculture and food production doubled between 1964 and 1999 in conjunction with a sevenfold increase in the use of N based fertilizer and a threefold increase in P based fertilizer (Tilman 1999).

Many studies have indicated that river riparian areas play a major role in controlling nutrient mass flux from groundwater and wetland systems to the in-stream environment (Duff et al. 2008, Cooper 1990, Peterjohn and Correll 1984, Jacobs and Gilliam 1985). To quantify this control and nutrient mass exchange, water and nutrient fluxes between the aquifer and the stream must be determined. Loading of solute mass from the aquifer to the stream often is estimated by applying the conservation of mass principle to a river reach during a defined time period (Jain, 1996; Jaworski et al., 1992; Teissier et al., 2008). Measurements of solute concentrations and water flow are taken at the upstream and downstream ends of the reach to provide an estimate of in-stream solute mass flux into and out of the reach, with differences attributed to either fluxes that

leave or enter the reach along its length or to changes in dissolved mass stored within the reach (Teissier et al. 2008, Martin and Gates 2014).

For many studies the mass balance approach has involved extensive data collection on many physico-chemical characteristics of the stream reach, including groundwater and surface water contributions, chemical reaction rates in bed sediments and soil media, hyporheic exchange, soil properties, and vegetative cover (Duff et al. 2008, House and Warwick 1998, Teissier et al. 2008). Many of these studies, however, are limited in their spatial scales. Studies performed on large, wide rivers (20 to 100 meters wide) are performed over long distances, typically tens of kilometers, but lack detailed examination of groundwater-surface water exchange, relying on existing stream gaging infrastructure for sampling locations and data (House and Warwick 1998, Teissier et al. 2008). In contrast, studies performed on smaller streams typically are confined to short reaches. Duff et al. (2008) collected detailed surface and groundwater data in three stream reaches about 1.0 km long, ranging in width from 4 to 11 meters and discharge rates between 0.14 m³/sec and 0.41 m³/sec, but did not expand their findings to a larger river. Published attempts to quantify nutrient mass exchange and associated groundwater-surface water interactions in large, wide rivers are lacking, as well as those comparing exchange water and nutrient dynamics between large and small streams within a given region.

This study seeks to monitor and quantify in-stream N loadings and concentrations, groundwater N loadings, and associated groundwater-surface water interactions within a major river and a contributing tributary in a semi-arid irrigated agricultural region. The Lower Arkansas River Valley (LARV) in southeastern Colorado is an alluvial, irrigated valley that suffers from high concentrations of nutrients and salts in the coupled groundwater-surface water system (Gates et al. 2009) due in large part to irrigation and drainage practices. Previous

regional-scale ($> 500 \text{ km}^2$) data collection and flow and contaminant transport modeling efforts (Gates et al. 2009, Bailey et al., 2015b) have indicated that riparian areas play a major role in controlling nutrient mass flux from the aquifer to the Arkansas River and its tributaries. However, the water and nutrient mass exchanges within the riparian-stream system have not yet been quantified. To accomplish this, two study reaches were selected and instrumented to be monitored through an entire growing season (April-November 2014). The study focuses on a 4.7 km reach of the main stem of the Arkansas River (average discharge = $12.3 \text{ m}^3/\text{s}$) and a 2.0 km reach of a major tributary, Timpas Creek (average flow = $1.7 \text{ m}^3/\text{s}$) to compare and contrast channel and riparian processes in streams of different scale. The field monitoring network consists of in-stream sampling sites and groundwater observation wells, with collected data used to quantify groundwater-surface interactions and a nitrate ($\text{NO}_3\text{-N}$) mass balance. A $\text{NO}_3\text{-N}$ mass balance for the Arkansas River study reach is performed to quantify the net daily loading of $\text{NO}_3\text{-N}$ mass to/from the study reach of the Arkansas River, with a stochastic simulation approach used to account for uncertainty in the input variables and parameters.

2. Materials and Methods

This section provides a description of the two reach-scale studies and the methods and instrumentation used to collect physical, hydrologic, and water quality data and to perform a nitrate ($\text{NO}_3\text{-N}$) mass balance for the Arkansas River reach.

2.1 Study Reaches

The location of the two study reaches within the so-called upstream study region (USR) of the LARV (Morway et al 2013) is shown in Figure 1A, with a detailed map of the Arkansas River reach shown in Figure 1B and a detailed map of the Timpas Creek reach shown in Figure

1C. The USR is so designated since it lies upstream of John Martin Reservoir, in contrast to a downstream study region (DSR) referenced in Section 3.2.3. The Arkansas River study reach is 4.7 km long, has an average width of 75 m, and is surrounded by a mixture of irrigated fields, fallowed fields, and pasture with moderate riparian vegetation composed primarily of cottonwood, willow, tamarisk, and a variety of grasses. Soils along this reach are mostly sand, loamy sand, and silty clay loam. Twenty-three years (1992-2014) of streamflow data for this site, which were collected by the United States Geological Survey (USGS) and the Colorado Division of Water Resources (CDWR), show an average discharge of 12.3 m³/s and a peak discharge of 233 m³/s. The Timpas Creek study reach (Figure 1C) is 2.0 km long, has an average width of 7.0 m, and is surrounded by fallowed fields, pasture, and irrigated fields. Riparian vegetation is present at the southern end of the reach but is sparse at the middle and northern end of the reach. Streamflow data collected at this location since 1965 by the USGS indicate an average discharge of 1.7 m³/s. The area is prone to flash floods during storm events of high intensity, with an estimated peak flow of 606 m³/s. One significant irrigation return flow surface ditch drains into the Timpas Creek study reach.

2.2 Characterizing Riparian-Stream Water Transfer

Groundwater table elevations in the riparian area were measured continuously in groundwater monitoring wells throughout the study period. Wells were positioned on both banks along three transects across the Arkansas River (ARKA, ARKB, ARKC) and along two transects across Timpas Creek (TIMA and TIMB), for a total of 20 wells. Monitoring wells were installed using a GiddingsTM auger drill mounted on a field truck or, for locations along Timpas Creek inaccessible by vehicle, by a hand auger. Each well was completed by placing a slotted 2-inch PVC pipe into the borehole, pouring sand down the annular space around the PVC as a filter

117 pack, placing 1-2 ft of bentonite near ground surface, and then using a bailer to develop the well.
118 Completion depths varied from 1.5 to 3.5 m depending on the study reach and location. Each
119 well was equipped with an Onset HOBO™ water level logger hanging from a static string. Water
120 levels were recorded every 15 minutes. In addition to water level loggers in the wells, one was
121 placed in the channel at each cross section on either the right or left bank. The choice of right or
122 left bank was determined by ease of access and the need to insure that the logger would remain
123 submerged throughout the growing season.

124 Stream discharge was measured at the upstream (ARKU and TIMU) and downstream
125 (ARKD and TIMD) ends of each study reach (see Figure 1) at continuous monitoring stations
126 using stage-discharge relationships. Upstream monitoring stations were paired with existing
127 USGS and CDWR streamflow gages at the Arkansas River and Timpas Creek sites, respectively.
128 To provide continuous monitoring at the downstream end of each reach, both reaches were
129 instrumented with an In-Situ AquaTroll™ 200 Data Logger (AT) to measure water stage. A total
130 of 6 and 8 discharge measurements were taken at the Arkansas River and Timpas Creek
131 downstream sites, respectively, using an Acoustic Doppler Velocimeter (ADV) periodically
132 throughout the study period to develop stage-discharge relationships. The stage-discharge
133 relationship at ARKD was divided into a high and low discharge rating curve with statistically
134 significant R^2 values of 0.98 and 0.99, respectively. The relationship at TIMD had a statistically
135 significant R^2 of 0.99. Due to high-water safety concerns, measurements were made in the
136 Arkansas River for discharges only below $13 \text{ m}^3/\text{s}$, which is approximately the average discharge
137 rate of the river reach. If the discharge rate was higher than $13 \text{ m}^3/\text{s}$ and if a steady flow
138 condition could be determined, then the discharge rate was assumed equal to the rate measured at
139 the upstream end. For Timpas Creek, a stage-discharge relationship also was developed for the

irrigation return flow ditch using a HOBO water level logger and periodic discharge measurements.

Water volume stored in the channel reach was calculated using a method similar to the USGS stage-storage method (Carter and Godfrey 1960). Relationships between stage, h , and channel top width, T_w , were developed for five surveyed channel cross sections along the Arkansas River reach and four cross sections along the Timpas Creek reach. A simple prism and wedge geometry was assumed to describe each channel subreach between the cross sections (Figure 2). Water storage in the riverbed and riparian zone as hyporheic flow is not included due to the strong hydraulic connection between the stream reach and the groundwater system and the associated rapid response of groundwater levels to river stage. To develop the h - T_w relationships, the channel cross section geometry was surveyed using a GNSS TopconTM GPS RTK unit, with the distance from left bank to right bank calculated at 0.1 m intervals of h for each cross section. The five cross sections are shown in Figure 1B. The generated h - T_w data points were plotted and divided into groups that could be modeled with up to a third-order regression equation. Daily values for storage change within the channel reach were calculated using the following steps:

- 1) Estimate the change in flow area, ΔA , for each cross section over the 24 hours using the channel T_w values estimated from the h - T_w relationship:

$$\Delta A = \frac{1}{2} (T_{w_a} + T_{w_b}) \Delta h \quad (1)$$

where T_{w_a} and T_{w_b} are the channel top widths at the cross sections estimated from measured h at the cross section at the beginning and end of the day, respectively, and Δh is the change in measured h over the day;

- 2) Estimate the daily change in stored volume within the subreach, ΔV_{sr} by multiplying the average ΔA over each subreach by the distance L between the upstream and downstream cross sections to define a prism:

$$\Delta V_{sr} = \frac{1}{2}(\Delta A_1 + \Delta A_2)L \quad (2)$$

where ΔA_1 and ΔA_2 are the daily change in flow area at the upstream and downstream cross sections of the channel subreach, respectively; and

- 3) Calculate the total daily change in storage, ΔV , along the entire stream reach by summing the ΔV_{sr} values for each subreach.

Assuming free surface evaporation and overland flow to be negligible, with the latter determined by period walk-throughs along both banks of each study reach during the study period, daily groundwater inflow Q_{GW} to the study reach along the Arkansas River was estimated using the following water balance:

$$Q_{GW} = \Delta V - Q_{US} + Q_{DS} \quad (3)$$

where Q_{US} is the average daily discharge at the upstream monitoring station and Q_{DS} is the average daily discharge at the downstream monitoring station. In Equation (3), positive values of Q_{GW} represent groundwater discharge to the reach, whereas negative values indicate seepage from the reach to groundwater. The sign of these values, i.e. the direction of groundwater flow, also is verified by comparing groundwater head levels in the monitoring well transects to stream stage. Average values of ΔV were found to be equivalent to 19% of the difference between Q_{US} and Q_{DS} , indicating that storage change within the Arkansas River reach over the study period has a significant effect on calculations of Q_{GW} .

For the reach along Timpas Creek, Q_{GW} was calculated as:

183
$$Q_{GW} = \Delta V - Q_{US} + Q_{DS} - Q_{dm} \quad (4)$$

184 where Q_{dm} is the average daily inflow from the surface drain. Average values of ΔV along
185 Timpas Creek were 0.75% of the difference between Q_{US} and Q_{DS} , thus contributing a negligible
186 amount to the overall water balance calculations. Relative contributions of Q_{dm} were
187 approximately 10%.

188 **2.3 Characterizing In-Stream and Riparian-Stream Nitrogen Dynamics**

189 **2.3.1 Water Quality Monitoring**

190 Throughout the study period water samples were collected at the upstream and downstream
191 locations of each study reach at approximately two week intervals (between June 11th and
192 November 8th) and measured for total N, NO₂-N, NH₄-N, NO₃-N, and all major salt ions. In
193 addition, the ATS logged measurements of specific conductance and temperature at 15 minute
194 intervals. Samples also were collected from the surface drain on Timpas Creek approximately
195 every two weeks. Surface water samples were collected in 1.0 L plastic bottles. Samples for
196 analysis of total N were taken by shaking the completely full (evacuated of air) 1.0 L collection
197 bottle to suspend all sediment and then decanting into a 0.25 L sample bottle. Dissolved samples
198 for NO₂-N, NH₄-N, NO₃-N, and dissolved salts were filtered in the field through a 0.45 µm filter
199 and into another 0.25 L sample bottle. Filters were changed for each sample and all sampling
200 equipment was cleaned with acid, phosphate free detergent, and two rinses with distilled water
201 between sampling sites. All water samples were stored on ice in coolers or refrigerated with a
202 maximum hold time of three days before being sent for analysis to Ward Laboratories, Inc. in
203 Kearney, Nebraska. Samples were analyzed using standard methods (e.g. USEPA 1983, Method
204 353.2 for NO₃-N).

Groundwater was sampled from the network of monitoring wells along both study reaches twice during the study period, once in June and again in October. Groundwater samples were collected at each monitoring well using a low flow QED Sample ProTM bladder pump, dual 0.635 cm (0.25 in) diameter polyethylene tubing, and a flow through cell. The pump was set to a flow rate between 0.10 to 0.20 L/min using a CO₂ power pack to minimize the disturbance in the flow through cell. Indicator properties of pH, electrical conductivity (EC, as specific conductance at 25 °C), temperature, dissolved oxygen (DO), and oxidation reduction potential (ORP) were monitored at approximately two minute intervals using an YSI 600QS Multiparameter Sampling System (YSI), which was routinely calibrated with standard solutions. The extracted water was considered representative of the surrounding groundwater when four parameters had stabilized for two consecutive readings: +/- 0.1 for pH, +/- 3% for EC, +/- 10% for DO, and +/- 10 mV for ORP. After stabilization was reached and values were recorded, the low flow cell was removed from the end of the pump tube and the pump rate was increased to between 0.20 and 0.30 L/min for sample collection.

In-stream pore water samples were collected at each well cross section from depths of approximately 0.3 meters on Timpas Creek and 1.0 meter on the Arkansas River. Samples were collected from below the channel bed using an MHE Products PushPointTM sampler. The PushPoint sampler consisted of a long hollow metal tube with eight, 1/8 inch slots at the bottom three centimeters ending in a point. A slender metal rod was held inside this tube when inserting the sampler into the bed sediments to provide structural support. At the desired depth, the interior metal rod was removed and a silicone pump tubing was attached to the top of the hollow tube. A peristaltic pump was then used to pull water through the perforations and out the top. At each cross section, pore water samples were taken from three evenly spaced locations across the

channel on Timpas Creek and the Arkansas River. Pore water samples were not collected from the Arkansas River in June due to high flows.

For both groundwater and pore water sampling, samples for total N were taken by pumping directly into the 0.25 L laboratory-provided plastic sample bottle while dissolved samples for NO₂-N, NH₄-N, NO₃-N, and dissolved salts were filtered through a 0.45 µm filter and into another 0.25 L sample bottle.

2.3.2 Arkansas River Nitrate Mass Balance

A mass balance approach was used to estimate the net daily loading of NO₃-N mass (M_{NO_3}) to/from the study reach of the Arkansas River. The mass balance equation is given as:

$$M_{NO_3} = \Delta V \cdot C_{NO_3,avg} - Q_{US} \cdot C_{NO_3,US} + Q_{DS} \cdot C_{NO_3,DS} \quad (5)$$

where $C_{NO_3,US}$ is the daily average concentration of NO₃-N at the upstream end of the study reach, $C_{NO_3,DS}$ the daily average at the downstream end, and $C_{NO_3,avg}$ the daily average concentration of NO₃-N along the length of the study reach, assumed to be the average of $C_{NO_3,US}$ and $C_{NO_3,DS}$. M_{NO_3} therefore accounts for any NO₃-N mass not included in the river flow into/out of the reach and in-reach storage changes, such as contributions from groundwater ($M_{NO_3,GW}$) and in-stream processes (e.g. sorption to bed sediments, denitrification, vegetation biological uptake) ($M_{NO_3,in-stream}$). Thus, $M_{NO_3} = M_{NO_3,GW} + M_{NO_3,in-stream}$.

C_{NO_3-N} at the upstream and downstream ends of the reach were estimated using relationships between EC (µS/cm) and NO₃-N (mg/L). This procedure has been used in other water quality studies to determine seasonal trends and storm event concentrations of nutrients, such as Iwanyshyn et al. (2009) in the Bow River near Calgary, Canada, and Gali et al. (2012) in the Hickory Grove Lake Watershed in Iowa. Medium to strong positive relationships between EC

and $\text{NO}_3\text{-N}$ were found in both studies. Simultaneous measurements of EC and $C_{\text{NO}_3\text{-N}}$ at the ARKU and ARKD monitoring stations were analyzed using least squares linear regression to estimate the statistically significant ($p < 0.05$) relationships shown in Figure 3. A squared residual analysis was used to determine outliers, with values having residuals > 2 standard deviations from the mean removed. Removal of one outlier value from each dataset resulted in a strong positive relationship at ARKU and a moderate positive relationship at ARKD with R^2 values of 0.91 and 0.65, respectively. These two relationships were used to estimate $C_{\text{NO}_3,US}$ and $C_{\text{NO}_3,DS}$ from values of EC measured at 15-min intervals at the ARKU and ARKD monitoring stations. This analysis was not performed on the Timpas Creek study reach due to a major flood event on July 13 2014 that prevented a continuous record of EC. The flood displaced the downstream AT installation, causing a significant gap in the TIMD data while equipment was repaired and replaced.

The portion of M_{NO_3} attributable to groundwater-surface water exchange, $M_{\text{NO}_3,GW}$, was estimated using the product of daily values of Q_{GW} (Equation 4) and $C_{\text{NO}_3\text{-N}}$ measured in the discharge or seepage water. During periods of groundwater discharge to the river, $C_{\text{NO}_3\text{-N}}$ observed in the groundwater samples from the monitoring wells in the riparian zone was used. These values ranged from < 0.1 mg/L to 1.8 mg/L for two samples at each of the 12 wells, with a mean of 0.31 mg/L. These concentrations are about one order of magnitude lower than the average concentration in the groundwater aquifer of the surrounding USR (Bailey et al. 2015a, Gates et al. 2016) and indicate that denitrification likely occurs in the shallow groundwater within the riparian corridor. However, since Q_{GW} is estimated for the entire length of the study reach, a composite value of $C_{\text{NO}_3\text{-N}}$ is required. For completeness of analysis and to determine the

effect of groundwater C_{NO_3-N} on mass balance results, two values (0.1 mg/L, 0.5 mg/L) spanning the range of measured values were assigned to the groundwater. During periods of river seepage to groundwater, (i.e. negative values of Q_{GW}), C_{NO_3-N} is assumed to equal the average of the upstream ($C_{NO_3,US}$) and downstream ($C_{NO_3,DS}$) values.

2.3.3 Nitrate Mass Balance Uncertainty Analysis

The values assigned to the variables in the NO_3-N mass balance of Equation (5) are not known with exactness, and hence an uncertainty analysis was performed to determine the possible range of values of M_{NO_3} . Three types of ambiguity were quantified for each of the input variables in Equation (5): 1) Error in measuring values; 2) Error in using the measured values to estimate the values of other essential variables, and 3) Error associated with non-continuous measurements in a system with wide spatial and temporal variations. These errors are captured in a stochastic version of Equation (5) solved using a Monte Carlo simulation, with each variable in Equation (5) treated as a random variable with an associated Probability Distribution Function (PDF).

The @RISK (version 7.5) software program was used to estimate the PDFs for parameters associated with discharge and NO_3-N concentrations and to produce random values (RVs) from those PDFs. The PDFs were defined by statistical characteristics of field data, by reference to instrumentation documentation, or by best judgement, with the latter applying only to stage-top width relationships for storage changes in the study reach. The @RISK software uses the highest ranking distributions for combined chi-square, Kolmogorov-Smirnov, and Anderson-Darling goodness-of-fit tests as well as Monte Carlo simulation to produce RVs of each distributed parameter (Palisade Corporation 2016). Each set of associated RVs for the parameters was used to calculate an RV for the variables in Equation (5), which was then solved for an RV of the

outputs M_{NO_3} and $M_{NO_3, in-stream}$. Finally, an estimate of the daily, length averaged NO_3 -N load (kg/day)/km removed due to in-stream processes over the sample period was obtained as the average of the calculated random $M_{NO_3, in-stream}$ values. The stochastic simulation is performed only between the time period of 1 September 2014 to November 8, during which time continuous measurements were available for all variables in Equation (5).

The degree of error in EC values was taken directly from the AquaTroll 200TM (AT) and Onset HOBOTM (HOBOTM) water level logger instrumentation documentation. The documentation for the AT stated that the EC detection (as specific conductance at 25°C) was accurate to within -0.5 and +0.5% of the reading plus 1 $\mu S/cm$ when reading less than 80,000 $\mu S/cm$ (In-Situ 2016). The instrument detection error was therefore assumed to be characterized by a normal distribution with fifth and 95th quantiles at -0.5 and +0.5%, respectively, plus the requisite 1 $\mu S/cm$. An RV was then obtained for EC from this distribution to be used in the EC and NO_3 -N regression equation.

The river stage errors for the ARKU and ARKD stations were assumed to be characterized by a normal distribution with fifth and 95th quantiles at -0.1 and +0.1% of the reading, also based on the AT instrumentation documentation (In-Situ 2016). An RV was then obtained from that distribution to use in the stage-top width relationship at ARKU and ARKD as well as the stage-discharge relationship at ARKD. The documentation for the HOBOTM water level logger stated that the maximum error in water level accuracy was within -0.1 and +0.1% of the reading (Onset 2016). The instrument detection error was therefore assumed to be characterized by a normal distribution with fifth and 95th quantiles at -0.1 and +0.1%, respectively. An RV was then obtained from that distribution to use in the stage-top width relationships at the ARKA, ARKB, and ARKC cross sections. The final sources of measurement error were at ARKU and ARKD

where discharge was reported based on a stage-discharge relationship developed by the CDWR or was calculated from the stage-discharge relationship developed from field data collected in this study, respectively. The discharge at ARKU was assumed to be characterized by a normal distribution with the 2.5th and 97.5th quantiles at -10.0 and +10.0% based on uncertainty found in discharge measurements at gaging stations by Turnipseed and Sauer (2010). An assessment of conditions at ARKD led to a similar supposition that flows calculated using the stage-discharge relationship developed in this study were subject to error of -15% and +15% at the 2.5th and 97.5th quantiles of a normal distribution.

The uncertainty associated with the groundwater C_{NO_3-N} was also assigned a distribution based on the variability in C_{NO_3-N} in the 12 wells. As mentioned previously, these values ranged from < 0.1 mg/L to 1.8 mg/L, with a mean of 0.31 mg/L and a standard deviation of 0.41 mg/L. These values were used to define a normal distribution for groundwater C_{NO_3-N} . An RV was then obtained from that distribution to use in the calculation of NO₃-N loading contribution to the river during periods of groundwater discharge to the river.

Error in regression relationships was accounted for through residuals analyses of the EC and NO₃-N concentration and stage-top width relationships. Values of residual error were estimated as the difference between laboratory determined NO₃-N concentrations, manual discharge measurements, and estimations of top width and the values predicted by their respective regression equations. The mean and standard deviation of each relationship's residuals were then used to define an assumed normal distribution of the residuals for each regression.

Uncertainty in the variation of geometry between surveyed cross sections was accounted for by assuming a common degree of uncertainty for each constant in the stage-top width relationship. In other stochastic mass balance studies a common form of stage-top width

regression equation is used at all surveyed cross sections, the only differences being the constants in those equations which were modeled as power functions of flow depth by Gates and Al-Zahrani (1996) and by Mueller Price and Gates (2008). By performing statistical analyses on the constants, a distribution can be determined that represents the spatial and temporal variability in the size and shape of the cross sectional geometry along a section of the river. In the present study, however, the stage-top width relationship equations were not similar and only a few surveyed cross sections were available; thus, a more subjective approach was taken. Coefficient of variation values reported for fitted distributions of constants in power functions of T_w versus h developed by Gates and Al-Zahrani (1996) for several rivers, along with observations of variability in channel geometry along the Arkansas River reach, guided the description of error in the constants of the $h - T_w$ relationships developed for use in this study. The error associated with spatial and temporal variability was accounted for by assuming that each constant in these relationships could be characterized by a normal distribution with 5th and 95th quantiles at -50.0% and +50.0%, respectively.

3. Results and Discussion

3.1 Groundwater-Surface Water Interactions

3.1.1 Arkansas River Study Reach

Stream discharge (m^3/s) at the upstream and downstream monitoring stations are shown in Figure 4 for both the Arkansas River study reach and the Timpas Creek study reach during the April 1 to November 8 2014 study period. Q_{DS} is less than Q_{US} within the Arkansas River study reach for the vast majority of the study period (Figure 4A), particularly during the spring and early summer snowmelt runoff period, with daily results for Q_{GW} (Figure 5) indicating that the

Arkansas River is a losing stream within the 4.7 km study reach. In Figure 5, positive values of Q_{GW} represent groundwater discharge to the river and negative values represent seepage from the river. These conditions for the study reach are different than those found from regional-scale groundwater flow modeling results presented in Morway et al. (2013) which show the USR river reach, which encompasses the study reach, to be a gaining segment. However, this difference likely is due to the scale of analysis of Morway et al. (2013), which used large (250 m) finite difference grid cells to characterize the groundwater flow patterns and the interaction between the aquifer and the Arkansas River. Their study also did not have monitoring points along the riparian corridor for model testing, and thus while able to replicate the general regional groundwater flow patterns, was not able to capture the local scale processes observed in this study.

The study period has been divided into four distinct periods for analyzing groundwater-surface water interactions (Figure 5): (1) Early irrigation season (coinciding with snowmelt runoff), (2) Mid irrigation season (corresponding with flood events), (3) Late irrigation season, and 4) End of irrigation season. Available data during Period 1 shows diminishing groundwater discharge to the river. During the high-flow Period 2, the exchange between the groundwater and river reverses direction and an average of $3.32 \times 10^5 \text{ m}^3/\text{day}$ ($0.82 \text{ m}^3/\text{s}$ per km) seeps from the river to the groundwater, which decreases to a smaller yet consistent seepage during Period 3, and finally a reoccurrence of groundwater discharge to the river occurs in Period 4 during the latter stages of the irrigation season. Groundwater discharge during this latter period is expected due to the lag of irrigation return flows to the river. Excluding the flooding events when Q_{DS} could not be determined accurately, the net river seepage to groundwater over the entire study period was approximately $1.3 \times 10^7 \text{ m}^3$, or $0.22 \text{ m}^3/\text{s}$ per km of the study reach.

The spatial and temporal patterns of hydrological interactions that combine to produce the time series of stream discharge and groundwater-surface water exchange flows in Figure 5 are presented in Figures 6 and 7. Figure 6A shows the general direction of groundwater flow based on comparison of continuous water level recording in the monitoring wells and in the Arkansas River. The length of the arrows indicates the magnitude of the groundwater hydraulic gradient. As seen in the figure, groundwater flows from west to east across the cross section ARKA, from groundwater to the river at cross section ARKB, and from south to north at cross section ARKC. Groundwater hydraulic gradients for each cross section are shown in Figure 7, with 15-minute gradient values computed from comparing water table elevation at pairs of monitoring wells. For example, the West time series plot for ARKA (Figure 7A) is computed from the two wells on the west side of the Arkansas River, with positive values indicating a gradient towards the river and negative values indicating a gradient away from the river. Whereas ARKA has consistent flow towards the river on the western side and away from the river on the eastern side, the other two cross sections (Figure 7B,C) have a complex pattern that often interchanges between flowing to/from the river. For ARKB (Figure 7B), river seepage occurred during the early snowmelt season (May 2014), but then groundwater flows to the river from both sides after July 1, with near-constant gradients during July-September.

3.1.2 Timpas Creek Study Reach

The streamflow hydrograph for Timpas Creek (Figure 4B) is shown using a log-scale since the flows during the flood (July 13 2014) are so much higher than the flows during the rest of the year. The daily flow average on July 13 reached 68 m³/s, with peak flow estimated to be 195 m³/s, corresponding to a 14-year event. The flow in the surface drain also is shown in Figure 4, and contributes minimally to the overall water balance, with flow rates generally below 0.5 m³/s.

Timpas Creek is not directly affected by the spring snowmelt and therefore exhibits no peak in the hydrograph in May (Figure 5B). Compared to the Arkansas River study reach, the interactions between groundwater and surface water are much less dynamic within the Timpas Creek study reach. Stream discharge measurements (Figure 4B) and water balance calculations (Figure 5B) indicate that the stream mainly is gaining groundwater during the study period, with a few short periods of losing water in the latter months (September-November) of the study period (Figure 5B). Over the study period, the net groundwater discharge was approximately $1.3 \times 10^6 \text{ m}^3$, or $0.05 \text{ m}^3/\text{s}$ per km of the study reach. These values are approximately one order of magnitude less than the net seepage rates for the Arkansas River study reach.

Groundwater discharge to the stream, however, seems to occur only in the southern half of the study reach (see flow patterns in Figure 6B), with enough groundwater discharge to overcome the stream seepage to groundwater that occurs in the northern section of the reach. This pattern is seen in the time series of groundwater hydraulic head in the monitoring wells in cross section A (TIMPA) and B (TIMPB) shown in Figure 8. For TIMPA (Figure 8A), the water table on the east side of the stream is as much as 6-7 m higher than the stream stage, providing a significant gradient that induces groundwater discharging to the stream. However, the stream stage is higher than the water table on the west side, indicating stream seepage. For TIMPB, groundwater is lower than the stream stage on both sides of the stream (Figure 8), although gradients are very small.

3.2 NO₃-N Mass Exchange and Fate

3.2.1 Arkansas River Study Reach

Results are shown based on in-stream water quality samples taken at the upstream and downstream end of both study reaches. A times series of stream water chloride (Cl), total

dissolved solids (TDS), total N, and C_{NO_3-N} at the upstream and downstream end in the Arkansas River 4.7-km study reach is shown in Figure 9 for the ten sampling events between June 10 2014 and November 8 2014.

Whereas differences between upstream and downstream concentration for Cl and TDS are small (Figure 9A,B), with a maximum percent decrease for Cl of 15% and for TDS of 23%, with downstream concentrations higher than upstream concentrations for several sampling events (e.g. August 4), differences for Total N and NO_3-N are quite large, particularly after the middle of August. This is shown quantitatively in Figure 10A, which shows the percent decrease from upstream to downstream end for each of the four species at the 10 sampling events. For total N, the average percent decrease on and after August 21 (sampling events 5-10) is 43%, and for NO_3-N the average percent decrease is 48%. For Cl and TDS, the corresponding average percent decrease is 7% and 10%, respectively. For total N and NO_3-N , the maximum percent decrease occurs on September 21 2014 with values of 58% (3.3 mg/L to 1.4 mg/L) and 64% (2.2 mg/L to 0.8 mg/L), respectively.

The large discrepancy in in-stream concentration between Cl, a conservative solute, and N, indicate that the percent decrease in total N and NO_3-N is due to in-stream chemical processes rather than mixing with incoming groundwater. Furthermore, as shown by the Q_{GW} results in Figure 5 and the groundwater hydraulic gradients in Figure 7, groundwater discharges to the reach mainly at the beginning (April) and end (October-November) of the study period. This is seen in the NO_3-N mass balance results for the study reach (Figure 11A), which shows the total daily unmeasured bulk M_{NO_3} (solid line) and daily load from groundwater $M_{NO_3, GW}$, with positive indicating NO_3-N mass loading from the aquifer to the stream and negative indicating loading from the stream to the aquifer. Using groundwater C_{NO_3-N} of 0.1 mg/L or 0.5 mg/L causes a

minimal change over the study period, due to the relatively few periods where groundwater discharges to the river along this study reach. However, since groundwater C_{NO_3} measured near the stream is markedly smaller than in-stream C_{NO_3-N} , groundwater discharge would contribute to stream dilution. The difference between M_{NO_3} and $M_{NO_3,GW}$ is assumed to be in-stream chemical processes $M_{NO_3,in-stream}$. On days when river water is seeping to the aquifer, the percent of unmeasured loading due to in-stream processes is estimated to be 77%.

Based on the results of the uncertainty analysis, the average daily value of $M_{NO_3,in-stream}$ during the time period of 1 September 2014 to 8 November 2014 is approximately 116.6 kg/day/km over the 4.7 km study reach. Figure 12 shows the mean value of $M_{NO_3,in-stream}$ and the distribution of estimated values as well as the 5th (124 kg/day/km) and 95th (108.9 kg/day/km) quantiles, with a 90% probability that the true value of $M_{NO_3,in-stream}$ is between these two values.

Figure 11B shows the stochastic mean value and the 90% prediction interval (between the 5th and 9th quantiles) for each day of the 1 September 2014 to 8 November 2014 study period. During the period of low river flow in September and early October the 90% prediction interval is relatively small due to the higher certainty in measuring low flows and cross sectional geometry. During the period of higher flows, however, from mid-October through early November the prediction interval expands due to the higher uncertainty in those same parameters, with the interval being > 150 kg/day/km during the middle week of October. For all but several periods of one or two days, however, the values show little likelihood of being positive, which would indicate addition of NO_3-N to the reach. Taking mean values, of the 78,100 kg of NO_3-N delivered to the study reach through the upstream cross-section during the 68-day period, approximately 42,100 kg (54% of total) was removed from the 4.7 km study

reach, with 5,300 kg (7% of total) removed via seepage to the aquifer and 36,800 kg (47% of total) removed through in-stream processes.

Comparing the temporal trend in N concentration percent decrease (Figure 9A) and stream discharge (Figure 4A) suggests that N mass is removed from the river water more effectively at lower discharge rates. This is shown in Figure 13, which shows the percent decrease in total N (Figure 13A) and C_{NO_3-N} (Figure 13B) as a function of Arkansas River discharge (m^3/sec). For NO_3-N , the highest percent decrease from upstream to downstream (64%) occurs at the lowest discharge rate ($2.12 m^3/sec$), with reduction in N concentration decreasing with increasing discharge rate. Though some dilution from groundwater recharge is occurring during the lower flow period, results suggest that more N is removed at lower discharge rates, likely due to the lower river stage enabling more of the water to interact with river bed sediments and undergo denitrification or vegetation uptake (McMahon and Böhlke, 1996; Puckett et al., 2008). The river stage during June 10 to August 4 averaged 0.84 m, which decreases to an average of 0.40 m during August 21 to November 8. Puckett et al. (2008) also suggested that a complex exchange due to coarse sediments and varying hydraulic gradients in the channel can create zones of denitrification in the river bed.

The influence of bed sediments in decreasing NO_3-N is further clarified by analyzing the pore water sampling results. For the October 4 sampling event (river discharge rates were too high in June 11 to allow sampling), average C_{NO_3-N} in pore water samples at the ARKA, ARKB, and ARKC cross sections was only 0.37 mg/L (high of 1.4 mg/L), with 8 of the 11 samples having undetectable NO_3-N , compared to the 1.4 mg/L average in the river water column and the 0.64 mg/L concentration in the riparian groundwater, suggesting denitrification in the bed sediments. This is in contrast to Cl in the pore water, which had an average (39 mg/L) higher

than the in the river water column (25-28 mg/L). For this time period the bed sediment had a total organic carbon (TOC) of 0.40%, averaged over 10 samples in the study reach, indicating the presence of an electron donor for denitrification to proceed. Dissolved organic carbon (DOC), which can more readily be used as an electron donor and thereby serve as a stronger indicator for denitrification, was not measured in this study.

3.2.2 Timpas Creek Study Reach

Similar to hydrologic results, water quality results for Timpas Creek are much different than observed for the Arkansas River. The magnitude of percent decrease in total N and $\text{NO}_3\text{-N}$ from the upstream end of the study reach to the downstream end was similar to Cl and TDS (Figure 9B). Average percent decrease over the 9 sampling events for total N and $\text{NO}_3\text{-N}$ was 2% and 4%, respectively, compared to 0% and 2% for Cl and TDS, respectively. The maximum decrease in $C_{\text{NO}_3\text{-N}}$ (31%) within the study reach occurred on August 4 2014, but Cl and TDS also decreased 20% and 17% from upstream end to downstream end.

With the percent of $C_{\text{NO}_3\text{-N}}$ decrease along the reach very low and similar in magnitude to conservative salts, results suggest that significant in-stream chemical processes do not effect N in Timpas Creek. When comparing $\text{NO}_3\text{-N}$ percent decrease to stream discharge, there is no observable trend for 8 of the sampling events (Figure 13C). If the August 4 sampling event is included (3.4 m^3/sec flow rate, 31% decrease of $C_{\text{NO}_3\text{-N}}$), a slight trend is observed ($R^2 = 0.55$), although this event coincides with 20% and 17% decrease in Cl and TDS, respectively. Conversely, the maximum percent decrease for $C_{\text{NO}_3\text{-N}}$ in the Arkansas River, 64%, occurred when percent decrease of Cl and TDS was 0% and 7%, signifying that in-stream chemical processes governed the fate of $\text{NO}_3\text{-N}$ for that time period.

3.2.3 Comparison to Regional Patterns in the LARV

Results from the Arkansas River study reach now are compared with results from data collected at the regional scale during the past decade. Figure 14 displays results of monitoring in-stream C_{NO_3-N} (mg/L) along two reaches of the Arkansas River: a 93 km reach upstream of John Martin Reservoir (Upstream Study Region) and a 74 km reach downstream of John Martin Reservoir (Downstream Study Region) (see Figure 1). Data were collected in the USR between June 20 2006 and July 12 2011, and data were collected in the DSR between July 28 2003 and August 16 2012. 14A displays C_{NO_3-N} at the upstream and downstream ends of the USR, demonstrating that C_{NO_3-N} at the downstream end generally is lower than at the upstream end. The percent decrease in C_{NO_3-N} between the upstream and downstream ends is shown in 14C, with data divided between low flow (September – April) and high flow (May – August) periods. The data reveal a pattern similar to that in the results from the 4.7 km Arkansas River study reach (see Figure 10A). Decrease in C_{NO_3-N} consistently occurs during low flow (23% average) with a mixture of increase and decrease occurring during high flow. For these same sampling periods, the in-stream TDS concentration (mg/L) increased on average by 70% from the upstream to downstream end, signifying that decrease in C_{NO_3-N} occurred due to biochemical processes.

By contrast, similar plots of data over 2003 – 2012 for a 74 km reach of the river along the DSR are shown in 14B and 14D. Here, where hydrological conditions and biochemical characteristics in the riparian and hyporheic zones affecting denitrification are indicated to be significantly different than in the USR, a consistent pattern of increase in C_{NO_3-N} (average of 80%) along the river is revealed.

3.2.4 Comparison with other Streams and Rivers

In regards to the Arkansas River, this study quantifies temporal patterns of groundwater-surface water interactions and stream-aquifer N mass exchange at a scale that typically has not been documented for large rivers. In addition, results of this study contain similarities and significant differences from N mass balance studies performed in other agricultural catchments. For small streams, typically the potential for in-stream NO_3 removal is high, although results can vary from stream to stream. The study performed by Cooper (1990) in a small (width of 1 m, discharge of 1.3 L/sec) headwater stream in New Zealand showed a percentage decrease of NO_3 -N flux along the study reach of up to 91%, although it varied during the year. Two of the five streams studied in Puckett et al. (2008) exhibited significant NO_3 retention, with the other three indicating NO_3 load increases due to large mass input of NO_3 from groundwater discharge. In contrast, and in agreement with results from Timpas Creek in this study, five headwater streams in agricultural streams in east-central Illinois (stream depths between 0.3 and 0.6 m; discharge rates up to 1.8 m^3/sec) had a very low efficiency of NO_3 -N removal (Royer et al., 2004). For Timpas Creek, the lack of $C_{\text{NO}_3-\text{N}}$ decrease along the study reach likely is a result of the channel being incised during high-flow events with consequent removal of organic-rich bed sediment.

Trends observed in water quality results for the Arkansas River study reach, in particular the rate of N concentration decrease along the reach, are not in agreement with the general conclusions from Howarth et al. (1996) and Alexander et al. (2000) regarding stream size and N removal, i.e. that the likelihood of NO_3 -N denitrification and associated decrease in $C_{\text{NO}_3-\text{N}}$ decreases significantly with increasing stream size. Typically, significant N removal rates (10% to 70%) occur in small streams (Birgand et al., 2007), with discharge rates below 2.0 m^3/sec (Royer et al., 2004; Duff et al., 2008; Puckett et al., 2008), whereas significant in-stream N

removal does not occur for large rivers. For example, N concentration percent decrease in the Arkansas River of up to 64% over the 4.7 km reach is in stark contrast to results from studies on two other large rivers, the River Swale in the United Kingdom (55 km reach, $> 50 \text{ m}^3/\text{sec}$ discharge rate) (House and Warwick, 1998) and the Garonne River in southwest France (30 km reach, $> 80 \text{ m}^3/\text{sec}$) (Teissier et al., 2008). For the River Swale, results indicated a 9.7% increase in $C_{\text{NO}_3-\text{N}}$ along the study reach in the spring and a 9.9% decrease in $C_{\text{NO}_3-\text{N}}$ in the autumn. For the Garonne River, $C_{\text{NO}_3-\text{N}}$ actually increased from upstream (mean of 1.32 mg/L) to downstream (mean of 1.61 mg/L) over a 3-day period in July 1999. The authors conclude that N dynamics is driven by variable discharge rather than by biochemical processes (Teissier et al., 2008). Results from the DSR of the LARV (see Figure 14B,D) agree with these studies of other large rivers.

As noted in Section 3.2.1, periods of significant decrease in $C_{\text{NO}_3-\text{N}}$ along the reach during the autumn months coincide with low river discharge rates and river stage. This phenomenon has been noted in other studies (Triska et al. 1993), but always for streams much smaller than the Arkansas River (mean discharge rate of $18.2 \text{ m}^3/\text{sec}$ over the 10 sampling events). The results of this study, therefore, suggest that high removal rates of $\text{NO}_3\text{-N}$ can occur even in large agricultural rivers. Results may be due to the small scale (4.7 km) of the reach analyzed, with study reaches of large rivers in other studies generally $> 25 \text{ km}$. Results in this study perhaps might be different, i.e., be more in agreement with previous studies, if the reach length were extended, and therefore $\text{NO}_3\text{-N}$ reductions found during this study may be less applicable to the entire region. Nevertheless, results indicate that more studies should be undertaken in agriculturally-influenced river systems to provide an improved conceptual model of in-river N fate and transport, with perhaps multiple small reaches ($< 5 \text{ km}$) within a larger river system compared and used to quantify the effects of scale.

4. Summary and Conclusions

Water quantity and quality monitoring throughout the 2014 growing season provided considerable insight into groundwater and surface water interactions and aquifer-stream nutrient mass exchange in the Arkansas River and Timpas Creek of the Lower Arkansas River Valley in southeastern Colorado. Water balance and N mass balance calculations were performed along a 4.7 km reach of the Arkansas River and a 2.0 km reach of Timpas Creek, using a network of in-stream monitoring sites and groundwater monitoring wells along the banks. Water table elevation and estimates of unaccounted-for flow in the Arkansas River suggest that stream water seeps to groundwater during periods of high flow. During the autumn months when river stage decreases, the groundwater hydraulic gradient is reversed and groundwater is discharged to the river. Groundwater discharged to Timpas Creek only on the east side of the upstream end, with creek water seeping to groundwater at all other locations.

Analysis of nitrogen (N) dynamics provides not only valuable comparison between the main stem of a major river and a contributing tributary, but also between streams and rivers of similar size in other watersheds worldwide. Drops in total N concentration along the Arkansas River study reach were on average 36% over ten sampling events between June 11 2014 and November 8 2014, with maximum drop (up to 58%) occurring during the autumn months when discharge is lower (average of 9 m³/sec) and a larger portion of river water has contact with organic-rich bed sediments. Comparison with changes in Chloride concentration along the reach indicates that N decrease is due to in-stream chemical processes (e.g. vegetation uptake, denitrification in river bed sediment) rather than hydrological processes. Overall, mass balance calculations indicate that about half of NO₃-N mass removed during the study period is due to in-

stream processes. In contrast to the Arkansas River, N removal rates in Timpas Creek were negligible, likely due to flood-event flows incising the channel and removing organic matter from the creek bed.

Of utmost importance is the stark contrast between N dynamics in the Arkansas River and in other large rivers. Typically, N dynamics in large rivers are driven by variable discharge (Teissier et al., 2008) with high flows limiting contact between N and streambed/riparian sediment and vegetation, and do not exhibit the ability to remove N at the rate found in this study. Results therefore point to the need for more studies on moderate to large rivers in agricultural watersheds to develop a more comprehensive conceptual model of in-stream N fate and transport. The information derived from this study provides knowledge of hydro-chemical processes on small to medium spatial and temporal scales and provides a valuable contrast in controlling processes between main-stem and tributary riparian areas. This project also provides a database for future small to medium scale groundwater-surface water modeling efforts in the Lower Arkansas River Valley to further elucidate processes that govern nutrient mass transport in the riparian-stream system, with implications for regional-scale processes.

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Figure Captions

Figure 1. (A) Lower Arkansas River Valley in southeastern Colorado, showing the locations of the Upstream Study Region (USR) and the Downstream Study Region (DSR); within the USR, short reaches along (B) the Arkansas River (4.7 km) and (C) Timpas Creek (2.0 km) are the focus of this study. Red crosses indicate stream gaging locations, and mark the upstream and downstream locations of each study reach; white circles indicate locations of groundwater monitoring wells in the riparian areas. The surveyed cross sections for the Arkansas River study reach are also shown in (B).

Figure 2. Diagram for water volume storage calculations within a sub-reach of the Arkansas River and Timpas Creek reaches.

Figure 3. The relationship between EC and C_{NO_3-N} at (A) the upstream end of the Arkansas River study reach ARKU and at (B) the downstream end ARKD.

Figure 4. Flow comparison of stream discharge at the upstream and downstream ends of the (A) Arkansas River study reach and the (B) Timpas Creek study reach during the 2014 growing season. For (A), the difference (upstream flow – downstream flow) also is shown.

Figure 5. Daily values of unaccounted for volumes ($m^3 \times 10,000$) of flow in the Arkansas River reach during the study period. Section 1 corresponds to the Snowmelt Period, Section 2 to Flooding Period, Section 3 to End of Summer Period, and Section 4 to End of Season Period.

Figure 6. Spatial map of groundwater flow direction and concentration of NO_3-N in each monitoring well in the (A) Arkansas River study reach and (B) Timpas Creek study reach, for the June 10-11, 2014 sampling event. Length of the flow direction arrows indicates relative magnitude of the groundwater hydraulic gradient.

Figure 7. Groundwater hydraulic gradients (measured every 15 minutes) during the study period at (A) ARKA cross-section, (B) ARKB cross-section, and (C) ARKC cross section. Each gradient is calculated using groundwater head values at two wells on the side of the Arkansas River. Positive values signify a gradient towards the river, and negative values away from the river.

Figure 8. Continuous groundwater hydraulic head in Timpas Creek study reach monitoring wells for both the A Cross Section and the B Cross Section (see Figure 6). The arrows on the diagram indicates direction of groundwater flow for the A Cross Section.

Figure 9. Measured in-stream concentrations at the upstream monitoring station (ARKU) and downstream monitoring stream (ARKD) of the Arkansas River study reach for (A) chloride, (B) total dissolved solids (TDS), (C) total N, and (D) NO_3-N . Values from 10 separate sampling events from June 10, 2014 to November 8, 2014 are shown.

Figure 10. Percent decrease in concentration from the upstream end to the downstream end for Total N, NO_3-N , Cl, and TDS for sampling events between June 10 2014 and November 8 2014 for (A) the Arkansas River study reach and (B) the Timpas Creek study reach.

Figure 11. Results of the season-long NO_3-N mass balance for the Arkansas River study reach (4.7 km), showing (A) the unmeasured NO_3-N load, the groundwater NO_3-N loading to the reach if average groundwater NO_3-N concentration is assumed to be 0.1 mg/L, and the groundwater loading if NO_3-N concentration is assumed to be 0.5 mg/L. The time period for which the uncertainty analysis was performed is bounded by a shaded gray box, with results shown in (B) for the daily NO_3-N removal due to in-stream processes (kg/day/km), showing the mean values and 5th and 95th quantile values.

Figure 12. Results of the stochastic mass balance uncertainty analysis to determine the range of possible values for NO_3-N removal due to in-stream processes showing average and 5th and 95th quantile values for the 1 September 2014 to 8 November 2014 time period.

Figure 13. Relationship between stream discharge (m^3/sec) and the percent decrease in N concentration from the upstream end to the downstream of the study reach for the sampling events between June 10 2014 and November 8 2014. (A) shows the relationship for C_{NO_3-N} in the Arkansas River study reach, (B) shows the relationship for total N in the Arkansas River study reach, and (C) shows the relationship for C_{NO_3-N} in the Timpas Creek study reach.

Figure 14. Results of monitoring in-stream NO_3-N concentration (mg/L) along two long reaches of the Arkansas River: concentration at the upstream and downstream ends of (A) the 93 km reach of the Upstream Study Region during 2006-2011 and (B) the 74 km reach of the Downstream Study Region during 2003-2012; and corresponding percent decrease in NO_3-N concentration for these same sampling events for (C) the Upstream Study Region and (D) the Downstream Study Region, with data divided into periods of Low Flow and High Flow in the Arkansas River.

Probability

Hydraulic Head (m)

1264
1262
1260
1258
1256
1254
1252

Cross Section A

4/1 5/2 6/2 7/3 8/3 9/3 10/4 11/4

Cross Section B

4/1 5/2 6/2 7/3 8/3 9/3 10/4 11/4

— Far Well
- - - Near Well
— Stream