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# NITRATE DYNAMICS IN AN ARID IRRGATION NETWORK: CAN NUTRIENT LOOPS BE CLOSED WITH MANAGEMENT TECHNIQUES?

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**by**

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**Nitrate Dynamics in an Arid Irrigation Network: Can nutrient loops be closed with management techniques?**

By

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**B.S. Environmental Science, 2017**

**M.S. Civil Engineering, 2019**

## ABSTRACT

Nutrients are the third leading cause of impairment in aquatic ecosystems, yet they remain necessary to support our growing agriculture system. Mining (as with phosphorus) and manufacturing (as with synthetic nitrogen) fertilizers deplete non-renewable resources and consume large amounts of energy. We have opportunities to optimize food-energy-water (FEW) resources, particularly in arid regions where wastewater, rather than agriculture, is the number one contributor of nutrients. This study evaluates the capacity of three unique channels (i.e., the Drain canal, the Delivery canal, and the Rio Grande River) within the agriculture system of the Middle Rio Grande Valley to process nutrients from the Albuquerque Wastewater Treatment Plant (ABQ WWTP). We used a mass balance approach paired with stable isotope analysis to determine the source and fate of $NO_3$-N within these channels over time (one year) and space. Our study revealed the growing season (March-October) is a key period of $NO_3$-N sink behavior

in the Rio Grande and Delivery canal, but the Drain (which carries nutrients back to the Rio Grande) was regularly a source of $NO_3$-N during this period. Additionally, we found that travel times are key to establishing source/sink $NO_3$-N dynamics, i.e., sites closest to the ABQ WWTP experienced source behavior and distal sites experienced sink behavior during the growing season. $NO_3$ stable isotope analysis revealed that $NO_3$ was primarily sourced from septic and manure waste (analogous to WWTP inputs), but during the growing season some $NO_3$ was sourced from $NH_4$, a common fertilizer used in this region. Stable isotope analysis also revealed the Drain canal experienced $NO_3$ production and the Rio Grande and Delivery canal experienced $NO_3$ uptake caused by microbial processing. With this information, we recommended areas of improvement to the agricultural system to promote nutrient processing in drains and downstream of the ABQ WWTP, while minimizing processing in the Delivery canal so as to increase nutrient delivery to crops. This study may pioneer new designs and strategies to promote the sustainable management of FEW resources in the Middle Rio Grande Valley.

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## *Introduction*

**Motivation**: Excess nutrients are one of the most common and disruptive disturbances to lotic aquatic ecosystems, with negative impacts observed in up to 90% of the streams in the U.S (EPA 2009). Due to the interconnected nature of fluvial networks, these impacts propagate from headwater streams to downstream rivers, lakes, aquifers and coastal waters that are highly susceptible to nutrient loading. Across the U.S., nutrient excess is the third leading cause of impairment in streams and rivers (after pathogens and sediments) and the second in lakes (after mercury) (EPA 2009). The most recent USGS Integrated Water Quality Assessment Report suggests that from the ~1 million miles of assessed streams nationwide, the median percentage with nutrient-related impairment across states is 10% (25$^{th}$ and 75$^{th}$ percentiles of 3% and 22% respectively, and a maximum of 88% in a given state). The median percentage of lakes with nutrient-related impairment across states is 18% (25$^{th}$ and 75$^{th}$ percentiles of 7% and 41%, respectively, and a maximum of 91% in a given state). These impacts are environmentally and economically costly, with estimated damage costs of 45-165 billion dollars per-year (Sobota et al. 2015) associated with N eutrophication alone in U.S. surface and groundwater systems. Thus, there is a strong need to develop methods to quantify and predict the transport and fate of nutrients along entire fluvial networks and their cumulative effects on water quality. Since humans interact ubiquitously with fluvial networks, it is imperative that we understand how our highly dynamic interventions and their cumulative effects (e.g., water uptake, agricultural runoff, effluent discharges from wastewater treatment plants, WWTPs) impact water quality and the fluvial and terrestrial ecosystems that depend on it.

While a significant body of research has identified the importance of streams and rivers in mediating the transport and export of nutrients (Kirchner et al. 2000; Wondzell 2011;

Zarnetske et al. 2012; Harvey and Gooseff 2015), most studies focus on solute-specific analyses (i.e., one nutrient is analyzed in each study), are mainly conducted in headwater streams (~90% of all reported studies), and occur primarily during summer baseflow conditions (Tank et al. 2008; Hall et al. 2013; González-Pinzón et al. 2015a). Thus, there are still fundamental knowledge gaps regarding 1) the mechanistic behavior of nutrient dynamics in fluvial networks, such as the role of physical characteristics, the impact of resource supply, quality, and stoichiometric constraints (the molar ratios of essential limiting nutrients including C, N and P), and 2) how these factors vary over time and space, considering anthropogenic disturbance regimes (Ensign and Doyle 2006; Tank et al. 2008; Marcé and Armengol 2009; Aguilera et al. 2013; Hall et al. 2013; González-Pinzón et al. 2015a). Currently, these knowledge gaps hinder the development of effective and enforceable environmental regulatory terms (e.g., total maximum daily loads, TMDLs) and successful restoration projects (a multibillion-dollar industry (Wohl et al. 2015)). Additionally, they limit our ability to identify and quantify natural and anthropogenic synergies and tradeoffs within the food-energy-water (FEW) nexus that could be optimized to close nutrient loops and reduce energy consumption (e.g., in wastewater nutrient removal, and in fertilizer production, transportation and application), as has been recently prioritized in national and international agendas (FAO 2014a; NSF 2014).

**The coupling between nutrient dynamics & the FEW nexus**: Projected rises in human population (>9 billion by 2050) and standards of living have accentuated the importance of the interconnections among FEW resources and the need for holistic approaches (the FEW nexus) to promote their sustainable production, distribution, and consumption (Hoff 2011; Finley and Seiber 2014). There is an urgent need to identify and quantify synergies and tradeoffs pertaining to the FEW nexus that support environmental sustainability (FAO 2014a; NSF 2014). This need is particularly relevant in arid-land regions, which represent the largest terrestrial biome on Earth, and are facing multiple pressures that stress FEW resources (e.g., rapid population growth, food insecurity, increased forest fires, and aridification due to climate change) (Kingsford 2006; Leemans 2009; Koohafkan 2012).

In arid-land fluvial networks, directly recycling wastewater nutrients into crop fields through irrigation may considerably reduce nutrient export, improve river water quality and help close nutrient loops because WWTP effluents are often the dominant source of bioavailable nutrients (Caraco et al. 2001; Dumont et al. 2005; Harrison et al. 2005). In addition, irrigation networks contain high densities of regulatory structures (e.g., dams and weirs) and infrastructure (e.g., supply canals and drainage ditches) that enhance nutrient retention via increased residence times, uptake in biochemically heterogeneous channels, and uptake by channel vegetation and crops (Soana et al. 2011; Bartoli et al. 2012; Lassaletta et al. 2012). Recent global estimates suggest that about 10 and 2 g/person/day of N and P, respectively, are available as nutrients from human metabolism in wastewater (Larsen et al. 2016). These magnitudes are comparable to major components of nutrient cycles. For example, the N available from the wastewater generated by 9 billion people would be on the same order of magnitude of anthropogenic production through the energy-intensive Haber-Bosh fixation process (forecasted as ~35 Mt of reactive N per year). Not surprisingly, recent sustainability assessments of N and P consistently suggest that the large, unresolved losses of nutrients in agricultural production will require sustained increases in nutrient recycling from wastewater effluents (Childers et al. 2011; Larsen et al. 2016). To date, there are several successful examples of environmentally sustainable nutrient recycling from wastewater: 1) in Sweden, the government set the goal of recovering and reusing 60% of all P in sewage (Cordell et al. 2009); 2) in California, ~61% ($0.5\times10^9$ m3/year) of the reused water is used for irrigation; and 3) on a global scale, ~1.7% ($7.7\times10^9$ m3/year) of the municipal water is reused, mostly in irrigation (Jimenez and Asano 2015). Without the recycling of wastewater nutrients, the continued energy-intensive manufacturing, transport, and application of synthetic fertilizers is required, despite their non-renewable and non-sustainable nature. The continued reliance on this method may not be possible as P—a major component of fertilizer—is scheduled to become scarce or exhausted in this century (Smil 2000; Cordell et al. 2009; Cordell and White 2011).

Irrigation with wastewater occurs globally, primarily in arid lands where wastewater is being used to increase food production by augmenting limited water supplies that would otherwise restrict agriculture and biofuels (Hamilton et al. 2007). With the future direction of wastewater treatment becoming more holistic in terms of resource recovery and environmental sustainability (Eddy & Metcalf 2013; NSF 2015), expanding wastewater reuse can help accomplish these goals through nutrient recycling and energy savings from reduced treatment, fertilizer production, and transportation. However, moving beyond managing each of the FEW sectors in isolation (the status quo, which has resulted in unsustainable, unclosed nutrient loops), to a more holistic approach, relies on accurately and dynamically identifying nutrient sources and sinks in fluvial networks, particularly in large rivers, where most of the population in arid-land basins resides (e.g., 50% of New Mexicans live in the Albuquerque metropolitan area along the Rio Grande Valley; similar cases occur in Idaho along the Snake River, and Arizona along the Gila River). This knowledge has been hampered by not utilizing rapid assessment methods that can provide timely insights into the crucial dimension of large rivers that has not been explicitly considered while investigating nutrient dynamics, i.e., anthropogenic disturbance and modification. With this in mind, a key question remains: Can the operation of WWTPs be tailored (e.g., switching between secondary and advanced tertiary treatment) to optimize environmental opportunities to grow crops, close nutrient loops and reduce energy expenses in advanced treatment? This study intends to address this question by investigating nutrient dynamics over a year using rapid assessment protocols and using the results to suggest opportunities for FEW resource management.

### *Methods*

**Site Description**: This study takes place in the Middle Rio Grande Basin (MRGB), NM, the most agriculturally productive and densely populated area along the 3,000 km length of the Rio Grande River (Figure 1). The MRGB is a ~300 km long reach bound by Cochiti Dam to the north and Elephant Butte Reservoir to the south. The Rio Grande (Figure 2C) is the main source of water for flood irrigation to over 4000 km$^2$ of crop, which consists primarily of alfalfa and pasture grass. Adjacent to the river is a complex network of irrigation channels, summing to ~2,100 km of canals, acequias (small irrigation ditches), and drains that carry water from the river to the fields and vice versa. We selected two major canals: Peralta Main Canal (PMC; Figure 2B) and Lower Peralta Riverside Drain (LPD; Figure 2A), here forth referred to as the Delivery canal and the Drain, within the central reach of the MRGB between Albuquerque and Belen, NM to isolate the biological and hydrological processes occurring within the irrigation network during the growing (March-October) and non-growing (November-February) seasons. Flows within the Delivery canal vary between 0.4-7 m$^3$/s from the point of diversion to the point of return to the Rio Grande during the growing season (the canal runs dry during the non-growing season). Turbidity is similar to that of the Rio Grande (~300 NTU on average) and primary productivity is limited to the edge of the wetted channel and its surrounding banks. The Drain flows vary between 0.4-2.5 m$^3$/s at the end of the reach. Turbidity is low (~20 NTU on average) in this channel, with the bed of the channel covered in filamentous algae and emergent macrophytes. The banks of the Delivery canal and the Drain are often lined with Coyote Willow (*Salix exigua)* and various species of grass (*Agrostis gigantea and Sporobolus wrightii*). The Drain persists entirely from intercepted groundwater leaving the Rio Grande and discharge ranges between 0.4-1.6 $m^3/s$.

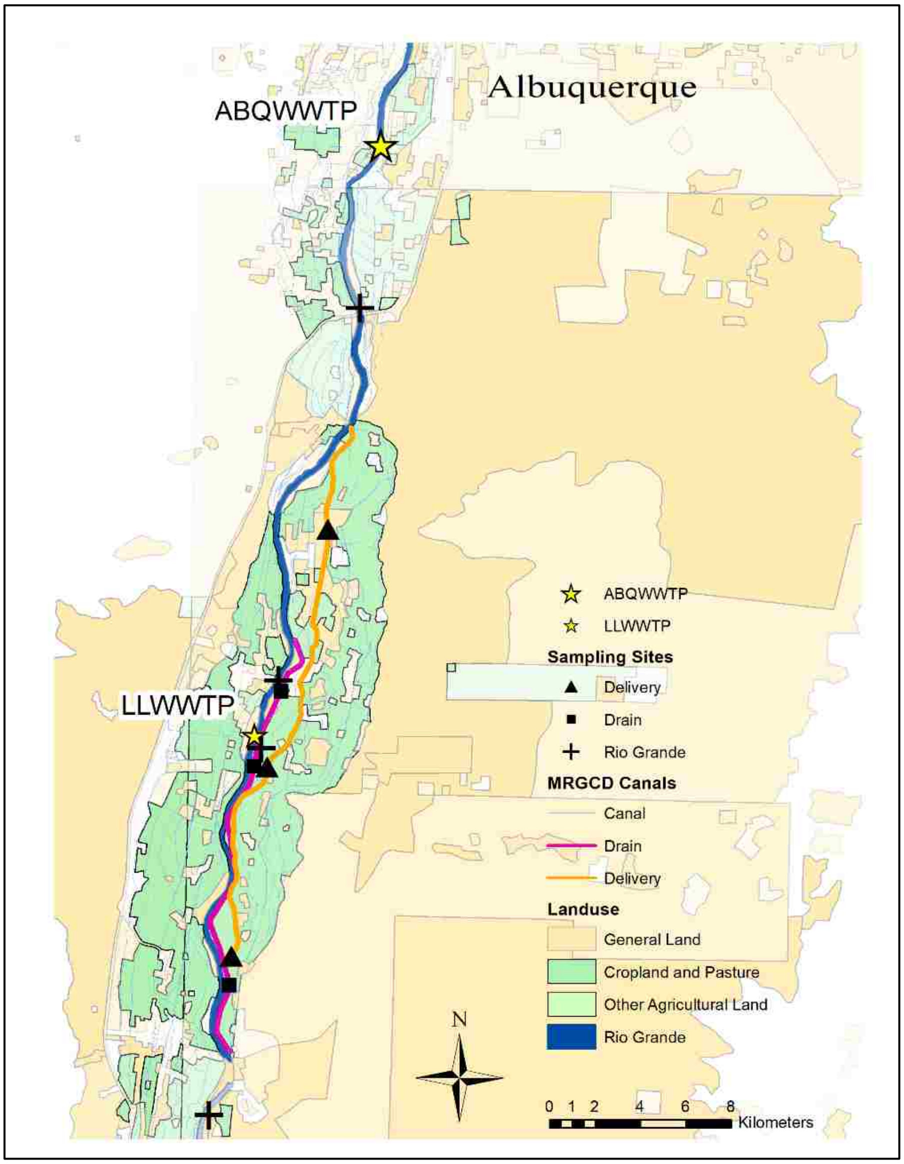


**Figure 1**. Study extent with the Rio Grande (navy), Drain (pink), and Delivery canal (orange) highlighted and sampling sites along each channel (black)

The Middle Rio Grande Conservancy District (MRGCD) is responsible for monitoring and maintaining the irrigation network. Water is diverted from the Rio Grande at Isleta Diversion Dam into the Delivery canal, which then carries water to agricultural users. Upon the start and end of the growing season, the Delivery canal is flushed with high flows to remove any debris from the channel. Returning water is captured by the Drain, which is dredged below the elevation of the water table to capture lateral groundwater from the river and drainage from the agriculture fields. Water in the Drain is returned to the Rio Grande ~50 km downstream where it was diverted, often to the floodplain to provide habitat to the endangered silvery minnow (Bartolino and Cole 2002).

**Figure 2**. Photos of sampling sites at the A) Drain, B) Delivery canal, and C) Rio Grande

Within our study reach, the Rio Grande receives inputs from the Albuquerque WWTP (ABQ WWTP) and the Los Lunas WWTP (LL WWTP) (Figure 1). The ABQ WWTP generally releases ~2.5 $m^3/s$ of water (ABCWUA)at concentrations between 3 and 5 mg/L of $NO_3$-N (ABQ WWTP permitted to release up to 15 mg/L of total inorganic nitrogen, but over 90% of the TIN is made up of $NO_3$, which is what we will be referring to henceforth (Mortensen et al. 2016)) into the Rio Grande upstream of the Isleta Diversion Dam, thus water in the Delivery canal is a mix of Rio Grande and ABQ WWTP effluent. LL WWTP releases ~1.4 $m^3/s$ (Village of Los Lunas)at concentrations ranging from 4 to 25 mg/L $NO_3$-N downstream of Isleta Diversion Dam (Van Horn 2010; Mortensen et al. 2016).

**Data Collection***:* We took samples every 3 weeks along the selected study reaches for the Drain (18 km), the Delivery canal (20 km), and the Rio Grande (50 km) beginning in October 2017 and ending in October 2018 (n=18). We identified four sampling sites along each reach (Figure 1) to track the longitudinal change in $NO_3$-N loads (kg/day) as water travels through the system. Inputs to each reach were also sampled to calculate a nutrient budget. Sampling sites were chosen due to their proximity to a gauging station operated by either the USGS or MRGCD (Table 1). At sites that were ungauged, discharge was measured using the SonTek FlowTracker handheld ADV (SonTek, San Diego, CA). The Delivery canal was not sampled during the non-growing season because the canal was dry. Grab samples were taken using 60 mL syringes and filtered with a 0.45-µm nylon filter. Filtered samples were stored in a cooler at 4°C until we returned to the lab. All filtered samples were placed in the freezer until analysis using ion chromatography (Pfaff 1996).

**Table 1.** Sampling sites and their distance from the Albuquerque WWTP are shown.

| | Site Name | Distance from ABQ WWTP (km) | Discharge Source |
|---|---|---|---|
| **Delivery** | Delivery 0 | 18 | MRGCD |
| | Delivery 1 | 29 | MRGCD |
| | Delivery 2 | 38 | MRGCD |
| **Drain** | Drain 0 | 25 | Manual |
| | Drain 1 | 29 | Manual |
| | Drain 2 | 39 | Manual |
| **Rio Grande** | Rio Grande 0 | -9 | USGS (08330000) |
| | Rio Grande 1 | 8 | USGS (08330875) |
| | Rio Grande 2 | 26 | USGS (08331160) |
| | Rio Grande 3 | 44 | USGS (08331510) |

**Nutrient Budget***:* We developed a fraction change (F) metric following Zarnetske et al. (2012) to understand source/sink behavior with a simple metric:

$$F = \frac{N_{dn}}{N_{up} + \sum N_{in}(\frac{l}{L})}$$

where $N_{dn}$ represents the $NO_3$-N load, $\delta^{15}N$ or $\delta^{18}O$ at the downstream point, $N_{up}$ is at the upstream point, and $N_{in}$ represents the summation of any $NO_3$-N entering the reach weighted by their distance to the downstream point ($l$) given the overall distance between the upstream and downstream point ($L$). The meaning of F for each variable is defined in the table below:

**Table 2**. Description and physical interpretation of F-values

| F-Value | Equation | Description | Physical Meaning |
|---|---|---|---|
| $F_{NO3}$ | $\frac{N_{load\,dn}}{N_{load\,up} + \sum N_{load\,in}(l/L)}$ | F>1: Source<br>F<1: Sink | *Source*: $NO_3$ being added to the system<br>*Sink*: $NO_3$ being removed from the system |
| $F^{15}N/^{18}O$ | $\frac{^{15}N_{dn}}{^{15}N_{up} + \sum {^{15}N} \cdot (l/L)}$<br>$\frac{^{18}O_{dn}}{^{18}O_{up} + \sum {^{18}O} \cdot (l/L)}$ | F>1: Heavy shift<br>F<1: Light shift | *Heavy*: Heavier isotopes ($^{15}N/^{18}O$) accumulate due to preferential removal of lighter $NO_3$ or mixing with heavier $NO_3$.<br>*Light*: Lighter isotopes ($^{14}N/^{16}O$) accumulate due to the production of $NO_3$ by nitrification or mixing with lighter $NO_3$. |

**Nutrient Uptake Experiments:** To assess uptake rates of the Drain, we performed 2 nutrient injection experiments in April 2018 and June 2018 on a 500m reach between Drain 1 and Drain 2. Nutrient injection experiments are used to quantify the reactive transport of NO¬3 using uptake metrics (Runkel 2007). We estimated NO3 uptake length (Sw; in m), uptake velocity (Vf, in m/s), and areal uptake (U, in mol/m2/s) (Stream Solute Workshop 1990)We added enough mass of a conservative (NaBr) and reactive (NaNO3) tracer to spike background concentrations by ~600 ppb and generated a breakthrough curve, which we used to calculate dynamic uptake metrics following the rationale behind the TASCC protocol (Covino et al., 2010). We determined NO3-N and Br (mg/L) concentrations from grab samples using Ion Chromatography. Uptake metrics were determined using a modified version of a Matlab (MathWorks, Natick, MA) code developed by Knapp et al. 2018, which models solute transport subject to advection, dispersion, sorption, transient storage, and reactivity to generate breakthrough curves that jointly fit to our experimental data (Knapp et al. 2018). The best fit curves identified using RMSE goodness of fit criterion were then used to calculate the uptake metrics defined below. The terms in each equation are defined by Covino et al. (2010) where $k_w$ (m-1) is the slope of the line between distance from the injection point and the ratio of reactive to conservative tracer concentration for each sample, Q is discharge (m3/s), $NO_3$-$N_{add\text{-}dyn}$ is the geometric mean of [NO3-N] through the experiment with respect to the initial, unreacted [NO3-N], and w is the wetted width of the stream (m).

$$S_{w-add-dyn} = -\frac{1}{k_{w-add-dyn}}$$

$$U_{add-dyn} = \frac{Q \times [NO_3 - N_{add-dyn}]}{S_{w-add-dyn} \times w}$$

$$V_{f-add-dyn} = \frac{U_{add-dyn}}{[NO_3 - N_{add-dyn}]}$$

**Stable Isotopes**: We employed dual nitrogen and oxygen isotopic analysis to determine if nitrate removal in the system was due to denitrification (dissimilatory process) or microbial assimilation (assimilatory process). A 20 mL aliquot from samples collected every month along the Rio Grande, the Delivery canal, and the Drain was analyzed for ambient nitrate isotopes.

Nitrate isotopes were determined using the denitrifier method (Sigman et al., 2001) at the University of Washington IsoLab. Values for $^{15}N$ and $^{18}O$ are reported in units of permil, which is defined as the ratio heavy to light isotope (R) in the sample vs. a standard.

$$\delta(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$$

Measured values of $^{15}N$ and $^{18}O$ of $NO_3$ are compared to international standards USGS35, USGS34, USGS32, and IAEANO3 and are reported with respect to atmospheric-$N_2$ and the Vienna Standard Meteoric Ocean Water (VSMOW), respectively.

*Results and Discussion*

**Wastewater Influence**: The Albuquerque WWTP is a major source of both water and nutrients to the Rio Grande, but its influence on the chemistry of the river depends on the seasonality of flow (Figure 3). For example, during the period of highest flow in December of 2017, discharge in the Rio Grande was at 35.1 $m^3/s$ at the USGS gauge over Central Bridge (#08330000) and 36.7 $m^3/s$ at I-25 Bridge (#08330875), which are located upstream and downstream, respectively of the WWTP outfall (i.e., ~1.0x or negligible discharge increase). For these same sampling locations, $NO_3$-N load was 191 kg/day upstream of the WWTP, which contributed 630 kg/day to the Rio Grande, increasing its load downstream to 713 kg/day (i.e., ~3.3x load increase). Conversely, during September of 2018, the 6.3 $m^3/s$ flow in the Rio Grande at Central Bridge was at the lowest during the study period, and increased to 8.6 $m^3/s$ at I-25 Bridge (i.e., ~1.4x discharge increase); the associated $NO_3$-N load from the WWTP was 1,055 kg/day, increasing the $NO_3$-N load in the Rio Grande from 114 kg/day upstream to 1,060 kg/day downstream (i.e., ~9.3x load increase).

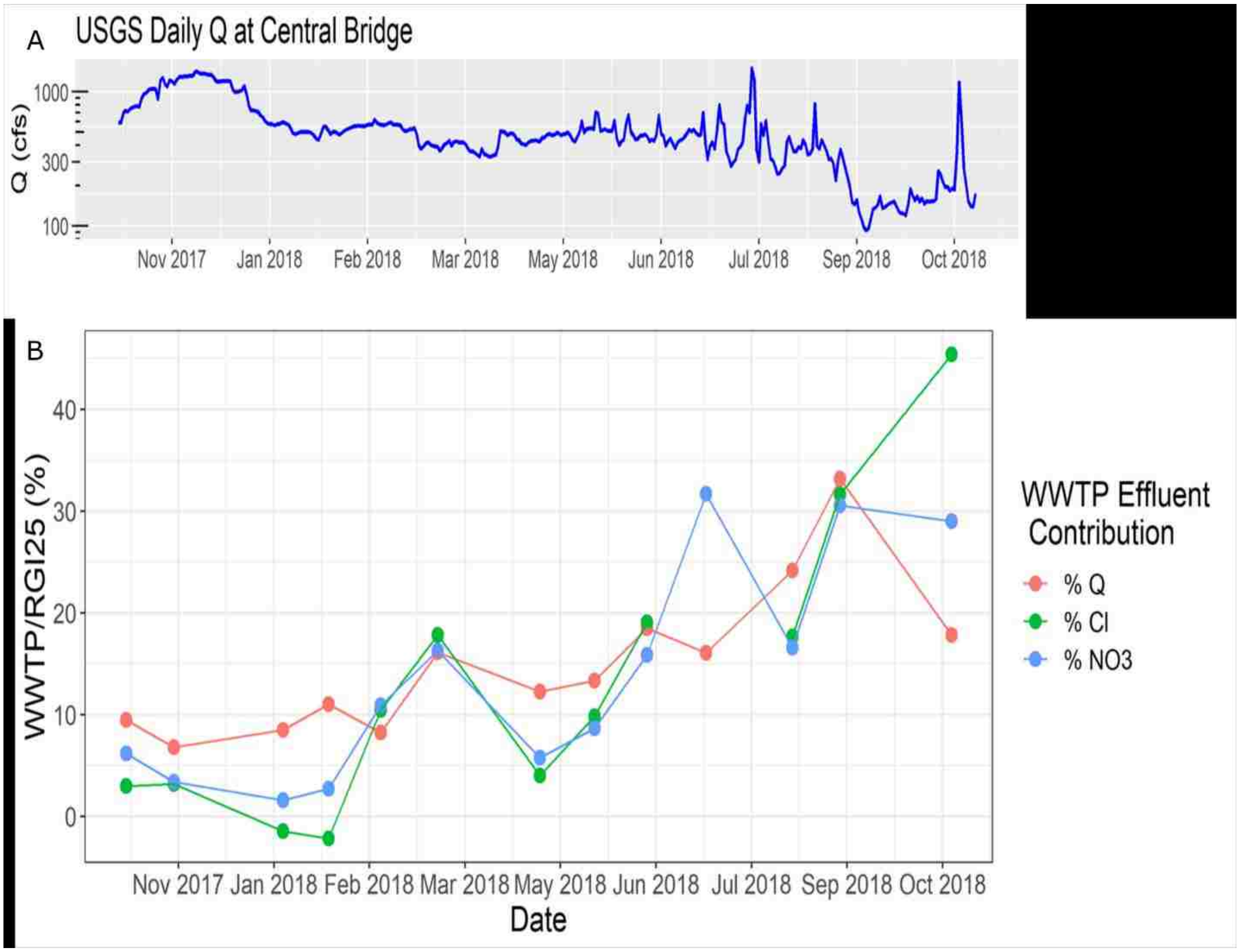


**Figure 3**. (A) Hydrograph of Rio Grande at Central Bridge in Albuquerque during study period. (B) Influence of Albuquerque WWTP on discharge (Q), Cl, and $NO_3$-N of the Rio Grande at Interstate 25 bridge ~9 km downstream.

**Temporal source/sink dynamics**: Differences in growing season vs. non-growing season source/sink behavior were apparent in all channels studied during the sampling period (Figure 4). During the non-growing season (white shading), most $F_{NO3\text{-}N} > 1$ indicating that the three channels were net sources of $NO_3$-N. The Delivery canal ranged between $0.004 < F_{NO3\text{-}N} < 3.5$ across all seasons, with minimum and maximum values occurring in the summer and the fall, respectively. The Drain ranged between $0.2 < F_{NO3\text{-}N} < 37.1$, with minimum values occurring in the summer and maxima in early fall and winter (when the system is flushed). The Rio Grande ranged between 0.05 < $F_{NO3-N}$ < 5.8, with minimum and maximum values occurring in the summer and the fall, respectively. Generally, source behavior ($F_{NO3-N}$>1) occurred in the fall and winter and sink behavior ($F_{NO3-N}$ < 1) in the summer (n>1=35, n=1=36, n<1=46). Results from a one-way ANOVA and Tukey's Test on the $\log_{10}$ transformed data suggest significant ($p<0.05$) differences in the $F_{NO3-N}$ between fall and summer, winter and summer, and winter and spring (Figure 4B).

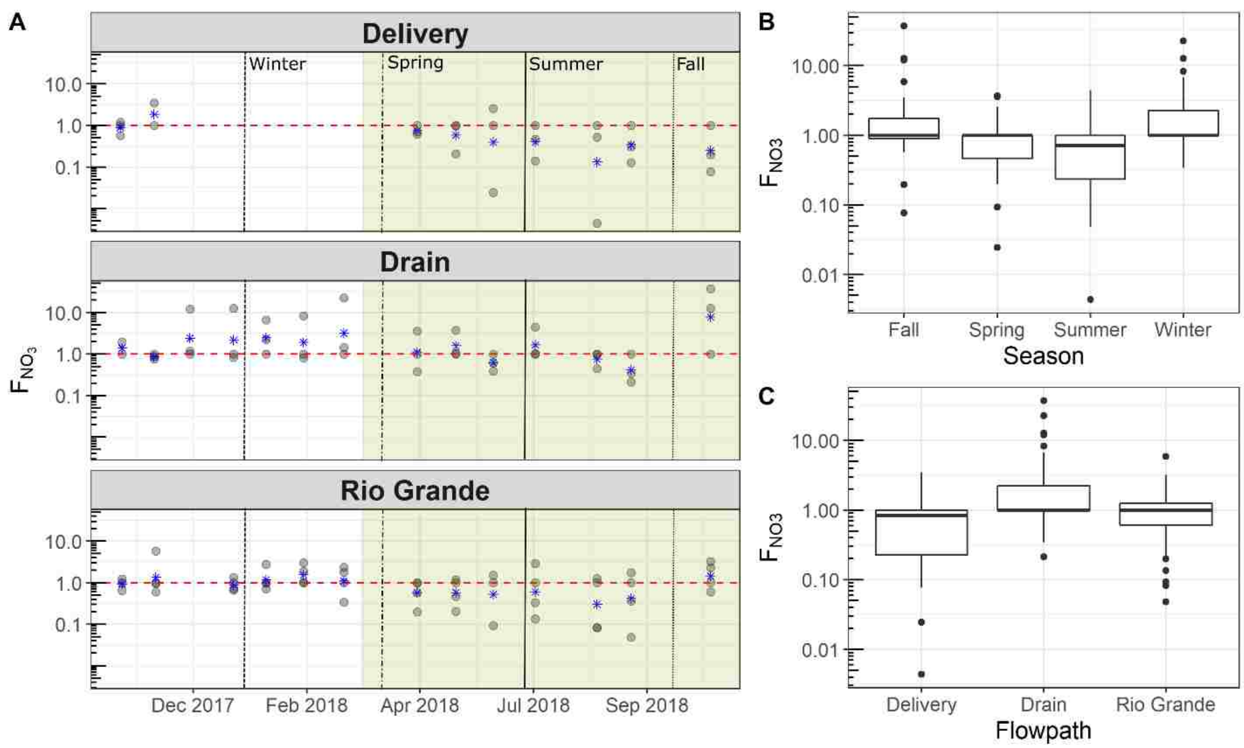


**Figure 4**. Seasonal source ($F_{NO3-N}$ >1) and sink ($F_{NO3-N}$ <1) behavior for the three channels for each sampling trip (A) (white and green shading represents non-growing and growing seasons). To the right is the F summarized by season (B) and channel (C).

Irrigation practices and infrastructure in arid regions, including vast portions of the western United States, Australia, Egypt, South Africa, Mexico, etc., are fundamentally different than in mesic or humid regions (FAO 2014b). In arid lands, water is withdrawn from large rivers at diversion dams, routed into canals that bifurcate until they form small channels, and is finally applied to fields through flood irrigation. This water then percolates through the soil column, enters the shallow alluvial aquifer, and flows via shallow groundwater channels to low-lying agricultural return drains. These drains gather water from numerous subsurface outflows, coalesce to form larger channels, and eventually return to the river at outflow points. This complex system effectively turns the flood plains of major rivers in arid regions into systems that can be highly nutrient retentive and provide the potential to close nutrient loops by recycling the nutrients from wastewater effluent (the main source) back into crops (Mortensen et al. 2016). Our channel-specific findings support the nutrient source-sink dynamic behavior identified by Mortensen et al. (2016) in the Middle Rio Grande watershed. That study suggested avenues for holistically closing nutrient loops, pointing the way forward to link FEW resources. However, it also highlighted that it is still unclear how we can maximize this retention considering synergies and tradeoffs among three main players: 1) the Albuquerque WWTP (main nutrient source); 2) the Middle Rio Grande Conservancy District (nutrient sink); and 3) New Mexico Environment Department (nutrient regulator). Therefore, understanding how nutrient inputs from the WWTP are processed within the conservancy district is a critical step into adopting a FEW nexus approach toward closing nutrient loops.

The sink behaviors observed during the spring and summer are expected due to warmer temperatures, lower discharges and corresponding longer residence times, and vascular plant activity (Zarnetske et al. 2012; Harvey and Gooseff 2015). However, this behavior is not ubiquitous, and our findings are at odds with observations in other arid and semi-arid river basins (Tank et al. 2008; Hall et al. 2013; González-Pinzón et al. 2015a), where low flow periods lead to nutrient saturation and, thus, net source behavior. We suggest that those systems may have other confounding factors such as nitrate-rich groundwater seeping into the rivers, nitrification without uptake, and stoichiometric imbalances (i.e., nutrient co-limitation) that lead to observed saturation at sites downstream of the WWTP input (Hall et al. 2013).

The Drain is designed to capture groundwater leaving the river, preventing water from flooding the agriculture fields. The water in this channel interacts with the riparian strip between the Rio Grande and the Drain and as a result the start of this reach is relatively low in $NO_3$-N concentrations (compared to the Rio Grande and Delivery canal), averaging ~0.1 mg/L through all seasons. In the Drain, the sink patterns observed in Figure 4 during the growing season are likely due to favorable water temperatures for biogeochemical processing (Zarnetske et al. 2012). The Rio Grande experienced well below average discharges between the months of July-September, and they were associated with sink behaviors (Figure 4). Discharge is likely important to this channel because it controls residence time and interaction with the hyporheic zone (Ensign and Doyle 2006; Marcé and Armengol 2009; Aguilera et al. 2013). Additionally, the input from sources chemically different from the Rio Grande itself (i.e., the WWTP and the agricultural drains) may create dynamic hotspots with extents controlled by discharge in the Rio Grande (FAO 2014a; NSF 2014; Wohl et al. 2015). As expected, most of the temporal dynamics observed in the Rio Grande are replicated in the Delivery canal (an artificial diversion of the Rio Grande), but as we will see below, distance from the WWTP also becomes crucial in defining its source/sink behavior.

**Spatiotemporal patterns of source/sink dynamics**: Figure 5 displays the spatial (x-axis) and temporal (columns) variation in source/sink (y-axis) behavior for each channel (rows). In the spring and summer, the Delivery canal and the Rio Grande generally become $NO_3$-N sinks ($F_{NO3-}$

$_{N}$ <1) with distance and the Drain tends to become a source. In the fall and winter, the Rio Grande and Drain tend to be net sources with distance downstream (Figure 4B).

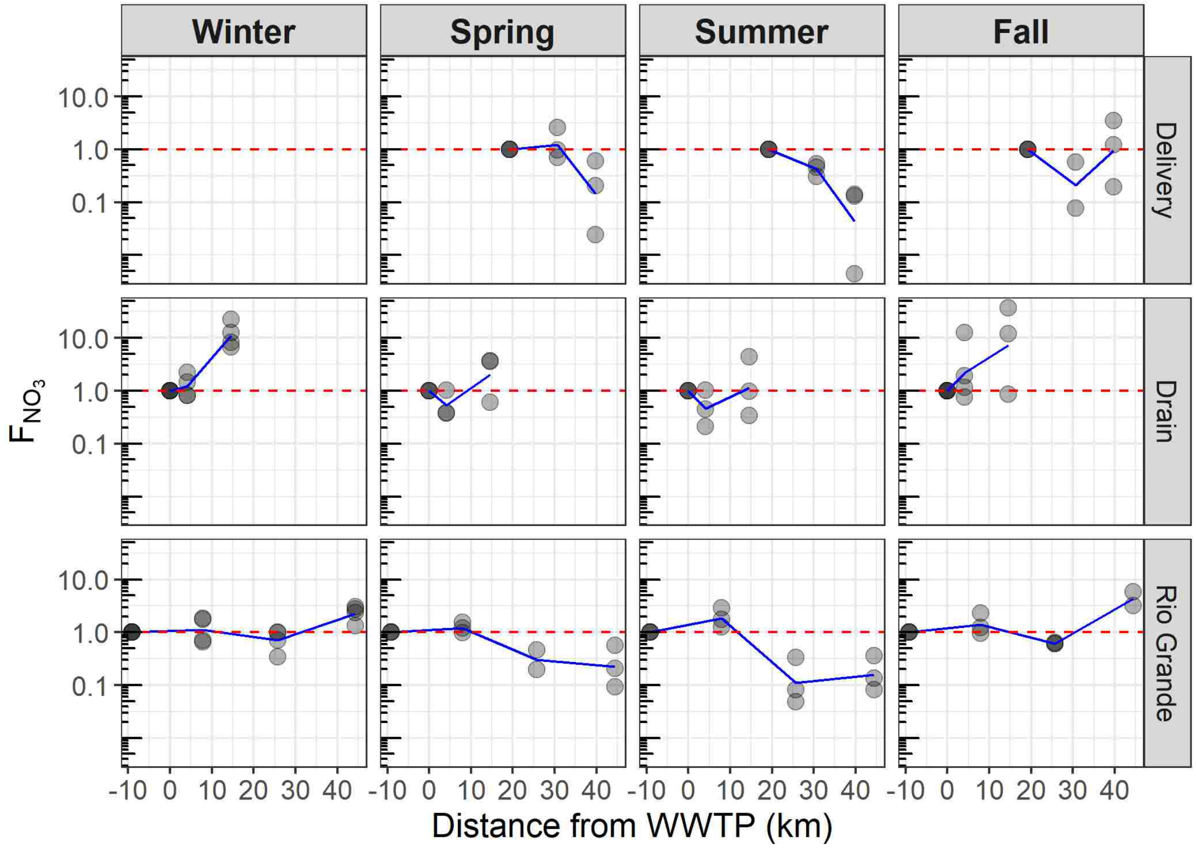


**Figure 5**. Source ($F_{NO3\text{-}N}$ >1) and sink ($F_{NO3\text{-}N}$ <1) behavior across channels (rows) through space and season (columns). Blue lines are mean F for all sampling events.

Our data suggest that the addition of $NO_3$-rich sources at 2 point-sources along our study reach in the Drain canal may contribute to nutrient uptake saturation. One of sources (the Deliver canal) results in increases in turbidity, which limits light availability and thus nutrient assimilation via photosynthesis by macrophyte communities (Camacho and González 2008; González-Pinzón et al. 2013). The Rio Grande and the Delivery canal, on the other hand, have consistent values of high turbidity (~300 NTU on average, often exceeding ~4,000 NTU during storm events), very little bankside vegetation due to the presence of fine and highly movable sediments, and lack lateral nutrient-rich inputs. Due to low flows in the Rio Grande that result in high temperatures and hydraulically disconnected compartments it is likely that denitrification drives the observed sink behavior in the spring and summer. This is supported by evidence suggesting that environments that experience drying and wetting (as with the Delivery canal and the Rio Grande) are prone to the development of denitrifying environments (González-Pinzón et al. 2012, 2015b).

**Quantifying $NO_3$ uptake**: Despite the net source behavior observed in the Drain, this channel is still optimal for nutrient processing because of the abundance of macrophytes, bankside vegetation, and turbidity (Fellows et al. 2006; Tank et al. 2010, 2018; Bernhardt et al. 2018). As such, we quantified $NO_3$ behavior in the Drain in terms uptake metrics ($S_w$, $V_f$, and U) from nutrient uptake experiments (Stream Solute Workshop 1990). The nutrient injection experiments revealed the Drain has a significant ability to process nutrients in a relatively short distance, however this ability is drowned out by the nutrient rich and turbid inputs that occur further downstream, leading to the source behavior noted in Figure 5. Before the influence of the turbid inputs, the Drain has an uptake length ($S_w$) of ~292 m in April, which decreased to ~228 m in June (Table 3). Because the calculated $S_w$ is less than the experiment reach length (500 m), we can confidently describe this reach as a $NO_3$ sink and quantify the uptake efficiency using uptake velocity ($V_f$) (Covino et al. 2010). $V_f$ increased between experiments, reflecting increased $NO_3$ uptake efficiency (faster uptake for the same experiment reach length). The study reach we selected was after an input from a nutrient rich (~3 mg/L) drainage canal had mixed with the Drain, indicating the Drain was efficiently able to process additional nutrients, despite already having received a dose of nutrients from the adjacent drainage canal. This type of behavior is supported by evidence from similar experiments done in other agriculture systems, indicating these type of canals have adapted to the constant load of nutrients and can process them as efficiently as headwater streams (Bernot et al. 2006; Mulholland et al. 2008; Covino et al. 2012). Quantifying uptake metrics is important because the Drain is likely a net source of $NO_3$ because of the quality of inputs added to it, not because it does not have a high processing capacity.

**Table 3.** Uptake metrics from nutrient injection experiments done in the Drain on April 2018 and June 2018. Experiment reach length was 500 m between Drain 1 and Drain 2.

| Date | Sw (m) | $V_f$ (m/s) | U (mol/m$^2$s) |
|---|---|---|---|
| April 2018 | 292.2 | $3.06 \times 10^{-4}$ | $4.24 \times 10^{-7}$ |
| June 2018 | 227.9 | $3.69 \times 10^{-4}$ | $1.89 \times 10^{-7}$ |

**Isotopes as fingerprints**: We used stable isotope analyses to identify $NO_3$-N sources and periods and locations of biologic uptake (i.e., assimilatory and dissimilatory). Table 3 presents the average $\delta^{18}O$ and $\delta^{15}N$ isotope values measured at the channels and Figure 6 displays all values gathered during the year of sampling, organized by channel (markers) and time (color). Also, we show regions and trends where known sources (e.g., fertilizer) and processes (e.g., microbial processing) are considered well understood in the literature (Wankel et al. 2006; Granger et al. 2008; Kendall et al. 2008)

**Table 4**. Average isotope values for the channels with ± one standard deviation.

| **Channel** | **$\delta^{15}N$ (‰)** | **$\delta^{18}O$ (‰)** |
|---|---|---|
| WWTP | 12.2±2.7 | -3.3±1.0 |
| Rio Grande River | 12.1±3.8 | -0.1±3.6 |
| Drain | 16.1±4.5 | 4.9 ±2.7 |
| Delivery | 13.5±2.7 | -0.7±2.9 |

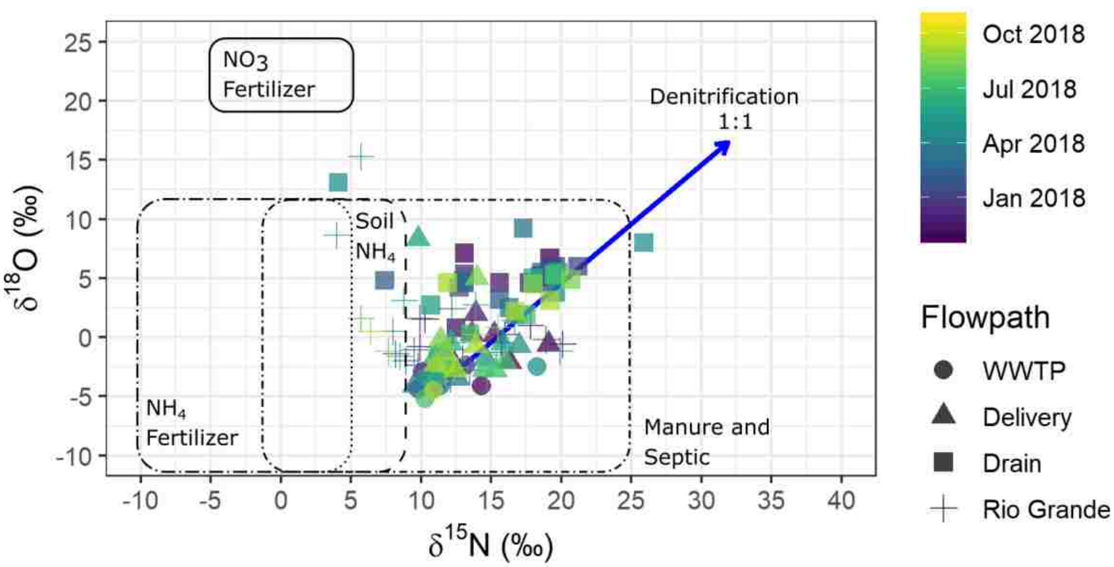


**Figure 6**. Isoplot of $^{18}\delta O$ and $^{15}\delta N$ displaying sources of $NO_3$ in this study. The blue line represents how $^{18}\delta O$ and $^{15}\delta N$ would grow in the presence of dissimilatory microbial $NO_3$ processing and discontinuous lines enclose known source regions (Granger et al. 2008; Kendall et al. 2008).

WWTP isotope values have a mean value of -3.3‰ for $\delta^{18}O$ and 12.2‰ for $\delta^{15}N$, which falls in the range of manure and septic waste (Kendall et al. 2008). The Rio Grande and Delivery canal have isotope signatures close to the WWTP signal, but the Rio Grande also shares isotope signatures from $NH_4^+$ derived from either fertilizers or soil erosion (Figure 6). The $NO_3$ derived from $NH_4^+$ in the Rio Grande occurs between April and May, likely reflecting the input from agricultural effluents that were minimally processed by the drainage network during the early part of the growing season. The Drain is statistically different from the Rio Grande by ~4‰ for $\delta^{15}N$ and ~5‰ for $\delta^{18}O$ ($p<0.05$) and likely reflects a manure or processed $NH_4^+$ fertilizer signal, depending on what the farmer used to fertilize their field. The Drain primarily reflects manure and septic waste (Figure 6), which agrees with observations of farmers tilling their soil with manure during the non-growing season. We found instances of the Drain reflecting soil $NH_4$-derived $NO_3$ and one instance of fertilizer $NH_4$ (Figure 6) when farmers apply N fertilizers (usually urea) in the spring/summer.

We explored correlations between $\delta^{18}O$ and $\delta^{15}N$ through space and time which, when positive, indicate the presence of biologically mediated $NO_3$ uptake (Granger et al. 2008; Kendall et al. 2008; Granger and Wankel 2016), and found positive correlations only at the most downstream sites on the Rio Grande and Drain, but not within seasons (Table 4). The lack of statistically significant trends within seasons may be due to mixing with different $NO_3$ sources within each channel, which may dampen or completely mask any processing pattern (Bedard-Haughn et al. 2003; Groffman et al. 2006). When we focus on one site, relationships independent of season begin to emerge leading to the results shown in Table 4 at the downstream sites on the Drain and Rio Grande River. The last sites on our study reaches represent $NO_3$ that has had the most interaction with the biota in the channel. Thus, the isotopes of $NO_3$ reflect the net effect of processing despite mixing with multiple sources of $NO_3$ (agriculture drains, groundwater, etc.) entering the reach upstream. Additionally, the slope of these lines is <1, indicating both nitrate production and uptake were occurring within these channels (Granger and Wankel 2016)

**Table 5**. Correlation factor (R-value) for $^{15}N$ and $^{18}O$ by site for each channel (*P<0.05).

| Channel | Site 0 | Site 1 | Site 2 | Site 3 |
|---|---|---|---|---|
| Delivery | -0.62 | 0.6 | 0.14 | |
| Drain | -0.58 | 0.26 | 0.65* | |
| Rio Grande | -0.64 | -0.5 | 0.022 | 0.63* |

Considering the $\delta^{18}O$ and $\delta^{15}N$ stable isotope values in the context of fractional changes (Table 2), values of F>1 are indicators of the accumulation of isotopically heavy molecules over time or downstream, suggesting selective uptake of lighter molecules (leaving behind the heavier) or mixing with a heavier source, and vice versa for F<1. We found that the Delivery canal had $0.76<F_{^{15}N}<1.6$ and $0.4<F_{^{18}O}<1.4$ for all seasons; the Drain had $0.14<F_{^{15}N}<2.1$ and $0.14<F_{^{18}O}<1.1$; and the Rio Grande had $0.2<F_{^{15}N}<3.1$ and $0.2<F_{^{18}O}<2.1$ (Figure 7).

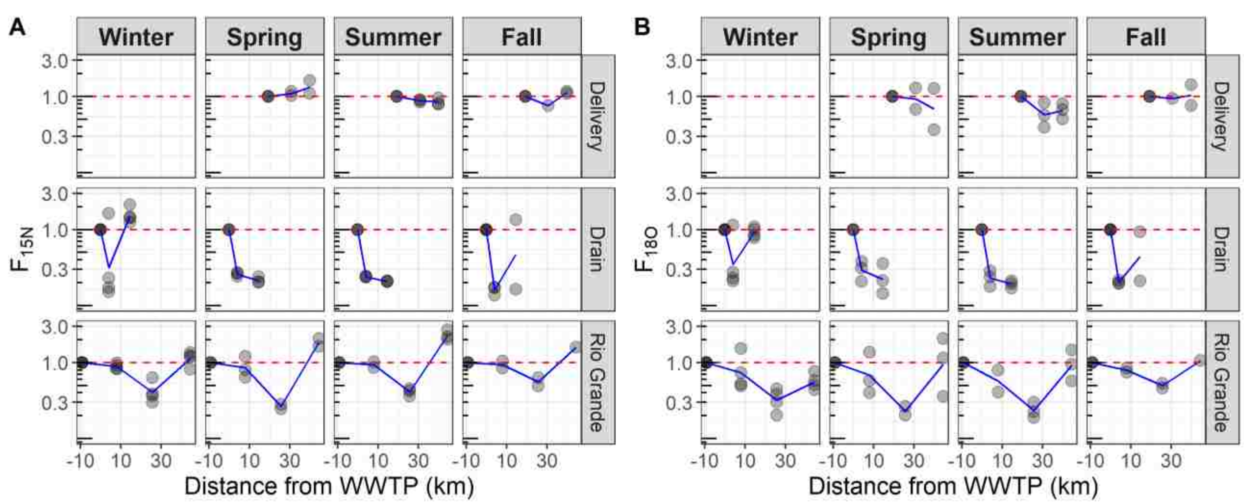


**Figure 7**. Spatial variation (distance from WWTP) by season (columns) and channel (rows) for $F_{^{15}N}$ (A) and $F_{^{18}O}$ (B).

The spatial patterns of $F_{^{15}N}$ and $F_{^{18}O}$ reflect the influence of different $NO_3$ sources on $NO_3$ processing. Several small channels (ungauged) branch off the Delivery canal to irrigate small fields and return to the main channel 1.8 km downstream, and the return of these small channels may influence the isotopic composition of $NO_3$ in the Delivery canal. $F_{^{15}N}$ values suggest that the inputs have little effect on the N isotopes along this channel, possibly because the $\delta^{15}N$ of the main channel and the returning canals have similar values. $F_{^{18}O}$ tells a different story involving the addition of isotopically light $NO_3$-$^{16}O$ in the spring and summer, suggesting these lateral extensions may have experienced nitrification or interacted with the soil yielding $NO_3$ with smaller $\delta^{18}O$ values (cf. the $NH_4^+$ soil and fertilizer boundaries in Figure 6) before returning to the main channel. The Drain has coupled $F_{^{15}N}$ and $F_{^{18}O}$ patterns, reflecting the influence of two different water types (i.e., an interior drain that likely carries $NH_4^+$ run-off from agriculture fields and the Delivery canal) on the processing capacity of this channel. In the winter, the Delivery canal is not flowing and thus does not enter the Drain. This is reflected by the $F_{^{15}N}>1$ and $F_{^{18}O}\sim1$ in the winter, implying that processing does occur through the reach but is masked by the Delivery canal input during the spring and summer. Finally the Rio Grande has correlated $F^{15}{}_{N}$ and $F^{18}{}_{O}$ values that reach a minimum at Site 2 (~ 25 km downstream of ABQ WWTP) due to the input of two major irrigation drains that enter the river upstream of this site, which likely alter water conditions to encourage both nitrification and uptake before the channel transitions to primarily $NO_3$ uptake between sites 2 and 3, where mean $F_{^{15}N}>1$ and $F_{^{18}O}\sim1$. $F_{^{15}N}$ and $F_{^{18}O}$ are dictated by the degree of dissimilatory $NO_3$ processing occurring; $F\sim1$ indicates little $NO_3$ processing or near equal processing and production, $F<<1$ indicates a degree of dissimilatory processing (e.g. denitrification) that is significant enough to be reflected by the $NO_3$ isotopes downstream, and $F>>1$ indicates $NO_3$ production.

**Rethinking Management of FEW resources**: The evaluation of the advantages of increasing wastewater reuse and nutrient recovery for agriculture is a complex problem involving supply (from WWTP effluent) and demand (agricultural uses), and the infrastructure linking the two. Critical considerations include a variety of technological options, including technologies for nutrient recovery, processes for different levels of nutrient removal from wastewater, specific water reuse treatment technologies, and appropriate disinfection (Singh et al. 2012; Eddy & Metcalf 2013; You et al. 2019). Since WWTPs consume large amounts of energy to degrade nutrients to minimize eutrophication in receiving waters, and large amounts of energy are also used to produce fertilizers, reusing wastewater for irrigation has dual benefits related to energy reduction and achieving environmental sustainability. Therefore, the choices that cities make concerning these systems can significantly affect energy consumption (Singh et al. 2012). It is important to highlight here that, despite the advanced (tertiary) treatment used by the Albuquerque WWTP, wastewater effluent is still the major source of nutrients to the Rio Grande (N loads of up to 1,330 kg N/day (Mortensen et al. 2016)). Also, because the WWTP is located <15 km upstream of the major diversion (Isleta Dam) that supports agriculture downstream of Albuquerque, wastewater is currently always being recycled after it is diluted with river water. In dry seasons during the early summer, discharges from the WWTP into the Rio Grande can represent up to 80% of the total river discharge. Thus, the irrigation network near Albuquerque provides an excellent system to investigate opportunities for closing nutrient loops in arid-land rivers, which are spread across the globe and share commonalities with the Rio Grande, while considering the fluxes and environmentally sustainable management of FEW resources.

**Non-physical Alternatives**: The seasonality observed in our data concerning nutrient sink/source behavior suggests opportunities to recycle nutrients from the WWTP effluent to holistically manage FEW resources. For example, our data show that in the spring and summer the Rio Grande processes nutrients more efficiently than during the fall and winter (Figure 4). Therefore, timing WWTP releases into the irrigation network during the growing season may supply needed nutrients without addition of fertilizers, and optimize or restore critical ecosystem services (e.g., nutrient retention, crop production) along the Rio Grande-irrigation network. The current paradigm guiding stream restoration projects pertaining to water quality is that a modification of the physical system to increase residence times will result in increased nutrient retention. Here, we proposed that instead of (or in addition to) restoring streams via modification of the physical system, it could be plausible to time WWTP effluent discharge and nutrient resource supply to optimize the retention of the nutrient(s) of concern in the river and the irrigation network.

Another angle less explored in the current body of research is the role of stoichiometry in modulating nutrient uptake. It is well understood that aquatic ecosystem and crop demands for macronutrients (carbon, nitrogen and phosphorous) are organized by the stoichiometric constraints of the biotic communities (Redfield 1958; Hecky et al. 1993; Klausmeier et al. 2004). The most influential study of ecological stoichiometry came from Redfield 1934 who noted that marine phytoplankton generally contained a ratio of C:N:P of 106:16:1 in their biomass, and that these ratios were similar to those available in their environment. This “Redfield ratio” suggests that an ecosystem requires an optimal distribution of available nutrients to flourish and has been used as a guide for many other environmental stoichiometry studies. In our context, stoichiometric constraints limit uptake of one nutrient (e.g., N) by the supply of another (e.g., P), and this may be manifested as saturation behaviors, such as those shown in Figures 4 and 5 during the fall and winter, even though the river does not reach eutrophication levels. Besides reducing nutrient retention capacity along channels, such stoichiometric imbalances may result in microbial community changes with repercussions across entire river food webs (Briggs et al. 2013; Hall et al. 2013; Wohl et al. 2015). With this in mind and recalling that WWTPs are the main sources of nutrients to our study reach, we propose that releasing stoichiometrically balanced WWTP effluents may be another non-physical restoration approach to create “hot spots” and “hot moments” (i.e. locations and periods of increased nutrient retention) along the Rio Grande-irrigation network.

**Physical Alternatives**: The Albuquerque WWTP is a major source of flow to the Rio Grande (Figure 3) and could be used to enhance floodplain and riparian zone interaction by releasing in pulses rather than at a constant discharge. This will help mimic natural flow pulses that have been lost or attenuated due to physical restoration and flow control structures. These flow pulses will help increase lateral connectivity between the river and its floodplain, which has been shown to enhance nutrient processing in rivers and wetlands (Goring et al. 2014; Covino 2017). Similarly, the Drain is a channelized gaining reach that acts as a pipe (such as those in drainage and sewage solutions) rather than a stream. Restoration techniques such as increased sinuosity and improved pool and riffle sequences could be used to enhance nutrient processing though increased water-sediment interactions, while creating enjoyable recreation environments.

The Delivery canal currently acts as a nutrient sink in the spring and summer, but it may be more ideal to make it carry treated wastewater with nutrients to the agricultural fields with minimal processing to supply more nutrients for crop production. Currently, the Delivery canal experiences sink behavior likely because of the numerous hydraulic jumps occurring at weir gauging stations, which contribute to water-sediment interactions with enhanced processing within the channel bed (Ensign and Doyle 2006). Thus, ensuring that flow is fast through this system by, for example, extending the length of the lining in the channel near hydraulic jumps would prevent interaction with the benthic hyporheic zone, limiting nutrient removal.

Finally, nutrients do not necessarily need to be released with the WWTP effluent and become a source to downstream waters. To avoid relying on the complexity and unpredictability of river systems, it might be best to remove nutrients at the WWTP and use them as dry fertilizers. While this would not have an immediate payoff, it could become cost-effective over time as we approach the exhaustion of mineral sources of nutrients such as P (Mortensen et al. 2016; You et al. 2019). While the science supports the possibility of this transition, laws do not and will need to be adjusted to allow the use of this unconventional source of fertilizer.

***Conclusion***

The idea of the Food-Energy-Water Nexus is to holistically manage our resources to prevent waste and maximize overall system efficiency; our system and many others are currently not equipped to seamlessly shift to recycling nutrient resources from WWTPs because of financial constraints, technological constraints, and management constraints. Breaking from the status quo will require collaboration between farmers, municipalities, and the federal government to adopt a FEW approaches to nutrient management. The reward of such cooperation could introduce a way to lower energy consumption by the WWTP and the farmers and possibly allow impacted systems to recover from nutrient degradation, hypoxia, and declining biodiversity.

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