

## Using $^{17}\text{O}$ to Investigate Nitrate Sources and Sinks in a Semi-Arid Groundwater System

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**ABSTRACT:** We apply a triple isotope approach for nitrate that utilizes  $\Delta^{17}\text{O}$  as a conservative tracer, in combination with  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$ , to assess source/sink dynamics of groundwater nitrate beneath alluvial washes in a semiarid urban setting. Other studies have used  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  to determine nitrate sources and cycling, but the atmospheric  $\delta^{18}\text{O}$  signature can be overprinted by biogeochemical processes. In this study,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values of nitrate were coupled with  $\delta^{17}\text{O}$  values of nitrate to quantify atmospheric nitrate inputs and denitrification amounts. Results show generally low groundwater nitrate concentrations (<0.2 mmol/L) throughout the basin; high nitrate concentrations (up to 1 mmol/L) with evidence for some denitrification were detected in areas where effluent was the predominant source of recharge to groundwater. Furthermore, the denitrification was inferred from elevated  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values which were reinforced by increases in observed  $\delta^{17}\text{O}$  values. Finally, relatively low, but significant atmospheric nitrate concentrations were measured in groundwater (up to 6% of total nitrate). This study concludes that the triple isotope approach improves determination of the proportion of atmospheric nitrate and the significance of denitrification in natural waters, allowing us to develop a conceptual model of the biogeochemical processes controlling nitrogen in an urban setting.



### ■ INTRODUCTION

Nitrate is a common contaminant in groundwater worldwide.<sup>1</sup> Concentrations above the maximum contaminant level (MCL; 0.71 mmol/L  $\text{NO}_3^-$ ; 10 mg  $\text{NO}_3^-/\text{N}/\text{L}$ )<sup>2</sup> have been measured in the unsaturated zone and shallow aquifers in arid regions of the world.<sup>3–8</sup> Often such areas depend on groundwater as the key source of potable water, so understanding the sources and processes affecting nitrate concentrations in arid and semiarid aquifers is of critical importance.

Researchers often use  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of nitrate to differentiate among various sources of nitrate.<sup>6,9,10</sup> This approach is known as the dual isotope technique, where assessing the relative importance of atmospheric, terrestrial, wastewater, and fertilizer nitrate is determined by interpreting the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  isotope data in isotope weighted mixing plots. However, the microbial process of denitrification often obscures the isotopic composition of the original nitrate source(s) by simultaneously modifying both the oxygen and nitrogen stable isotope ratios, typically by isotopic enrichment in the residual nitrate pool.<sup>10</sup> The enrichment process combined with significant overlap in isotopic values among a variety of nitrate sources can often result in ambiguous interpretation of dual  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  isotope data. This ambiguous interpretation creates problems when attempting to delineate possible nitrate sources and the importance of the processes that influence the concentration of nitrate in natural waters.

A promising new technique employs  $\Delta^{17}\text{O}$  as a conservative tracer of atmospheric nitrate to better constrain its proportion in soils and groundwater.<sup>11</sup> In most biogeochemical processes

that fractionate isotopes,  $\delta^{17}\text{O}$  is directly related to  $\delta^{18}\text{O}$  by a factor of 0.52. In contrast, photochemical production of nitrate in the atmosphere has an excess  $^{17}\text{O}$  based on what is expected from the  $\delta^{18}\text{O}$  value and this excess in the  $\delta^{17}\text{O}$  signature is designated as  $\Delta^{17}\text{O}$  ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \cdot \delta^{18}\text{O}$ ). This approach should allow  $\Delta^{17}\text{O}$  to be used as a way of transforming dual isotope plots by removing the atmospheric nitrate contribution<sup>12,13</sup> and allow a better constraint on the significance of bacterially mediated denitrification. Coupling nitrate concentration data with fractionation trends in  $\delta^{15}\text{N}$  and both  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values, could improve quantification of nitrate sources and the importance of denitrification in groundwater systems.

It has been shown that anthropogenic sources of N are significant in arid and semiarid urban areas,<sup>13,14</sup> such as Tucson, Arizona in the southwestern United States (U.S.). Like much of the southwestern U.S., Tucson is characterized as semiarid with limited soil moisture content, sparse vegetation density, warm temperatures (highs of 45 °C), and an urban population near 1 million. Sources of nitrate found in local soils and surface waters include atmospheric deposition (8-year average wet nitrate deposition in the Tucson area is 3.8 kg  $\text{ha}^{-1} \text{yr}^{-1}$  measured by the National Atmospheric Deposition Program), the discharge of treated wastewater into ephemeral streams, the use of fertilizers in park lawns, and animal wastes from areas

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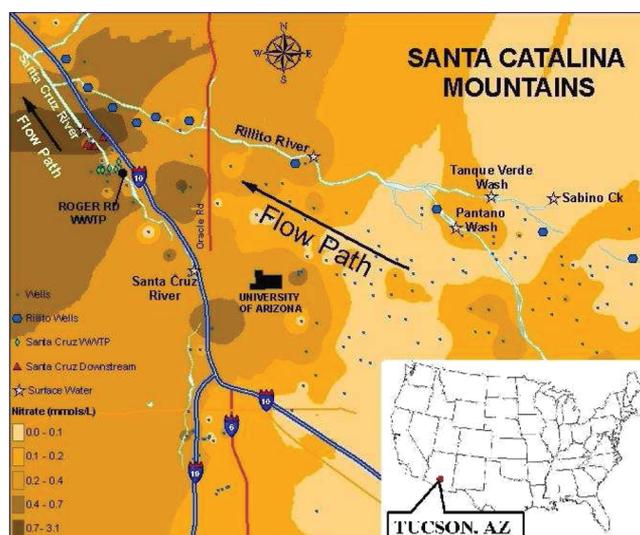
with ranching activity. These nitrate sources have the potential of leaching into the groundwater thereby degrading the water quality of this important water resource; groundwater provides all of the potable water for Tucson Water (personal communication with Ralph Marra, Hydrologist, Tucson Water). Here we use a comparison between the ephemeral Rillito (ephemeral) and Santa Cruz (effluent dominated) Rivers to better understand the underlying controls on the sources and sinks of nitrate in semiarid groundwater systems.

The current study (i) uses a triple stable isotope approach to quantify the contribution of atmospheric nitrate to surface waters and the proportion reaching the Tucson groundwater system, and to transform  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  data to assess the importance of denitrification and other nitrate sources in the Tucson groundwater system; (ii) utilizes available geochemical data to estimate the contribution of wastewater effluent to nitrate in the groundwater; and (iii) synthesizes the results of the study to develop a conceptual model of nitrogen biogeochemistry in an arid and semiarid system.

## EXPERIMENTAL SECTION

**Study Area.** The study sites are in the Santa Cruz and Rillito River floodplains, which are located within the Tucson basin. In general, groundwater in the alluvial aquifer beneath the Santa Cruz and Rillito Rivers can be considered oxic because of the high porosity and low organic material content of aquifer materials. These conditions are similar to most basin and range aquifers of the western United States that have been generally found to be oxic.<sup>15</sup> There are no perennial streams in the basin other than short reaches along the Santa Cruz River that have continuous discharge of effluent from Wastewater Treatment Plants (WWTPs). Based on hydraulic gradients, the direction of groundwater flow in the Tucson Basin is from east and southeast to northwest.<sup>16</sup> The depth to the water table increases from 38 to 52 m with downstream distance along the Rillito River and it varies between 42 and 47 m beneath the Santa Cruz River.

Wells were sampled adjacent to the Rillito River and the wastewater effluent dominated Santa Cruz River floodplains (Figure 1), where significant groundwater recharge occurs.<sup>16</sup> To examine lateral and longitudinal hydrologic and biogeochemical processes along the Santa Cruz, two well transects were selected, one near the Roger Road WWTP and the other one 1.4 km downstream (Figure 1). The groundwater transect along the Rillito River consisted of a series of monitoring and pumping wells arrayed longitudinally downstream where urbanization increases from low-density residential to high-density commercial along the transect. Surface water was also sampled along the Santa Cruz River and the Rillito River and at the outlet of ephemeral channels that were discharging into the river during a summer rain event to obtain preinfiltration nitrate concentrations and isotopic signatures of possible source waters (Figure 1). Water sources likely evolve along the Rillito groundwater flow path; beginning in the east with inputs from Catalina Mountain runoff through wash infiltration before transitioning to more urban runoff from outlets of the urban drainage system during storms. Conversely, wastewater dominates recharge in the Santa Cruz River floodplain and thus it was assumed that our effluent samples represent the Santa Cruz River during nonstorm flow conditions. Because previous groundwater nitrate concentrations have varied by less than 0.02 mmol/L over 4 years of sampling (City of Tucson, unpublished water quality data) a one-time sampling campaign was determined sufficient to capture steady-state groundwater concentrations and isotopic signatures along our sampling transects.



**Figure 1.** Wells sampled along the Rillito River (blue circles), and at two Santa Cruz River cross sections: upstream near the wastewater treatment plant (green diamonds) and downstream (red triangles). Runoff samples were collected in major washes (stars) during a summer rain event. Shading represents nitrate concentrations modeled with data from 230 wells. Concentrations generally increase from the southeast to the northwest, with the darkest shade representing concentrations above the MCL.

**Sample Collection and Analysis.** All samples were collected using established field protocols and analyzed for nutrient concentrations using published methods. To avoid sampling stagnant water, three well casing water volumes were pumped and discarded prior to groundwater sample collection. Samples for the combined analysis of anions and nitrate stable isotopes were collected in triple-rinsed HDPE bottles. A subset of these samples was collected and stored in amber glass bottles for the analysis of total nitrogen (TN) and dissolved organic carbon (DOC). After collection, the samples were returned to the lab, filtered (0.45- $\mu\text{m}$  nylon), and stored at 4 °C in the dark. The samples were then analyzed for anions (chloride and nitrate) using ion chromatography (Dionex 4000i) and for DOC and TN by 680 °C combustion and catalytic oxidation (Shimadzu TOC-V). Chloride data were useful to study the fate of nitrate and to trace source water contributions using chloride concentrations since chloride is considered a conservative tracer because it is generally inert to biological and chemical transformation in most hydrologic systems. DOC and TN were measured to shed light on the role of biological processes during recharge, as organic matter is required for denitrification.

Aliquots of the samples were processed for nitrate isotopes using recently established methods. Samples were preconcentrated using anion exchange resin and converted to  $\text{AgNO}_3$ .<sup>17</sup> The oxygen isotopes  $\delta^{18}\text{O}_{\text{NO}_3}$  and  $\delta^{17}\text{O}_{\text{NO}_3}$  were measured by isotope ratio mass spectrometry (IRMS) at the Purdue Stable Isotope facility using previously described  $\text{AgNO}_3$  thermal decomposition method<sup>11</sup> with analytical precisions of  $\pm 0.5\%$  and  $\pm 0.2\%$ , respectively. Analysis of  $\delta^{15}\text{N}_{\text{NO}_3}$  was carried out with an Elemental Analyzer IRMS using 2 mg of  $\text{AgNO}_3$  salt<sup>18</sup> with analytical precision of  $\pm 0.05\%$ .

**Quantifying Nitrate Sources Using a Multiple Isotope Mixing Model.** When nitrate from different sources is mixed together, if each source has a unique isotopic composition, the relative importance of each source can be determined using an isotope mixing model assuming conservative mixing. In the

Tucson system, three sources are likely to play an important role in the nitrate budget: atmospheric deposition ( $\text{NO}_3^-_{\text{atm}}$ ), nitrification of  $\text{NH}_4^+$  from sewage and nitrification of  $\text{NH}_4^+$  from plant or other biological material ( $\text{NO}_3^-_{\text{sew}}$ ), and nitrification of plant or other biological material ( $\text{NO}_3^-_{\text{bio}}$ ). We are interested in the relative importance, or fraction ( $f$ ), of these three sources in the nitrate mixture found in groundwater. However, since biogeochemical processes such as denitrification, fractionate oxygen and nitrogen isotopes in  $\text{NO}_3^-$  based on their relative mass differences, the isotopic composition of the mixture does not remain fixed but can change according to the enrichment factor ( $\epsilon$ ) of the process. This can be written as follows:

$$\delta^{18}\text{O}_{\text{NO}_3\text{mix}} = f_{\text{atm}} \times \delta^{18}\text{O}_{\text{NO}_3(\text{atm})} + f_{\text{sew}} \times \delta^{18}\text{O}_{\text{NO}_3(\text{sew})} + f_{\text{bio}} \times \delta^{18}\text{O}_{\text{NO}_3(\text{bio})} + \epsilon^* f_{\text{removed}} \quad (1)$$

$$\delta^{15}\text{N}_{\text{NO}_3\text{mix}} = f_{\text{atm}} \times \delta^{15}\text{N}_{\text{NO}_3(\text{atm})} + f_{\text{sew}} \times \delta^{15}\text{N}_{\text{NO}_3(\text{sew})} + f_{\text{bio}} \times \delta^{15}\text{N}_{\text{NO}_3(\text{bio})} + \epsilon^* f_{\text{removed}} \quad (2)$$

$$f_{\text{atm}} + f_{\text{sew}} + f_{\text{bio}} = 1 \quad (3)$$

Because there is a linear relationship between the enrichment factor for oxygen and nitrogen during denitrification the system has three equations and four unknowns ( $f_{\text{atm}}$ ,  $f_{\text{sew}}$ ,  $f_{\text{bio}}$ , and  $\epsilon$ ) ( $f_{\text{removed}}$  can be calculated using mass loss of nitrate compared to a conservative tracer such as  $\text{Cl}^-$ ) and no exact solution to the mixing model can be attained.

Determining the amount of atmospheric nitrate in the nitrate mixture can be accomplished applying an isotopic mass balance using  $\Delta^{17}\text{O}$ , which removes one degree of freedom and allows the above equations to be solved. Biological or chemical processes that produce nitrate usually fractionate the oxygen isotopes in a mass-dependent manner, resulting in a linear relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ :

$$\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O} \quad (4)$$

Atmospheric photochemical reactions, however, can fractionate oxygen isotopes “independently of mass”, resulting in a higher  $\delta^{17}\text{O}_{\text{NO}_3}$  than the expected relationship ( $\delta^{17}\text{O}_{\text{atm}} > 0.52 \times \delta^{18}\text{O}$ ). The difference between measured and expected  $\delta^{17}\text{O}$  values is quantified by the following:<sup>13</sup>

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} \quad (5)$$

Atmospheric nitrate is known to have positive  $\Delta^{17}\text{O}$  values and they are unaffected by terrestrial processes, such as denitrification or assimilation because the fractionation by these processes will vary as  $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ .<sup>11</sup> In this case, the nitrate mixture is considered to have only two sources of nitrate: atmospheric nitrate with a mole fraction  $f_{\text{atm}}$  and terrestrial nitrate with a mole fraction of  $f_{\text{terr}} = f_{\text{sew}} + f_{\text{bio}}$  and  $f_{\text{atm}} + f_{\text{terr}} = 1$ . This leads to the general  $\Delta^{17}\text{O}$  mass balance equation

$$\Delta^{17}\text{O}_{\text{NO}_3\text{mix}} = f_{\text{NO}_3\text{atm}} \times \Delta^{17}\text{O}_{\text{NO}_3\text{atm}} + f_{\text{NO}_3\text{terr}} \times \Delta^{17}\text{O}_{\text{NO}_3\text{terr}} \quad (6)$$

where  $\Delta^{17}\text{O}_{\text{NO}_3\text{atm}}$  and  $\Delta^{17}\text{O}_{\text{NO}_3\text{terr}}$  are the  $\Delta^{17}\text{O}$  values of the atmospheric and terrestrial nitrate, respectively, and  $\Delta^{17}\text{O}_{\text{NO}_3\text{mix}}$  is the  $\Delta^{17}\text{O}$  value of the nitrate mixture, which is measured in the nitrate collected from the well and river samples discussed above.

The  $\Delta^{17}\text{O}$  values of atmospheric and terrestrial nitrate have been documented in several other studies. Atmospheric deposi-

tion studies have measured a  $\Delta^{17}\text{O}$  range of 20–30‰ in atmospheric nitrate samples.<sup>11,19</sup> The higher values occur briefly during winter and most  $\Delta^{17}\text{O}$  values of atmospheric nitrate cluster around an average value of 23‰ with a standard deviation of 3‰.<sup>19</sup> Terrestrial nitrate is from nitrification whose source of reduced N could be from sewage, fertilizer, and microbial or plant N mineralization. Oxygen atoms incorporated into terrestrial nitrate during nitrification are derived from both atmospheric  $\text{O}_2$  or soil/groundwater  $\text{H}_2\text{O}$  molecules<sup>10</sup> both of which have  $\Delta^{17}\text{O}$  values of zero.<sup>11,12</sup> Because the nitrification process is a normal mass-dependent kinetic process, the  $\Delta^{17}\text{O}_{\text{NO}_3\text{terr}}$  value is assumed to be zero, which reduces eq 3 to

$$\Delta^{17}\text{O}_{\text{NO}_3\text{mix}} = f_{\text{NO}_3\text{atm}} \times \Delta^{17}\text{O}_{\text{NO}_3\text{atm}} \quad (7)$$

Using the average  $\Delta^{17}\text{O}_{\text{NO}_3\text{atm}}$  value of 23‰, the estimated proportion of atmospheric nitrate and terrestrial nitrate can be calculated as follows:

$$f_{\text{NO}_3\text{atm}} = \Delta^{17}\text{O}_{\text{NO}_3\text{mix}} / 23\text{‰} \quad (8)$$

$$f_{\text{NO}_3\text{terr}} = 1 - f_{\text{NO}_3\text{atm}} \quad (9)$$

Using an annual average value for  $\Delta^{17}\text{O}_{\text{NO}_3\text{atm}}$  is appropriate in this circumstance since groundwater is by definition an integration of a large number of aqueous fluxes over an extended time scale.

An advantage of using the  $\Delta^{17}\text{O}$  value to determine the atmospheric nitrate fraction is that that fraction can then be used to transform the terrestrial nitrate  $\delta^{18}\text{O}$  value. This is important because atmospheric nitrate is known to have high  $\delta^{18}\text{O}$  values relative to V-SMOW (40–90‰), and even a small fraction of atmospheric nitrate can elevate nitrate  $\delta^{18}\text{O}$  values in the mixture. For example, only 10% atmospheric nitrate could raise the mixture nitrate  $\delta^{18}\text{O}$  value by up to 9‰. If elevated nitrate  $\delta^{18}\text{O}$  values are inferred to be the result of denitrification,<sup>10</sup> then removing the atmospheric nitrate  $\delta^{18}\text{O}$  contribution is crucial. Analysis of available atmospheric nitrate isotope data<sup>11–13</sup> shows that the correlation between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  can be fitted to the equation

$$\delta^{18}\text{O}_{\text{NO}_3\text{atm}} = (2.287 \times \Delta^{17}\text{O}_{\text{NO}_3\text{atm}} - 10.1) \pm 10 \quad (10)$$

all in units of permil. Using this equation to estimate the  $\delta^{18}\text{O}$  value of atmospheric nitrate and the  $f_{\text{NO}_3\text{atm}}$  from eq 5, the transformed terrestrial nitrate  $\delta^{18}\text{O}_{\text{NO}_3\text{terr}}$  value can be estimated as

$$\delta^{18}\text{O}_{\text{NO}_3\text{terr}} = \delta^{18}\text{O}_{\text{NO}_3\text{mix}} - f_{\text{NO}_3\text{atm}} \times \delta^{18}\text{O}_{\text{atm}} \quad (11)$$

A similar isotope transformation approach could be used for mixed nitrate samples by removing the effect of atmospheric nitrate fractionation processes on the  $\delta^{15}\text{N}$  signature.<sup>20</sup> Atmospheric nitrate (aerosol and dissolved nitrate) from Tucson has  $\delta^{15}\text{N}$  values that exhibit a distinct seasonal trend range from a maximum of +12‰ in the winter to –2‰ in the summer with respect to air  $\text{N}_2$ .<sup>21</sup> The mass weighted average  $\delta^{15}\text{N}$  value of atmospheric nitrate over the course of a year is  $+4 \pm 5\text{‰}$  which can be used along with  $f_{\text{NO}_3\text{atm}}$  obtained from the  $\Delta^{17}\text{O}$  analysis to correct the  $\delta^{15}\text{N}$  of terrestrial nitrate using

$$\delta^{15}\text{N}_{\text{NO}_3\text{terr}} = \delta^{15}\text{N}_{\text{NO}_3\text{mix}} - f_{\text{NO}_3\text{atm}} \times \delta^{15}\text{N}_{\text{atm}} \quad (12)$$

This correction is minor because the  $\delta^{15}\text{N}$  is close to zero and the  $f_{\text{NO}_3\text{atm}}$  is typically small in mixed systems.

Using conservative tracers in combination with nitrate concentrations can permit an estimate of how much nitrate, organic carbon, or total nitrogen is lost along a flow path. The conservative tracer confirms the fraction of a specific water source that arrives at a point. The nonconservative chemicals (e.g., nitrogen and carbon chemical species) can then have the amount of mass lost between source and sample location calculated as

$$\%X \text{ Removal} = 100 \times \left( \frac{[X]_{\text{effluent}} - [X]_{\text{groundwater}}}{[X]_{\text{effluent}}} \right) \quad (13)$$

In this example all groundwater is assumed to originate as effluent and thus any lower concentration of the constituent in question [X] is attributed to a loss versus a higher concentration would be attributed to a gain.

**Uncertainty Estimation.** Propagation of uncertainty from the underlying water sampling and isotopic analysis procedures developed in this study can be done using a method developed by Phillips and Gregg.<sup>22</sup> This uncertainty estimation approach assumes a simple direct mixing approach of two sources as in eq 3. The resulting variance estimate of the fraction of atmospheric nitrate is

$$\sigma_{f\text{NO}_3}^2 = \frac{1}{(\Delta_{\text{O}_3} - \Delta_{\text{non-atm}})^2} \left[ \sigma_{\Delta_{\text{sampl}}}^2 + f_{\text{NO}_3}^2 \sigma_{\Delta_{\text{O}_3}}^2 + (1 - f_{\text{NO}_3})^2 \sigma_{\Delta_{\text{non-atm}}}^2 \right] \quad (14)$$

where  $\sigma^2$  is variance of each potential nitrate source or that of the sample. The standard deviation (the variance<sup>-1/2</sup>) for the  $\Delta^{17}\text{O}$  value for each individual sample was estimated at 0.3‰ based on past analytical results.<sup>11,19</sup> The standard deviation for the  $\Delta^{17}\text{O}$  value for nonatmospheric samples was assumed to be 0.3‰ based on laboratory experience that nonatmospheric test materials always return values of 0 for  $\Delta^{17}\text{O}$  (thus this value is an overestimate of uncertainty). Finally, a value of 3‰ was used as the standard deviation of the atmospheric nitrate based on prior literature results.<sup>11,19</sup> The variance and results standard error of the estimate were calculated using an excel spreadsheet available from the EPA (<http://www.epa.gov/wed/pages/models.htm>).

RESULTS AND DISCUSSION

**Atmospheric Proportion.** In contrast to previous studies that have measured significant atmospheric deposition in urban settings of the southwestern U.S.,<sup>13,14</sup> the direct atmospheric contribution of nitrate to Tucson’s groundwater measured in this study is relatively minor (Figure 2). Low  $\Delta^{17}\text{O}_{\text{NO}_3\text{mix}}$  values (0.7–1.4‰) in the groundwater samples suggest 3–6% of groundwater nitrate is unprocessed atmospheric nitrate. In contrast the proportion of atmospheric nitrate was significantly higher in the runoff samples, up to 43%. This indicates that a significant fraction of atmospheric nitrate is processed by N cycling when it recharges through river sediments to the groundwater. Processes at the soil level (including plant uptake and mineralization) and mixing with other nitrate sources (fertilizers, soil N, manure/septic) modify the original  $\Delta^{17}\text{O}_{\text{NO}_3\text{atm}}$  value of the sample, thereby removing its atmospheric imprint<sup>10,11</sup> (Figure 2). Although all groundwater samples had similar fractions of nitrate from atmospheric contributions, a slightly higher fraction was measured beneath the Santa Cruz River (6%). This result was likely due to higher recharge rates to groundwater in this setting due to the consistent flow of effluent in the channel. Previous studies suggested that nitrate originating from precipitation is

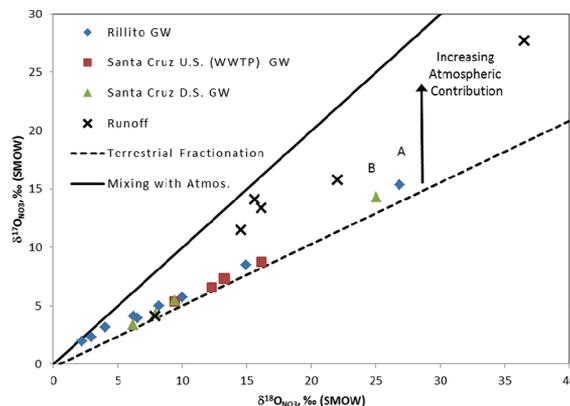


Figure 2. Plot of  $\delta^{17}\text{O}$  vs  $\delta^{18}\text{O}$ . The greater the vertical deviation from the terrestrial fractionation line ( $\Delta^{17}\text{O}$ ) the greater the atmospheric influence. The furthest away from the terrestrial N range, the greater the effect of terrestrial fractionation. Runoff samples have the most atmospheric influence. The downstream Santa Cruz samples underwent less terrestrial fractionation than the WWTP samples (except for Sample B). Among groundwater samples, A and B had the most atmospheric input (6%) and underwent the most terrestrial fractionation.

distinguishable based on its elevated  $\delta^{18}\text{O}_{\text{NO}_3}$  value. Few of our nitrate samples had  $\delta^{18}\text{O}_{\text{NO}_3\text{mix}}$  values greater than 20‰ in both surface and subsurface samples and would indicate no atmospheric nitrate fraction based on known terrestrial  $\delta^{18}\text{O}_{\text{NO}_3}$  values<sup>9,12,13,23,24</sup> (Figure 3). This highlights the sensitivity of

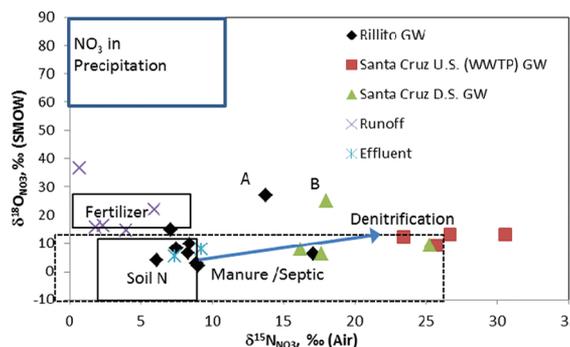
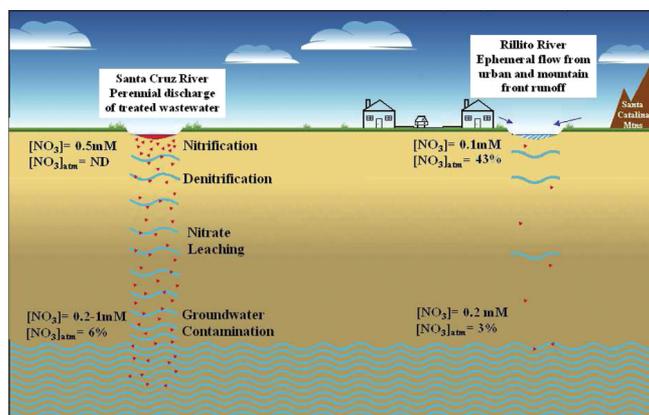


Figure 3. Plot of  $\delta^{18}\text{O}$  vs  $\delta^{15}\text{N}$ . Most Rillito groundwater samples plotted within the soil N range and the Santa Cruz samples within the manure/septic range with a denitrification trend from stream level to groundwater. The runoff data plotted near the lower values of the precipitation range. The elevated  $\delta^{18}\text{O}$  of samples A and B are likely due to mixing with atmospheric nitrate or to sample processing errors and denitrification. US and DS stand for upstream and downstream transects along the effluent-dominated reach of the Santa Cruz.

$\Delta^{17}\text{O}$  analysis for detecting even trace amounts of atmospheric nitrate in mixed nitrate systems.

Uncertainty analysis for using the oxygen isotopes of nitrate to determine isotopic fraction originating as atmospheric versus terrestrial sources indicates that individual sample results should be looked upon skeptically but averaging across samples can result in robust estimates of atmospheric contribution to the nitrate observed in individual samples. For individual samples ( $n = 1$ ) the applied method results in a sample error of the estimate of 8% atmospheric nitrate meaning that a sample result of





**Figure 6.** Conceptual model showing nitrate infiltration patterns beneath the Santa Cruz and the Rillito Rivers. Red triangles represent nitrate molecules. Due to continuous discharge of nitrate-rich treated wastewater on the Santa Cruz, more nitrate reaches the groundwater. N cycling is measured beneath the Santa Cruz with significant denitrification. The opposite is true in the Rillito River with small sources of nitrate measured during ephemeral flows. Groundwater had low atmospheric nitrate (3–6%) with slightly more measured in the Santa Cruz groundwater.

affected by denitrification with changes in  $\delta^{17}\text{O}$  values of up to 11%. These results show the utility of  $\delta^{17}\text{O}$  isotopic analysis as a powerful tool to shed light on the degree of denitrification undergone by water samples.

Whereas previous studies have associated elevated nitrate concentrations with fertilizers, human and animal wastes, and  $\text{N}_2$  fixation by rhizobia bacteria at the root level of plants in arid regions of the world,<sup>3–8</sup> these studies were not able to quantify the atmospheric contribution to nitrate contamination. Using  $\delta^{17}\text{O}_{\text{NO}_3}$ , we are able to quantify contributions of atmospherically derived nitrate with higher certitude. Furthermore, this technique allows us to remove the atmospheric signal from the analysis to better constrain the remaining sources of nitrate to groundwater, and biogeochemical processes, such as denitrification, that may be a sink for nitrate.

**Conceptual Model.** As a whole our results have led us to develop a conceptual model of the difference in processes controlling the sources and sinks of nitrate beneath the Santa Cruz and Rillito Rivers (Figure 6). These two rivers represent divergent recharge and biogeochemical conditions. The Rillito represents a relatively pristine river system dominated by ephemeral flow conditions, whereas the Santa Cruz represents an effluent-dominated system. A key result here is that the more consistent flow conditions enabling direct hydrologic connections between the surface and groundwater aquifers<sup>16</sup> combined with consistent surface flow of nutrient rich waters, as seen in the effluent dominated Santa Cruz River, facilitates the transport of nitrate to the aquifer after biogeochemical processing along the recharge flow path. Additionally locations of more ephemeral connections (e.g., the Rillito) and thus intermittent recharge seem to limit the transport of nitrate to the groundwater resulting in lower nitrate concentrations and more limited impact of atmospherically derived nitrate along the ephemeral Rillito River. The evidence for this model is that the effluent-dominated reach has greater percentages of atmospheric nitrate in the subsurface despite effluent itself having no atmospheric signal (the atmospherically sourced nitrate thus coming from episodic runoff events).

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