USING ^{15}N, ^{18}O, AND ^{17}O TO DETERMINE NITRATE SOURCES AND REMOVAL PROCESSES FROM GROUNDWATER, TUCSON, ARIZONA

By

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Abstract

Nitrate is a common groundwater contaminant. Due to adverse health effects, waters above the Maximum Contaminant Level (MCL) of 10 mg NO_3-N/L or 0.71 mmols/L, are banned from domestic consumption by the EPA. Studies have measured elevated nitrate concentrations in arid land soils and groundwater around the world. These elevated concentrations could be detrimental to the environment and to human health. Thus, it is important to consider the different sources and processes affecting nitrate concentrations Here, a novel triple isotope system approach was employed, coupling $\delta^{17}O$ with $\delta^{18}O$ and $\delta^{15}N$ of nitrate to determine the sources (atmospheric, terrestrial, fertilizer, wastewater) and removal processes influencing nitrate concentrations in the Tucson basin groundwater system. Results show low groundwater nitrate concentrations (0.2 mmols/L) where wastewater was not a predominant source of water, versus high concentrations (1 mmols/L) above the MCL in groundwaters where wastewater was the dominant water source. Furthermore, groundwater up to 1.6 Km away from the wastewater stream was contaminated with effluent recharge waters. In addition, denitrification was inferred from $\delta^{18}O$ and $\delta^{15}N$ data with this inference reinforced by $\delta^{17}O$ data and $\delta^{15}N$ enrichments up to 26‰. Finally, low atmospheric nitrate was measured in groundwater, representing up to 6% of total nitrate. The triple isotope approach studied here is ideal for determining the proportion of atmospheric nitrate versus other terrestrial nitrate sources and the significance of nitrate removal processes.

1 Introduction

Nitrate is a common contaminant in groundwater around the world (WHO, 2006). In high concentrations, nitrate can cause eutrophication of aquatic ecosystems and methemoglobinemia (blue baby syndrome) by conversion to nitrite in infants (Adam, 1980; Fan et al., 1996). In Arizona, nitrate contamination is the leading cause for removing wells from production for domestic use (AZDEQ, 2002). The Environmental Protection Agency (EPA) has set the maximum contaminant level (MCL) for nitrate in drinking water to 0.71 mmols/L or 10 mg NO_3-N/L (EPA, 2006). High nitrate concentrations have been measured in the unsaturated zone and shallow aquifers in arid regions of the world with mean vadose zone nitrate profiles up to 14.5 mmol/L NO_3 (203 mg/L NO_3–N) in Senegal (Deans et al., 2005), 10 mmols/L NO_3 (140 mg/L NO_3–N) in Niger's groundwater (Girard & Hillaire-Marcel, 1997), 200 mmols/L NO_3 (2800mg/L NO_3–N) in Sudan's groundwater (Edmunds et al., 1992), 3.1 mmols/L NO_3 (43.4 mg/L NO_3-N) of natural origin in the Kalahari desert groundwater (Heaton, 1984), and as high as 143 mmols/L NO_3 (2000 mg/L NO_3–N) in southwestern U.S. soil profiles (Hunter et al., 1982; Walvoord et al., 2003). In light of health concerns and existing observed concentrations, understanding the sources and processes affecting nitrate concentrations in arid and semi-arid aquifers is of critical importance. In this study, we used elemental chemistry and stable isotopes of NO_3 (^{15}N, ^{18}O, and ^{17}O) to determine the sources and removal processes of nitrate in a semi-arid aquifer influenced by atmospheric, terrestrial and wastewater N sources.

Four major sources of nitrate found in groundwater and streams (Kendall, 1998; Mayer et al., 2002) include: (1) nitrate from fertilizer, which mainly comes from the addition of nitrogen as a nutrient to agricultural fields and lawns (Walvoord et al., 2003; McMahon & Bohlke, 2006); (2) nitrate from animal and human waste rich in organic nitrogen that decomposes and oxidizes to nitrate (Schmidt, 1973; Esposito, 1993; Aravena et al., 1993; Aravena & Robertson, 1998); (3) nitrogen originating from the decomposition of plant materials (mineralization) that cycles in the soil layer (Mayer et al., 2002; Johnson et al., 2005; Sirulnik et al., 2006) and (4) nitrate formed by photochemical reactions in the atmosphere. In the latter, nitrogen released from fossil fuel combustion, lightning N_2 fixation and degassing processes, oxidizes through cycling in the atmosphere before depositing in the biosphere (Michalski et al., 2004a-b; Ewing et al., 2007).

Nitrates are lost from soil and groundwater systems through three main processes. The first and most important process of nitrate removal is denitrification (Aravena & Robertson, 1998) where organisms break down nitrate to produce N_2 gas under anoxic conditions and in the presence of electron donors such as organic matter (Heaton, 1984; Aravena et al., 1993; Aravena & Robertson, 1998; Kendall, 1998):

$$4NO_3^- + 5C + 2H_2O \longrightarrow 2N_2 + 4HCO_3 + CO_2 \qquad (1).$$

Second, plants and microorganisms compete for nitrogen in the soil. They take up nitrate and ammonium as nutrients and convert them to organic N, a process known as immobilization (Johnson et al., 2005; Deans et al., 2006). Finally, due to its high mobility, nitrate can be lost from shallow soils and transported by recharge waters

(leaching). Leaching represents not only a loss of nitrate to the soil but also a source of nitrate to groundwater (Heaton, 1984; Walvoord et al., 2003; Deans et al., 2005; Johnson et al., 2005; McMahon & Bohlke, 2006).

Traditionally, researchers have used ^{15}N and ^{18}O of nitrate to differentiate between various N sources and to determine if denitrification is occurring (Aravena et al., 1993; Heaton, 1984; Kendall, 1998). However, microbial and physical processes can modify both the oxygen and nitrogen stable isotope ratios. For example, although precipitation nitrate has enriched $\delta^{18}O$ values compared to terrestrial nitrate, processes in the soil (immobilization and mineralization) can decrease its elevated isotopic mass ratio (Kendall, 1998). A recently developed technique employs the Oxygen-17 isotope of nitrate to better constrain the proportion of atmospheric nitrate and to evaluate the significance of isotopic fractionation (Michalski et al., 2003). Although most processes that fractionate oxygen molecules in NO_3 are mass dependent, giving $\delta^{17}O$ a direct relation to $\delta^{18}O$, atmospheric photochemical reactions fractionate oxygen molecules independent of mass, resulting in a higher $\delta^{17}O_{NO3}$ due to the oxygen's ozone origin (Thiemens et al., 1999). Using the ^{17}O, ^{15}N and ^{18}O of nitrate along with major element analysis of water solutes, we were able to: (1) evaluate the impact of nitrate-rich effluent on groundwater quality in the Tucson Basin, (2) determine if denitrification significantly reduced groundwater nitrate, and (3) quantify the proportion of atmospheric-derived nitrate in surface water and groundwater.

2   Background

2.1   Isotope Definitions

Isotopes are molecules of the same element that have different atomic mass due to different numbers of neutrons in the nucleus of the atom. For example, the most common oxygen molecule found on Earth, Oxygen-16 (denoted ^{16}O) which makes up 99.76% of Earth's oxygen, has 16 nucleons (protons + neutrons), whereas the two less common oxygen isotopes, ^{17}O (0.04%) and ^{18}O (0.2%) are heavier with 17 and 18 nucleons, respectively. A commonly used approach to express the isotopic variation between samples is the delta notation (Kendall, 1998):

$$\delta ‰ = [(R_s / R_{std}) - 1] \times 1000 \qquad (2),$$

where R denotes the $^{18}O/^{16}O$, $^{17}O/^{16}O$ or $^{15}N/^{14}N$ ratio of a compound in the sample (s) or standard (std). Oxygen isotopic mass ratios (expressed in ‰) are based on the Vienna Standard Mean Ocean Water (VSMOW) and nitrogen mass ratios are based on air N_2.

As compounds undergo chemical, physical, or biological reactions, the elements can fractionate, thereby changing their isotopic mass ratios. The fractionation, α, is:

$$\alpha_{p-s} = (1000 + \delta_p) / (1000 + \delta_s) \qquad (3),$$

where the subscripts p and s stand for product and substrate, respectively. A more common expression of isotope fractionation used is the enrichment factor (Equation 4).

$$\varepsilon = 1000 \times (\alpha - 1) \qquad (4)$$

For small fractionations, the enrichment is roughly equal to the change in isotopic mass

ratios between the product and the substrate:

$$\varepsilon = \delta_p - \delta_s \qquad (5).$$

For example, in biologically mediated denitrification, organisms preferentially break

down nitrate compounds with lighter isotopic mass ratios, leaving the substrate nitrate

more enriched in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, and producing N_2 and N_2O depleted in

$\delta^{15}N$ and $\delta^{18}O$. Like many other kinetic and equilibrium processes, isotopic fractionation

during denitrification follows the Rayleigh equation:

$$\delta_p = \delta_s - \varepsilon_{p-s} \text{ x } \ln(C_p/C_s) \qquad (6),$$

where the enrichment (ε) is related to both the change in isotopic mass ratios ($\delta_p - \delta_s$) and

the initial (C_s) and remaining (C_p) concentrations. A wide range of $\delta^{15}N$ enrichment

factors (5-40‰) have been measured in groundwater systems impacted by denitrification,

with corresponding fractionation factors ranging between 1.005-1.040 (Vogel et al.,

1981; Aravena & Robertson, 1998; Kendall, 1998).

2.2 Nitrate Isotopic Mass Ratios

Previous studies attempted to distinguish sources of nitrate based on their $\delta^{15}N$ isotopic

signatures (Heaton, 1984; Girard & Hillaire-Marcel, 1997). Due to their overlapping

$\delta^{15}N$ signatures, this approach was greatly improved by coupling $\delta^{15}N$ with $\delta^{18}O$ of

nitrate (Figure 1).
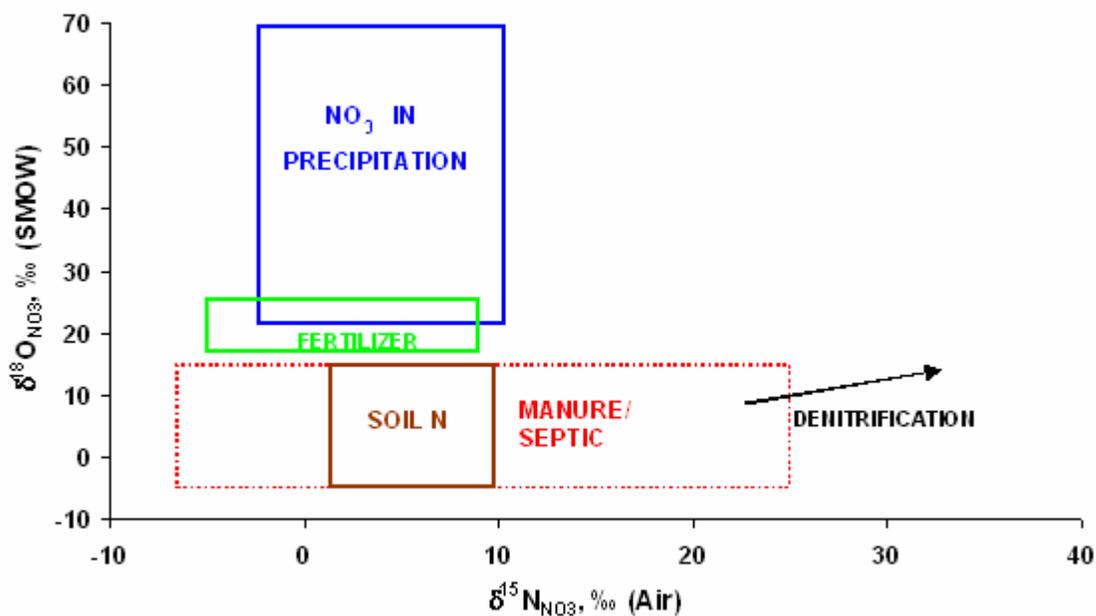
Figure 1. Plot of δ^{18}O vs δ^{15}N for the different nitrate sources. Precipitation nitrate has the highest δ^{18}O values. Although with similar mass ratios, manure/septic N can usually be distinguished by a more elevated δ^{15}N signature. More difficult to tease apart are nitrates from fertilizers and precipitation. Denitrification follows a 1:2 increase of δ^{18}O with respect to δ^{15}N along a flow path.

Fertilizer nitrate has δ^{18}O values near 22 ± 3‰. Although manure/septic and soil N have overlapping δ^{15}N and δ^{18}O ranges, studies have shown that manure/septic nitrates tend to have higher δ^{15}N values, at times exceeding 20‰ (Girard & Hillaire-Marcel, 1997; Kendall, 1998; Aravena et al., 1993; Mayer et al., 2002). Soil nitrates have δ^{15}N values generally between 3 and 10‰ (Girard & Hillaire-Marcel, 1997). Precipitation nitrate has the highest δ^{18}O values, ranging from 25‰ to 70‰ and overlapping with fertilizer nitrate isotopic mass ratios (Figure 1).

2.3 Denitrification

In addition to identifying sources of nitrate, isotopic data are useful for determining whether nitrates are affected by fractionating processes. For example, denitrification can be discerned by an increase of both $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ on a 1:2 slope (Figure 1). Furthermore, in biologically mediated denitrification, organisms reduce nitrate and produce N_2 gas, changing nitrogen from N^{+5} to N^0. This process requires electron donors, typically carbon in organic matter (Aravena & Robertson, 1998; Hedin et al., 1998; Kendall, 1998). During the redox reaction, carbon is oxidized from C^0 to C^{+4} as the dissolved organic matter is converted to CO_2 (Equation 1).

2.4 Atmospheric nitrate characterization

In most reactions, isotope fractionations are mass-dependent, occurring because of differences in isotopic mass ratios. Due to higher energy required to break down the bonds of the heavier isotope, biological or physical processes prefer to use the lighter from the heavier isotope. For example, due to ^{17}O's intermediate mass between ^{18}O and ^{16}O, the resultant $\delta^{17}O$ values in kinetic and equilibrium reactions are directly related to $\delta^{18}O$ via:

$$\delta^{17}O = 0.52 \times \delta^{18}O \qquad (7).$$

However, recent studies have found that in photochemical reactions occurring in the atmosphere, ^{17}O fractionates mass-independently (Thiemens et al., 1999; Michalski et al., 2003) giving it a distinctly elevated isotopic signature:

$$\delta^{17}O > 0.52 \times \delta^{18}O \qquad (8).$$

This distinction in the type of isotopic fractionation can be employed to quantify atmospheric from terrestrially derived nitrate. The difference between measured and expected $\delta^{17}O$ values from kinetic and equilibrium reactions ($\delta^{17}O = 0.52 \times \delta^{18}O$) is termed $\Delta^{17}O$ (capital delta seventeen O):

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \qquad (9).$$

Atmospheric deposition studies conducted in southern California (Michalski et al., 2003; Michalski et al., 2004b) and Chile (Michalski et al., 2004a; Ewing et al., 2007) measured a $\delta^{17}O$ range of 60-80‰ in atmospheric nitrate samples, whereas terrestrially derived nitrate had $\delta^{17}O$ values close to 0‰ (Figure 2) (Michalski et al., 2003). The enrichment in ^{17}O for atmospherically derived compounds (e.g. NO_3, SO_4…) is a result of atmospheric photochemical reactions (See Appendix B).

When atmospheric-derived nitrate mixes with terrestrial nitrate in the soil layer, the $\delta^{17}O$ signature of nitrate decreases (Figure 2). If the new nitrate pool undergoes further fractionation by terrestrial processes (immobilization, denitrification), its $\delta^{17}O$ value varies parallel to the terrestrial fractionation line with a slope of 0.52, as expressed in Equation 7, thereby preserving its original $\Delta^{17}O$ signature (Figure 2). Since processes can

alter the $\delta^{18}O_{NO3}$ values, the conservation of $\Delta^{17}O$ values is ideal for tracing back the proportion of atmospheric nitrate present in a sample (Michalski et al., 2003; Michalski et al., 2004a,b; Ewing et al., 2007).
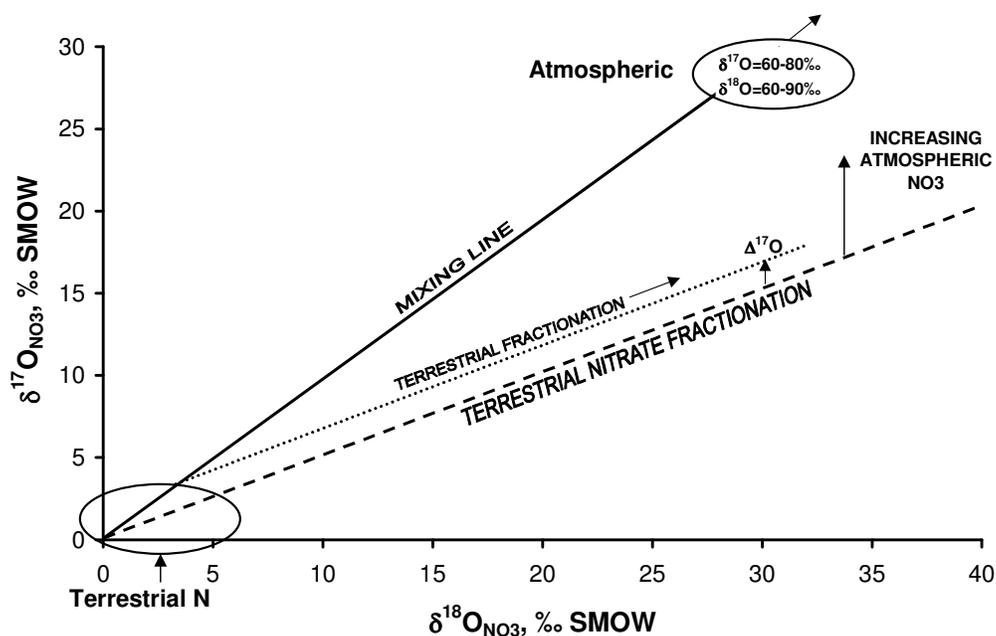
Figure 2. Plot of $\delta^{17}O$ vs $\delta^{18}O$ for nitrate. Terrestrial and atmospheric nitrate have distinct isotopic ranges. The figure illustrates the evolution of $\delta^{17}O_{NO3}$ as atmospheric nitrate deposits and mixes with terrestrial nitrate (solid line) and then undergoes processes at the soil level ("Terrestrial Fractionation" dotted line), preserving its $\Delta^{17}O$ signature. The greater the $\Delta^{17}O$, the more the atmospheric influence.

3   Methods

3.1   Study Area

The Tucson basin is an ideal hydrogeologic setting in which to examine groundwater

nitrates. In this semi-arid basin, there are no perennial streams other than short effluent-

dominated reaches from wastewater treatment plants on the Santa Cruz River. Studies

have shown that significant groundwater recharge occurs along the Rillito River

floodplain (Eastoe et al., 2004) and from treated wastewater outflows into the Santa Cruz

River. Furthermore, golf courses, agricultural activity, houses with septic tanks, landfills,

and atmospheric deposition (combustion of fossil fuels) are possible N sources in the

basin. In the last eight years, the National Atmospheric Deposition Program has measured

an average of 3.8 Kg/ha/yr wet nitrate deposition in a station near Tucson (NADP, 2008).

Nitrate concentration data of 230 Tucson wells measured in 2006-2007 was obtained

from the City of Tucson. From this data, a contour map was generated using an Inverse

Distance Weighted technique where each pixel point on the map was assigned a

groundwater nitrate concentration value based on the closest 12 wells. The weight of each

well on the pixel concentration was inversely proportional to the distance between the

well and pixel. A general trend of increasing nitrate concentrations was observed from

southeast to northwest, with concentrations exceeding the EPA's MCL near the effluent-

fed Santa Cruz River (Figure 3).
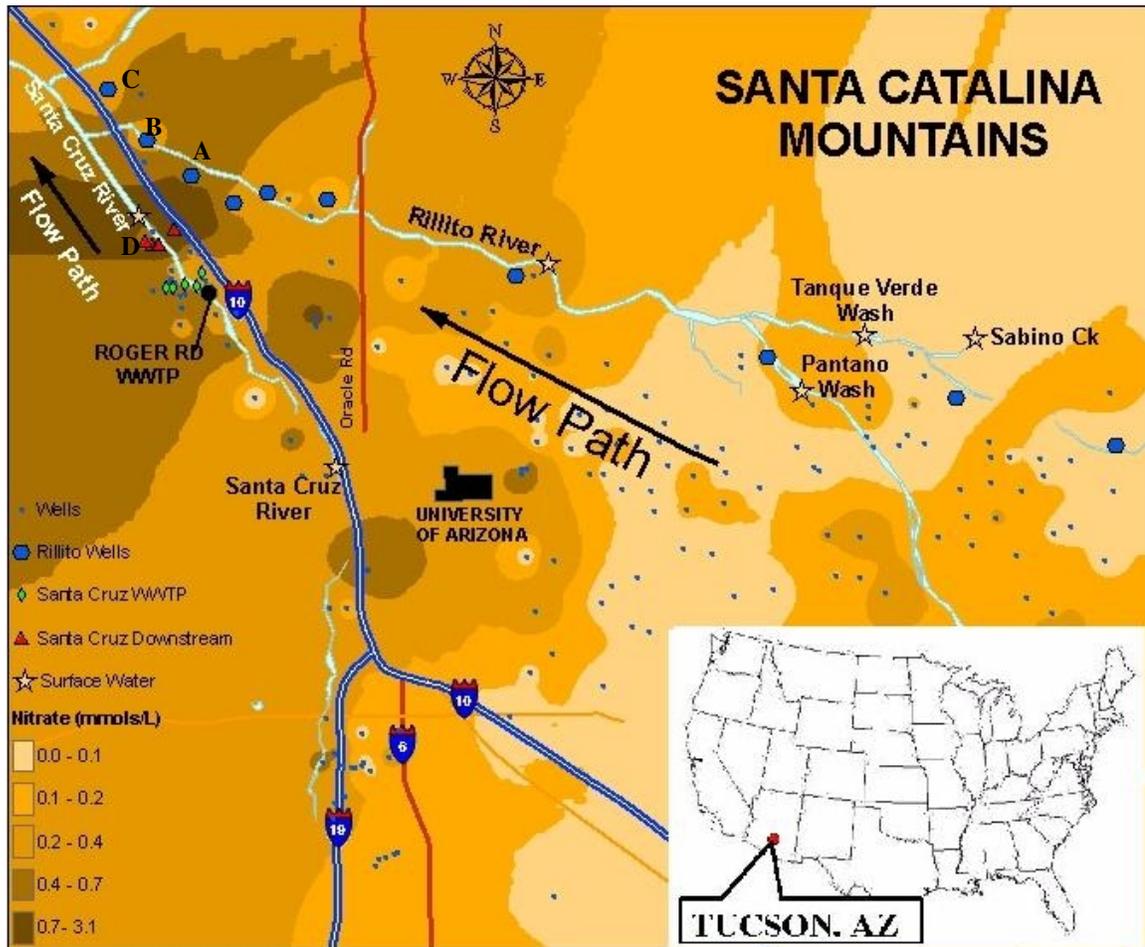
 Figure 3. Wells sampled along the Rillito River (blue circles), and at two Santa Cruz River cross-sections: near the wastewater treatment plant (green diamonds) and downstream (red triangles). Runoff samples were collected in major washes (stars) during a summer rain event. Shading represent nitrate 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.

A previous study characterized Tucson's groundwater regions based on their age, origin

and flow paths (Eastoe el al., 2004). The general direction of flow based on the gradient

was determined to be from east and southeast to west and northwest Tucson. Based on

this previous study, groundwater quality was analyzed along a flow path beneath the

Rillito River. Water sources likely evolve along this flow path from more mountain front

to more urban runoff dominated recharge. The depth to water table increases along the

Rillito River from 38 to 52m (Figure 4).

Since a significant source of recharge to Tucson's groundwater is treated effluent,

groundwater beneath a wastewater effluent fed wash, the Santa Cruz River was also

investigated. To examine both lateral and longitudinal processes, two well cross-sections

were selected along the Santa Cruz, one near the Roger Road Wastewater Treatment

Plant (WWTP) and the other one 1.4 Km downstream (See Figure 3). Along the Santa

Cruz, the water table varies between 42 and 47m below the land surface (Figure 4).
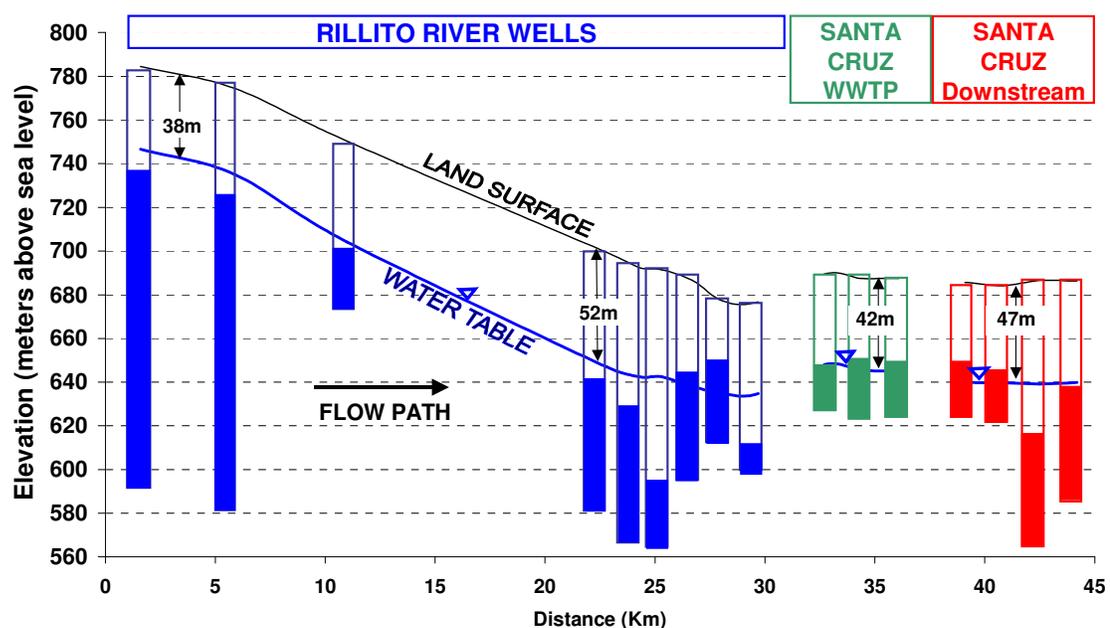
Figure 4. Surface-groundwater profile. The land surface, water table, screening top and bottom (hatching) of wells are shown along the Rillito River, and along the Santa Cruz River, at transects near and downstream from the Roger Road Wastewater Treatment Plant.

3.2   Sample Volume

Previous research (Chang et al., 1999; Silva et al., 2000) determined that 100-200 μmoles

of [NO$_3$] was needed for the analysis of nitrate isotopes $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. Based on

analysis of groundwater nitrate concentrations obtained from Tucson Water utility

company, 4 liters of sample per well (2 2-liter HDPE bottles were used) was required for

the combined analysis of anions, nitrate stable isotopes, water isotopes (δ^2H_{H2O} and

$\delta^{18}O_{H2O}$) and sulfur isotope ($\delta^{34}S_{SO4}$). In addition, a 125ml amber glass bottle sample was

collected for the analysis of Total Nitrogen (TN) and Dissolved Organic Carbon (DOC).

For this analysis, an amber glass bottle was necessary to minimize the entrance of light

into the bottle (limit bacterial activity) and to prevent carbon contamination from plastic

surfaces.

3.3   Water Sample Collection

A temporal analysis of Tucson groundwater nitrate concentrations obtained from Tucson

Water utility company showed very little variability in nitrate concentration. In four

years, nitrate concentrations did not fluctuate more than 0.02 mmols/L (Figure 5),

therefore, a one-time sampling campaign was sufficient to capture groundwater

concentrations and isotopic compositions.
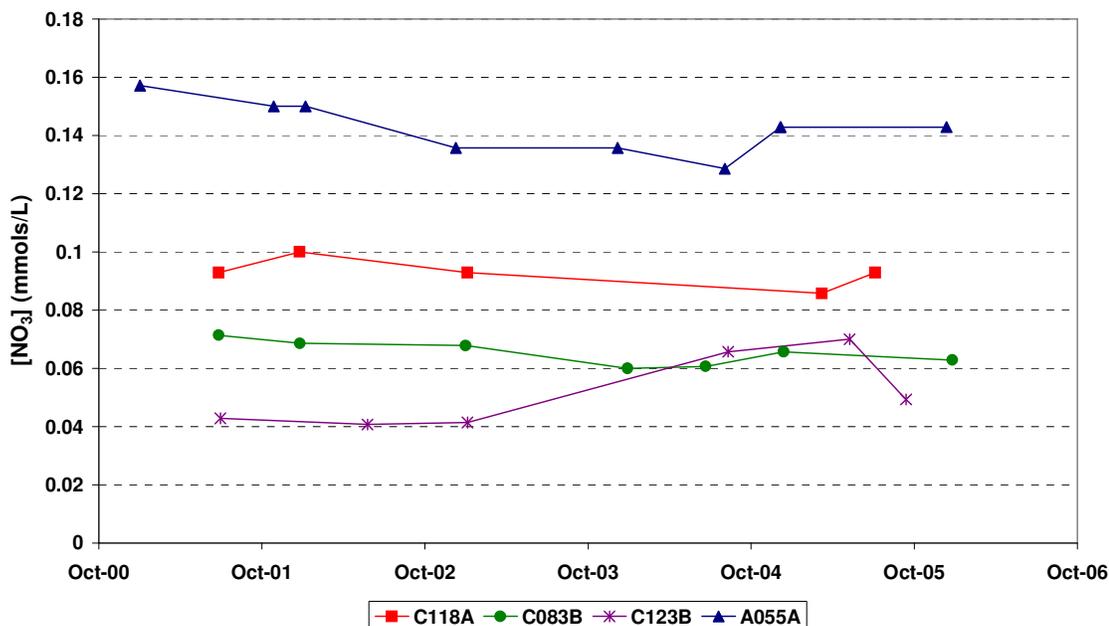
Figure 5. Temporal variability of groundwater nitrate concentrations. Little variability of nitrate concentrations was observed in four Tucson wells with less than 0.02 mmol/L change within 4 years.

To sample groundwater, one needs to be careful to not sample water standing for a long duration inside the well casing. To address this concern and sample fresh groundwater from monitoring wells, three well casing water volumes were pumped before sample collection. Using the known well casing depth and diameter, a measure of the water table depth was taken with a sounder to calculate the casing volume. All production wells were running, and hence, the need of purging three well casings before sampling was already met. In addition, pH, temperature and dissolved oxygen were measured in the field from fresh water sample collected in a rinsed bucket (Appendix C).

3.4 Surface Water Sample Collection

In addition to groundwater samples, surface waters were sampled to obtain the pre-infiltration concentrations and isotopic signatures of possible source waters. Samples were collected from the Rillito River and other ephemeral channels during a summer rain event. The Tanque Verde Wash, Sabino Creek, and Pantano Wash were sampled before their discharge into the Rillito River. In addition, samples were collected from the wastewater-fed Santa Cruz River and from the Central Arizona Project (Colorado River water), currently used to recharge Tucson's groundwater. All washes were sampled from a bridge, using a bucket tied to a rope and rinsing the bucket three times before sample collection. The CAP water was sampled from a well at the Central Avra Valley Storage and Recovery Project and a wastewater effluent sample was collected from a pond at the Sweetwater Recharge Facility.

3.5 Water Sample Analysis

After collection, the samples were returned to the lab, filtered (0.45μm nylon) and stored at 4 ℃ in the dark. Within two days, the sample alkalinity was analyzed by end point titration (ASTM, 2006). The samples were then analyzed for anions (fluoride, chloride, nitrite, bromide, nitrate, sulfate and phosphate) using Ion Chromatography (Dionex 4000i) and for Dissolved Organic Carbon (DOC) and Total Nitrogen (TN) through 680°C combustion catalytic oxidation with a Shimadzu TOC-V.

Once nitrate concentrations were determined, the volume containing 150μmols (100-200

μmols needed) of [NO_3] was calculated for each sample. These sample volumes were

then passed through ion-exchange columns to capture all nitrate (Silva et al., 2000) and

other anions in the sample (See Appendix A for details). The columns were then shipped

to the Department of Earth and Atmospheric Science at Purdue University for nitrate

isotopic analysis. As described by Silva and others (2000), the nitrate was eluted from the

column, precipitated as $AgNO_3$ and converted to gas (N_2 and O_2). The nitrate isotopes

$\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and $\delta^{17}O_{NO3}$ were measured by isotope ratio mass spectrometry (IRMS)

(Silva et al., 2000; Michalski et al., 2003) with analytical precisions of ±0.05‰, ±0.5‰

and ±0.2‰, respectively. In addition, the water isotopes (δ^2H_{H2O} and $\delta^{18}O_{H2O}$) were

measured by IRMS with a gas-source Finnigan Delta S Isotope Ratio Mass Spectrometer

(analytical precision of ±0.9‰ for δD and ±0.08‰ for $\delta^{18}O$). The $\delta^{34}S_{SO4}$ isotope was

measured by combustion in O_2 and continuous flow isotopic ratio mass spectrometry

(CFIRMS) with a Finnigan Delta Plus and Costech Element Analyzer (±0.13‰ analytical

precision). Both sulfur and water isotope analyses were conducted at the University of

Arizona Environmental Isotope Laboratory.

3.6   Atmospheric nitrate proportions

Oxygen in atmospheric compounds are derived from either ozone (O_3) or water (H_2O)

molecules (Thiemens et al., 1999) (Appendix B). Therefore,

$$\Delta^{17}O_{sample} = f_{ozone} \times \Delta^{17}O_{ozone} + f_{H2O} \times \Delta^{17}O_{H2O} \qquad (10),$$

where f_{ozone} and f_{H2O} are the fractions of ozone and water derived oxygen atoms,

respectively. A $\Delta^{17}O$ value of 0 has been measured for water vapor (likely due to the

effect of mass-dependent fractionation processes such as evaporation), thereby

simplifying Equation 10 (Michalski et al., 2003):

$$\Delta^{17}O_{sample} = f_{ozone} \times \Delta^{17}O_{ozone} \qquad (11).$$

Atmospheric deposition studies have measured a $\Delta^{17}O$ range of 20-30‰ in atmospheric

nitrate samples. Using an average value of 23‰ (Ewing et al., 2007), the estimated

proportion of atmospheric nitrate is calculated to be

$$f_{ozone} = \Delta^{17}O_{sample} / 23‰ \qquad (12).$$

To determine what sources contribute to the measured isotopic signature, the atmospheric

imprint must be subtracted from the $\delta^{18}O$ signature. The non-atmospheric signature is

$$\delta^{18}O_{non\text{-}atm} = \delta^{18}O - f_{ozone} \times \delta^{18}O_{atm} \qquad (13),$$

where $\delta^{18}O_{atm}$ is estimated to be 75‰ from atmospheric deposition studies (Michalski et

al., 2003; Ewing et al., 2007). The atmospheric nitrate concentration is calculated using

the estimated atmospheric proportion: $[NO_3]_{atm} = f_{ozone} \times [NO_3]_{sample}$.

3.7   Solute removal calculation

In the Santa Cruz system, the percentage of solute removal and potential denitrification

along the recharge path is calculated to be

$$\% \text{ X Removal} = 100 \text{ x } ([X]_{\text{effluent}} - [X]_{\text{groundwater}}) / [X]_{\text{effluent}} \qquad (14),$$

where "X" represent the solute. This removal estimate assumes that there is no mixing

between waters with distinctly different solute concentrations and that there are no other

sources along the recharge path. In case of significant unaccounted sources during

recharge, the removal estimates are an underestimate.

4   Results

4.1   Water Sources

Water isotopes were used as tracers to determine sources of recharge to the Rillito and

Santa Cruz groundwater. The δ^{18}O and δD values for the Rillito groundwater were lower

than the Santa Cruz groundwater (Figure 6). This observation is likely due to the fact that

the Rillito groundwater is predominantly recharged from high-elevation precipitation in

the Santa Catalina mountains. In addition, the Tucson Basin groundwater is dominated by

winter recharge with relatively negative δ^{18}O and δD values (Eastoe et al., 2004).
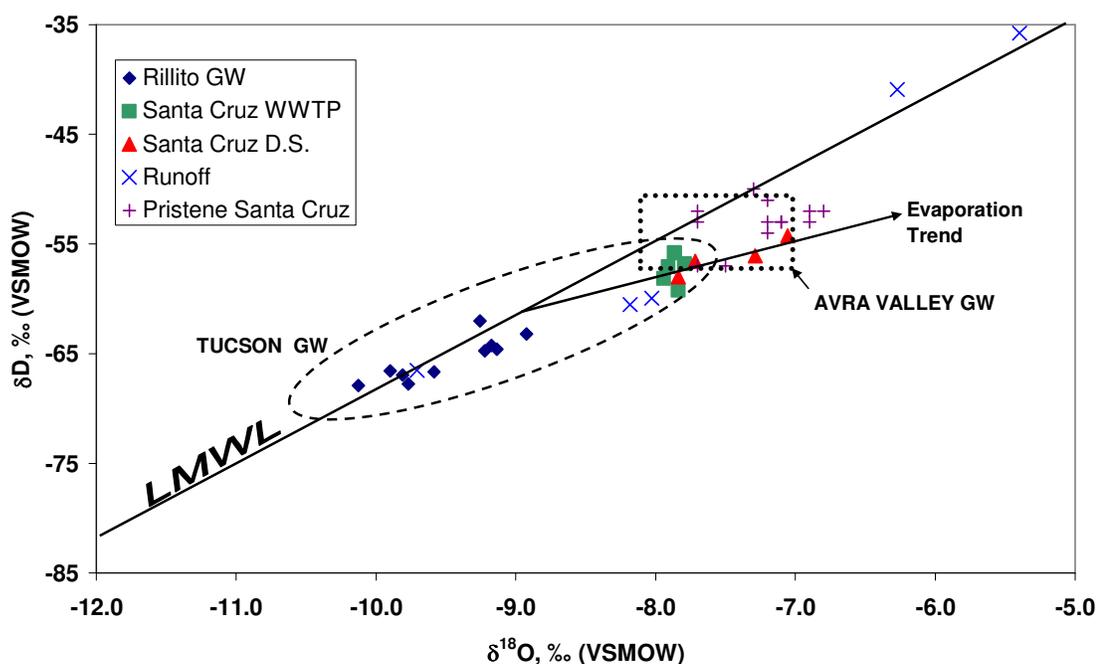
Figure 6. Water isotopes for groundwater and surface water samples. Rillito groundwater plots within the expected Tucson groundwater range (broken oval). The Santa Cruz groundwater represents a mixture of Avra Valley groundwater (dotted rectangle), Tucson groundwater (broken oval), CAP (broken rectangle) and pristine Santa Cruz groundwater (+). The Santa Cruz samples' isotopic mass ratios are more elevated and follow an evaporation trend at an angle from the local meteoric water line (LMWL).

Groundwater samples beneath the Rillito River plot along the local meteoric water line (LMWL), indicating little to no evaporation, and within the range of groundwater from Eastoe (2004)'s long-term study of Tucson groundwater (Figure 6).

In contrast, the more enriched Santa Cruz groundwater reflects a mixture of infiltrated low-elevation precipitation and pre-development Santa Cruz groundwater with wastewater effluent recharge. Most of the domestic water that ends up as wastewater originates from Tucson Basin groundwater, Avra Valley groundwater (west of Tucson) and, more recently, from the Colorado River water delivered from the Central Arizona Project (CAP). The signature range of Avra Valley groundwater is similar to pristine Santa Cruz groundwater and both water sources are more enriched in $\delta^{18}O$ and δD than Tucson Basin groundwater and CAP water (Figure 6). Due to the many different sources of water to Tucson's water supply, their relative proportions and their large variation in isotopic values, it is difficult to attribute Tucson's wastewater effluent to a specific isotopic signature range. Hence, water isotopes are an inadequate tracer for wastewater inputs. However, they can be used to infer that evaporation is a significant process affecting the Santa Cruz groundwater, given the departure from Tucson's Local Meteoric Water Line (Figure 6).

4.2   Wastewater influence

Groundwater beneath the upstream reach of the Rillito River had low nitrate concentrations (~0.2 mmols/L). Nitrate concentrations increased and reached the EPA's

MCL (0.71 mmols/L or 10 mg NO_3-N/L) near the confluence with the Santa Cruz

(Sample A, Figure 7). Concentrations then decreased further downstream to pre-Santa

Cruz groundwater influence concentrations (samples B, C). The Santa Cruz samples had

high nitrate concentrations with four of the nine samples reaching or exceeding the MCL

and showed an overall increase in nitrate from the WWTP to the downstream transects,

with average concentrations of 0.5 and 1.5 mmols NO_3/L, respectively.
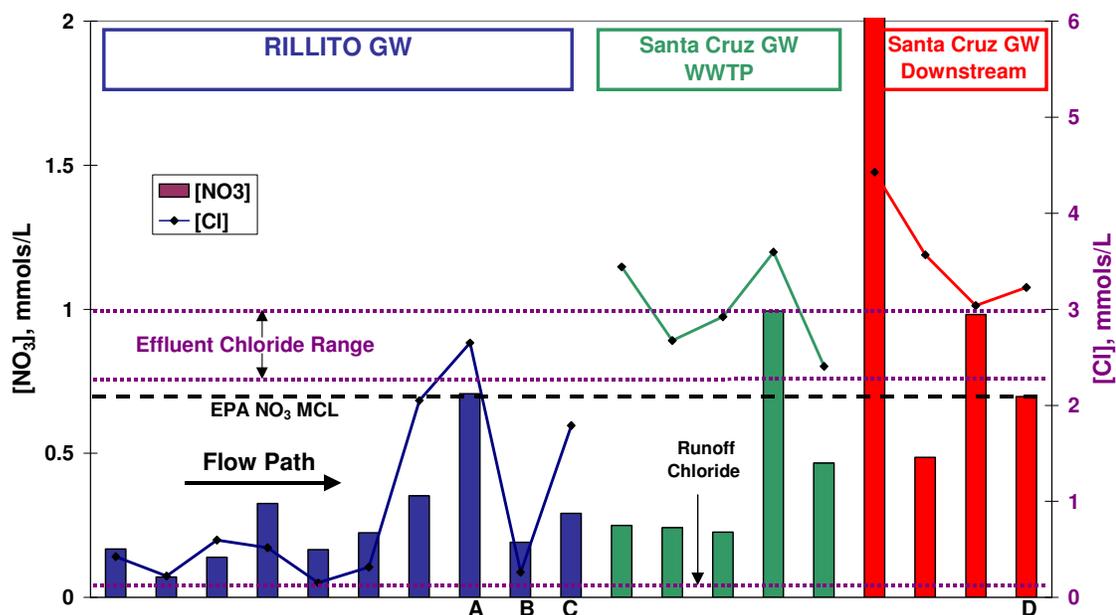
Figure 7. Nitrate (bars, left axis) and chloride (connected dots, right axis) concentrations in groundwater beneath the Rillito River, and in Santa Cruz transects near the WWTP and downstream. The lines shown are the EPA's nitrate MCL (broken line), the chloride concentration range for the wastewater effluent stream (upper dotted lines) and the runoff chloride level (lower dotted line).

In previous studies conducted by Schmidt (1973) and Esposito (1993) on the recharge of

Santa Cruz River effluent waters, elevated chloride values (and chloride/bromide ratios)

were found to be a good tracer of wastewater influence. The runoff samples in our study

had distinctly low chloride concentrations (Figure 7). The groundwater chloride data

reveal that all Santa Cruz samples and Rillito samples A and C are influenced by wastewater recharge. Peculiarly, sample B, between A and C, had little wastewater influence.

4.3 Sources of Nitrates
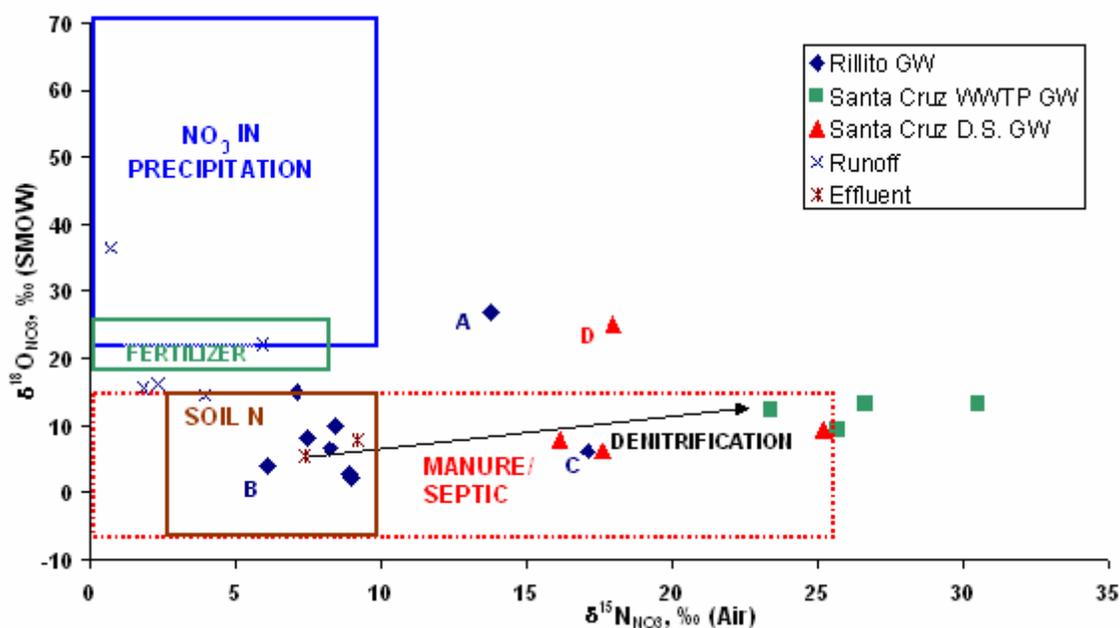
Figure 8. Plot of $\delta^{18}O$ vs. $\delta^{15}N$. Most Rillito groundwater samples plotted within the Soil N range and the Santa Cruz samples within the manure/septic range with a denitrification trend from stream level to groundwater. The runoff data plotted near the lower values of the precipitation range.

Coupling the $\delta^{18}O$ and $\delta^{15}N$ values of nitrate, it is possible to differentiate between nitrate sources in the Tucson Basin groundwater system. The runoff samples plot within or near the lower portion of the precipitation $\delta^{18}O$ range (17-22‰). The depleted $\delta^{18}O$ values may be due to mixing with fertilizer and/or soil nitrate or by nitrate cycling in the soil through plant immobilization and mineralization. The Rillito groundwater samples

generally fell within the soil nitrification range (δ^{15}N=6-9‰ and δ^{18}O=1-10‰). The Santa Cruz groundwater samples plot within the manure/septic range, with isotopic mass ratios significantly more elavated (δ^{15}N>16‰) than the wastewater stream samples (δ^{15}N=7-9‰) (Figure 8).

Several samples showed evidence for mixing with effluent and/or denitrification. Sample C had a δ^{15}N value larger than most Rillito groundwater samples. As observed with the chloride data, this result is probably due to mixing with wastewater. Samples A and D have peculiar isotopic signatures (Figure 8). Similar to Sample C, their δ^{15}N values are within the range for soil N and manure/septic mixing. However, their δ^{18}O values are elevated, and likely influenced by a third end-member: possibly atmospheric nitrate. Sample B was not affected by effluent recharge (Figure 7) and had isotopic mass ratios within the soil N range.

4.4   Denitrification

The Santa Cruz samples follow a denitrification trend along the recharge path between treated wastewater stream and groundwater, as δ^{18}O values increase with increasing δ^{15}N on a 1:2 slope (Figure 8). Denitrification rates were higher near the WWTP, with δ^{15}N enrichments up to 26‰ (α = 1.026) and 54% of nitrate removal, than downstream with 11‰ enrichments of δ^{15}N and an actual increase in nitrate concentration. High concentrations of DOC in the wastewater effluent likely facilitates denitrification in the organic-poor alluvial aquifer (Figure 9).
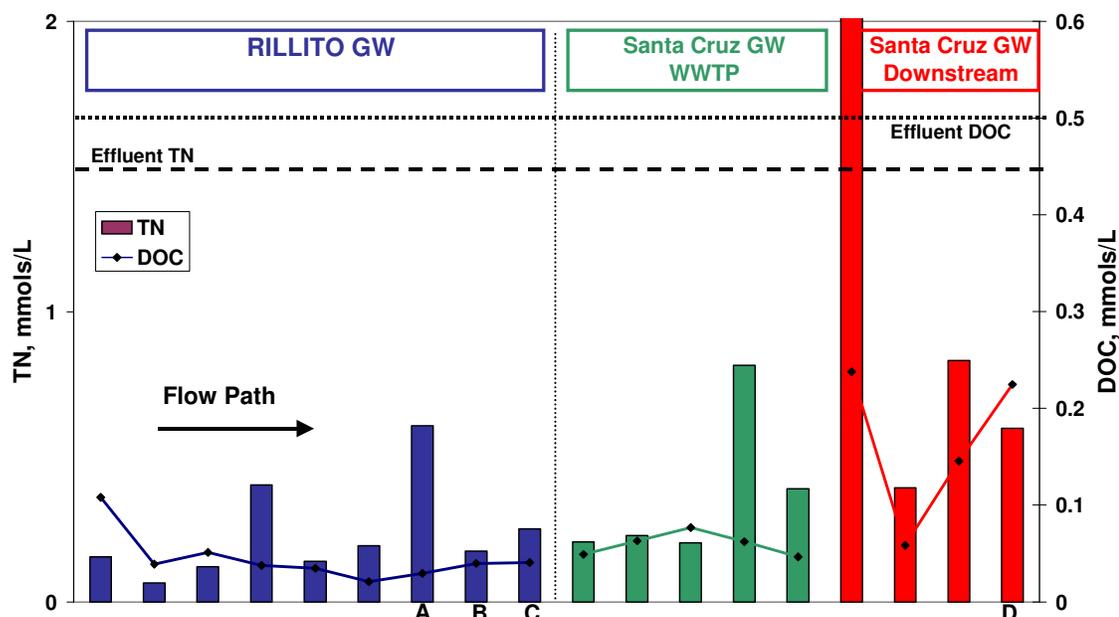
Figure 9. Total Nitrogen (bars) and Dissolved Organic Carbon (connected dots) for Rillito River (blue), Santa Cruz WWTP (green) and Santa Cruz downstream (red) groundwater samples. The effluent TN (broken line) and DOC (dotted line) are shown.

Significant amounts of DOC were consumed between the effluent stream level and the

groundwater, with 88% and 67% average removal rates at the upstream WWTP and

downstream transects, respectively (Figure 9). TN average removal rates along the Santa

Cruz recharge pathway were 76% at the WWTP and 21% downstream.

4.5   Atmospheric contributions of NO_3

Proportions of atmospheric nitrate were higher in the runoff samples (up to 43%) than in

the groundwater (up to 6%). The Rillito groundwater appears to have a higher

atmospheric input (3.5% average) than the Santa Cruz groundwater (1.9% average)

(Figure 10). Although Rillito groundwater samples had the highest atmospheric

percentages, their actual atmospheric derived concentrations (0.01 mmol/L average) were within the range of the upstream (0.007 mmol/L average) and downstream (0.02 mmol/L average) Santa Cruz samples.
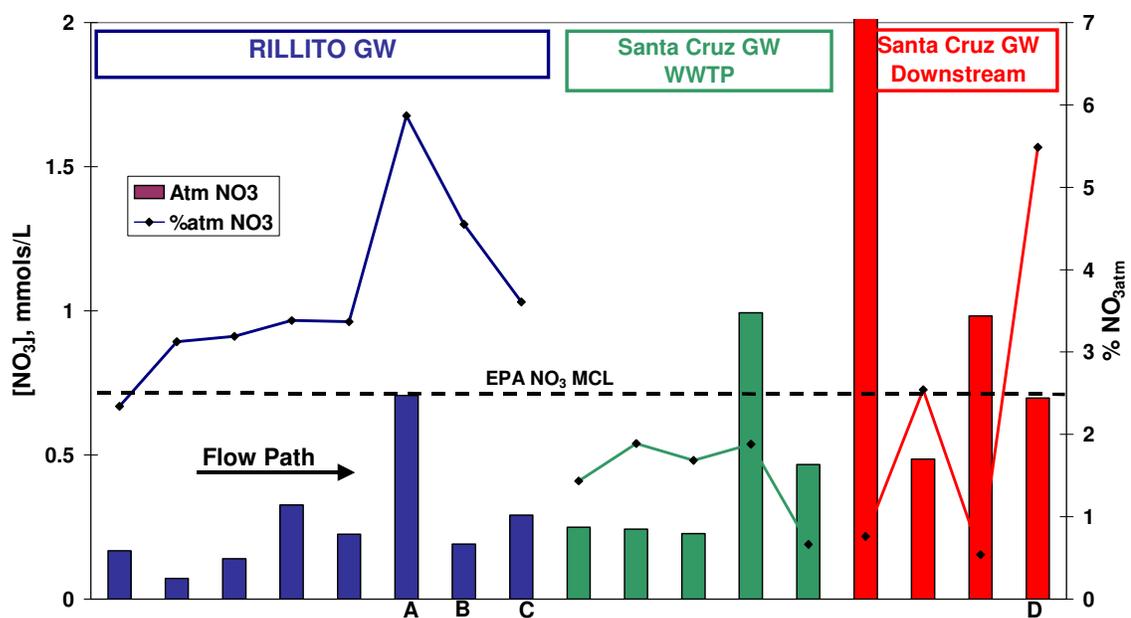
Figure 10. Nitrate concentration (bars, left axis) with % atmospheric nitrate (connected dots, right axis). Although Rillito groundwater had the highest atmospheric %, its atmospheric nitrate concentrations were comparable to the Santa Cruz groundwater.

Samples A and D represent the groundwater samples with the greatest atmospheric input (6%) and are shown to have undergone the most terrestrial fractionation (Figure 11). Interestingly, these samples have some of the highest nitrate concentrations. The Santa Cruz WWTP transect samples have undergone more terrestrial fractionation than the downstream samples, as evidenced by higher $\delta^{18}O_{NO3}$ and $\delta^{17}O_{NO3}$ values.
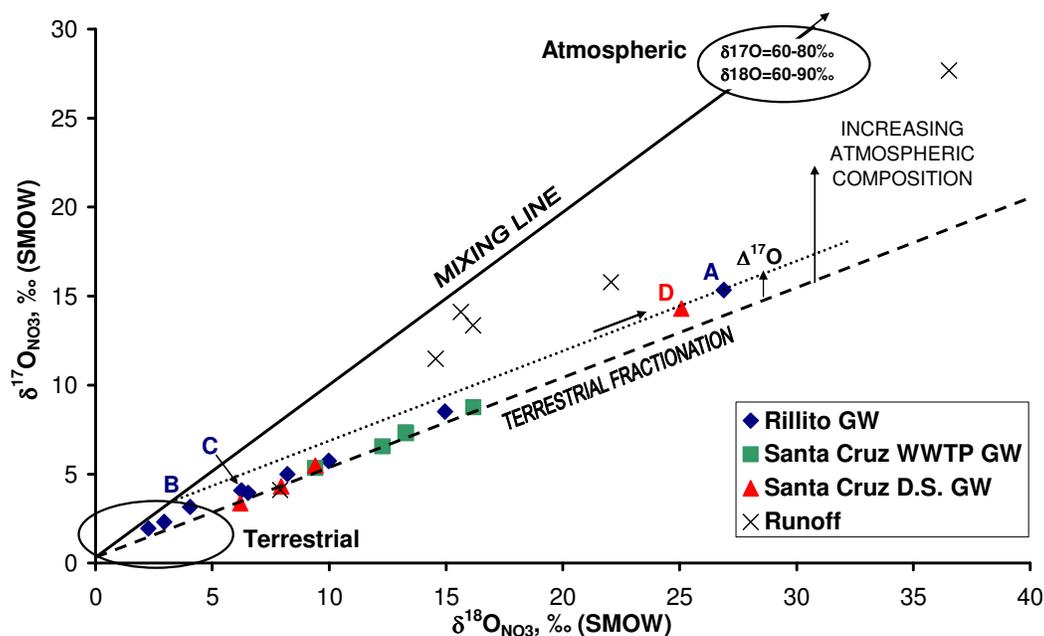
Figure 11. Plot of $\delta^{17}O$ vs $\delta^{18}O$. The greater the vertical deviation from the terrestrial fractionation line ($\Delta^{17}O$) the greater the atmospheric influence. The furthest away from the terrestrial N range, the greater the effect of terrestrial fractionation. Runoff samples have the most atmospheric influence. Among groundwater samples, A and D had the most atmospheric input and underwent the most terrestrial fractionation.

Since both fertilizers and precipitation have elevated $\delta^{18}O_{NO3}$ values, the atmospheric

imprint was removed from the nitrate $\delta^{18}O$ signatures to better define the different

sources and processes affecting groundwater nitrate concentrations. Nearly all corrected

$\delta^{18}O$ values were within the soil N and manure/septic range. Runoff samples were the

most affected by this change. The atmospheric correction of samples A and D still result

in their $\delta^{18}O$ being higher than soil N and manure/septic ranges (Figure 12). Other

processes may have affected their $\delta^{18}O$ values.
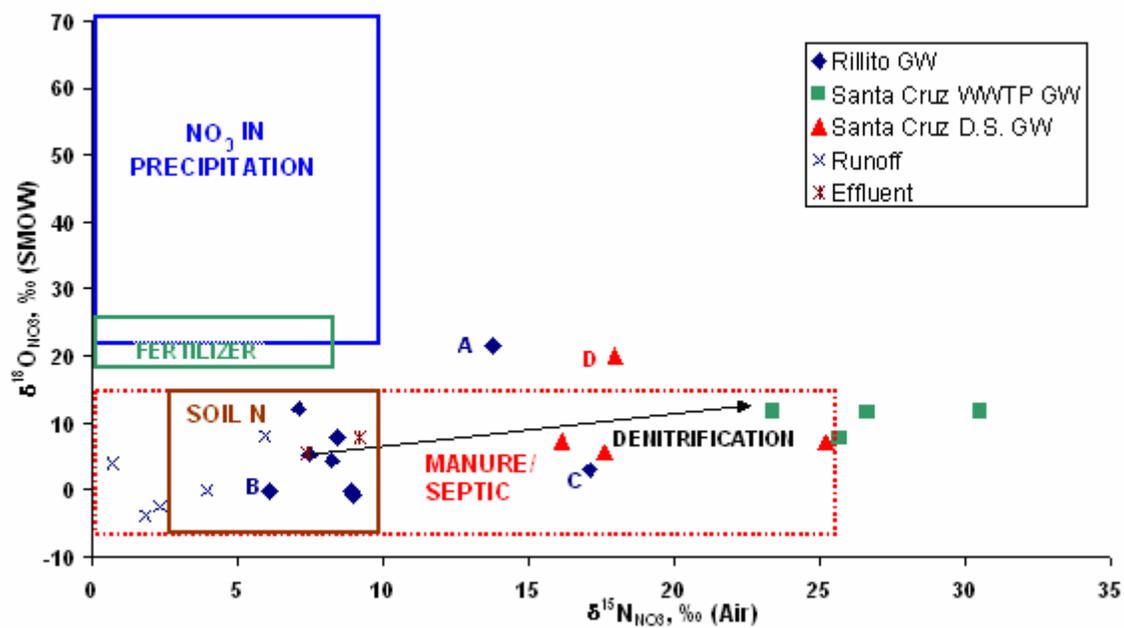
Figure 12. Removal of atmospheric imprint. Dual isotope plot after removal of atmospheric imprint to the $\delta^{18}O$ signatures (Equation 14). Nearly all $\delta^{18}O$ signatures are within the soil N and manure/septic range. Other processes are affecting samples A and D.

5   Discussion

5.1   Wastewater impact on groundwater

Previous studies have found groundwater to be contaminated with nitrate from

manure/septic sources. Girard and Hillaire-Marcel analyzed groundwater nitrate

compositions of wells in Niger (1997). Due to distinctly elevated δ^{15}N values of latrine

nitrate (15.2‰), they concluded that the elevated groundwater nitrate concentrations (up

to 11.6 mmols/L or 162.4 mg/L NO_3-N) were predominantly due to latrine

contamination. In Ontario, Canada, workers were able to trace a septic plume in

groundwater with septic δ^{15}N values above 8‰ (Aravena et al., 1993). In Israel,

groundwater nitrate concentrations exceeding 1.7 mmols/L (23.7 mg/L NO_3-N) were

associated with nitrate inputs from septic ponds and manure as shown by elevated δ^{15}N

values (7-15‰) (Oren et al., 2004).

Based on previous studies conducted in the Santa Cruz River (Schmidt, 1973; Esposito,

1993), we used chloride as a conservative tracer for wastewater. Low measured chloride

concentrations implied little influence of effluent recharge in the Rillito groundwater,

with nitrate concentrations generally low upstream (0.2 mmols/L). Nitrate and chloride

concentrations increased downstream in groundwater beneath the Rillito River proximal

to the Santa Cruz River. Two of the samples (A and C) had elevated chloride

concentrations due to mixing with effluent recharge waters. Sample B is peculiar as it is

between samples A and C and was not affected by effluent waters (soil N isotopic

signature and low chloride). This result could be due to (1) the sampling depth for well B

was shallower than for wells A and C (Figure 4) and/or (2) geologic features isolated this well from surrounding groundwater. Due to elevated chloride concentrations, all Santa Cruz groundwater samples are inferred to be largely influenced by wastewater.

The wastewater influence conclusion was reinforced with the DOC data. The average DOC for samples with little to no wastewater influence was 0.05 mmols/L whereas the samples with the most wastewater influence had a higher DOC average of 0.09 mmols/L.

Furthermore, the average nitrate concentration was significantly higher in the wastewater influenced Santa Cruz (1 mmols/L) than in the Rillito groundwater (0.2 mmols/L). As found in previously mentioned studies, wastewater influenced samples were clearly distinguished based on their elevated $\delta^{15}N_{NO3}$ values (>12‰).

These results allow us to construct a conceptual model of the hydrological and biogeochemical processes influencing the transport of effluent to the aquifer. Greater hydrologic connectivity between surface water and groundwater is achieved in the Santa Cruz River than in the Rillito River, due to continuous stream flow. This condition enhances the transport of nutrients from treated wastewater to the groundwater. The aquifer is contaminated with nutrient-rich recharge waters, with groundwater up to 1.6 Km away from the Santa Cruz River (well A) reaching the nitrate MCL of 0.71 mmols/L.

5.2 Nitrate removal by denitrification

Many studies of aquifer systems have observed significant nitrate removal via

denitrification (Vogel et al., 1981; Heaton, 1984; Esposito, 1993; Aravena et al., 1993;

Girard & Hillaire-Marcel, 1997; Aravena & Robertson, 1998; Oren et al., 2004). While

mixing trends generally exhibit a positive temporal or spatial correlation between $\delta^{15}N$

and [NO$_3$] (Girard & Hillaire-Marcel, 1997), this correlation is negative for

denitrification trends (Heaton, 1984; Mayer et al., 2002).

The Santa Cruz groundwater isotopic signatures showed a denitrification trend along the

stream-to-groundwater flow path, with samples near the wastewater treatment plant more

denitrified ($\varepsilon = 26‰$ and $\alpha = 1.026$ of $\delta^{15}N$) than downstream samples ($\varepsilon = 11‰$ and $\alpha = 1.011$ of $\delta^{15}N$) (Figure 8). This result was reinforced with groundwater samples having

less nitrate (76% removal), and organic carbon (88% removal) than the wastewater

stream. These enrichment values (ε) are within the range of enrichments measured in

other studies of 5-40‰ (Vogel et al., 1981; Aravena & Robertson, 1998; Kendall, 1998).

A previous study showed Santa Cruz River recharge waters affected by denitrification at

the seepage level and nitrification of ammonia in the vadose zone before recharging the

aquifer (Esposito, 1993). The well transect at the wastewater treatment plant are near the

Sweetwater Recharge Facility, where surface ponds are filled with treated effluent water

that percolates and replenishes a perched aquifer. Reclaimed water used to irrigate lawns

in parks and golf courses all over Tucson is pumped from this aquifer. Ponds follow

wet/dry cycles, encouraging nitrification during dry periods and denitrification during wet periods (Chipello, 1999). This soil aquifer treatment (SAT) creates ideal conditions for denitrifying bacteria to thrive, which may explain the low nitrate concentrations in the WWTP groundwater transect.

Due to the influence of wastewater treatment plant effluent discharged to the Santa Cruz River, the downstream transect groundwater had higher nitrate, TN, and DOC concentrations than the WWTP transect. Furthermore, the isotopic signatures of the downstream samples showed denitrification affecting nitrate compositions to a lesser extent than the samples near the WWTP transect (Figure 8). This observation is confirmed by the $\delta^{17}O$ data showing that these samples underwent less terrestrial fractionation than the WWTP transect groundwater samples (Figure 10). Lower removal rates were measured in downstream groundwater samples (21% TN and 67% DOC removal), along with an increase in nitrate (46% increase) from the effluent stream. Higher groundwater nitrate concentrations may be due to lower denitrification rates, greater leaching, and ammonia nitrification in the vadose zone. Aside from recent effluent, another possible source of NO_3 to the groundwater may be from the flushing of vadose zone nitrate from large mid-20th century agricultural fields in the area, that were irrigated with wastewater effluent (Schmidt, 1973).

A previous study investigated two potential electron donors required for denitrification using $^{15}N_{NO3}$, $^{18}O_{NO3}$, $^{34}S_{SO4}$, $^{18}O_{SO4}$, ^{13}C and biogeochemical data (Aravena & Robertson,

1998). If pyrite oxidation is the electron donor, an increase of [SO$_4$] is observed with a decrease in $\delta^{34}S_{SO4}$ values. In the case of organic matter as the electron donor, a conversion of organic carbon to dissolved inorganic carbon is expected with a decrease of $\delta^{13}C$ values. Aravena and Robertson found a combination of both pyrite and organic matter oxidation to be electron donors (1998). In the present study, the sulfate concentrations and $\delta^{34}S_{SO4}$ data were inconclusive. Due to a higher pool of organic matter present and the observed decrease of DOC along the recharge flow path, organic matter is more likely to be the electron donor than pyrite.

Constant moisture content, more nutrient sources from wastewater, and greater vegetation density make the Santa Cruz system a biogeochemical hot spot (McClain et al., 2003) for N cycling with denitrification and nitrification in the vadose zone.

5.3 Atmospheric proportion

Although nitrate originating from precipitation is distinguishable based on its elevated $\delta^{18}O_{NO3}$ value (Figure 1), studies, including the present one, have measured few $\delta^{18}O_{NO3}$ values greater than 20‰ in both surface and subsurface samples (Aravena et al., 1993; Mayer et al., 2002; Michalski et al., 2004b; McMahon & Bohlke, 2006; Ewing et al., 2007). Processes at the soil level, including plant uptake and mineralization modify the original $\delta^{18}O_{NO3}$ value of the sample, thereby removing its atmospheric imprint (Kendall, 1998; Michalski et al., 2003). The $\delta^{17}O_{NO3}$ data is therefore essential to account for atmospheric contributions.
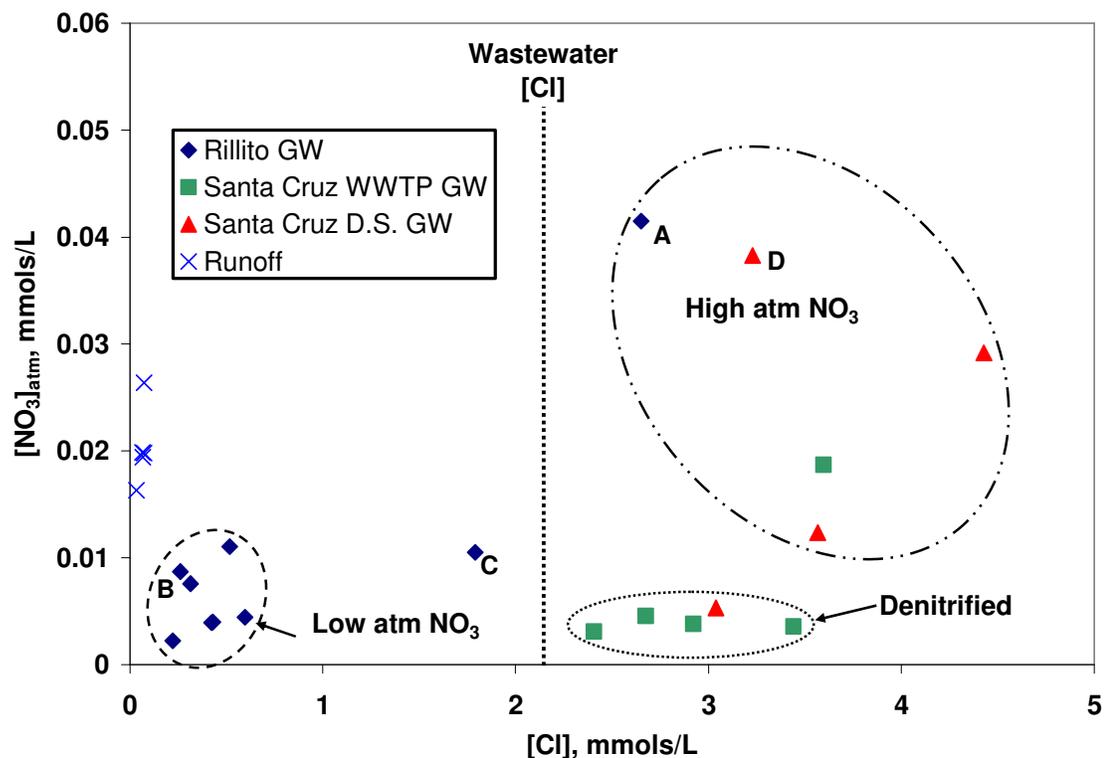
Figure 13. Atmospheric nitrate vs. chloride concentrations. The high chloride concentrations distinguish samples with wastewater influence from those with little to no influence. The highest atmospheric nitrate concentrations were detected in runoff and wastewater influenced waters.

Although a few studies have measured significant atmospheric deposition in urban

settings of the southwestern US (Michalski et al., 2004b; Lohse et al., 2008), the

atmospheric contribution of nitrate to Tucson's groundwater is relatively minor. Up to

6% atmospheric nitrate was measured in samples A and D. Although Rillito samples had

the highest atmospheric percentages, their atmospheric concentrations (average 0.01

mmols/L) were similar to the Santa Cruz samples (average 0.013 mmols/L). While the

highest atmospheric nitrate concentrations were measured in wastewater-influenced

waters (up to 0.04 mmols/L), the ones affected the most by denitrification had the least

amount of $[NO_3]_{atm}$, with an average of 0.004 mmols/L (Figure 13). Samples A and B

provide good examples of wastewater recharge waters having more $[NO_3]_{atm}$. Although

both samples had some of the highest percentages of atmospheric nitrate, sample B had a

lower nitrate concentration (0.009<0.04 mmols/L) due to very little wastewater influence.

Samples A and D had the highest $\delta^{18}O$ (Figure 8) values of NO_3, which we hypothesized

to be due to mixing with atmospheric nitrate. To test this hypothesis, we removed the

atmospheric imprint, however these samples still had relatively high $\delta^{18}O$ values (Figure

12). Several mechanisms can explain this enrichment in $^{18}O_{NO3}$. First, there could be

errors in estimating their atmospheric proportion and this source may have been

underestimated. Second, these samples may have been influenced by both denitrification

and atmospheric nitrate mixing. The pre-denitrified nitrate may have had isotopic

signatures similar to wastewater effluent (sample D) and fertilizers (sample A) or a

mixture of both. Third, another process that affects $\delta^{18}O_{NO3}$ is nitrification, which has

been shown to occur before recharging the aquifer (Esposito, 1993). Experiments have

shown that, during the oxidation of nitrate, bacteria produce nitrate obtaining 2/3 of the

oxygen molecules from water and 1/3 from O_2 (Kendall, 1998). Therefore, the $\delta^{18}O$ value

of bacterially derived nitrate is related to the $\delta^{18}O$ of water. One way to get elevated

$\delta^{18}O_{H2O}$ values is through evaporation, which has been found to affect groundwater and

may be even more significant at shallow depths where nitrification and denitrification

likely occur. Fourth, analytical errors may have occurred during sample processing for

nitrate isotopic analysis. Finally, their enriched $\delta^{18}O_{NO3}$ values may be due to a

combination of processes, including mixing with atmospheric nitrate, nitrification, denitrification, and analytical errors.

The greater surface-groundwater connection beneath the Santa Cruz River may explain the larger atmospheric nitrate concentrations. More atmospheric (and wastewater) nitrate can potentially make it to the groundwater due to higher infiltration rates. This result implies that atmospheric nitrate can be found in soils beneath the Rillito River.

6   Conclusions

The use of $\delta^{17}O$ data to determine the proportions of atmospheric derived nitrate is a relatively new method currently applied on surface water samples. In this study, we applied this method to groundwater beneath alluvial washes in a semi-arid urban setting to shed light on proportions of atmospheric nitrate in aquifers.

Little nitrate was measured in Rillito groundwater and this may be due to minimal vegetation density and recharge rates. Nitrate sources were predominantly from soil nitrification. Little atmospheric-derived nitrate (up to 6%) reached the aquifer due to limited surface water-groundwater connection with a relatively deep water table (>40m).

The conditions are significantly different in the wastewater influenced Santa Cruz system. The greater hydrologic connectivity between surface water and groundwater created by a perennial stream accelerates the transport of solutes, including atmospheric nitrate and organic carbon, to groundwater and enhances nutrient cycling along the recharge path. After several decades of wastewater discharge practice, wells up to 1.6 Km away from the wastewater stream are contaminated with nitrate, with concentrations exceeding the EPA's MCL.

Furthermore, in organic rich wastewater systems, bacterially mediated denitrification represents one of the most efficient avenues of nitrate removal. The enrichment rates up to 26‰ observed in the Santa Cruz groundwater were within the range measured by other

studies for denitrification. Organic matter was more likely than pyrite oxidation to be the electron donor. Human intervention to encourage denitrification, such as soil aquifer treatment (SAT) practiced at the Sweetwater Recharge Facility, may be of great interest in other wastewater-influenced systems around the world.

Finally, $^{17}O_{NO3}$ is not only ideal to determine the atmospheric proportion present in groundwater nitrate; it is also useful to determine and/or confirm the relative extent of fractionation processes (i.e. denitrification) affecting nitrate concentrations in groundwater. While previous studies have associated elevated nitrate concentrations to fertilizers, human and animal waste and N_2 fixation by rhizobia bacteria at the root level of plants, these studies were not able to quantify the significance of atmospheric nitrate contamination. Using $^{17}O_{NO3}$, we are able to quantify atmospheric derived nitrate and investigate denitrification with higher certitude.

Appendix A: Preparation of the Anion Exchange Column

1. Analyze the water sample for anions (IC)
2. Determine the total anionic strength in meq/ml. The resin column can exchange up to 1.2meq/ml (2.4meq for 2ml column)
3. Determine the volume of sample needed to have 100-200μeq. Aim for 150μeq to account for inexact volumes and water loss during run.
4. Use a graduated cylinder to measure the volume of sample needed.
5. Store the sample in the fridge until needed.
6. Assemble a flask, rubber stopper, and funnel with stopcock assembly as in the Silva et al. (2000) paper, and connect it to a vacuum pump. The rubber stopper needs to be able to hold the column (#7). If no funnel is available, a burette can be used although it holds less volume than a funnel and water samples will need to be added more often.
7. Place about 5g of dry resin in a beaker (the amount depends on the number of columns to be prepared; a batch may be needed)
8. Add some DI water and mix until a slurry is obtained
9. Poor the slurry into the column until the 2ml marc.
   If the slurry is not poured uniformly, some large bubbles are observed in the column and/or chunks of dried slurry have deposited above the 2ml marc:
   a) Stop pouring
   b) Using a small metallic rod, push all the resin in the column filling up (as best as possible) the voids
   c) Place the column onto the flask/rubber stopper assembly
   d) Add some DI water until all the resin is submerged.
   e) Vacuum out the water.
   f) Lift the column out and inspect for remnant air voids and heterogeneities.
   g) Repeat a-f until homogeneity is best achieved.

Note: As the water is vacuumed out of the resin, the little resin beads are forced against each other, filling up the voids.

   h) Add or remove resin until the resin level is a few millimeters above the 2ml mark. This is important because the top of the resin column will be disturbed by the addition of a water sample. This disturbance will break the homogeneity in the top portion.
10. Prepare a solution of 1.25M $CaCl_2$
11. Place the column on the assembly and pass 2ml of $CaCl_2$ through the resin column. This is to saturate the resin with chloride.
    a) Papers and manuals do not agree on a flow rate. To be on the safe side and to have better control on the flow out of the column, the ideal flow rate is achieved when water drips fast enough that you can count the drops
    b) This can be achieved by carefully adjusting the vacuum strength.

Appendix A: Preparation of the Anion Exchange Column (Continuation)

12. Rinse the resin with 2ml of DI water
   a) Follow the same flow rate as in 11a.
   b) If these columns are to be preserved for later use, keep about 0.5ml of DI in the column. The columns are ready.
13. Pass the water samples through the column
   a) Set the outflow rate as in 11a.
   b) Adjust the inflow rate (stopcock or burette valve) so as to get about the same flow rate into and out of the resin column. This is to prevent overflow from the column. Monitor and adjust.
   c) Add the water sample as needed
   d) If the volume of sample added is higher than the flask, you will have to interrupt the flow to empty out the flask. Once set, the vacuum strength doesn't need to be changed throughout the whole process.
14. Once the water sample is passed through, cap the column in both ends, label it and store it at room temperature.
15. Collect 5ml of the eluant for anion analysis. Only chlorine should be present.
16. Clean all the instruments used for the next sample.

Appendix B: Cycling and production of atmospheric nitrate
(adapted from Michalski et al., 2003)

The largest pool of nitrogen on Earth is N_2 gas, which constitutes 78% of the atmosphere by volume. N_2 is highly unreactive due to its strong triple bonds. Requiring up to 911 KJ/mol, only a few processes can break these bonds and produce reactive N (fixation). In the biosphere, N fixers include bacteria (i.e. cyanobacteria) and plants (i.e. legumes). In the atmosphere, only lightning discharges and combustion processes (i.e. automobiles and factories) can break these bonds. With high temperatures, N_2 oxidizes and produces reactive NO:

$$O_2 + N_2 \longrightarrow 2NO \quad (B.1)$$

NO further gets oxidized to NO_2 by mixing with ozone (B.2) and HO_2 (B.3). The opposite reaction also occurs where NO is reformed by uv/vis photolysis (B.4). Ozone gets recreated subsequently (B.5).

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (B.2)$$

$$NO + HO_2 \longrightarrow NO_2 + OH \quad (B.3)$$

$$NO_2 + hv \longrightarrow NO + O \quad (B.4)$$

$$O_2 + O + M \longrightarrow O_3 \quad (B.5)$$

In the last three reactions, a great deal of O cycling occurs where ozone and NO are both created and destroyed. During this cycle, NO_2 is created with O molecules from ozone. The greater the cycling, the more the incorporation of ozone molecules. NO_2 oxidizes even more to NO_3 as nitric acid along three pathways (B6, B7, B8). Although NOx compounds do deposit on the earth and are available to the biosphere, the deposition rates of nitric acid are significantly higher.

$$NO_2 + OH + M \longrightarrow HNO_3 + M \quad (B.6)$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (B.7a)$$

$$NO_3 + HC (DMS) \longrightarrow HNO_3 \quad (B.7b)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \quad (B.8a)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad (B.8b)$$
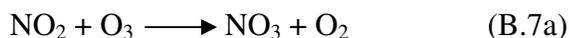
Reaction B.6 occurs during the day as NO_2 reacts with hydroxy radicals. On a separate pathway, NO_2 can react again with ozone and produce NO_3 (B.7a) that later forms HNO_3

Appendix B: Cycling and production of atmospheric nitrate (Continuation)

(B7.b) on aerosol surfaces (i.e. HC, or DMS). In the third nitric acid creation process, NO_2 reacts with previously formed NO_3 to form N_2O_5 (B.8a) that then hydrolyzes on wet surfaces to yield HNO_3 (B.8b). Processes B.7 and B.8 are more significant during the night due to rapid photolysis during daylight.

The processes above follow a series of chemical and photochemical reactions. Whereas kinetic and equilibrium reactions in the biosphere fractionate elements with mass dependence (MDF), photochemical reactions in the atmosphere follow mass independent fractionations (MIF). For example, in biotic reactions, organism breakdown O compounds leaving the $\delta^{17}O$ signature always proportional to $\delta^{18}O$ by a factor of 0.52 ($\delta^{17}O = 0.52 \times \delta^{18}O$). However, larger $\delta^{17}O$ enrichment is measured in photochemical reactions. The difference between the measured and the mass dependent fractionated $\delta^{17}O$ is termed "capital delta 17O" ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$). Due to its nature, $\Delta^{17}O$ of a compound is preserved through further terrestrial fractionation processes (i.e. denitrification) and represents an ideal conservative tracer for atmospheric derived compounds.

From reactions B.6-B.8, we realize that atmospheric nitrate is only produced from the oxidation of NO_2, which is oxidized from NO with either ozone or HO_2 (B.2-B.3). Therefore,

$$\Delta^{17}O_{NO2} = f_{NO} \times \Delta^{17}O_{NO} + f_{O3} \times \Delta^{17}O_{O3} \qquad (B.2.1)$$

$$\Delta^{17}O_{NO2} = f_{NO} \times \Delta^{17}O_{NO} + f_{HO2} \times \Delta^{17}O_{HO2} \qquad (B.3.1)$$

Where f_x is the proportion of element x. For example, in B.2.1, $f_{NO} + f_{O3} = 1$. The O in NO originates from O_2 and since $\Delta^{17}O_{O2} = 0$, $\Delta^{17}O_{NO} = 0$. Furthermore, studies measured $\Delta^{17}O_{HO2} \sim 1‰$, and for simplification, we assume $\Delta^{17}O_{HO2} = 0‰$. Therefore,

$$\Delta^{17}O_{NO2} = f_{O3} \times \Delta^{17}O_{O3} \qquad (B.2.2)$$

From reaction B.6 we get:

$$\Delta^{17}O_{NO3} = f_{NO2} \times \Delta^{17}O_{NO2} + f_{OH} \times \Delta^{17}O_{OH} \qquad (B.6.1)$$

Since 2 out of 3 O molecules came from NO_2, $f_{NO2} = 2/3$. Studies measured $\Delta^{17}O_{OH} = 0$ due its water vapor origin (equilibrium fractionation). Therefore,

$$\Delta^{17}O_{NO3} = 2/3 \times f_{O3} \times \Delta^{17}O_{O3} \qquad (B.6.2)$$

Appendix B: Cycling and production of atmospheric nitrate (Continuation)

Similar analysis is performed for B.7-B.8 to obtain $\Delta^{17}O_{NO3}$ as a function of f_{O3} and $\Delta^{17}O_{O3}$. We get:

$$\Delta^{17}O_{NO3} = 2/3 \text{ x } f_{O3} \text{ x } \Delta^{17}O_{O3} + 1/3 \text{ x } \Delta^{17}O_{O3} \qquad (B.7.2)$$

$$\Delta^{17}O_{NO3} = 1/3 \text{ x } f_{O3} \text{ x } \Delta^{17}O_{O3} + \tfrac{1}{2} \text{ x } [2/3 \text{ x } f_{O3} \text{ x } \Delta^{17}O_{O3} + 1/3 \text{ x } \Delta^{17}O_{O3}] \qquad (B.8.2)$$

Equations B.6.2, B.7.2 and B.8.2 can then be used in models to compute the atmospheric proportion f_{O3}. Although, $\Delta^{17}O_{O3}$ has never been measured, models have estimated it around 35‰. If β, γ, κ are the proportions of NO_{3atm} derived from B.6.2, B.7.2 and B.8.2, respectively, then

$$\Delta^{17}O_{NO3} = \beta \text{ x } (Eq. \ B.6.2) + \gamma \text{ x } (Eq. \ B.7.2) + \kappa \text{ x } (Eq. \ B.8.2) \qquad (B.9)$$

Since all 3 equations have a common denominator of $(f_{O3} \text{ x } \Delta^{17}O_{O3})$, the solution can be simplified to:

$$\Delta^{17}O_{NO3} = \phi \text{ x } f_{O3} \text{ x } \Delta^{17}O_{O3} \quad (B.10)$$

Atmospheric deposition studies in Southern California have measured $\Delta^{17}O_{NO3}$ between 20-30‰ with an average of 23‰. Assuming that $\phi \text{ x } \Delta^{17}O_{O3} = 23‰$, we get

$$\Delta^{17}O_{NO3} = f_{O3} \text{ x } 23‰ \quad (B.11)$$

To summarize, the O molecules incorporated in the NO_3 compound are either derived from O_2, O_3 or H_2O. Since $\Delta^{17}O_{O2} = \Delta^{17}O_{H2O} = 0$ and $\Delta^{17}O_{O3} = 35‰$, $\Delta^{17}O_{NO3}$ is directly proportional to $\Delta^{17}O_{O3}$ by a factor f_{O3}. Cycling (reactions B.1-B.8) occurs in the atmosphere where ozone O molecules get incorporated into the formation of NO_{3atm}. The greater the cycle through ozone, the larger will be f_{O3}.

Appendix C: Data

Well code	Latitude	Longitude	Ground Elevation (m.a.s.l.)[*]	Casing Top Depth (m)	Casing Bottom Depth (m)	Water Depth (m)
Rillito River Groundwater						
C075B	32.2391	-110.7732	784.15	42.7	183	37.88
C83B	32.2502	-110.8164	774.09	48.8	189.1	39.33
WR146A	32.2602	-110.8679	750.00	45.445	73.2	46.20
UA Ag Farms[£]	32.2798	-110.9362	NA	NA	NA	NA
A55A	32.2978	-110.9869	699.09	53.68	114.68	52.39
A57B	32.2995	-111.0033	692.07	61	231.8	49.94
Z002	32.2972	-111.0123	691.16	94.245	135.42	48.98
Z005	32.3036	-111.0240	686.28	39.65	91.5	48.46
WR369A	32.3119	-111.0361	676.83	27.45	64.05	42.38
Z015	32.3237	-111.0463	676.52	59.78	71.98	42.12
Santa Cruz WWTP Cross-section						
WR201	32.28088	-111.02149	689.33	39.65	61	41.55
EW005	32.27806	-111.02270	689.94	NA	NA	NA
EW006	32.27822	-111.02627	689.94	NA	NA	NA
WR066B	32.27876	-111.02889	687.20	35.075	61	41.97
WR063B	32.27740	-111.02957	687.20	35.075	61	42.91
EW004	32.27753	-111.03115	688.41	NA	NA	NA
Santa Cruz Downstream Cross-section						
WR203	32.29094	-111.02876	685.37	35.075	61	45.49
WR200	32.28728	-111.03279	683.84	39.65	61	44.42
EW007	32.28750	-111.03471	686.28	67.1	146.4	47.45
PK001A	32.28825	-111.03650	685.98	45.14	94.245	46.46

[*] m.a.s.l = meters above sea level
[£] University of Arizona Agricultural Research Center at 4101 N. Campbell Avenue

Appendix C: Data (Continuation)

Well Code	Water Depth (m)	Temp (℃)	pH	DO† (mg/L)	Alk§ (mg/L)	DOCⱵ (mmols/L)	TN‡ (mmols/L)
Rillito River Groundwater							
C075B	124.25	21.40	6.88	5.50	1.92	0.108	0.155
C83B	129.01	21.60	7.09	4.60	2.07	0.039	0.066
WR146A	151.52	21.90	7.11	6.80	3.69	0.051	0.121
UA Ag Farms	NA	NA	NA	NA	NA	0.038	0.403
A55A	171.84	22.20	7.30	6.40	1.83	0.035	0.140
A57B	163.80	23.50	7.64	5.40	2.37	0.021	0.194
Z002	160.67	25.10	7.46	9.00	1.94	NA	NA
Z005	158.96	25.00	7.49	6.20	2.16	0.029	0.607
WR369A	139.00	21.00	7.31	4.40	1.88	0.040	0.175
Z015	138.15	24.90	7.25	4.50	2.23	0.041	0.251
Santa Cruz WWTP Cross-section							
WR201	136.30	24.40	7.06	4.20	2.34	0.049	0.207
EW005	NA	23.90	7.32	3.60	2.5	0.063	0.229
EW006	NA	23.90	7.08	4.60	2.21	0.077	0.204
WR066B	137.66	24.80	6.54	4.40	1.97	NA	NA
WR063B	140.74	25.00	6.65	3.40	2.24	0.062	0.815
EW004	NA	24.90	7.15	6.00	2.07	0.047	0.390
Santa Cruz Downstream Cross-section							
WR203	149.22	22.70	7.01	5.80	2.42	0.238	2.902
WR200	145.71	24.40	6.81	6.80	2.17	0.058	0.393
EW007	155.64	28.50	7.21	3.60	2.47	0.146	0.831
PK001A	152.38	24.10	7.30	3.80	2.3	0.225	0.598

† DO = Dissolved Oxygen
§ DOC = Dissolved Organic Carbon
‡ TN = Total Nitrogen

Appendix C: Data (Continuation)

Well code	F (mmols/L)	Cl (mmols/L)	NO$_2$ (mmols/L)	NO$_3$ (mmols/L)	Br (mmols/L)	SO$_4$ (mmols/L)	PO$_4$ (mmols/L)
Rillito River Groundwater							
C075B_D	0.031	0.430	0.000	0.171	0.001	0.504	0.001
C075B	0.031	0.424	0.000	0.167	0.003	0.522	0.001
C83B	0.011	0.222	0.000	0.071	0.001	0.626	0.001
WR146A	0.017	0.597	0.000	0.139	0.001	0.331	0.000
UA Ag Farms	0.006	0.518	0.000	0.326	0.002	0.115	0.000
A55A	0.008	0.152	0.000	0.166	0.000	0.149	0.000
A57B	0.007	0.315	0.000	0.225	0.001	0.214	0.000
Z002	0.008	2.050	0.000	0.352	0.003	0.693	0.001
Z005	0.007	2.651	0.000	0.707	0.004	1.969	0.006
WR369A	0.010	0.261	0.000	0.191	0.001	0.620	0.001
Z015	0.011	1.790	0.000	0.291	0.001	1.023	0.002
Santa Cruz WWTP Cross-section							
WR201	0.018	3.442	0.000	0.250	0.004	1.349	0.002
EW005	0.038	2.674	0.001	0.242	0.004	1.377	0.002
EW006	0.040	2.923	0.001	0.227	0.004	1.303	0.002
WR066B	0.027	3.715	0.001	0.846	0.004	1.263	0.002
WR063B	0.034	3.598	0.000	0.994	0.004	1.290	0.002
EW004	0.049	2.406	0.000	0.467	0.004	1.762	0.003
Santa Cruz Downstream Cross-section							
WR203	0.003	4.429	0.000	3.832	0.000	6.472	0.024
WR200	0.033	3.567	0.001	0.486	0.004	1.355	0.003
EW007	0.042	3.039	0.001	0.982	0.004	1.859	0.004
PK001A	0.040	3.229	0.001	0.698	0.005	1.324	0.001
Surface Water Samples							
CAP	0.017	2.271	0.000	0.010	0.001	2.230	0.006
Santa Cruz R.	0.012	0.072	0.003	0.106	0.000	0.122	0.002
Rillito R.	0.010	0.073	0.006	0.135	0.000	0.193	0.000
Rillito R.(2)	0.008	0.064	0.001	0.080	0.000	0.045	0.000
Pantano W.	0.006	0.033	0.001	0.038	0.000	0.051	0.002
Tanque Verde W.	0.009	0.066	0.001	0.075	0.000	0.050	0.001
Sabino Ck.	0.007	0.053	0.001	0.059	0.000	0.040	0.001
Effluent WWTP[#]	0.041	3.826	0.130	0.417	0.005	1.575	0.024
Effluent DS[$]	0.049	3.413	0.122	0.516	0.005	1.599	0.021

[#] WWTP = Wastewater Treatment Plant
[$] DS = Downstream

Appendix C: Data (Continuation)

Well code	$\delta^{18}O_{H2O}$ ‰	$\delta^{2}H_{H2O}$ ‰	$\delta^{34}S_{SO4}$ ‰	$\delta^{15}N_{NO3}$ ‰	$\delta^{17}O_{NO3}$ ‰	$\delta^{18}O_{NO3}$ ‰	$\Delta^{17}O_{NO3}$ ‰	ATM[∞] %
Rillito River Groundwater								
C075B_D	NA	NA	NA	8.43	5.73	9.98	0.54	2.34
C075B	-9.2	-64	6.3	8.28	3.94	6.54	0.54	2.34
C83B	-9.8	-68	NA	7.12	8.5	14.96	0.72	3.13
WR146A	-9.3	-62	5.8	7.49	5	8.2	0.73	3.19
UA Ag Farms	-9.8	-67	5	9	1.95	2.25	0.78	3.38
A55A	-10.1	-68	4.8	NA	NA	NA	NA	NA
A57B	-9.6	-67	6.9	8.93	2.3	2.93	0.77	3.37
Z002	-9.2	-65	8.3	NA	NA	NA	NA	NA
Z005	-9.1	-65	8.5	13.77	15.33	26.88	1.35	5.87
WR369A	-9.9	-67	6.2	6.13	3.15	4.04	1.05	4.55
Z015	-8.9	-63	8.3	17.12	4.08	6.24	0.83	3.61
Santa Cruz WWTP Cross-section								
WR201	-7.9	-57	8.5	NA	8.74	16.17	0.33	1.43
EW005	-7.9	-56	6.9	25.69	5.33	9.41	0.43	1.89
EW006	-7.8	-57	7	30.52	7.3	13.29	0.39	1.68
WR066B	-7.8	-59	3.9	NA	NA	NA	NA	NA
WR063B	-7.9	-58	3.9	26.66	7.33	13.26	0.43	1.88
EW004	-7.9	-56	6.2	23.41	6.54	12.28	0.15	0.66
Santa Cruz Downstream Cross-section								
WR203	-7.7	-57	8.8	16.16	4.31	7.95	0.18	0.76
WR200	-7.8	-58	8.8	25.24	5.48	9.41	0.58	2.54
EW007	-7.3	-56	8.5	17.63	3.35	6.2	0.12	0.54
PK001A	-7.1	-54	12	17.98	14.3	25.07	1.26	5.49
Surface Water Samples								
CAP	-9.7	-82	4.1	NA	NA	NA	NA	NA
Santa Cruz R.	-6.3	-41	6.9	5.96	15.77	22.06	4.3	18.68
Rillito R.	-5.4	-36	NA	3.97	11.47	14.57	3.9	16.96
Rillito R. (2)	-10.9	-73	NA	2.36	13.36	16.15	4.96	21.57
Pantano W.	-8	-60	NA	0.74	27.68	36.52	8.69	37.77
Tanque Verde	-8.2	-61	NA	1.84	14.1	15.63	5.97	25.96
Sabino Ck	-9.7	-67	NA	NA	4.11	7.9	NA	NA
Effluent WWTP	-11	-73	3.7	7.39	2.8	5.51	NA	NA
Effluent DS	-10.6	-72	2.6	9.22	4.11	7.9	NA	NA

[∞] ATM = percentage of total nitrate that is atmospheric derived

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