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ISOTOPE INVESTIGATION OF NITRATE IN SOILS AND AGRICULTURAL DRAIN WATERS OF THE LOWER YAKIMA VALLEY, WASHINGTON

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ISOTOPE INVESTIGATION OF NITRATE IN SOILS AND AGRICULTURAL DRAIN WATERS OF THE LOWER YAKIMA VALLEY, WASHINGTON

A Thesis
Presented to
The Graduate Faculty
Central Washington University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Geological Sciences

by
Dallin Paul Jensen
May 2017
CENTRAL WASHINGTON UNIVERSITY

Graduate Studies

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ABSTRACT

ISOTOPE INVESTIGATION OF NITRATE IN SOILS AND AGRICULTURAL DRAIN WATERS OF THE LOWER YAKIMA VALLEY, WASHINGTON

by

Dallin Paul Jensen

May 2017

Nitrate in the groundwater of the Lower Yakima Valley, Washington has long been known to frequently exceed the EPA maximum contaminant level standard for potable water (10 mg/L), adversely impacting communities with disadvantaged socio-economic status. In this research, nitrogen and oxygen isotopic signatures were determined for nitrate soil leachates and irrigation return flow collected in the Lower Yakima Valley, Washington and compared to previous isotopic studies of nitrate in Central Washington. $\delta^{15}$N, $\delta^{18}$O and $\Delta^{17}$O values are used to constrain sources of NO$_3^-$ to groundwater. Isotope signatures for nitrate from soil leachate largely overlapped with the point cloud of data for nitrate in groundwater in a local EPA study. The groundwater nitrate was largely attributed to a mixture of manure and fertilizer. However, isotope signatures in this study also overlapped with isotopic values attributed to naturally occurring soil nitrate from a study at the nearby Hanford Site, Washington. A mass balance calculation based on $\Delta^{17}$O data suggests that there is a $\sim$9% atmospheric contribution to nitrate in soil accumulations below caliche layers at several locations. This atmospheric input was
consistent across multiple sites. We argue that the consistent atmospheric component implies the nitrate in these soil samples at depth appears to have a largely predominately non-anthropogenic origin, because a significant anthropogenic input would dilute and cause variation in this atmospheric signature. We suggest the flushing of naturally occurring soil nitrate to groundwater during land use conversion to irrigated agriculture may represent a previously overlooked, significant, nitrate input to shallow alluvial aquifers in this region.
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CHAPTER I

INTRODUCTION

Groundwater quality and abundance is of increasing concern globally. In the arid western United States, climate change is resulting in increased evapotranspiration, altered precipitation patterns, and reduced snow storage.\textsuperscript{1} These changes, combined with population growth result in strained freshwater resources. The Yakima River Basin, an extensively irrigated agricultural area in central Washington state, is an example of this water resource challenge, with problems of both water availability and water quality. In the Lower Yakima River Valley, repeated findings of nitrate contamination in groundwater has spurred efforts to determine potential sources.\textsuperscript{2}

There has been much debate about the sources of nitrate in the Lower Yakima River Valley, with dairy farms and agricultural fields being discussed primarily. There has been little discussion of natural accumulation of nitrate in soils although soils similar to those found in the Lower Yakima Valley often accumulate atmospheric nitrate over millennial time scales.\textsuperscript{3} Other research has suggested millennia old biological soil crusts may be an important source of nitrate to similar arid and semiarid soils\textsuperscript{4}. These solutes are then flushed into groundwater upon land use changes from a natural hydrologic setting to irrigated farmland.\textsuperscript{4,5} This study attempts to determine whether naturally occurring nitrate in soils could represent a potential input of nitrate to groundwater in the Lower Yakima Valley, after widespread irrigation was implemented in the 20\textsuperscript{th} century.
CHAPTER II
LITERATURE REVIEW
The Hydrology of the Yakima River Basin

The Yakima River Basin aquifer system underlies 16,000 km² in south-central Washington and is hydraulically connected to the Yakima River (Figure 1). The eastern, central and southwestern parts of the basin are largely made up of layered flood basalt flows of the Columbia River Basalt Group (CRBG), with discontinuous and weakly consolidated sedimentary interbeds. Most water in the CRBG is located at the top of basalt flows in the entablature and in interbeds. The lowlands are underlain by unconsolidated valley fill of glacial, glacio-fluvial, lacustrine, alluvial, and fluvial origins. The CRBG, which composes the bedrock of most of this region, is fractured down to depths of up to 100–150 meters below the surface, creating networks of connected joints. Wells installed in basin-fill aquifers yield on average three times as much water as those drilled through CRBG.

The Yakima River Basin has a variable climate with annual precipitation varying from 15 cm in central Washington near Royal City, to 270 cm along its western margin on the crest and humid east slopes of the Cascade Range. Precipitation occurs most frequently between November and February as snow which establishes a seasonal snow pack.
FIGURE 1. The Yakima River Basin.

This seasonal snow pack melts as early as January at lower elevations, and progressively later at high elevations. Irrigation occurs during the dry season, from early April until late October.
The water used for irrigation is largely stored via a system of dams and reservoirs constructed in the early 20th century. During low flow periods, irrigation artificially recharges shallow alluvial aquifers and accounts for up to 75 percent of stream flow in this basin. Groundwater levels in basin-fill units of the Yakima Valley tend to be stable with declines of less than 7 m relative to the 1990s. Groundwater levels in aquifers with lower replenishment rates in the CRB group tend to be declining with total falls of up to 60 meters.

The Yakima Basin is divided into upper and lower portions by a hydrologic restriction at Union Gap, Washington (Figure 1). Farmers in this region, particularly in the upper Yakima Basin, commonly use rill irrigation, a process involving inundating the higher portion of a field and allowing water to travel across the field through rills. With this farming practice, much of the irrigation water recharges shallow aquifers. Studies have shown this inefficient irrigation practice has increased recharge of these shallow aquifers from 0.0-0.3 cm to 51.1-127.0 cm annually, and induces seasonal variation in groundwater tables (Figure 2).

The Geochemistry of the Yakima Basin

A recent upper Yakima Basin study described the geochemical relationship between surface and groundwater in regions of the Yakima Basin with irrigated agriculture. The study characterized groundwater geochemistry along a transect in the upper Yakima River Basin into four main hydro-chemical groups. The first group
showed temporal increases in Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, and Mg\textsuperscript{2+} concentrations during the irrigation season, and elevated δ\textsuperscript{18}O and δD values similar to the Yakima river, suggesting substantial connectivity with irrigation water. This group showed nitrate concentrations as high as 11 mg/L. Two other groups show interaction with local lithologies, the Columbia River basalts (non-modern, high-Na groundwater), and the
Ellensburg Formation’s ash and lahar deposits (Ca-Mg-HCO₃ type waters). The fourth group has been influenced in part by both the Ellensburg Formation and, to a lesser extent, surface water causing some temporal variation in solute concentrations. Some groundwater samples exhibit solute concentrations close to the average for all groundwater samples obtained, suggesting that areas of groundwater mixing exist.⁹ This study showed shallow alluvial aquifers in the Yakima Basin are strongly influenced by irrigated agriculture, which highlights a potential for soil constituents, such as nitrate, to be flushed from agricultural soils to groundwater.

A Primer on Nitrate Stable Isotope Analysis

Frequently, stable isotope ratios can be used for the identification of contamination sources as they lend source-specific signatures, and biologic cycling changes these signatures in predictable ways (Figure 3). The two stable isotopes of nitrogen are ¹⁵N and ¹⁴N. In the atmosphere there are 272 ¹⁴N atoms for every one ¹⁵N atom. Nitrogen isotopes are reported in per mil (‰) relative to atmospheric ratios which are calculated using the following formula¹⁰:

\[
\delta^{15}N_x = \left( \frac{\frac{^{15}N}{^{14}N}_x}{\frac{^{15}N}{^{14}N}_{air}} - 1 \right) \times 1000
\]

Most materials on Earth contain δ¹⁵N compositions between -20 and +30‰, although substances have been found with values varying from -49 to +102‰.¹⁰
Nitrogen in soils tend to have values between -2 to +6‰,\(^\text{11}\) while synthetic fertilizer has values of -8 to +7‰ and manure is generally between +10 and +25‰. Once in soil the NO\(_3^-\) from synthetic fertilizer has average δ\(^{15}\)N values of +0.7 to +10.1‰, while nitrate in soil from manure has δ\(^{15}\)N values from +5.2 to +22.8‰.

Atmospheric nitrogen sources tend to have δ\(^{15}\)N values between -15 and +15‰.\(^\text{10}\)

More recent studies in Washington State have found δ\(^{15}\)N values of nitrate in wet deposition ranging from -11‰ to +3.5‰.\(^\text{11}\)

The overlapping δ\(^{15}\)N values found among various nitrate sources require the incorporation of δ\(^{18}\)O to better constrain potential nitrate inputs. δ\(^{18}\)O values for

**FIGURE 3. Nitrate isotope data from previous Lower Yakima studies. Data**
from EPA\textsuperscript{2} in orange and Cavanaugh\textsuperscript{21} in red, plotted with ranges displayed for discreet sources from modern literature,\textsuperscript{11} and a blue ovoid showing the point cloud for natural soil nitrate at the Hanford Site.\textsuperscript{23}

Nitrate are, like δ\textsuperscript{15}N values, reported per mil and are calculated via comparison to a standard VSMOW (Vienna Standard Mean Ocean Water) using a similar δ equation:

$$
\delta^{18}O_x = \left( \frac{\frac{^{18}O}{^{16}O}}{\frac{^{18}O}{^{16}O}}_{\text{VSMOW}} - 1 \right) \cdot 1000 \quad (2)
$$

Synthetic fertilizers have been found to have δ\textsuperscript{18}O values of nitrate between +17 and +25 ‰. Nitrate from the nitrification of ammonium fertilizers tends to have δ\textsuperscript{18}O values from -5 to +15‰.\textsuperscript{11} Microbial nitrate and nitrate from animal waste typically have δ\textsuperscript{18}O values between -10 and +10‰.\textsuperscript{10} The range of δ\textsuperscript{18}O values found for atmospheric nitrate from wet deposition was found to be from +63 to +94‰ in a study surveying precipitation across the United States.\textsuperscript{12} Atmospheric nitrate has a variety of inputs, natural and anthropogenic, but fossil fuel combustion is thought to represent the largest NO\textsubscript{x} input to the atmosphere. The largest sink of NO\textsubscript{x} is oxidation to nitric acid (HNO\textsubscript{3}), which then dissociates to nitrate when deposited during precipitation as wet deposition.\textsuperscript{11}

Dry deposition of nitrate represents the largest source of nitrate deposition in arid climates in much of the western United States. Dry deposition is the transfer of nitrate species directly to the Earth’s surface without precipitation. This source is poorly understood due to difficulty obtaining measurements, a multitude of
potential sources (aerosols, dry gases, and peroxyacetyl nitrate) and limited
monitoring of dry deposition. Measurements of $\delta^{15}$N in nitrate from dry deposition
have ranged from -1 to +11 ‰.\(^{11}\)

If nitrate in groundwater or surface water is the product of mixing from two
sources with discrete isotopic signatures, it is possible to determine the proportion
of nitrate originating from each source. A simple test to see if $\delta^{15}$N and $\delta^{18}$O values
can be explained by mixing is to plot $\delta$ values vs $1/NO_3^-$.
If data plots on a straight line, two discrete sources likely explain variability in $\delta^{15}$N and $\delta^{18}$O values.\(^{11}\)
Unfortunately, there are rarely only two nitrate sources and so this method is not
effective at assigning quantitative values to relative nitrate contributions in most
cases.\(^{11}\)

Denitrification Method for Analysis of $\delta^{15}$N and $\delta^{18}$O in Nitrate

This study employs the bacterial denitrification method to analyze $\delta^{15}$N and $\delta^{18}$O
in Nitrate. The bacterial denitrification method of nitrate isotopic analysis in
freshwater overcomes many limitations found in earlier methods. This method
involved the analysis of nitrous oxide gas ($N_2O$) produced from nitrate by
denitrifying bacteria under anaerobic conditions. Typical denitrifying bacteria have
a series of enzymes which are utilized in each step of the following pathway:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$  \(3\)

Researchers have found that naturally occurring denitrifying bacteria lacking
active N₂O reductase, which prevents N₂O from being reduced to N₂, can be used for extracting nitrate from waters. This method requires first cultivating an appropriate strain of bacteria in a soy broth containing nitrate and ammonium. The bacteria are then removed from the medium utilizing a centrifuge, then suspended in a medium to increase bacterial populations. Each vial is then purged using N₂ gas to remove any nitrous oxide produced from the growth mediums, and to ensure anaerobic conditions. The freshwater sample is then added to the bacteria and a N₂O extraction system flushes the sample with helium gas, carrying the nitrous oxide gas into a portion of a glass U-tube in a liquid nitrogen bath. Once the nitrous oxide gas has been isolated in the U-tube, and cryogenically concentrated, it can be analyzed using an isotope ratio mass spectrometer. This allows the measurement of nitrogen and oxygen isotopic ratios in nitrate with an error of less than one per mil.

The Coupling of δ¹⁷O with δ¹⁵N and δ¹⁸O to Identify Atmospheric Deposition as a Source of Nitrate Contamination

Analysis of δ¹⁷O in nitrate when coupled with δ¹⁵N and δ¹⁸O data is a promising new method to isolate the proportion of nitrate with an atmospheric origin. This method has not yet been utilized in the Lower Yakima Basin. While most processes which fractionate oxygen are mass dependent, the atmospheric photochemical reactions which form atmospheric nitrate are mass independent resulting in higher
\( \delta^{17}O_{\text{NO}_3} \) values. In mass dependent kinetic and equilibrium reactions:\(^{14}\)

\[
\delta^{17}O = 0.52 \times \delta^{18}O
\]  
(4)

While in atmospheric photochemical reactions:

\[
\delta^{17}O > 0.52 \times \delta^{18}O
\]  
(5)

Therefore, by using the measure:

\[
\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O
\]  
(6)

it is possible to identify the total proportion of nitrate from atmospheric photochemical reactions by seeing how close \( \Delta^{17}O \) is to the value expected if \( \delta^{17}O \) and \( \delta^{18}O \) values fell along the atmospheric mixing line.\(^{15}\) As oxygen in atmospheric compounds has either an ozone (O\(_3\)) or water (H\(_2\)O) origin:

\[
\Delta^{17}O_{\text{Sample}} = f_{\text{ozone}} \times \Delta^{17}O_{\text{ozone}} + f_{\text{H}_2\text{O}} \times \Delta^{17}O_{\text{H}_2\text{O}}
\]  
(7)

where \( f_{\text{ozone}} \) and \( f_{\text{H}_2\text{O}} \) are the fractions of ozone and water derived atoms. Studies of atmospheric deposition have measured \( \Delta^{17}O \) values ranging from 20-30‰, with an average value of 23‰. Therefore, the estimated proportion of atmospheric nitrate in a sample is \( f_{\text{ozone}} = \Delta^{17}O_{\text{Sample}} / 23‰ \). The atmospheric nitrate concentration of a sample can then be calculated using the equation:

\[
[\text{NO}_3^-]_{\text{atm}} = f_{\text{ozone}} \times [\text{NO}_3^-]_{\text{Sample}}
\]  
(8)

The \( \delta^{18}O \) signature of the nitrate of non-atmospheric origin may then be determined as \( \delta^{18}O_{\text{non-atm}} = \delta^{18}O - f_{\text{ozone}} \times \delta^{18}O_{\text{atm}} \).\(^{16}\) This technique has the potential to identify the proportion of nitrate from atmospheric deposition in soils and groundwater of the Lower Yakima Valley.
Naturally occurring soil nitrate will retain only a fraction of this isotope signature as nitrate from atmospheric deposition will be incorporated into biota upon deposition to varying degrees based on the limits mean annual precipitation (MAP) places on biological productivity. A recent study measured soil nitrate $\Delta^{17}$O values across transects of several deserts with orographic effects to develop an empirical equation to describe this loss of the atmospheric $+23$ per mil $\Delta^{17}$O signature where:

$$\ln\left(\frac{\text{MAP}}{253.8}\right) - 0.12 = \Delta^{17}\text{O} \quad (9)$$

Based on the MAP of Mabton, Washington (190 mm), naturally occurring soil nitrate in the Lower Yakima Valley would be expected to exhibit a $\Delta^{17}$O value of approximately $+2.5$ per mil.

Discussion of EPA Study

Multiple investigations into groundwater quality in the Lower Yakima Valley in Washington State have revealed nitrate at concentrations above the U.S Environmental Protection Agency (EPA) maximum contaminant levels (MCL; 10 mg/L of N-NO$_3$) in many locations in the Toppenish and Benton sub-basins. Nitrate is a contaminant of concern because it is linked methemoglobinemia (blue baby syndrome) in infants. In 2008, the *Yakima Herald Republic* ran a series of articles
drawing attention to the nitrate contamination issue, and to the concern that these nitrate contaminated wells disproportionately impact disadvantaged Latino fruit pickers unable to advocate for themselves.²

In 2013, the EPA subsequently conducted a three-phased study to better understand sources of nitrate contamination in the Lower Yakima Valley.² Phase 1 estimated the total nitrogen inputs from all potential sources by using land use data. Through this method, it was concluded livestock operations represent 65 percent of total nitrate inputs, cropland 30 percent, biosolids 3 percent, and 2 percent other sources. The EPA focused the Phase 2 and Phase 3 efforts on these three sources.² Phase 2 involved testing the drinking water of over three hundred private well dependent homes and found roughly 20 percent showed nitrate levels above the MCL (Figure 4).

This led to further testing of wells downgradient of potential sources such as large dairy operations during Phase 3. During this phase, the EPA found concentrations of nitrate, and the antibiotics monensin and tetracycline (commonly used in livestock), increased in downgradient wells with proximity to the Haak Dairy, and an identified dairy cluster. This was additionally significant as there are few regulations regarding the construction of manure lagoons by dairy farms. For example, it is permissible under current law to construct lagoons without an impermeable barrier to prevent infiltration of manure solutes to groundwater.¹⁸ One limitation of the EPA study is that well depths were not often recorded, making
it difficult to determine what aquifer residential wells are drawing from and whether they are connected hydraulically to the dairy farms. However, the EPA did utilize isotopic techniques to determine nitrate sources of concern. Their isotope data suggests that animal waste was the source of many instances of contamination.

The EPA analysis of nitrate contamination found a range of $\delta^{15}$N and $\delta^{18}$O signatures in nitrate-contaminated water using the bacterial denitrification method (Figure 3). The limited depth data available suggested an inverse correlation between well depth and nitrate concentrations. This result agrees with the Taylor and Gazis study, which concluded nitrate contamination occurs in the upper Yakima Valley when agricultural discharge enters shallow local aquifers. $\delta^{15}$N and
δ\textsuperscript{18}O signatures were also analyzed. In the EPA study\textsuperscript{2}, samples with δ\textsuperscript{15}N and δ\textsuperscript{18}O values indicating manure as the primary source frequently were found in locations which may be downgradient from two identified dairy clusters, suggesting that these samples came from shallow aquifers hydraulically connected to the dairy manure piles.

The EPA also collected other solute data which could be used to characterize the various groundwater bodies tested for nitrate contamination, adding clarity about which water bodies were tested. The EPA additionally tested for a suite of agricultural chemicals including tetracycline and monensin, antibiotics used on ruminants, and found them both in wells that appear to be downgradient from dairy farms\textsuperscript{2}. This represented the strongest support that some residential drinking wells were contaminated by the dairy farms’ waste streams.

However, some contaminated wells near each identified dairy cluster had δ\textsuperscript{15}N and δ\textsuperscript{18}O signatures more similar to those expected from atmospheric and fertilizer sources, indicating a more comprehensive understanding of potential nitrate sources, the hydrogeology, and the geochemistry of the Lower Yakima Basin is needed to fully trace the origins of all instances of nitrate contamination in this area.

Samples with nitrate with a predominant atmospheric nitrate source contained up to 69.6 mg/L, almost seven times the MCL\textsuperscript{2}. Another potential source of nitrate to soils in a semi-arid shrub steppe environment is biological soil crusts which have been shown in similar setting to export nitrate and ammonium to the soil
These biological soil crusts have previously been identified in Yakima County suggesting that this may be an additional source of nitrate to soils in the Lower Yakima Valley. Studies in other similar arid soils have found abundant nitrate which can then be exported to groundwater upon land use conversion to irrigated agriculture, a regime change that occurred in the early 1900’s, altering the Lower Yakima Valley to one of the most prolific agricultural regions in the American West.

U.S. Geological Survey Particle Backtracking

In 2011 a transient three-dimensional groundwater-flow model of the Yakima River Basin was completed utilizing MODFLOW-2000. This used the particle tracking code MODPATH 5.0 to backtrack simulated particles from some wells with nitrate levels above the MCL for the period from October 1959 to September 2001. Path-lines terminating at the water table were then linked to a land surface area and were not specific to any land use practice or contaminant (Figure 5).

These path-lines identified land surfaces where nitrates in groundwater may have originated. This modeling effort did not attempt to incorporate any groundwater interactions with soil during transport, or any water quality impairments due to subsurface features such as septic systems. This modeling effort was made more uncertain by the unknown well depths for many of the 121 nitrate contaminated wells identified by the EPA. To complete the modeling for these wells,
it was assumed nearby wells had similar depths. In addition, the model did not

**FIGURE 5.** Simulated zones of contribution for nitrate contaminated wells in the Lower Yakima Basin\(^{18}\), against soils containing significant carbonate content\(^{22}\).
include the cones of depression for the contaminated groundwater wells. Thus, the modeled capture areas of each of the wells should be interpreted as the centroids of the true capture areas. Many dairy farms are located within these capture areas, along with significant areas containing carbonate rich soils (color coded in Figure 4) which may contain abundant natural soil nitrate.

Cavanaugh Atmospheric Nitrate Investigation

The EPA investigation\(^2\) included some nitrate samples showing \(\delta^{15}\text{N}\) and \(\delta^{18}\text{O}\) signatures indicative of significant atmospheric contribution; this was identified as a subject worthy of investigation for an undergraduate thesis at Central Washington University. Because the EPA report\(^2\) suggested that caliche may be a potential nitrate source, calcareous soils were sampled in addition to ground waters near EPA samples with possible atmospheric nitrate isotopic signatures. This study analyzed \(\delta^{15}\text{N}\) and \(\delta^{18}\text{O}\) compositions of the caliche samples and four well water samples via the denitrification method.\(^21\)

The investigation utilized linear and polynomial trend lines to attempt to analyze relationships between pairs of solutes, and was able to find an approximately linear relationship between Cl\(^{-}\) and SO\(_4^{2-}\), solutes associated with irrigation recharge. The researcher also attempted to attribute \(\delta^{15}\text{N}\) and \(\delta^{18}\text{O}\) values to source signatures, using nitrate fields in Kendall and McDonnell.\(^{10}\) Two additional
samples had δ^{15}N values below -11‰ and δ^{18}O values below +50‰ (Cavanaugh, 2013), for at least one of these samples it seems likely fractionation occurred during the conversion of NH$_4^+$ to NO$_3^-$ demonstrating the uncertainty in identifying nitrate sources using stable isotopes.$^{11}$ While data from this undergraduate thesis are incongruent with other local studies for unclear reasons, useful data was gathered (Figure 3).

Carbonate-Rich Soils in the Lower Yakima Valley

Carbonate rich soils form in arid and semi-arid areas when precipitation is insufficient to flush carbonates from soils for millennia, and indicate inconsequential groundwater recharge. These soils represent the primary potential source of atmospheric nitrate in the semi-arid Lower Yakima Basin as their presence indicates other soil solutes, such as nitrate, may also accumulate without flushing from groundwater.$^{21}$

In 1985 a soil survey of the Yakima County Area identified significant areas of calcareous soils (Figure 5), indicating that solutes such as nitrate may accumulate in these soils. These well drained, carbonate containing soils, occur on slopes of less than 30 percent and are predominately silt loams. These soils do not effervesce until a depth of 50–75 cm is reached, indicating these depths represent the zone of accumulation.$^{22}$

At the Hanford Site ~80 km east of the Lower Yakima Valley, carbonate rich
caliche soils have been found to contain abundant soil nitrate. At this location, historic nuclear activities at this location caused substantial unnatural groundwater infiltration from dilute wastewater being disposed of onto the ground surface. This process was shown to have resulted in the flushing of this abundant soil nitrate to local groundwater, leading to concentrations in exceedance of the EPA MCLs. The δ¹⁵N and δ¹⁸O values of nitrate in the Hanford study were broadly similar to those identified in the EPA² report to represent a manure nitrate source. This similarity suggests that naturally occurring nitrate in this region may be mistaken for other inputs. This Hanford study is significant as it shows anthropogenic groundwater infiltration may result in a substantial naturally occurring soil nitrate flux to groundwater in a nearby setting climatically and biologically similar to that of the Lower Yakima Valley.

Carbonate rich soils are of particular interest to understanding input of nitrate to soils. Studies in other areas have found these soils represent a significant nitrate input to groundwater upon flushing of soil solutes to groundwater due to land use conversion to irrigated agriculture. This land use conversion to irrigated agriculture occurred on a large scale in the Lower Yakima Valley during the 20th century.⁴,⁶

Discussion

A growing body of evidence suggests dairy farms in the Lower Yakima Valley are an important source of nitrate contamination in groundwater. However, some
groundwater has nitrate in excess of the MCL with an isotopic signature suggestive of an atmospheric source.\(^2\) Nitrate is known to be transported through atmospheric dry deposition,\(^{11}\) or fixated in biological soil crusts present in the Yakima Valley\(^2^0\) and transported from the soil surface during percolation events\(^1^9\). Calcareous soils additionally have the potential to accumulate atmospheric nitrate, and then interact with groundwater either during precipitation events or groundwater mounding during the irrigation season. At the nearby Hanford site, which is climatically similar to the Yakima River basin, it has been shown that artificial groundwater infiltration has led to transport of nitrate from soils to groundwater.\(^2^3\)

The limited research on atmospheric and soil nitrates conducted in this area provides the background for this study. To further explore these nitrate sources, \(\delta^{15}N\), \(\delta^{18}O\), and \(\delta^{17}O\) analyses are combined to with more methodical soil sampling to better understand the origins of nitrates in the groundwater of the Lower Yakima Valley.

**Literature Cited**


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CHAPTER III

JOURNAL ARTICLE
An isotope investigation of nitrate in soils and agricultural drains of the Lower Yakima Valley, Washington

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Nitrate in the groundwater of the Lower Yakima Valley, Washington has long been known to frequently exceed the EPA maximum contaminant level standard for potable water (10 mg/L), adversely impacting communities with disadvantaged socio-economic status. In this research, nitrogen and oxygen isotopic signatures were determined for nitrate soil leachates and irrigation return flow collected in the Lower Yakima Valley and compared to previous isotopic studies of nitrate in central Washington. Isotope signatures for nitrate from soil leachate had significant overlap with both the point clouds of isotope signatures for nitrate in groundwater in an EPA study that was attributed to manure and fertilizer application,¹ and naturally occurring soil nitrate at the nearby Hanford Site, Washington.² A mass balance calculation based on $\Delta^{17}O$ data suggests that there is a ~9% atmospheric contribution to nitrate in soil accumulations below caliche layers at several locations. This atmospheric input agreed with other research on the atmospheric contribution to naturally occurring soil nitrates in areas with similar Mean Annual Precipitation values, and is consistent across multiple sites. We argue that this consistent ~9% atmospheric component indicates that soil nitrate at depth is
dominated by naturally occurring soil nitrate across multiple sites. We suggest the flushing of naturally occurring soil nitrate to groundwater during land use conversion to irrigated agriculture may represent a previously overlooked significant nitrate input to shallow alluvial aquifers in this region.

**Introduction**

The aquifers of the Lower Yakima Valley, Washington (Figure 6) have been known since 2002 to contain water with nitrate in excess of the Environmental Protection Agency’s (EPA) Maximum Contamination Level (MCL) for drinking water of 10 mg/L. Concentrations of nitrate in the aquifers of this region are now known to have been increasing since at least the 1970s. In 2008, a series of articles in the *Yakima Herald Republic* highlighted that nitrate contaminated private drinking water wells were disproportionately impacting a disadvantaged community. This spurred the EPA to conduct an investigation largely assigning contamination to local dairy farms based on stable isotope data, the presence of monensin and tetracycline in both dairy manure lagoons and downgradient wells, along with the assumption that anthropogenic inputs dominate nitrate sources to groundwater. In addition, the EPA study found nitrate in a few disparately distributed wells and soil samples to be anomalously enriched in $^{18}$O suggesting potential atmospheric nitrate inputs to drinking water wells. A separate study at the Hanford Site 80 km away concluded that naturally occurring soil nitrate was flushed into groundwater after land use
Figure 6. Map of the Lower Yakima Valley, Washington and sampling sites. Approximate surface area of contribution to nitrate contaminated wells\textsuperscript{18} is shown in salmon shading. Soil samples are as follows; Road Cut 1 (RC1), Road Cut 2 (RC2), Natural 1 through 4 (N1-4), Irrigated Agriculture (I), Irrigated and Natural (IN).
changes resulting in elevated groundwater nitrate. The study reported here investigates further the role of soils and atmospheric inputs as a potential source of nitrate to groundwater in the Lower Yakima Valley.

Site Description

The Lower Yakima Valley naturally experiences limited groundwater recharge,\(^6\) due to a strong orographic effect, which has allowed for the development of carbonate rich soils across a large fraction of the study area.\(^7\) The soils and groundwater recharge were substantially altered during the 20\(^{th}\) century, after diversion of snowmelt from the adjacent Cascade range and widespread implementation of rill irrigation, which caused high rates of modern groundwater recharge to shallow alluvial aquifers.\(^1,6,8\) This region supports a diverse array of agricultural crops, and widespread animal husbandry operations such as dairy farms.\(^1\) Manure, fertilizer and natural soil nitrate are all possible sources of nitrate to groundwater.

Methods and Materials

Soil Samples. Soil samples were selected based on sampling site access, proximity to the surface area of contribution to nitrate contaminated drinking water wells\(^9\) and the presence of soil types\(^7\) known to occur within the area of contribution. At eight locations soil samples were collected from soil pits, or road cuts at regular depth intervals to a depth of approximately 1 meter. The collection of
soil samples from soil series containing significant carbonate content was emphasized as the presence of carbonate was used as a potential indicator for the accumulation of atmospheric chemicals. Soil samples were immediately frozen and stored at -20° C in a dark environment. Soil sample sites included four shrub steppe sampling sites (N1 through N4), one irrigated apple orchard (I), a site with a mix of irrigated agriculture and unutilized shrub steppe (IN), and two road cuts adjacent to un-irrigated farm land which offered easy sampling access (RC1 and RC2). Locations RC1, RC2, and IN were selected for closer chemical and isotopic analysis after preliminary results showed nitrate concentrations greater than 2 mg/l for some soil leachates. At location IN two pits and one road cut were sampled to compare nitrate in a roadcut with a shrub steppe setting (IN1) uncultivated road right of way (IN4), and in an apple orchard (IN3). Water samples were also collected from two agricultural drains for analysis and comparison of nitrate isotope signatures.

Sampling locations were limited due to extensive private land ownership, landowners suspicious of investigations into nitrate sources, and sparse sites in a truly natural setting.

**Chemical Analysis.** A subset of each sample (~3 g) was mixed with a mass of deionized (DI) water 10 times the mass of the soil sample for 10 minutes. The water samples and the resultant slurry was then filtered using a 0.45 μm quartz fiber filter and then analyzed for nitrate, chloride, sulfate, and phosphate with a Dionex ion chromatograph after EPA method 300.10 Minor nitrate cross
contamination from the pre-filtration process was observed in the procedural blanks (<0.13 mg/L), and subtracted from the nitrate analytical results. A subset of each sample was tested for carbonate content by measuring the amount of carbon dioxide gas produced upon reaction with hydrochloric acid, this involved placing a soil sample in a closed 40 mL screw cap vial with a rubber septum, and placing a small vial containing 1 ml of hydrochloric acid in the container. The screw cap vial was then sealed, shaken, and the pressure inside was measured using a digital manometer and compared to ambient atmospheric pressure. Approximately 1 g of each soil sample was tested for moisture content by measuring the mass difference after being placed in an oven at 110°C for 24 hours. Loss on ignition was then obtained for each oven dried sample by measuring the percentage of mass lost after being placed in a muffle furnace at 950°C for 6 hours. Total organic content of soil samples was estimated by subtracting percentage carbonate content from percentage loss on ignition. Soil pH was determined by mixing 5 g of soil with 10 ml of DI water, and measured after allowing the resulting slurry to sit for 10 minutes.

Isotope Analysis. DI water leachates from four sampling locations were selected for isotope analysis after it was determined they contained significant nitrate. Due to cost constraints only leachates with nitrate concentrations greater than 2.5 mg/L, and the agricultural drain water samples were analyzed at the University of Pittsburgh’s Regional Stable Isotope Laboratory to obtain $\delta^{17}O_{NO_3}$, $\delta^{18}O_{NO_3}$, and $\delta^{15}N_{NO_3}$ values using the Sigman--Casciotti bacterial denitrifier.
method, and a continuous flow GV Instruments IsoPrime™ stable isotope ratio mass spectrometer. The remaining leachates with nitrate concentrations between 1.0 mg/L and 2.5 mg/L were also analyzed using the same method at the Washington State University Stable Isotope Core Laboratory for δ^{18}O_{NO_3} and δ^{15}N_{NO_3} using a Gas Bench II and a ThermoFinnigan Delta V Ratio Mass Spectrometer. Stable isotopic compositions of oxygen and nitrogen in nitrate were used to identify likely nitrate sources in soil using known source values. All oxygen isotope data presented are calculated with respect to Vienna Standard Mean Ocean Water (VSMOW) and reported in per mil. The relationship between δ^{18}O_{NO_3} and δ^{15}N_{NO_3} values during mass dependent fractionation was used to calculate Δ^{17}O_{NO_3}.

**Results and Discussion**

Nine soil sites and two irrigation return flow sites were sampled in this study. Analytical data for these soil and water samples are presented in Table 1. For the nine soil sampling locations, nitrate in soil leachate was detected at levels typically in abundance of at least 1 mg/L for at least some portion of the soil profile. Of the nine soils sites samples, three were found to have leachate nitrate concentrations above 5 mg/L and selected for detailed analysis.

Two of these sampling sites were from road cuts, while the third was obtained from a moist silt loam likely wetted by irrigation water, all of which
TABLE 1.– Major anion concentrations, $\delta^{18}O_{\text{NO}_3}$ and $\delta^{15}N_{\text{NO}_3}$ values for soil samples, soil leachates, and water samples.

<table>
<thead>
<tr>
<th>Site Location</th>
<th>Depth (cm)</th>
<th>Moisture Content (%)</th>
<th>Organic Content (%)</th>
<th>CaCO$_3$ (%)</th>
<th>pH</th>
<th>$\text{NO}_3^-$ (mg/L)</th>
<th>F$^-$ (mg/L)</th>
<th>Cl$^-$ (mg/L)</th>
<th>PO$_4^{3-}$ (mg/L)</th>
<th>$\text{SO}_4^{2-}$ (mg/L)</th>
<th>$\delta^{15}N$</th>
<th>$\delta^{18}O$</th>
<th>$\Delta^{17}O$</th>
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<td>Road cuts adjacent to unirrigated farmland</td>
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<td></td>
<td></td>
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<tr>
<td>RC2 46.141 N, 120.026 W</td>
<td>0 to 15</td>
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<td>18</td>
<td>ND</td>
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<td>12.3</td>
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<td>δ¹⁸O</td>
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*Number after sample pit represents which soil pit sample was taken from if applicable. **/ represents not measured. ***ND represents not detected.
allowed particularly easy access for soil sampling. In the two roadcut soils, the highest nitrate concentrations lie within the caliche horizon. This spatial pattern suggests a sampling bias between road cuts and soil cores; hard calcareous soils at depth may have limited access to nitrate-rich samples at depth using corers. IN3 (apple orchard) and IN1 (shrub steppe roadcut) had relatively low nitrate concentrations, however IN4 (shrub steppe eight meters south of orchard) had nitrate concentrations as high as 9.49 mg/L.

Notably, soil leachates from the two orchard locations (IN4, and I1) had the lowest concentrations of nitrate out of any produced during this study, including natural settings, despite known fertilizer application. It is highly probable that any naturally occurring or added nitrate once present in these soils has been transferred to the groundwater by irrigation.

$δ^{18}O$ and $δ^{15}N$ nitrate data collected are plotted in Figure 7, along with typical source ranges, data from an EPA groundwater study, and the range of values found in natural pore water nitrate at the Hanford Site (~50 km east). The EPA groundwater study largely attributed well water nitrate contamination to dairy manure with several outliers indicative of a significant atmospheric nitrate contribution. The values determined for soil samples in this study overlapped range of values found to occur in groundwater in the EPA study. However, overlap in typical nitrate source values make it difficult to distinguish between a natural soil nitrate versus a mixture of manure and ammonium fertilizer without prior land use.
information or other chemical tracers which can differentiate between these sources.

**FIGURE 7.** Plot of $\delta^{18}O_{NO_3}$ versus $\delta^{17}O_{NO_3}$ for soils and agricultural drains sampled in the Lower Yakima Valley, the trend for caliche containing soils at depth, and the Terrestrial Fractionation Line (TFL) for mass dependent fractionation.

Farmers commonly apply a mixture of ammonium fertilizer and synthetic nitrate fertilizer$^{15}$ which will tend to result in higher $\delta^{18}O$ values and lower $\delta^{15}N$ values when mixed with either naturally occurring nitrate or manure in soils. During denitrification reactions, the remaining nitrate will move along 1:1 and 2:1 trajectories on at $\delta^{18}O - \delta^{15}N$ plot$^{5}$ (Figure 6). $\delta^{15}N$ values for ammonium fertilizer may additionally experience enrichments of up to 15‰ during ammonium
devolatilization, this fertilizer may then be converted to nitrate. $\Delta^{17}O$ nitrate values ranged from -1.2 to +2.2‰ (Figure 7). It is unknown why $\Delta^{17}O$ values may deviate negatively from the mass dependent $^{17}O$ versus $^{18}O$ line.

However significantly negative values occurred exclusively in irrigation return flow and irrigation influenced soils (IN4). Other negative values have been reported before for biogenic soil nitrate in a forested catchment. Positive $\Delta^{17}O$ values were used to determine the fraction of nitrate from atmospheric sources ($f_{atm}$) which can be estimated based on mass balance considerations with the equation:

$$f_{atm} = \frac{\Delta^{17}O}{+23.4‰} \quad (1)$$

Atmospheric contributions to nitrate in soil samples were found to vary between 10 and 0 percent (Figures 8c, 8f, and 8h).

Soil samples taken from RC2 presented complex trends in $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ (Figure 8d). The shallowest sample analyzed had values typical of naturally occurring nitrate, potentially due to biotic processing in the root zone (Figure 8e). The 30-45 cm soil interval showed anomalously high values of $\delta^{15}N_{NO_3}$ (+12.6‰) and $\delta^{18}O_{NO_3}$ (+12.9‰) (Figure 8d), which may be explained through either denitrification fractionation of natural soil nitrate or from an initial commercial
fertilizer with a common mix of ammonium and nitrate which had undergone enrichment during ammonium volatilization. The next three depth intervals

Figure 8. Trends in nitrate isotope ratios (a, d, g) nitrate and carbonate concentrations (b, e, h) and percent of nitrate with atmospheric origin (c, f, i) versus depth. Caliche was observed in the field where carbonate contents was found to exceed five percent.
(45–60 cm, 60–75 cm, and 75–90 cm) all yielded $\delta^{15}\text{N}_{\text{NO}_3^-}$ (+1.0 to 4.6‰) and $\delta^{18}\text{O}_{\text{NO}_3^-}$ (+10.8 to 6.3‰) values that likely indicate a mixture of commercial fertilizer and natural soil nitrate. This depth interval also has relatively low leachate nitrate concentrations between 1.5 and 1.0 mg/L. Nitrate concentrations then increase for the depth intervals 90–105 cm, and 105–120 cm, to 2.8 and 3.0 mg/L, while $\delta^{15}\text{N}_{\text{NO}_3^-}$ (+2.7 to 6.4‰) and $\delta^{18}\text{O}_{\text{NO}_3^-}$ (+6.3‰) more strongly reflect naturally occurring soil nitrate. $\Delta^{17}\text{O}$ values were near zero from 15–45 cm, but were 1.8–2.3‰ from 90–120 cm (Figure 8d).

These nitrate isotope characteristics are interpreted to be the result of a surficial commercial fertilizer input, with increased naturally occurring nitrate concentrations with depth, particularly at and below the relatively impermeable carbonate rich caliche layer at the depth interval 90–105 cm. The positive $\Delta^{17}\text{O}$ values below 90 cm indicate between 8 and 10 percent of this largely natural soil nitrate is atmospheric in origin and has not been biologically mediated (Figure 10f).

RC1 soil leachate $\delta^{15}\text{N}_{\text{NO}_3^-}$ and $\delta^{18}\text{O}_{\text{NO}_3^-}$ values to a depth of 60 cm were broadly like those of RC2, also likely from soil and fertilizer inputs, with leachate nitrate concentrations of 2.4 to 10.6 mg/L (Figures 8a and 8b). The depth interval of 90–105 cm yielded $\delta^{15}\text{N}_{\text{NO}_3^-}$ and $\delta^{18}\text{O}_{\text{NO}_3^-}$ values of +25.4 and +17.9 respectively, values that are interpreted as $^{15}\text{N}$ and $^{18}\text{O}$ enrichment due to fractionation during denitrification. This depth interval had a leachate nitrate concentration of 2.91
mg/L, the lowest of any depth interval at this location supporting the possibility of ongoing bacterial denitrification. $\Delta^{17}O$ values were near zero to a depth of 60 cm, and 2.1–2.2‰ between 60 and 105 cm. Like deeper soil at RC2, this indicated soil nitrate below 60 cm at RC1 had a 9–10% atmospheric contribution (Figure 8c). $\Delta^{17}O$ values were not obtained below 105 cm (Figure 8a).

Based on the isotopic evidence, we suggest that soil nitrate at site RC1 largely stems from fertilizer and natural soil nitrate sources and that the constant atmospheric content of nitrate (~10%) below 60 cm depth is due to the caliche layer, which is relatively impermeable, protecting the underlying soil nitrate from surface inputs. Thus, the soils below the caliche layer are dominated by naturally occurring nitrate, both biologically-mediated nitrate that is fixed by bacterial processes and direct atmospheric deposition of nitrate. This interpretation is supported by the similarity to deeper soils at the nearby RC2 sampling location. These soils have a significant atmospheric nitrate contribution contained the highest nitrate concentrations in leachate for any soils sampled (10.6 mg/L for 90-105 cm at RC1).

All samples from soil pit IN4 (Figures 8g-i), with the exception of the sample taken from 75–90 cm, exhibited $\delta^{15}N_{\text{NO}_3}$-values above the ammonium chemical fertilizer range of -10 to +4,\textsuperscript{5} and within the natural soil range observed at the Hanford site of +3‰ to +8‰.\textsuperscript{2} It is particularly challenging to uniquely determine nitrate sources in an area with abundant natural soil nitrate\textsuperscript{2} and known usage of
both chemical ammonia and manure fertilizer. However, the land leaser at site IN stated only chemical ammonia fertilizer has been used on the site since at least 2004. $\Delta^{17}O$ values were slightly negative, indicating no significant atmospheric nitrate was present. As what is interpreted to be natural soil nitrate in RC1 and RC2 has an atmospheric component of between 7 and 10 percent, the absence of this atmospheric component in IN4 is interpreted as largely reflecting agricultural inputs. However, higher nitrate cycling from increased moisture availability via throughflow from a nearby irrigated orchard may be an alternate explanation for the lack of positive $\Delta^{17}O$ values. The $\delta^{15}N_{NO_3^-}$ and $\delta^{18}O_{NO_3^-}$ values for IN4 are similar to those for RC1 and RC2, demonstrating the difficulty associated with distinguishing natural soil nitrate from anthropogenic inputs in this area using only $\delta^{15}N_{NO_3^-}$ and $\delta^{18}O_{NO_3^-}$.

The Marion Drain, and the Sulfur Creek Wasteway samples yielded $\delta^{15}N_{NO_3^-}$ values of 7.1 and 10.1 respectively and $\delta^{18}O_{NO_3^-}$ values of $-4.23$ and $-1.9$ respectively (Figure 9). These values are not incongruent with a complex mixture of nitrate produced from nitrification of ammonium in fertilizer and manure, natural soil nitrate, and nitrate fertilizer. $\Delta^{17}O_{NO_3^-}$ values were $-0.9$ and $-1.4$, indicating no atmospheric contribution (Figure 7).

We conclude that natural soil nitrate represents a potential source of nitrate in groundwater upon flushing during irrigation which may lead to elevated nitrate
FIGURE 9. Chart of δ^{18}O vs δ^{15}N for soil leachate and agricultural drain samples. Typical nitrate isotope source ranges after Kendall et al. (2007), shaded region of natural soil pore water values for a study at the Hanford Site\textsuperscript{2} (80 km east), groundwater values plotted for an EPA study\textsuperscript{1} and soil leachate values from this study. Two agricultural drain samples from the Marion Drain, and the Sulfur Creek Wasteway are also plotted. Arrows signify typical alteration of isotope signatures from bacterial denitrification from arbitrarily selected δ^{18}O and δ^{15}N values. Drains contain agricultural run-off from a large portion of the study area.
concentrations. Isotope values in soil leachate nitrate overlapped with many of the values for nitrate in groundwater in the EPA\textsuperscript{1} study, which concluded nitrate in groundwater samples largely has a mixed manure and fertilizer input, with manure predominating. A nearby Hanford site study found naturally occurring soil pore water with nitrate concentrations of up to 500 mg/L.\textsuperscript{2} We interpret our soil leachate data to reflect naturally occurring soil nitrate, and commercial fertilizer as well as denitrification within the soil.

A potential mechanism for large quantities of nitrate to be transported into soils is millennial atmospheric deposition, followed by partial biologic processing. A recent study\textsuperscript{19} has shown that nitrogen cycling in soils depends on mean annual precipitation (MAP) with $\Delta^{17}$O values that are increasingly shifted away from the atmospheric value with increasing MAP due to biological mediation. An empirical equation was developed to describe this shift:

$$\ln\left(\frac{\text{MAP}}{253.8}\right) - 0.12 = \Delta^{17}\text{O} \quad (2)$$

Based on the MAP in the Lower Yakima Valley (~190 mm/yr), naturally occurring soil nitrate would be expected to exhibit a $\Delta^{17}$O value of approximately +2.5 per mil. This is similar to $\Delta^{17}$O values observed at depth at sample sites RC2 and RC1 of +1.8 to +2.3 per mil (Figures 7 and 8).
The deposition of atmospheric nitrate and the cycling of nitrogen in soils may work in conjunction with the formation of biological soil crusts, symbiotic communities of fungi, cyanobacteria, bryophytes, algae and lichens. Studies in the cold deserts of the Colorado Plateau, southwest Utah, the Mohave Desert, and the Sonora Desert have investigated nitrogen cycling in these communities using micro sensors, acetylene reduction assays to measure $\text{N}_2$ fixation rates, acetylene inhibition assays to measure denitrification rates, and measurements of ammonium oxidation rates.\textsuperscript{20–22} The results indicate that biological soil crusts fix an order of magnitude more nitrate than is denitrified, leading to a flux of nitrate to the soil below during percolation events.\textsuperscript{20–22} These biological soil crusts have been documented to cover between 15 and 20 percent of the ground surface of the Yakima Military Training Ground to the north of the study area.\textsuperscript{23,24} Therefore it is very possible a similar process has occurred prior to agriculture in the Lower Yakima Valley.

Studies such as EPA (2013) use elevated $\delta^{18}\text{O}_{\text{NO}_3}$, characteristic of atmospheric nitrate, in groundwater to assess if natural soil nitrates in caliche may represent a significant input to nitrate contaminated water. However, this study has found nitrate in soil with the potential to impact groundwater lacking this well-known signature. Studies into nitrate contamination of groundwater in this, and other semi-arid regions, should therefore be careful to avoid assigning contamination entirely to a mixture of agricultural fertilizer and manure based
purely on the absence of $\delta^{18}O_{\text{NO}_3}$ enrichment. Other studies have also found nitrate-containing soils can be a significant input in an agricultural setting upon land use conversion to irrigated agriculture. Further study may be warranted to investigate the contribution of soil nitrate in groundwater contamination in the Lower Yakima Valley.

As IN4 and the agricultural return drains all exhibited negative $\Delta^{17}O$ values of up to $-1.4\%$ (Figure 7), the use of a two end member mixing model of $0\%$ for non-atmospheric nitrate and $+23\%$ for atmospheric nitrate may underestimate the abundance of atmospheric nitrate in soils and water. It is possible atmospheric nitrate was present in these agriculturally impacted samples but had its characteristic positive $\Delta^{17}O$ anomaly obscured by mixing with nitrate sources with the observed negative values. If an endmember of $-1.4\%$ is used instead of $0\%$, atmospheric contributions to soil nitrate in sample RC2 90 to 105 cm are as high as 15%, and atmospheric nitrate is present in all soil samples for which $\Delta^{17}O$ data was collected.

In the future, modeling may be used to estimate total natural nitrate inputs of soil series by simulating irrigation to groundwater and transport to better understand the significance of this potential contribution. As irrigation commenced with the implementation of widespread agriculture in this area it is likely these soils contributed an initial nitrate load to groundwater which has received subsequent additions through fertilizer and manure application.
This study was limited by the availability of land for which sampling permission was obtainable and further soil sampling of more site locations is warranted to determine the chemical variability of these soils. Soils sampled tended to be in upland areas on the valley margins which have less intensive land use and more widespread public ownership. It is likely the lowlands in the study area which have intensive private land use as irrigated agriculture had a higher atmospheric contribution to soil nitrate than soils sampled prior to land use conversion due to slightly lower MAP. Future researchers should make great efforts to locate any extent soils which have not undergone flushing through irrigation to better constrain the potential nitrate flux to groundwater which occurred during land use conversion.

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CHAPTER IV

CONCLUSION

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This study found soil nitrate which represents a potential source to groundwater upon flushing during irrigation. Isotope values were broadly congruent to the isotope results for nitrate in groundwater in the EPA study,\(^1\) which concluded nitrate in groundwater samples largely has a mixed manure and fertilizer input, with manure predominating. However, a nearby Hanford site study found naturally occurring soil pore water with nitrate concentrations of up to 500 mg/L.\(^2\)

Once biota incorporate nitrate, the positive $\Delta^{17}O$ anomaly and associated atmospheric signature is removed. With increasing levels of MAP (mean annual precipitation) and a corresponding increase in biological activity, less of this atmospheric signature is retained. A recent study\(^3\) explored the relationship between MAP and the fraction of atmospheric nitrate retained, and developed an empirical relationship based on transcripts across several deserts with orographic effects. This study found regions with MAPs similar to the Lower Yakima Valley (188 mm/yr and 190.5 mm/yr) for nearby Sunnyside and Mabton, Washington respectively) have soils which only partially atmospheric $\Delta^{17}O$ values due to biological mediation.

Using the empirical equation developed\(^3\) (equation 9 in the literature review), naturally occurring soil nitrate in the Lower Yakima Valley would be expected to exhibit a $\Delta^{17}O$ value of between +2.5 and +2.35 per mill. This is similar to $\Delta^{17}O$ values observed at depth at sample sites RC2 and RC1 of +1.8 to +2.3 per mill.
We interpret our data to reflect naturally occurring soil nitrate, and commercial fertilizer as well as denitrification within the soil, and not from manure application to fields. We suggest naturally occurring soil nitrate may be a significant overlooked contributor to nitrate contaminated private drinking water wells in the EPA Lower Yakima Valley study\textsuperscript{1} in addition to nitrate from dairy manure management or fertilizer application. A potential mechanism for large quantities of nitrate to be transported into soils is millennial scale atmospheric deposition, followed by partial biologic processing.

This mechanism may work in conjunction with the formation of biological soil crusts, symbiotic communities of fungi, cyanobacteria, bryophytes, algae and lichens. Studies using micro sensors, acetylene reduction assays to measure N\textsubscript{2} fixation rates, acetylene inhibition assays to measure denitrification rates, and measurements of ammonium oxidation rates have investigated nitrogen cycling in these communities. The results have been to find that biological soil crusts fix an order of magnitude more nitrate than is denitrified, leading to a flux of nitrate to the soil surface below during percolation events. These studies were conducted in the cold deserts of the Colorado Plateau, southwest Utah, the Mohave Desert, and the Sonora Desert\textsuperscript{4-6}. Biological soil crusts have been documented to cover between 15 and 20 percent of the ground surface of the Yakima Military Training Ground to the north of the study area\textsuperscript{7,8}. Therefore it is possible that a similar process has occurred prior to agriculture in the Lower Yakima Valley.
This atmospheric deposition, incomplete nitrogen cycling by biological soil crusts, accumulation of nitrate in the subsurface, and subsequent flushing to groundwater upon land use conversion to irrigated agriculture may be a significant source of groundwater contamination in the shallow alluvial aquifers of the Lower Yakima Valley. Studies such as EPA (1) often look for elevated $\delta^{18}O_{\text{NO}_3}$ in groundwater to access if natural soil nitrates may represent a significant input to nitrate contaminated water, however this study has found nitrate in soil with the potential to impact groundwater lacking this well-known signature. Studies into nitrate contamination of groundwater in this, and other semi-arid regions, should therefore be careful to avoid assigning contamination entirely to a mixture of agricultural fertilizer and manure based purely on the absence of $\delta^{18}O_{\text{NO}_3}$ enrichment. Other studies have also found nitrate-containing soils be a significant input in an agricultural setting upon land use conversion to irrigated agriculture$^9$. Further study may be warranted to investigate the contribution of soil nitrate in groundwater contamination in the Lower Yakima Valley.

$\Delta^{17}O$ values may slightly deviate from expected (+1.8 to +2.3‰ instead of 2.3‰ to 2.5‰). due to sites being located at a higher elevation than Sunnyside, or Mabton and thus may receive slightly higher values of precipitation due to a strong orographic effect in this area, reducing observed $\Delta^{17}O$ values. Alternatively, an anthropogenic nitrate input of ~10 to 30% would produce a similar reduction in $\Delta^{17}O$ values. As IN4 and the agricultural return drains all exhibited negative $\Delta^{17}O$
values of up to -1.4‰, the use of a two end member mixing model of 0‰ for non-atmospheric nitrate and +23‰ for atmospheric nitrate may substantially underestimate the abundance of atmospheric nitrate in soils and water. It is possible atmospheric nitrate was present in these agriculturally impacted samples but had its characteristic positive $\Delta^{17}O$ anomaly obscured by mixing with nitrate sources with the observed negative values. If an endmember of -1.4‰ is used instead of 0‰, atmospheric contributions to soil nitrate in sample RC2 90 to 105 cm are as high as 15%.

Soils sampled tended to be in upland areas on the valley margins which have less intensive land use and more widespread public ownership. If the proposed flushing of natural soil nitrate to groundwater is widespread, it is likely the lowlands in the study area which have intensive use as irrigated agriculture had a higher atmospheric contribution to soil nitrate than soils sampled prior to land use conversion due to lower amounts of precipitation in this area. Future researchers should make efforts to locate the limited extent soils which have not undergone flushing through irrigation to better constrain the potential nitrate flux to groundwater which occurred during land use conversion.

Future work may then use geochemical and groundwater modeling to estimate total natural nitrate inputs of soil series upon irrigation to groundwater to better understand the significance of this potential contribution. As irrigation commenced with the implementation of widespread agriculture in this area it is
likely these soils represented an initial nitrate load to groundwater which has received subsequent additions through fertilizer and manure application. This study was limited by the availability of land for which sampling permission was obtainable and further soil sampling of more site locations is warranted to better understand the chemical variability of these soils.

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