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LETTER

Coupling the dual isotopes of water (δ2H and δ18O) and nitrate (δ15N and δ18O): a new framework for classifying current and legacy groundwater pollution

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Abstract

Nitrate contamination of groundwater is a concern globally, particularly in agricultural regions where decades of fertilizer nitrogen (N) use has led to a legacy of N accumulation in soils and groundwater. Linkages between current management practices and groundwater nitrate dynamics are often confounded by the legacy effect, and other processes unrelated to management. A coupled analysis of dual stable isotopes of water (δH2O = δ2H and δ18O) and nitrate (δNO3− = δ15N and δ18O) can be a powerful approach to identify sources and processes responsible for groundwater pollution. To assess how management practices impact groundwater nitrate, we interpreted behavior of δH2O and δNO3−, together with nitrate concentrations, in water samples collected from long-term monitoring wells in the Southern Willamette Valley (SWV), Oregon. The source(s) of nitrate and water varied among wells, suggesting that the nitrate concentration patterns were not uniform across the shallow aquifer of the valley. Analyzing the stability versus variability of a well’s corresponding δH2O and δNO3− values over time revealed the mechanisms controlling nitrate concentrations. Wells with stable δH2O and δNO3− values and nitrate concentrations were influenced by one water source with a long residence time and one nitrate source. Variable nitrate concentrations of other wells were attributed to dilution with an alternate water source, mixing of two nitrate sources, or variances in the release of legacy N from overlying soils. Denitrification was not an important process influencing well nitrate dynamics. Understanding the drivers of nitrate dynamics and interaction with legacy N is crucial for managing water quality improvement. This case study illustrates when and where such coupled stable isotope approaches might provide key insights to management on groundwater nitrate contamination issues.

1. Introduction

Chronic inputs of nitrogen (N) for agricultural production over time can lead to accumulation of surplus N in soils and groundwater. This legacy N contamination of nitrate (NO3−) to groundwater systems has far-reaching consequences for human health and the environment, including impacts to drinking water sources or to groundwater-dependent ecosystems, like wetlands, rivers, and coastal areas (Hansen et al 2017). The U.S. Environmental Protection Agency (EPA) established a maximum contaminant level (MCL) for public drinking water of 10 mg NO3−–N L−1 primarily to reduce risk of methemoglobinemia in infants (USEPA 1995). Ingestion of water with NO3− concentrations at or even below the current MCL can increase risk of cancers, birth defects, and other adverse health effects (Hinsby et al 2012, Ward et al 2018). Furthermore, the leaching of legacy NO3− to the groundwater, and its subsequent discharge to surface waters, can cause eutrophication and seasonal hypoxia (Lewis et al 2011, Davidson et al 2012, Tesoriero et al 2013, Weitzman et al 2014, McLellan et al 2015, Chen et al 2018, Van Meter et al...
2018). Thus, understanding the current and legacy drivers of NO$_3^-$ concentrations in groundwater is critical for water quality management.

Across the US, agricultural activities are the main source of N inputs to landscapes (Ruddy et al. 2006, Galloway et al. 2008, Sobota et al. 2013, Sabo et al. 2019). Nitrate concentrations in groundwater are driven by N inputs to the land, physical features impacting the flow rates of water through soils and aquifers, and redox conditions (DeSimone et al. 2014). More than 20% of shallow domestic wells in agricultural areas of the US are reported to exceed 3 mg NO$_3^-$ of N inputs are attributed to agricultural practices in the Willamette Valley (SWV) in Oregon, where 90% of groundwater used for US public water supplies are largely influenced by cropland area, precipitation, and agricultural lands with a legacy of N applications (Peñin et al. 2020). Such elevated concentrations can persist for decades in groundwater aquifers, especially beneath agricultural areas of the US are reported to exceed 3 mg NO$_3^-$ concentrations (Dieter et al. 2007, Exner et al. 2014, Dwivedi and Mohanty 2016), may lead to significant lags between management efforts and improvements to groundwater quality (Lindsey et al. 2003, Howden et al. 2010, Meals et al. 2010, Van Meter et al. 2016).

In 2015, approximately 47% of the U.S. population was estimated to rely on groundwater for domestic purposes including drinking water (Dieter et al. 2018). This percentage was much higher in Oregon, where ~70% of the state population relies at least partially on groundwater for domestic use, with close to 95% of rural populations entirely dependent on groundwater from private domestic wells (ODEQ 2017a). Over the past three decades, water samples collected from both private and public wells across the state have shown widespread groundwater NO$_3^-$ contamination (ODEQ 2017b). Specifically, an extensive groundwater survey of the southern Willamette Valley (SWV) in Oregon, where 90% of N inputs are attributed to agricultural practices (LCOG 2008), revealed that much of the shallow groundwater of the region was chronically contaminated with NO$_3^-$ at concentrations exceeding natural levels, i.e. $>3$ mg NO$_3^-$~N L$^{-1}$, indicating anthropogenic causes (Madison and Brunett 1985). Designated as a Groundwater Management Area (GWMA) in 2004, the Oregon Department of Environmental Quality (ODEQ) has since sought to control NO$_3^-$ contamination in the area by promoting best management practices (BMP’s) that reduce N inputs. However, despite 15 years of mitigation efforts 57% of wells in the SWV–GWMA exhibit increasing NO$_3^-$ concentrations (Piscitelli 2019).

Increasing trends emphasize the urgency to link management practices to variations in groundwater NO$_3^-$ concentrations. However, the legacy of past management and N accumulation have complicated these simple linkages. Given the prevalence of legacy NO$_3^-$ in agricultural areas (Van Meter et al. 2016), simply tracking changes in NO$_3^-$ concentrations over time has been inadequate to evaluate long-term effectiveness of management practices (Nestler et al. 2011, Utom et al. 2020). Rather, the addition of isotopic tools to identify sources and transformations of N in groundwater may be an effective means for classifying wells based on unique patterns (figure 1). This approach may be especially important when legacy effects confound the ability to directly link current NO$_3^-$ levels with improved agriculture.

Different sources of groundwater and nutrients have distinct isotopic compositions, and thus, the dual stable isotopes of water ($\delta$H$_2$O: $\delta^{18}$H--H$_2$O and $\delta^{18}$O--H$_2$O) and NO$_3^-$ ($\delta$NO$_3^-$: $\delta^{15}$N--NO$_3^-$ and $\delta^{18}$O--NO$_3^-$) have both been used as tools for identifying sources, inferring processes, and determining the contributions of various inputs (Sulzman 2007). Specifically, $\delta$H$_2$O values can reveal the origin of water sources to groundwater (McGuire and McDonnell 2007, Palmer et al. 2007, Brooks et al. 2012), while $\delta$NO$_3^-$ values can differentiate between source inputs of NO$_3^-$ in groundwater (e.g. Kendall et al. 2007, Xue et al. 2009, Suchy et al. 2018, Qin et al. 2019). Trends between $\delta$NO$_3^-$ values and groundwater NO$_3^-$ concentrations can also be used to ascertain N transformation processes (e.g. Mayer et al. 2002, Minet et al. 2017, Veale et al. 2019, Utom et al. 2020). However, identification of NO$_3^-$ sources and/or processing based solely on the analysis of $\delta$NO$_3^-$ can be complicated by overlapping source $\delta$NO$_3^-$ values, potential mixing of NO$_3^-$ sources, and isotopic changes from biogeochemical processes (Kendall et al. 2007, Xue et al. 2009, Zhang et al. 2018, Zhu et al. 2019). Legacy effects may also impact interpretation, as $\delta$NO$_3^-$ values in groundwater could represent a mixture of different sources and times (Hu et al. 2019). Thus, for more accurate interpretation, multiple investigative tools should be used simultaneously (Hu et al. 2019, Zhu et al. 2019, Jung et al. 2020). Combining $\delta$NO$_3^-$ with $\delta$H$_2$O to identify hydrologic parameters could provide a mechanistic approach for understanding groundwater NO$_3^-$ dynamics and help to distinguish areas vulnerable to long-term N contamination due to legacy effects.

The main objectives of this study were to assess whether coupling of dual stable isotopes of $\delta$H$_2$O and $\delta$NO$_3^-$ can resolve questions about sources and transformations of N in groundwater systems, and to develop an approach to identify some key mechanisms influencing NO$_3^-$ dynamics (figure 1 and table 1). To meet these objectives, NO$_3^-$ concentrations, as well as the dual stable isotopes of $\delta$H$_2$O and $\delta$NO$_3^-$, were measured in groundwater and domestic wells of the SWV–GWMA. We hypothesized that...
coupled isotopic indicators of $\delta H_2O$ and $\delta NO_3^-$ would act as a powerful tool for classifying wells based on N movement, potential N sources with distinct isotopic signals, and transformations of N in the groundwater, allowing for identifying wells where management practices might address contamination issues.

2. Materials and method

2.1. Study location

The Willamette Valley, Oregon, USA, is a productive agricultural area with fine textured soils originating from the Missoula floods (O’Connor et al. 2001). Characterized as having a modified maritime climate regime, the SWV–GWMA has cool, wet winters and warm, dry summers. Yearly precipitation ranges from 1020 to 1270 mm (with ~80% occurring from October to March) and mean monthly air temperatures range from 3°C–5°C in January to 17°C–20°C in August (Uhrich and Wentz 1999). Though relatively flat-lying with very low relief (figure 2), a series of gently sloping and smoother terrace and floodplain surfaces have given the landscape an undulating or rolling topography moving out from the Willamette River (Roberts 1984). The region’s mild climate and flat terrain is suited to produce orchard crops, nursery crops, blueberries, hay, and many types of grass grown for seed (Mueller-Warrant et al. 2015).

Flowing mostly northward (figures 2 and S1), groundwater generally follows the contour of the land, similar to the flow of the Willamette River (Herrera et al. 2014). Groundwater within the topmost shallow aquifer of the SWV–GWMA generally flows through the upper sediments unit, which is characterized by high permeability, high porosity, and high well yield (Conlon et al. 2005). Horizontal hydraulic conductivities range from $1.06 \times 10^{-7}$ to $8.64 \times 10^{-2}$ m s$^{-1}$, vertical hydraulic conductivities from $7.06 \times 10^{-6}$ m s$^{-1}$, and storage coefficients from $3.00 \times 10^{-3}$ to $2.00 \times 10^{-1}$. Flow tends to occur under unconfined conditions with typical water table fluctuations between 1.5 and 6 m of the surface (Conlon et al. 2005). Data from USGS indicates that >80% of groundwater used throughout the Willamette Valley, which is principally recharged by direct infiltration of valley precipitation, is pumped from the uppermost alluvial aquifer layer (consisting of sand and gravel deposits) (Hinkle 1997) and used mostly for irrigation (Conlon et al. 2005). Thus, regional water-quality monitoring has focused on the shallow groundwater (<25 m below land surface), which is likely most affected by anthropogenic activities (Hinkle 1997).

The southern part of the Willamette Valley was identified as a hot spot for N loading (Hoppe et al 2014) with $NO_3^-$ contaminated groundwater (ODEQ 2004, Kite-Powell and Harding 2006). The SWV–GMWA (figure 2), which covers ~600 km$^2$ of lowlands, was established in 2004 because of the high density of domestic and groundwater wells with elevated $NO_3^-$ concentrations. The SWV–GWMA extends from Albany south to the city of Eugene. The boundaries approximate the limits of the underlying shallow alluvial aquifer, with the Willamette River flowing south-to-north through the center of the GWMA (figure 2). Agricultural land uses cover approximately 93% of the SWV–GWMA area (LCOG 2008).  

2.2. Shallow groundwater sampling

Since 2006, shallow groundwater samples were analyzed for $NO_3^-$ concentrations, hereafter referred to as $[NO_3^-]$, by ODEQ from 16 domestic wells (installation dating from the 1970s; well depth 6–24 m) and 23 ODEQ groundwater monitoring wells (installation dating between 2003 and 2006; well depth 4–15 m) across the SWV–GWMA. Quarterly sampling for water isotopes ($\delta H_2O$, $\delta^2H–H_2O$ and $\delta^{18}O–H_2O$) in all wells began in 2012, but in 2016 sampling frequency decreased to once a year (May/June) in all but 12 wells. Analysis for $NO_3^-$ isotopes ($\delta NO_3^-$; $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) also began in 2016. We report monitoring results from 2012 to 2020 for water isotopes and 2016–2020 for $NO_3^-$ isotopes (Compton 2021). Sampling and analytical techniques are detailed in the supplementary material.
Stable N/A Legacy groundwater

Stable/Variable No apparent

Variable 

Stable/Variable 

Table 1. Well behavior categories defined in terms of [NO$_3^-$] trends, H$_2$O and NO$_3^-$ source stability over time, and correlative relationships between parameters.

| Category                  | [NO$_3^-$] Nitrate concentration | $\delta^{15}$H–H$_2$O Water source | $\delta^{15}$N–NO$_3^-$ Nitrate source | Trends | Description |
|---------------------------|----------------------------------|-------------------------------------|----------------------------------------|--------|-------------|
| Stable                    | Stable                           | Stable                              | Stable                                  | N/A    | Legacy groundwater; [NO$_3^-$] disconnected from present-day changes at the surface. |
| Dilution                  | Variable                         | Variable                            | Stable                                  | [NO$_3^-$] correlated with $\delta^{15}$H–H$_2$O, but no correlation with $\delta^{15}$N–NO$_3^-$; dual $\delta$NO$_3^-$ not variable. |
| Mixing                    | Variable                         | Variable                            | Variable                                | [NO$_3^-$] correlated with $\delta^{15}$H–H$_2$O and $\delta^{15}$N–NO$_3^-$; dual $\delta$NO$_3^-$ correlated. |
| Leaching                  | Variable                         | Stable/Variable                      | Stable                                  | [NO$_3^-$] not correlated with $\delta^{15}$H–H$_2$O or $\delta^{15}$N–NO$_3^-$; dual $\delta$NO$_3^-$ not variable. |
| Denitrification           | Variable                         | Stable                              | Variable                                | [NO$_3^-$] negatively correlated with $\delta^{15}$N–NO$_3^-$, but no correlation with $\delta^{15}$H–H$_2$O; dual $\delta$NO$_3^-$ positively correlated. |
| Multi-Process             | Variable                         | Variable                            | Variable                                | No apparent correlations. |
| Likely NO$_3^-$ source in agricultural fields (across all categories) | Stable/Variable                  | Stable/Variable                      | Stable                                  | $\delta^{15}$N–NO$_3^-$ more isotopically enriched (e.g. >10 ‰). |

2.3. Well categorization

Relationships between isotopic signatures and [NO$_3^-$] were used to categorize well behavior in terms of H$_2$O and NO$_3^-$ source stability over time, revealing patterns about N transformation and transport mechanisms across the landscape (figure 1). For each well, the variance across sampling times (one SD) in three parameters—[NO$_3^-$], $\delta^{15}$H–H$_2$O values, and $\delta^{15}$N–NO$_3^-$ values—was used as an initial assessment of parameter stability. The SDs ranged from 0.2 to 9.0 mg NO$_3^-$–N l$^{-1}$ for [NO$_3^-$], 0.3‰–4.8‰ for $\delta^{15}$H–H$_2$O values, and 0.1‰–7.0‰ for $\delta^{15}$N–NO$_3^-$ values. When the SD of a parameter was <10% of its variability range, the parameter was initially identified as stable over time, and when it was >10%, it was initially identified as variable over time. We then assessed whether variable parameters were correlated within a well to further classify the behavior (figure 1 and table 1).

3. Results

3.1. Nitrate concentrations and isotopic values

Across all wells sampled from 2012 to 2020, [NO$_3^-$] ranged from 0.0 to 41.8 mg NO$_3^-$–N l$^{-1}$, with a median of 6.1 mg NO$_3^-$–N l$^{-1}$. Values of $\delta^{15}$H–H$_2$O ranged from −81.5‰ to −50.5‰, with a median of −62.6‰, and $\delta^{18}$O–H$_2$O ranged from −11.6‰ to −6.9‰, with a median of −8.9‰. Meanwhile, $\delta^{15}$N–NO$_3^-$ and $\delta^{18}$O–NO$_3^-$ values ranged from −0.1‰ to +40.9‰, with a median of +4.5‰, and −3.2‰ to +17.4‰, with a median of +1.6‰, respectively. These ranges and median values did not differ significantly between DW and GW wells.
3.2. Classification of wells
Theoretically, specific processes such as dilution with an alternate groundwater source, mixing of two groundwater sources with differing NO$_3^-$ sources, leaching of legacy NO$_3^-$ from overlying soils, and denitrification have unique isotopic signatures in this coupled dual isotope approach (figure 1 and table 1). When the relationships between [NO$_3^-$] and δ$^{15}$N–NO$_3^-$ values, [NO$_3^-$] and δ$^2$H–H$_2$O values, and δ$^{15}$N–NO$_3^-$ and δ$^{18}$O–NO$_3^-$ were taken together, clear distinctions among sources and processing of NO$_3^-$ became apparent in most of the wells of the SWV–GWMA (figure 3). However, well category was not related to well location across the SWV–GWMA (figure 4). Of the 39 total sampled wells, [NO$_3^-$] in 28 wells varied over time. Nitrate trends in 85% of the wells (i.e. 33) could be classified based on concentration and isotopic patterns (figures 3(a)–(i)); overlapping processes in six wells, categorized as ‘multi-process’ (figures 3(j)–(l)), make classification difficult using the coupled dual isotope approach alone.

3.2.1. Stable wells
We classified 11 wells with relatively unchanging behavior in all measured parameters (figures 3(a)–(c)) as stable. The SD stability thresholds averaged 0.5 mg NO$_3^-$–N l$^{-1}$, 0.7 ‰ δ$^2$H–H$_2$O, and 0.4 ‰ δ$^{15}$N–NO$_3^-$. Each stable well occupied a unique space with distinct isotopic values and [NO$_3^-$], indicating that both H$_2$O and NO$_3^-$ sources were unique. Nitrate concentrations ranged from 0.2 to 11.2 mg NO$_3^-$–N l$^{-1}$, with four wells (DW-6, DW-10, GW-9, GW-27) having concentrations >7 mg NO$_3^-$–N l$^{-1}$ throughout the majority of the sampling period (figure 3(a)). Values of δ$^2$H–H$_2$O were used to separate water into two distinct sources: Willamette River water (range: −81.1‰ to −73.5‰) and valley precipitation (range: −67.4‰ to −59.0‰) collected from Corvallis, OR (supplementary material). Water in most stable wells was similar to valley precipitation, with δ$^2$H–H$_2$O values spanning the entire range of precipitation values (figure 3(b)). One well (DW-3), however, had more depleted isotopic values indicating mixing with Willamette River water (figure 3(b)).

Nitrate derived from fertilizers, soil organic matter, and animal manure/septic waste tend to have overlapping δ$^{18}$O–NO$_3^-$ values, in the range of...
3.2.2. Dilution and mixing wells

Wells where $[\text{NO}_3^-]$ varied with shifting water sources (correlated with $\delta^{2}H$–$\text{H}_2\text{O}$) but which had a stable $\text{NO}_3^-$ source (stable $\delta\text{NO}_3^-$) were classified as diluting wells (table 1). Variable $[\text{NO}_3^-]$ in eight wells were positively correlated with $\delta^{2}H$–$\text{H}_2\text{O}$ values (figure 3(e)) and had stable $\delta\text{NO}_3^-$ values. In these wells, $[\text{NO}_3^-]$ ranged from 0.3 to 29.5 mg $\text{NO}_3^-$–$\text{N}$ $\text{l}^{-1}$. The highest $[\text{NO}_3^-]$ were found within the valley precipitation $\delta^{2}H$–$\text{H}_2\text{O}$ range, and $[\text{NO}_3^-]$ decreased as $\delta^{2}H$–$\text{H}_2\text{O}$ values decreased from dilution by Willamette River water (figure 3(e)). Synthetic fertilizer was likely the main $\text{NO}_3^-$ source to these wells ($\delta^{15}N$–$\text{NO}_3^-$ range: $+1.6$ to $+6.7$‰, $\delta^{18}O$–$\text{NO}_3^-$ range: $-2.2$ to $+9.7$‰, figure 3(f)).

The four other wells where $[\text{NO}_3^-]$ increased with $\delta^{2}H$–$\text{H}_2\text{O}$ (figure 3(e)) had variable $\delta^{15}N$–$\text{NO}_3^-$ values that were correlated with $\text{NO}_3^-$ levels...
J N Weitzman

were values (range: $\delta^3$H–H$_2$O signatures from overlying soils, leading to the values ranged from 0.1 to 40.9‰. Negative correlations between $[\text{NO}_3^-]$ and $\delta^{15}$N–$\text{NO}_3^-$ in tandem with positive correlations between the dual $\delta$NO$_3^-$ isotopes would seem to suggest denitrification processes are at play in wells DW-1524, GW-4S, GW-7, GW-18, and seasonally in GW-10 (table 1, figures 3(j) and (l)). However, the variability in $\delta^2$H–H$_2$O and $\delta^{15}$N–$\text{NO}_3^-$ values for the wells suggests that the influence of multiple sources cannot be ruled out. Thus, denitrification was not a dominant transformation pathway in any of the six wells (or in any of the wells throughout the SWV–GWMA).

While we cannot distinguish the primary influences accounting for the variable $[\text{NO}_3^-]$ within the multi-process wells, (i.e. whether multiple N transformation processes are occurring simultaneously, or mixing of water sources, and NO$_3^-$ sources, or both), synthetic fertilizers and manure/septic sources appear to be the main contributors (figure 3(l)).

4. Discussion

Given that NO$_3^-$ is highly mobile and primarily originates from non-point sources, tracking its origins can be difficult. However, by analyzing $\delta^2$H–H$_2$O and $\delta$NO$_3^-$ in tandem we were able to identify multiple mechanisms and sources controlling groundwater $[\text{NO}_3^-]$. We created a new framework for categorizing groundwater behavior (figure 1 and table 1), revealing insights into groundwater-contaminant interactions and helped identify where to target appropriate land management practices (Hansen et al. 2017) to reduce groundwater $[\text{NO}_3^-]$. While the overlap in isotopic values for multiple sources and the influence of isotopic fractionation pose limits, applying the coupled dual isotope approach at other locations could lead to more mechanistic understanding of the movement of water and contaminants within the groundwater. Experimenting with different management techniques in areas where groundwater $[\text{NO}_3^-]$ are known to be linked to contemporary land management practices could allow for unambiguous assessments of BMP’s, eliminating the confounding effects of legacy lag-times (Meals et al. 2010, Van Meter et al. 2016).
4.1. Application of approach at SWV-GWMA

The variance in $[\text{NO}_3^-]$ and values of the coupled dual isotopic indicators of $\delta^{2}H_2O$ and $\delta^{15}N$ across space and time within the wells of the SWV–GWMA revealed the complex nature of groundwater $\text{NO}_3^-$ transport throughout the relatively uniform shallow aquifer. We classified well behavior at this test site into five categories, with the percentage of wells in each category, from greatest to least, as follows: 28% stable, 26% leaching, 21% dilution, 15% multi-process, and 10% mixing. These results suggest that managing groundwater $[\text{NO}_3^-]$ in the region will require integration of different approaches, such as controlling $\text{NO}_3^-$ sources and/or enhancing $\text{NO}_3^-$ sinks across the landscape (Stigter et al. 2011).

Synthetic fertilizers (69%), manure/septic sources (5%), or a mixture of the two (26%) were found to be the main sources of $\text{NO}_3^-$ to the SWV–GWMA groundwater. These results align with a surface water modeling study based on conditions in the Willamette River Basin in 2002 that found agricultural fertilizer (27.2%) and animal manure (10.9%) were the largest contributors to incremental $N$ stream loads (Wise and Johnson 2011). Similarly, Compton et al. (2020) showed that agricultural activities accounted for 78% of the annual total $N$ inputs to the entire Willamette River Basin for the years 2002–2006, with 69% of total inputs attributed to synthetic fertilizers and 7% to manure waste from permitted confined animal feeding operations (CAFOs) used as fertilizer. These numbers closely match those within the boundaries of the SWV–GWMA where agricultural crop activities contribute 90% of $N$ inputs and CAFOs contribute 6% (LCOG 2013). Most of the nursery crops and grass seed of the region require significant inputs of synthetic $N$ fertilizers (100–250 kg N ha$^{-1}$ year$^{-1}$) (Compton et al. 2020) where a substantial amount can leach from the rooting zone into streams or the groundwater, especially when temporal asynchrony occurs between fertilizer application, crop $N$ uptake, and hydrologic movement (Lin et al. 2019).

Eight permitted CAFOs within the SWV–GWMA make up ~2% of the land, and together contribute ~6% of the total $N$ inputs (LCOG 2008). The three largest operations account for ~94% of the total CAFO $N$ contributions and are closest to wells DW-10, GW-3, and GW-12. Average $\delta^{15}N$–$\text{NO}_3^-$ values for these nearby wells are 8.8‰, 6.5‰, and 4.6‰, respectively. Typical values for manure waste tend to have $\delta^{15}N$–$\text{NO}_3^-$ values $\geq 10$‰ (Kendall et al. 2007), suggesting that a well’s distance from a currently-permitted CAFO may not be the best parameter for revealing the true influence of animal agriculture on groundwater $[\text{NO}_3^-]$ in the region. The manure source signatures seen in two wells (DW-5 and GW-8) of the SWV-GWMA that are not close to any currently-permitted CAFOs could be due to the direct application of manure as a crop fertilizer to the surrounding agricultural fields, the legacy impact of past animal agriculture in the area, or the flow path and direction of groundwater.

Water isotopes were useful in elucidating the contributions of varying water sources and hydrological processes to the SWV–GWMA groundwater. Local valley precipitation was the main water source to the groundwater in 64% of the wells across the region, with evidence of Willamette River hyporheic water mixing with valley groundwater (Kendall and Caldwell 1998) in the remaining 34% of wells, which diluted $[\text{NO}_3^-]$ (figure S2). This method worked well because the two sources were isotopically unique; however, the $\delta^{2}H$–$H_2O$ values of groundwater in each stable well were also isotopically distinct within the precipitation range (figure 3(b)). These slight isotopic differences suggest that the shallow aquifer of the SWV–GWMA consists of highly compartmentalized groundwater pools that have limited lateral connectivity (Joshi et al. 2018), likely due to the heterogeneity of the alluvial aquifer material. The slight but consistent isotopic differences also indicate that water isotopes could be a powerful tool even in locations without a broad range of isotopically distinct water sources.

4.2. Management implications for wells

Stable wells, i.e. those with relatively unchanging $[\text{NO}_3^-]$ and $\delta^{2}H_2O$ and $\delta^{15}N$–$\text{NO}_3^-$ values (figures 3(a)–(c)), are unlikely to be immediately impacted by any new management modifications at the land surface. The stability of $\delta^{2}H$–$H_2O$ values suggests one slow-moving groundwater source to each stable well with long residence time (Broxton et al. 2009, Thomas et al. 2013). Given this, the stable $\delta^{15}N$–$\text{NO}_3^-$ values, which indicate fertilizer- or manure/septic-derived $\text{NO}_3^-$ sources, are likely signatures from past $N$ inputs. While the $[\text{NO}_3^-]$ in stable wells appear to be disconnected from current surface inputs, the relatively low concentrations found in some wells (e.g. DW-9, GW-8, GW-15) suggest that land around them may be less susceptible to leaching of $\text{NO}_3^-$ into the groundwater, or inputs of $N$ in the past were more efficiently managed. The higher groundwater $[\text{NO}_3^-]$ of other stable wells (e.g. DW-10, GW-9, GW-27), however, could signify a long-term legacy of contaminated groundwater, which immediate land management changes could not resolve readily.

We found $[\text{NO}_3^-]$ variation was driven by dilution of an alternate groundwater source (Ogrinc et al. 2019), the mixing of two $\text{NO}_3^-$ sources (Kendall et al. 2007), or the leaching of present-day (Minet et al. 2017) or legacy N (Hu et al. 2019) from overlying soils. The variable $\delta^{2}H$–$H_2O$ values in leaching wells suggest that groundwater within them has a short residence time (Broxton et al. 2009, Thomas et al. 2013), and thus the impact of surface management changes on groundwater $[\text{NO}_3^-]$ could potentially be
assessed over relatively short timeframes. The residence time of groundwater in the dilution and mixing wells, however, is not as discernable. The source of high \([\text{NO}_3^-]\) could be from a stable groundwater pool with a long residence time, suggesting once again that legacy sources could be responsible for the contamination. Concentrations only decrease on the short-term when the contaminated water is influenced by another water supply (like the Willamette River) or another \(\text{NO}_3^-\) source (figure S2). These wells could thus have long-term \([\text{NO}_3^-]\) contamination problems that are not addressed as quickly because evidence of other events (i.e. dilution by ‘cleaner’ river water or mixing with a lower concentration \(\text{NO}_3^-\) source; figure S2) appear to diminish the issue.

The high \([\text{NO}_3^-]\) of the valley groundwater could be due to high N input levels, low plant uptake, re-application of high \([\text{NO}_3^-]\) irrigation water, or N-leaching legacy effects. Reducing new fertilizer inputs (Chen et al. 2018), optimizing uptake of legacy nutrients (Hu et al. 2019), or incorporating perennial vegetation or cover crops to more efficiently sequester excess \(\text{NO}_3^-\) (Brandi-Dohrn et al. 1997, Feaga et al. 2010, Van Meter et al. 2017) could all help in reducing the groundwater \(\text{NO}_3^-\) pool. These changes, however, are not likely to show a short-term effect on N loading in wells impacted by nutrient legacies due to the documented N-leaching lag effect (Hamilton 2012, Van Meter et al. 2018). Wells characterized as leaching with high variability in \(\delta^2\text{H–H}_2\text{O}\) and \([\text{NO}_3^-]\) are the most likely to see short-term effects from management.

Denitrification was not found to be a dominant process in any of the wells of the SWV–GWMA. While many have found high denitrification in groundwater (Böttcher et al. 1990, Tesoriero et al. 2013, Minet et al. 2017), others found it to be insignificant (Howard 1985, Wassenaar et al. 2006, Jia et al. 2020). In shallow, and even deep, aquifer systems, anaerobic conditions known to promote high levels of denitrification may be elusive (Hamilton and Helsel 1995, Lorite-Herrera and Jiménez-Espinoza 2008). The absence of an adequate carbon source can also limit denitrification in soils and groundwater (Hiscock et al. 1991, Rivett et al. 2008, Weitzman et al. 2014). Thus, the conditions necessary for denitrification were likely lacking across the SWV–GWMA. However, strategies that slow the movement of water through the soil profile or supplement low-organic soils with organic-rich carbon sources could increase denitrification.

5. Conclusions

Using the coupled dual isotope approach, we built a framework for classifying different processes responsible for groundwater \([\text{NO}_3^-]\) dynamics and confirmed the prevalence of legacy \(\text{NO}_3^-\) as a main contributor to groundwater contamination in an agricultural setting. Including \(\delta\text{H}_2\text{O}\) and \(\delta\text{NO}_3^-\) analyses with standard \([\text{NO}_3^-]\) data could enable land managers to more effectively evaluate groundwater BMP’s. The value of different improved N management strategies, such as the optimization of fertilizer use (rate, timing, location, and form), irrigation management, soil and tissue testing, cover crop adoption, and soil health promotion (Feaga et al. 2004), may vary depending on the underlying behavior of the groundwater. Future work to elucidate fate and transport of groundwater N may benefit from the coupling of \(\delta\text{H}_2\text{O}, \delta\text{NO}_3^-\), and another discriminate isotope (e.g. boron, strontium, sulfate) or chemical tracers to further elucidate \(\text{NO}_3^-\) sources or processes.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.23719/1519089.

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