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Coupling the dual isotopes of water (δ^2H and δ^{18}O) and nitrate (δ^{15}N and δ^{18}O): 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 ($\delta H_2O = \delta^2H$ and $\delta^{18}O$) and nitrate ($\delta NO_3{}^- = \delta^{15}N$ and $\delta^{18}O$) 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 δH_2O and $\delta NO_3{}^-$, 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 δH_2O and $\delta NO_3{}^-$ values over time revealed the mechanisms controlling nitrate concentrations. Wells with stable δH_2O and $\delta NO_3{}^-$ 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 ($NO_3{}^-$) 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 $NO_3{}^-$–N l^{-1} primarily to reduce risk of methemoglobinemia in infants (USEPA 1995). Ingestion of water with $NO_3{}^-$ 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 $NO_3{}^-$ 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 the MCL (Dubrovsky *et al* 2010, DeSimone *et al* 2014). In addition, drinking water NO_3^- violations in groundwater used for US public water supplies are largely influenced by cropland area, precipitation, and annual N surplus in the source area (Pennino *et al* 2020). Such elevated concentrations can persist for decades in groundwater aquifers, especially beneath agricultural lands with a legacy of N applications (Repert *et al* 2006, Puckett *et al* 2010, Katz *et al* 2014). Even if new N inputs cease, the release of diffuse sources of N, coupled with slow natural attenuation of groundwater NO_3^- in shallow aquifers (Mastrocicco *et al* 2010, 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 aboveground agricultural practices (Meals *et al* 2010, Hamilton 2012).

Different sources of groundwater and nutrients have distinct isotopic compositions, and thus, the dual stable isotopes of water (δH_2O: $\delta^2H–H_2O$ and $\delta^{18}O–H_2O$) and NO_3^- (δNO_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, δH_2O values can reveal the origin of water sources to groundwater (McGuire and McDonnell 2007, Palmer *et al* 2007, Brooks *et al* 2012), while δNO_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 δNO_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 δNO_3^- can be complicated by overlapping source δNO_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 δNO_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 δNO_3^- with δH_2O 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 δH_2O and δNO_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 δH_2O and δNO_3^-, were measured in groundwater and domestic wells of the SWV–GWMA. We hypothesized that

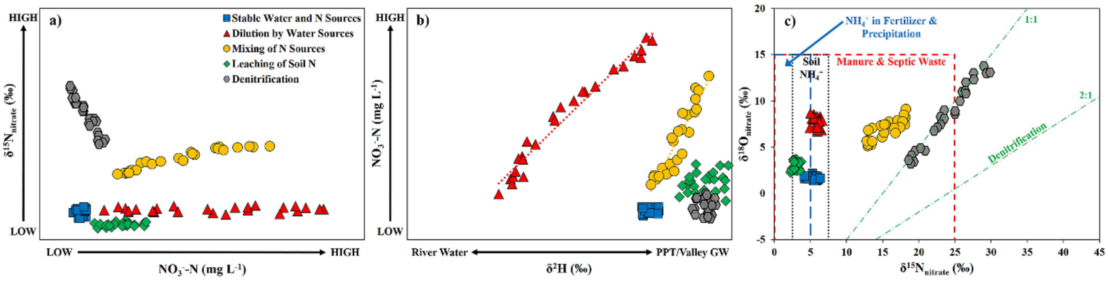

Figure 1. Conceptual figure depicting expected groundwater parameter relationships of different well behavior categories. Plots consist of: (a) [NO_3^-] vs $\delta^{15}N$–NO_3^-; (b) δ^2H–H_2O vs [NO_3^-]; and, (c) dual isotopes of δNO_3^- (i.e. $\delta^{15}N$–NO_3^- vs $\delta^{18}O$–NO_3^-). Colored dashed lines in (c) represent approximated isotopic ranges for common agricultural NO_3^- sources and denitrification processes (adapted from Kendall *et al* 2007. John Wiley & Sons. Copyright © 2007 Blackwell Publishing Ltd.). Colored symbols across plots (a)–(c) distinguish between well behavior categories as follows: blue squares = stable; red triangles = dilution; yellow circles = mixing; green diamonds = leaching; and, gray hexagons = denitrification.

coupled isotopic indicators of δH_2O and δNO_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% occuring 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 sedimentary unit, which is characterized by high permeability, high porosity, and high well yield (Conlon *et al* 2005). Horizontal hydraulic conductivities range from 1.06×10^{-7} to 8.64×10^{-2} m s^{-1}, vertical hydraulic conductivities from 7.06×10^{-6} m s^{-1}, and storage coefficients from 3.00×10^{-3} to 2.00×10^{-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 (δH_2O: δ^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 (δNO_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.

Table 1. Well behavior categories defined in terms of $[\mathrm{NO_3}^-]$ trends, H_2O and $\mathrm{NO_3}^-$ source stability over time, and correlative relationships between parameters.

Category	$[\mathrm{NO_3}^-]$ Nitrate concentration	δ^2H–H_2O Water source	δ^{15}N–$\mathrm{NO_3}^-$ Nitrate source	Trends	Description
Stable	Stable	Stable	Stable	N/A	Legacy groundwater N; $[\mathrm{NO_3}^-]$ disconnected from present-day changes at the surface.
Dilution	Variable	Variable	Stable	$[\mathrm{NO_3}^-]$ correlated with δ^2H–H_2O, but no correlation with δ^{15}N–$\mathrm{NO_3}^-$; dual $\delta\mathrm{NO_3}^-$ not variable.	Dilution of a high $[\mathrm{NO_3}^-]$ water source with another low $[\mathrm{NO_3}^-]$ water source.
Mixing	Variable	Variable	Variable	$[\mathrm{NO_3}^-]$ correlated with δ^2H–H_2O and δ^{15}N–$\mathrm{NO_3}^-$; dual $\delta\mathrm{NO_3}^-$ correlated.	Mixing of $\mathrm{NO_3}^-$ sources, each with distinct $[\mathrm{NO_3}^-]$, δ^2H–H_2O, and $\delta\mathrm{NO_3}^-$ isotopic signatures.
Leaching	Variable	Stable/Variable	Stable	$[\mathrm{NO_3}^-]$ not correlated with δ^2H–H_2O or δ^{15}N–$\mathrm{NO_3}^-$; dual $\delta\mathrm{NO_3}^-$ not variable.	Release of stored soil $\mathrm{NO_3}^-$; potential identifier of legacy effects (seasonally variable),
Denitrification	Variable	Stable	Variable	$[\mathrm{NO_3}^-]$ negatively correlated with δ^{15}N–$\mathrm{NO_3}^-$, but no correlation with δ^2H–H_2O; dual $\delta\mathrm{NO_3}^-$ positively correlated.	Decreasing $[\mathrm{NO_3}^-]$ due to transformation of $\mathrm{NO_3}^-$ to N_2O or N_2 via denitrification.
Multi-Process	Variable	Variable	Variable	No apparent correlations.	Unknown, multiple processes.
Likely $\mathrm{NO_3}^-$ source in agricultural fields (across all categories)	Stable/Variable	Stable/Variable	Stable	δ^{15}N–$\mathrm{NO_3}^-$ more isotopically enriched (e.g. >10 ‰).	Manure/septic waste as $\mathrm{NO_3}^-$ source.
	Stable/Variable	Stable/Variable	Stable	δ^{15}N–$\mathrm{NO_3}^-$ more isotopically depleted (e.g. <10‰).	Synthetic Fertilizer as $\mathrm{NO_3}^-$ source.

2.3. Well categorization

Relationships between isotopic signatures and $[\mathrm{NO_3}^-]$ were used to categorize well behavior in terms of H_2O and $\mathrm{NO_3}^-$ 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—$[\mathrm{NO_3}^-]$, δ^2H–H_2O values, and δ^{15}N–$\mathrm{NO_3}^-$ values—was used as an initial assessment of parameter stability. The SDs ranged from 0.2 to 9.0 mg $\mathrm{NO_3}^-$–N l^{-1} for $[\mathrm{NO_3}^-]$, 0.3‰–4.8‰ for δ^2H–H_2O values, and 0.1‰–7.0‰ for δ^{15}N–$\mathrm{NO_3}^-$ 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, $[\mathrm{NO_3}^-]$ ranged from 0.0 to 41.8 mg $\mathrm{NO_3}^-$–N l^{-1}, with a median of 6.1 mg $\mathrm{NO_3}^-$–N l^{-1}. Values of δ^2H–H_2O ranged from −81.5‰ to −50.5‰, with a median of −62.6‰, and δ^{18}O–H_2O ranged from −11.6‰ to −6.9‰, with a median of −8.9‰. Meanwhile, δ^{15}N–$\mathrm{NO_3}^-$ and δ^{18}O–$\mathrm{NO_3}^-$ 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.

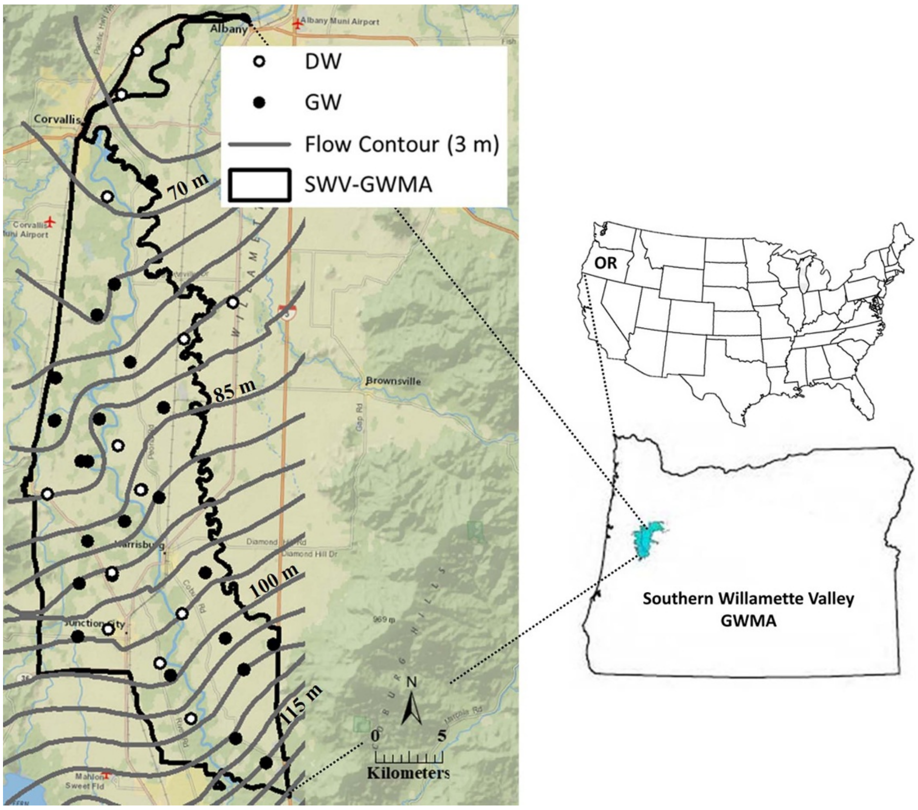

Figure 2. Southern Willamette Valley Ground Water Management Area (SWV–GWMA) in western Oregon, USA. The symbols depict sampled well locations with white circles representing domestic wells (DW) and black circles representing groundwater wells (GW). Gray lines represent interpolated groundwater elevation contours above sea level at 3 m intervals for Spring 2017 (which is representative of most seasons and years (figure S1 (available online at stacks.iop.org/ERL/16/045008/mmedia))). (See supplementary material for groundwater contour kriging methods.)

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^2H–H_2O 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^2H–H_2O, 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_2O 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^2H–H_2O 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 (Figure 3(a)). Values of δ^2H–H_2O 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^2H–H_2O 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

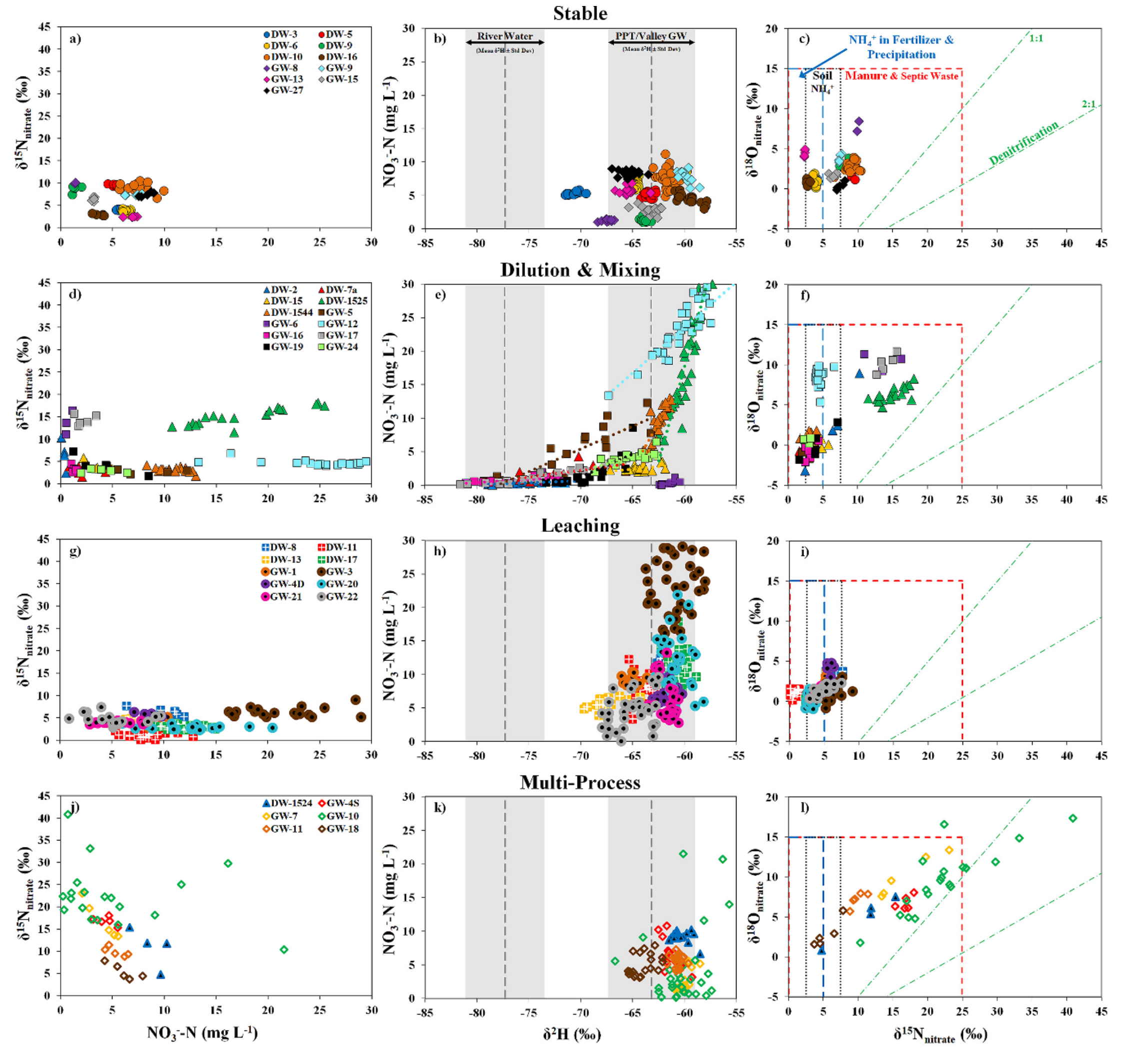

Figure 3. Plots of specific parameter relationships (down columns) used for well behavior classification (across rows). Categories were determined via: (a), (d), (g) and (j) plots of [NO_3^-] vs $\delta^{15}N$–NO_3^-; (b), (e), (h) and (k) plots of δ^2H–H_2O vs [NO_3^-]; and (c), (f), (i) and (l) dual isotope plots of δNO_3^- (i.e. $\delta^{15}N$–NO_3^- vs $\delta^{18}O$–NO_3^-). Gray boxes in the plots of the second column represent the long-term ranges in δ^2H–H_2O values for the Willamette River and Corvallis precipitation, with dashed lines representing long-term averages and boxes extending ± SD (supplementary material). Colored dashed lines in the plots of the third column represent approximated isotopic ranges for common agricultural NO_3^- sources and denitrification processes (adapted from Kendall *et al* 2007. John Wiley & Sons. Copyright © 2007 Blackwell Publishing Ltd.). Across each row wells with similar behavior patterns were grouped together into the following categories: (a)–(c) stable; (d)–(f) dilution and mixing; (g)–(i) leaching; or, (j)–(l) multi-process.

−15‰ to +15‰ (Kendall *et al* 2007). Values of $\delta^{18}O$–NO_3^- in the 11 stable wells fell near the center of this range, extending from +0.2‰ to +8.5‰ (figure 3(c)). However, $\delta^{15}N$–NO_3^- values tend to be more distinct, allowing for better discernment among these sources. Most synthetic fertilizers have $\delta^{15}N$–NO_3^- values in the range of −4‰ to +4‰, with some measured in the range of −8‰ to +7‰, while manure/septic waste tends to be more enriched in $\delta^{15}N$–NO_3^-, with typical values that range from +10‰ to +20‰ (Kendall *et al* 2007). Values of $\delta^{15}N$–NO_3^- in the stable wells ranged from 2.3‰ to 10.2 ‰ (figure 3(c)). Together, the dual isotopes of δNO_3^- showed that synthetic fertilizer was the dominant agricultural NO_3^- source contributing to groundwater NO_3^- in the stable wells, with wells DW-5 and GW-8 potentially influenced by manure/septic waste sources (figure 3(c)).

3.2.2. *Dilution and mixing wells*

Wells where [NO_3^-] varied with shifting water sources (correlated with δ^2H–H_2O) but which had a stable NO_3^- source (stable δNO_3^-) were classified as diluting wells (table 1). Variable [NO_3^-] in eight wells were positively correlated with δ^2H–H_2O values (figure 3(e)) and had stable δNO_3^- values. In these wells, [NO_3^-] ranged from 0.3 to 29.5 mg NO_3^-–N l^{-1}. The highest [NO_3^-] were found within the valley precipitation δ^2H–H_2O range, and [NO_3^-] decreased as δ^2H–H_2O values decreased from dilution by Willamette River water (figure 3(e)). Synthetic fertilizer was likely the main NO_3^- source to these wells ($\delta^{15}N$–NO_3^- range: +1.6 to +6.7 ‰, $\delta^{18}O$–NO_3^- range: −2.2 to +9.7 ‰, figure 3(f)).

The four other wells where [NO_3^-] increased with δ^2H–H_2O (figure 3(e)) had variable $\delta^{15}N$–NO_3^- values that were correlated with NO_3^- levels

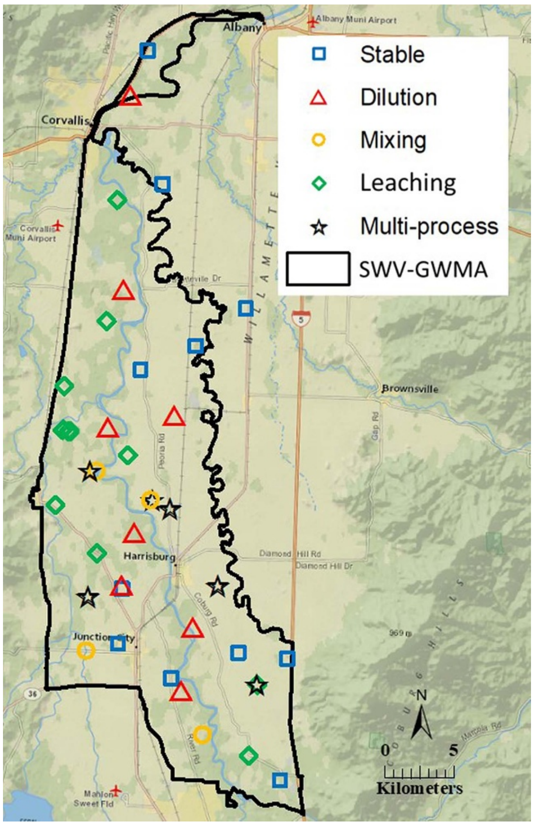

Figure 4. Map of sampled well locations within the Southern Willamette Valley Ground Water Management Area (SWV–GWMA). The colored symbols represent the behavior category to which each specific well was assigned, as follows (with the number of wells within each category listed in parentheses): blue squares = stable (11), red triangles = dilution (8), yellow circles = mixing (4), green diamonds = leaching (10), and black stars = multi-process (6).

(figure 3(d)), and dual δNO_3^- were correlated, too (figure 3(f)). These wells were classified as mixing of two nitrate sources with distinct $[NO_3^-]$ and δNO_3^- and δ^2H–H_2O signatures (table 1). While the groundwater composition of the wells was clearly impacted by a combination of NO_3^- sources, such as fertilizer sources, crop residues, and soil mineralization, our data precludes us from ascertaining the specific sources that mixed.

3.2.3. Leaching wells

In ~25% of wells (i.e. ten wells), changes in $[NO_3^-]$ that ranged from 0.0 to 29.1 mg NO_3^-–N l^{-1} were classified as leaching of soil NO_3^-. The groundwater NO_3^- in these wells lacked any correlation with δ^2H–H_2O values (range: −69.7 to −58.0 ‰), or $\delta^{15}N$–NO_3^- values (range: −0.1 to 9.0‰) (figures 3(g)–(i)). Values of δ^2H–H_2O indicated valley precipitation, (figure 3(h)) and δ^2H–H_2O variability within a well provided evidence of some seasonal precipitation variability. Values of $\delta^{15}N$–NO_3^- were largely stable, and when combined with the $\delta^{18}O$–NO_3^- values (range: −0.9 to 4.8‰), revealed synthetic fertilizer to be the main NO_3^- source to the wells (figure 3(i)). Seasonal precipitation and/or irrigation events are likely responsible for the release of fertilizer NO_3^- from overlying soils, leading to the leaching of excess NO_3^- into the groundwater.

3.2.4. Multi-process wells

For the six remaining wells, the $[NO_3^-]$ and isotopic patterns did not indicate one dominant process as being responsible for the NO_3^- trends, so they were given the categorization of multi-process (figures 3(j)–(l)). Concentrations of NO_3^- in these wells ranged from 0.1 to 21.5 mg NO_3^-–N l^{-1}, while δ^2H–H_2O values ranged from −66.7 to −55.7‰ and $\delta^{15}N$–NO_3^- values ranged from 0.1 to 40.9‰. Negative correlations between $[NO_3^-]$ and $\delta^{15}N$–NO_3^- in tandem with positive correlations between the dual δNO_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 δ^2H–H_2O and $\delta^{15}N$–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 $[NO_3^-]$ 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 δH_2O and δNO_3^- in tandem we were able to identify multiple mechanisms and sources controlling groundwater $[NO_3^-]$. 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 $[NO_3^-]$. 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 $[NO_3^-]$ 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 [NO_3^-] and values of the coupled dual isotopic indicators of δH_2O and δNO_3^- across space and time within the wells of the SWV–GWMA revealed the complex nature of groundwater 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 [NO_3^-] in the region will require integration of different approaches, such as controlling NO_3^- sources and/or enhancing 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 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 2008). Most of the nursery crops and grass seed of the region require significant inputs of synthetic N fertilizers (100–250 kg N ha^{-1} y^{-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 $\delta^{15}N–NO_3^-$ values for these nearby wells are 8.8‰, 6.5‰, and 4.6‰, respectively. Typical values for manure waste tend to have $\delta^{15}N–NO_3^-$ values $\geqslant$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 [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 [NO_3^-] (figure S2). This method worked well because the two sources were isotopically unique; however, the $\delta^2H–H_2O$ 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 [NO_3^-] and $\delta^2H–H_2O$ and $\delta^{15}N–NO_3^-$ values (figures 3(a)–(c)), are unlikely to be immediately impacted by any new management modifications at the land surface. The stability of $\delta^2H–H_2O$ 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 $\delta^{15}N–NO_3^-$ values, which indicate fertilizer- or manure/septic-derived NO_3^- sources, are likely signatures from past N inputs. While the [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 NO_3^- into the groundwater, or inputs of N in the past were more efficiently managed. The higher groundwater [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 [NO_3^-] variation was driven by dilution of an alternate groundwater source (Ogrinc *et al* 2019), the mixing of two 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 $\delta^2H–H_2O$ 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 [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 [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 NO_3^- source (figure S2). These wells could thus have long-term [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 NO_3^- source; figure S2) appear to diminish the issue.

The high [NO_3^-] of the valley groundwater could be due to high N input levels, low plant N uptake, re-application of high [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 NO_3^- (Brandi-Dohrn *et al* 1997, Feaga *et al* 2010, Van Meter *et al* 2017) could all help in reducing the groundwater 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 δ^2H–H_2O and [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-Espinosa 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 [NO_3^-] dynamics and confirmed the prevalence of legacy NO_3^- as a main contributor to groundwater contamination in an agricultural setting. Including δH_2O and δNO_3^- analyses with standard [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 δH_2O, δNO_3^-, and another discriminate isotope (e.g. boron, strontium, sulfate) or chemical tracers to further elucidate 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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