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Vadose zone flushing of fertilizer tracked by isotopes of water and nitrate

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Abstract

A substantial fraction of nitrogen (N) fertilizer applied in agricultural systems is not incorporated into crops and moves below the rooting zone as nitrate (NO_3^-). Understanding mechanisms for soil N retention below the rooting zone and leaching to groundwater is essential for our ability to track the fate of added N. We used dual stable isotopes of nitrate ($\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) and water ($\delta^{18}O–H_2O$ and $\delta^2H–H_2O$) to understand the mechanisms driving nitrate leaching at three depths (0.8, 1.5, and 3.0 m) of an irrigated corn field sampled every 2 weeks from 2016 to 2020 in the southern Willamette Valley, Oregon, USA. Distinct periods of high nitrate concentrations with lower $\delta^{15}N–NO_3^-$ values indicated that a portion of that nitrate was from recent fertilizer applications. We used a mixing model to quantify nitrate fluxes associated with recently added fertilizer N versus older, legacy soil N during these "fertilizer signal periods." Nitrate leached below 3.0 m in these periods made up a larger proportion of the total N leached at that depth (~52%) versus the two shallower depths (~13%–16%), indicating preferential movement of recently applied fertilizer N through the deep soil into groundwater. Further, N associated with recent fertilizer additions leached more easily when compared to remobilized legacy N. A high volume of fall and winter precipitation may push residual fertilizer N to depth, potentially posing a larger threat to groundwater than legacy N. Optimizing fertilizer N additions could minimize fertilizer losses and reduce nitrate leaching to groundwater.

1 | INTRODUCTION

Nitrogen (N) fertilizer is important for agricultural yield, yet a substantial fraction of applied N is not incorporated into the crop, increasing its potential to move below the rooting zone and into groundwater systems as nitrate (NO_3^-). Groundwater nitrate concentrations tend to be highest in aquifers

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Abbreviations: d-excess, deuterium excess; NO_3^-, nitrate; QC, quality control; $\delta^{15}N–NO_3^-$, stable nitrogen isotope ratio ($^{15}N/^{14}N$) in nitrate; $\delta^{18}O–H_2O$, stable oxygen isotope ratio ($^{18}O/^{16}O$) in water; $\delta^{18}O–NO_3^-$, stable oxygen isotope ratio ($^{18}O/^{16}O$) in nitrate; $\delta^2H–H_2O$, stable hydrogen isotope ratio ($^2H/^1H$) in water.

underlying agricultural areas across the United States (Burow et al., 2010). Residents in these rural areas often rely on private domestic wells as sources for drinking water (Johnson et al., 2019). Within agricultural regions, >20% of these domestic wells are known to exceed the federal maximum contaminant level (MCL; 10 mg NO_3^-–N·L^{-1}) for public drinking water (DeSimone et al., 2014; Dubrovsky et al., 2010; Pennino et al., 2020). Many adverse health effects, including increased risk of cancers and birth defects, have been linked to the consumption of drinking water at or above the MCL (Hinsby et al., 2012; Ward et al., 2018). The loss of excess N as nitrate into waterways is also known to detrimentally impact the environment, with nutrient imbalances leading to eutrophication, seasonal hypoxia, and other ecosystem functioning impairments (Ascott et al., 2021; Chen, Shen, et al., 2018; Hamilton, 2012; Tesoriero et al., 2013; Weitzman et al., 2014).

The application of N fertilizer via agricultural activities is the largest contributor to total N inputs to landscapes in the United States and accounted for 33% of such inputs in 2012 (Sabo et al., 2019). In many regions across the globe, N fertilizer not removed by crops has been accumulating within vadose zone soils over the past several decades (Ascott et al., 2016, 2017; Tesoriero et al., 2013; Van Meter et al., 2016, 2018; Xin et al., 2019). This accumulation of surplus N over time in agricultural soils, classified as legacy N, has created a pool of N that can leach into the groundwater out of sync with current N fertilizer applications (Basu et al., 2022; Compton et al., 2021; Onsoy et al., 2005; Rosenstock et al., 2014) and has the potential to act as a long-term source of elevated nitrate concentrations to groundwater and streams (Exner et al., 2014; Howden et al., 2011; Johnson & Stets, 2020; Metson et al., 2020; Puckett et al., 2011). The movement and transformation of N through the vadose zone are controlled by hydrological factors, like the timing and magnitude of precipitation and/or irrigation, and hydrogeological features that control water flow rates and water residence time, and in turn redox conditions (DeSimone et al., 2014; Green et al., 2008; Hansen et al., 2017; Quemada et al., 2013; Rivett et al., 2008). The dynamics of legacy N accumulation within agricultural systems have complicated our ability to accurately predict the fate of newly added N, as groundwater nitrate is not decreasing despite increased implementation of land management improvements (Howden et al., 2010; Kim et al., 2020; Lindsey et al., 2003; McDowell et al., 2021; Meals et al., 2010; Van Meter et al., 2016).

The agriculturally productive Willamette Valley, Oregon, USA, is an example where groundwater nitrate contamination is widespread (DeSimone et al., 2014; Hoppe et al., 2011; ODEQ, 2017). New inputs of N have been increasing over the last 80 years in the region, with N fertilizers most recently accounting for 70%–90% of local N inputs (Compton et al., 2020; Lin et al., 2019; Metson et al., 2020), leading to elevated groundwater nitrate levels in response. However, a concomitant increase in riverine N exports from the Willamette River Basin has not been observed (Metson et al., 2020) prompting questions about the fate of surplus N.

Core Ideas

- A total of 11% (22.7 kg N·ha^{-1}·year^{-1}) of recently applied fertilizer was leached below 3 m with the onset of fall rain.
- Processed legacy nitrogen (N) comprised up to 18% (32.8 kg N·ha^{-1}·year^{-1}) of nitrate lost to leaching.
- Denitrification was not an important process contributing to N removal.
- Residual fertilizer N posed a greater immediate threat to groundwater than soil legacy N.
- N sources and potential processing information can link soil surface practices with nitrate leaching.

Soil surplus N can be lost through gaseous releases, such as via the process of denitrification, leached to the groundwater, or accumulated within the soil profile. Denitrification, or the process by which nitrate is sequentially reduced to molecular dinitrogen under mostly anaerobic conditions, largely depends on various factors like soil type, reduction capacity, degree of saturation, and water residence time (Lenhart et al., 2021; Oh et al., 2023), which can impact oxygen concentrations and the presence of electrons donors (i.e., reactive organic carbon or reduced minerals). However, most studies in agricultural settings have shown that denitrification tends to be very limited in the unsaturated vadose zone (Green et al., 2008; Onsoy et al., 2005; Parkin & Meisinger, 1989; Rivett et al., 2007; Chen, Wang, et al., 2018). Concentrations of organic carbon tend to decline with depth in the soil (Chen, Wang, et al., 2018; Parkin & Meisinger, 1989), resulting in lower reaction rates and smaller microbial populations (Holden & Fierer, 2005; Kieft & Brockman, 2001). During unsaturated conditions, atmospheric oxygen can fill pore spaces in the soil resulting in more aerobic environments throughout the vadose zone (Green et al., 2008). Legacy N storage, or the accumulation of N within systems, was confirmed in the high-input agricultural soils and groundwater along the Mississippi River Basin (Van Meter et al., 2016, 2023) and more recently within agricultural soils of the Willamette Valley (Weitzman et al., 2022). Thus, storage of surplus N within the soils and groundwater of the Willamette Valley is likely responsible for minimizing surface water N exports, as opposed to denitrification, explaining the incongruity in the mass balance of N inputs (high N fertilizer applications) and outputs (low stream N exports) for the region.

Annual nitrate leaching rates significantly decreased with depth in a 4-year field study (the same study detailed herein) that measured the transport of nitrate through the vadose zone underlying a fertilized and irrigated sweet corn crop in Corvallis, OR (Weitzman et al., 2022). Of new annual surface N inputs across the study years, less than a third (~29%) was found to leach below the 3.0-m soil depth. And, though a substantial fraction of annual N inputs was removed in crop harvest (~44%), a considerable amount of the annual N inputs was found to remain in the soil below the rooting zone (~27%) (Weitzman et al., 2022). We had originally hypothesized that the total annual leached nitrate would be correlated with varying N inputs at the surface across the study years, and that decreased leaching across the vadose zone would be driven by water flow dynamics and agricultural N management practices (Weitzman et al., 2022). However, these external factors, like fertilizer amount and precipitation (and irrigation) amount, were not significant predictors of nitrate leaching below 3.0 m. Rather, the variation in leaching across depths and years appeared to be influenced by postharvest soil nitrate, which itself is controlled by internal N cycling processes within the vadose zone (Weitzman et al., 2022).

A significant amount of water and contaminants pass below the root zone downward through the soil vadose zone before reaching the groundwater (Gurevich et al., 2021; Harter et al., 2005; Liao et al., 2012). This movement and processing of water and N may occur at various rates through the soil and deeper lithology, contributing to legacy N accumulation within agricultural systems (Van Meter et al., 2016; Weitzman et al., 2022; Zhu et al., 2021). Our understanding of soil–water interactions below the rooting zone (which in corn is generally less than ~1.0 m) is limited, especially concerning the mechanisms of N retention in soil and leaching to groundwater. Being able to discriminate between current and legacy N contributions to different ecosystem N pools could help us to better predict the fate of N below the rooting zone. The dual stable isotopes of water (δH_2O: $\delta^{18}O–H_2O$ and $\delta^2H–H_2O$) and nitrate (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 (Böhlke & Denver, 1995; Sulzman, 2007; Weitzman, Brooks, et al., 2021). Specifically, δH_2O values can reveal the origins, residence times, and flowpaths of different water sources (e.g., Brooks et al., 2012; McGuire & McDonnell, 2007; Sprenger et al., 2019; Sprenger, Erhardt, et al., 2016; Sprenger, Seeger, et al., 2016), while δNO_3^- values can differentiate between source inputs of nitrate and reveal dominant N transformation processes (e.g., Kendall et al., 2007; Mayer et al., 2002; Qin et al., 2019; Suchy et al., 2018; Utom et al., 2020; Xue et al., 2009).

Nitrogen can be quickly transformed from one form to another as it is added to and transported through the soil (Hobbie & Ouimette, 2009; Robinson, 2001). These transformations impart predictable isotopic fractionation signatures, which cause $\delta^{15}N–NO_3^-$ values to either become more enriched or more depleted (Denk et al., 2017). Most N cycling processes that dominate in the soil cause enrichment above the source isotopic value (Kendall et al., 2007). For example, soil processes that might lead to reduced nitrate leaching through the soil system, like denitrification (typical of fine-grained, saturated soils with lower concentrations of dissolved oxygen) or ammonia volatilization (a common occurrence following the addition of ammonia-based fertilizers in soils with pH >7.0), are enriching processes, yielding residual nitrate with much higher $\delta^{15}N–NO_3$ values (e.g., as high as +15‰ to +30‰ for denitrification and +20‰ to +27‰ for ammonia volatilization) (Kendall, 1998). Thus, the utilization of such stable isotopes could help us better track the transport and transformation of nitrate through the vadose zone. Specifically, legacy N, regardless of the form in which it is stored in the soil, is assumed to have undergone some processing (e.g., immobilization by microbes or rapid uptake into organic matter). As such, legacy N could be identified as being relatively enriched in $\delta^{15}N–NO_3^-$ compared to newer N sources that have not been processed in the soil.

In this study, we employed a dual stable isotope approach (δH_2O and δNO_3^-) at the study site of Weitzman et al. (2022), in order to understand the mechanisms driving the declining rates of nitrate leaching with depth. We intensively monitored the movement and concentration of nitrate in the vadose zone over multiple years and depths beneath a sweet corn field in the Willamette Valley (Weitzman et al., 2022). With this approach, we sought to address the following three main objectives:

1. determine whether denitrification or soil N storage (i.e., legacy N) is a more important process for the reduction in nitrate leaching seen at depth;
2. estimate the magnitude of leaching by different sources (contemporary vs. legacy) through the vadose zone at different depths and time periods; and
3. reveal water sources (irrigation or precipitation), transit time, and the extent of mixing with depth, and link the hydrologic findings with the measured rates and sources of nitrate leaching.

2 | MATERIALS AND METHODS

2.1 | Study site

The study site (44°34′26.1″N, 123°14′35.2″W) was a ~0.8-ha agricultural field located within Oregon State University's Vegetable Research Farm in Corvallis, OR, lying ~400 m east of the Willamette River. It is characterized as having a relatively flat-lying, low-relief terrain with fine-textured alluvial-derived silty clay loam that is slightly acidic to neutral (i.e., pH range ~5.5–7.0) from the Chehalis soil series (Cumulic Ultic Haploxeroll) in the upper 1.5 m (Soil Survey Staff, 2019). Silt loam and loam layers intermix below the silty clay loam layer, followed by a layer of sandy loam and loamy sand, which then transitions to a gravel/rock matrix at depths of ~4.3–6.7 m below the ground surface (Hutchins et al., 2022; Weitzman et al., 2022).

The field site is located within the Willamette Valley, an agriculturally productive region with more than 50% of its land in production (Morlan et al., 2010) as either pasture, hay, grass seed, or other variety of specialty field crops (Metson et al., 2020). With cool, wet winters and warm, dry summers, the Mediterranean climate regime typical of the Willamette Valley means very little precipitation occurs during the summer, leading to a higher use of irrigation in the summer for some crops (Taylor & Bartlett, 1993), including the corn grown in this study. Generally, the groundwater table fluctuated no more than 2.4–3.4 m annually, with groundwater ranging from depths below the ground surface of 3.0–6.7 m during the study (Hutchins et al., 2022).

2.2 | Experimental design and field management

The field study was established in Summer 2016 with the uniform planting of a sweet corn crop across the whole ~0.8-ha site and replanted with sweet corn in either June or July of each year through Summer 2020. The field was fertilized with N twice during the growing season and spray-irrigated with well-collected groundwater (containing measurable concentrations of nitrate included in the N budget) approximately every week throughout the summer months. Rates of N application, crop and cover crop varieties, as well as corn harvest and cover crop termination dates and techniques are detailed in Weitzman et al. (2022) and Hutchins et al. (2022). Field-scale N budgets for the study are reproduced here (from Weitzman et al., 2022) (Table 1) and reported on a "fertilizer year" basis (July–June, straddling two calendar years) in order to better capture the influence of timing-specific agronomic management practices, such as fertilizer application, irrigation, and crop harvest. The relationships between different N input and export components serve as distinctive indicators of management performance. For example, fractional leaching export is used to understand how much N may be exported to the groundwater, and N-use efficiency (NUE) tends to provide a benchmark for N management effectiveness, while N surplus and N remainder are considered proxies for N loss to the environment (Table 1). Here, we present the full 4-year dataset, with interpretation based on three complete fertilizer years spanning from July 2017 through June 2020.

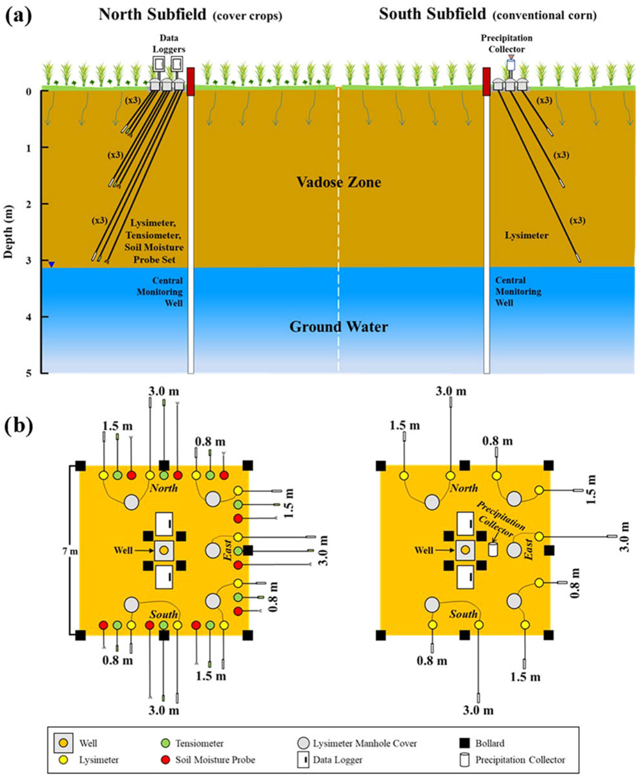

FIGURE 1 Schematics of monitoring networks within two subfields, North subfield interseeded with cover crops (left) and South subfield with conventional corn (right), of the field site located at OSU's Vegetable Research Farm. (a) Lateral cross-sectional view of vadose zone devices and lysimeters buried across depths (0.8, 1.5, and 3.0 m) in the two subfields. (b) View from above depicting directional orientation (North, East, and South) of replicate vadose zone devices and lysimeters buried across depths. Reproduced from Weitzman et al. (2022).

2.2.1 | Monitoring networks

Two monitoring networks within the field were instrumented to track changes in soil solution chemistry as rainwater or irrigation water infiltrated the surface soil and percolated through the vadose zone and into the groundwater (Hutchins et al., 2022; Weitzman et al., 2022). Each network was equipped with three replicate suction lysimeters ($n = 3$) at three depths each—0.8, 1.5, and 3.0 m (Figure 1)—for a total of six lysimeters at each depth. Replicate soil moisture probes ($n = 3$) and tensiometers ($n = 3$) included at the three depths recorded data every 30 min over the 4-year study period. All vadose zone devices were installed in 8.26-cm outer diameter (OD) boreholes constructed at 45° using a Geoprobe 6610DT Direct Push Drill Rig (Geoprobe Systems) and backfilled with soil (Hutchins et al., 2022; Weitzman et al., 2022). A precipitation collector device constructed to minimize evaporative losses over time (Gröning et al., 2012) was mounted in the

TABLE 1 Annual nitrogen (N) fluxes (inputs and exports) across the three fertilizer years (Summer–Spring) and three soil depths (0.8, 1.5, and 3.0 m) investigated at the field site. Leached nitrate (NO_3^-–N) fluxes are expressed as depth averaged mean values and one standard error in parentheses. Fractional leaching export rate (%) is expressed as the amount of N leached at the 3.0-m depth, divided by the total N inputs (fertilizer + irrigation water + deposition). Crop N uptake includes both cover crop N (retained on site) and corn crop N (removed from the site, i.e., "harvested" N). Surplus N gives an indication of what is lost or retained by the environment and is estimated as the total N inputs minus crop N harvest (where crop N harvest for this study is equal to corn crop N uptake). Nitrogen remainder is defined as the total N exports (leached + corn crop N harvest) subtracted from the total N inputs. Nutrient-use efficiency (NUE) is calculated as the percent of corn crop N harvest divided by total N inputs. Annual averages (with standard error) are based on six replicate lysimeters at each depth during each fertilizer year, except at the 0.8-m depth during the last fertilizer year for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed). Reproduced from Weitzman et al. (2022).

Year	N inputs			NO_3^-–N leached by depth			Fractional leaching export rate	Crop N uptake		Surplus N	N remainder by depth			NUE
	kg ha^{-1}·year^{-1}			kg ha^{-1}·year^{-1}			%	kg ha^{-1}·year^{-1}		kg ha^{-1}·year^{-1}	kg ha^{-1}·year^{-1}			%
	Fertilizer	Irrigation water	Deposition (wet + dry)	0.8 m	1.5 m	3.0 m	Total to 3.0 m	Cover crops	Corn		0.8 m	1.5 m	3.0 m	Total
Year 1: Summer 2017 to Spring 2018	121	44.0	5.00	149 (21.2)	123 (17.0)	81.1 (11.6)	47.7	18.5	77.6	92.5	−56.8	26.8	41.4	46
Year 2: Summer 2018 to Spring 2019	183	28.4	5.00	75.2 (12.4)	76.3 (21.2)	60.8 (13.5)	28.2	90.5	256	−42.5	−118	−1.14	15.5	120
Year 3: Summer 2019 to Spring 2020	224	18.4	5.00	86.5 (26.4)	63.6 (16.6)	24.8 (6.80)	10.0	54.7	258	−10.0	−97	22.9	38.8	104

Note: Leached nitrate (NO_3^-–N) fluxes are expressed as depth averaged mean values and one standard error in parentheses. Fractional leaching export rate (%) is expressed as the amount of N leached at the 3.0-m depth, divided by the total N inputs (fertilizer + irrigation water + deposition). Crop N uptake includes both cover crop N (retained on site) and corn crop N (removed from the site, i.e., "harvested" N). Surplus N gives an indication of what is lost or retained by the environment and is estimated as the total N inputs minus crop N harvest (where crop N harvest for this study is equal to corn crop N uptake). Nitrogen remainder is defined as the total N exports (leached + corn crop N harvest) subtracted from the total N inputs. Nutrient-use efficiency (NUE) is calculated as the percent of corn crop N harvest divided by total N inputs. Annual averages (with standard error) are based on six replicate lysimeters at each depth during each fertilizer year, except at the 0.8-m depth during the last fertilizer year for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed). Reproduced from Weitzman et al. (2022).

field to capture rainwater and irrigation water for isotopic analyses.

2.2.2 | Water sampling and analysis

Lysimeter soil pore water samples and precipitation and/or irrigation water were collected every 2 weeks over the 4 years of the study for analysis of a suite of water chemistry parameters (Hutchins et al., 2022). Lysimeters were primed by applying a vacuum (−60 kPa) 1 week prior to sample collection. Total water volume in each lysimeter bottle was recorded, then subsamples of the soil solution were created based on a predetermined analytical priority: (1) nitrate concentration, and (2) stable isotopes of nitrate (δNO_3^-: $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) and stable isotopes of water (δH_2O: $\delta^{18}O–H_2O$ and $\delta^2H–H_2O$). A total of 1849 samples were analyzed for nitrate concentrations, 1377 for δNO_3^-, and 1804 for δH_2O. All the data are publicly available (Weitzman et al., 2024).

For nitrate concentration, an aliquot of the solution was collected in an HDPE Nalgene bottle and acidified in the field with sulfuric acid (H_2SO_4) to pH <2. Concentrations were measured at the EPA's Robert S. Kerr Environmental Research Center (Ada, OK, USA) using colorimetric analysis via a Lachat QuickChem 8000 Flow Injection Ion Analyzer (Lachat Instruments). Sample aliquots for both stable isotope analyses (water and nitrate) were filtered in the field through 0.45-μm syringe filters into separate HDPE 20-mL scintillation vials and delivered to the EPA's Integrated Stable Isotope Research Facility (ISIRF, Corvallis and Newport, OR, USA) for analysis. Poly-seal conical caps and parafilm were used to minimize evaporation for δH_2O-designated samples, which were then stored upside down at room temperature prior to analysis using a Laser Absorption Liquid-Water Isotope Spectrometer (Model DLT-100; Los Gatos Research). Samples for δNO_3^- analysis were placed in a −20°C freezer until measurement procedures could commence to prevent oxygen exchange and bacterial activity. The full suite of analytes measured as part of the broader study, including other nutrients, metals, and so forth, can be found in Hutchins et al. (2022).

Samples for δNO_3^- analysis were prepared following the bacterial denitrifier method using *Pseudomonas aureofaciens* (Casciotti et al., 2002; Sigman et al., 2001), which under anerobic conditions cannot produce the nitrous oxide (N_2O) reductase enzyme needed for complete denitrification to dinitrogen (N_2) but, rather, quantitatively reduce nitrate to nitrous oxide. The produced nitrous oxide serves as the analyte gas, allowing the isotopic composition of the sample to be analyzed using a gas-chromatography-based GasBench II (Thermo Electron Corporation) inlet with cryogenic trapping connected to an isotope ratio mass spectrometer (DELTA V Plus; Thermo Electron Corporation) operating in continuous-flow mode. The bacterial denitrifier method can introduce fractionation and exchange issues that could interfere with the accurate measurement of $\delta^{18}O–NO_3^-$ (Casciotti et al., 2002). To account for these complications, the fractionation and exchange rate values were determined for each set of samples prepared with the same batch culture of *P. aureofaciens*, along with the $\delta^{18}O–H_2O$ value for each sample, to correct the $\delta^{18}O$ value in the nitrous oxide analyte (Weitzman, Brooks, et al., 2021).

2.3 | Nitrate leaching fluxes

Nitrate leaching losses across the three lysimeter depths (0.8, 1.5, and 3.0 m) were estimated using measured lysimeter nitrate concentrations along with simulated water flux rates from a HYDRUS-1D model, as presented in Weitzman et al. (2022). Daily mass flux rates were integrated over time, averaged for each depth to estimate annual mass flux of nitrate ($kg{\cdot}ha^{-1}{\cdot}year^{-1}$) across the whole field. Note that in the last year of the study (Fertilizer Year 3, July 2019 to June 2020), the two East position lysimeters at the 0.8-m depth were found to have potentially been impacted by a fertilizer application error (Weitzman et al., 2022), and so they were excluded from all analyses at this shallowest depth for the final year; however, the data from these lysimeters are available in Weitzman et al. (2024).

2.4 | Isotopic analysis

Analysis of the natural abundance stable isotopes of δH_2O (i.e., $\delta^{18}O–H_2O$ and $\delta^2H–H_2O$) and δNO_3^- (i.e., $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) in the lysimeter pore water samples are reported in standard delta (δ) notation as the relative abundance per mil (‰), which is defined as

$$\delta\,(‰) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right] \times 1000,$$

where R represents the isotopic ratio of the heavy to light isotope abundance for the sample (R_{sample}) and a standard reference material (R_{standard}). All $\delta^2H–H_2O$, $\delta^{18}O–H_2O$, and $\delta^{18}O–NO_3^-$ values are expressed relative to Vienna-Standard Mean Ocean Water (V-SMOW), and $\delta^{15}N–NO_3^-$ values are expressed relative to standard atmospheric dinitrogen (N_2) (AIR).

For δH_2O on the laser spectrometer, calibration to the international scale was made for each analytical set of samples using three internal standards (range −1.7 to −111.4 for $\delta^2H–H_2O$ and −1.8 to −14.8 for $\delta^{18}O–H_2O$) with a separate QC (quality control) standard to test accuracy. Internal standards were annually calibrated to internationally certified standards (V-SMOW, GISP, and SLAP). Measurement accuracy for analyzed samples was determined on 86 repeated measures of QC standards spanning the range of sample values and estimated to be 0.02‰ ± 0.23‰ (±standard deviation [SD]) and 0.05‰ ± 0.08‰ for δ^2H–H$_2$O and δ^{18}O–H$_2$O, respectively (Brooks et al., 2022). Measurement precision across the study was determined on 176 repeated measures of study samples and estimated to be ±0.3‰ and ±0.1‰ for δ^2H–H$_2$O and δ^{18}O–H$_2$O, respectively. Deuterium excess (d-excess) was calculated as an index of how much evaporation has affected the isotopic value of each water sample using the following equation (Clark & Fritz, 1997; Dansgaard, 1964):

$$\text{d} - \text{excess} = \delta^2\text{H–H}_2\text{O} - 8 \times \delta^{18}\text{O–H}_2\text{O}.$$

Ocean water tends to have an average d-excess ~0, while the average d-excess for precipitation is ~10. Water in terrestrial environments with d-excess values <10 is presumed to have undergone some evaporation (Brooks et al., 2012, 2014).

For δNO$_3{}^-$ analyses, calibration to the international scale was made for each analytical set of samples using three NIST standards (ranging 180.0 to −1.8 for δ^{15}N–NO$_3{}^-$ and 58.8 to −27.9 for δ^{18}O–NO$_3{}^-$) with an additional independent QC standard. Measurement accuracy for the IRMS across the study was determined on 93 repeated measures of QC standards spanning the range of sample values and estimated to be −0.02‰ ± 0.16‰ and −0.10‰ ± 0.19‰ for δ^{15}N–NO$_3{}^-$ and δ^{18}O–NO$_3{}^-$, respectively. Measurement precision across the study was determined on 96 repeated measures of study samples and estimated to be ±0.1‰ and ±0.4‰ for δ^{15}N–NO$_3{}^-$ and δ^{18}O–NO$_3{}^-$, respectively. Overall uncertainty for the corrected δ^{18}O–NO$_3{}^-$ values (which relied on δ^{18}O–H$_2$O measurements) was 0.4‰.

2.5 | Fertilizer signal identification and isotopic mixing model

An isotopic mixing model approach was used to differentiate periods across the three fertilizer years when contributions to nitrate fluxes were likely associated with recently added fertilizer N (in this study typically: δ^{15}N ≅ 0‰) versus older, processed soil legacy N with higher δ^{15}N values. The dataset did not provide us the ability to identify the exact form in which legacy N is stored in the soil, but we assumed legacy N had been immobilized by microbes or undergone other N cycling processes, which would cause it to be relatively enriched in ^{15}N compared to newly applied fertilizer. Isotopic indicators of denitrification were rare (i.e., represented by a sequence of time over which nitrate concentrations decrease simultaneously as δ^{15}N–NO$_3{}^-$ and δ^{18}O–NO$_3{}^-$ values increase), and thus a denitrification fractionation effect was not included in the mixing model.

The statistical significance of monotonic (increasing or decreasing) trends in nitrate concentrations and δ^{15}N–NO$_3{}^-$ values across the study period were assessed by using the nonparametric Mann–Kendall test. Autocorrelation was taken into account with the Hamed and Rao method (Hamed & Rao, 1998). Data from the replicate lysimeters at each soil depth ($n = 6$) were normalized to the beginning of the time period being analyzed so as to avoid issues arising from differences in values across the lysimeters, and instead focus on the absolute change across the time series. Periods with fertilizer influences were termed “fertilizer signal periods” marked by the mixing of more isotopically enriched soil nitrate with more isotopically depleted fertilizer N. Such instances were thus identified by times when nitrate concentrations increased and δ^{15}N–NO$_3{}^-$ decreased in replicate lysimeters over consecutive dates. We considered the fertilizer signal period to persist until the δ^{15}N–NO$_3{}^-$ started increasing, which would indicate mixing with mineralized soil N.

We utilized a two-endmember linear mixing model, with the mean proportion of source A in the mixture calculated as f_a according to the following:

$$f_{\text{a}} = \frac{\bar{\delta}_{\text{M}} - \bar{\delta}_{\text{B}}}{\bar{\delta}_{\text{A}} - \bar{\delta}_{\text{B}}},$$

where $\bar{\delta}_{\text{M}}$, $\bar{\delta}_{\text{A}}$, and $\bar{\delta}_{\text{B}}$ represent the mean isotopic signatures (e.g., δ^{15}N–NO$_3{}^-$) for the mixture M and the sources A and B, respectively. In our mixing model, we used the average isotopic value of the fertilizer sources applied to the field for each of the three complete fertilizer years. We estimated the isotopic value of the applied fertilizer to be the average measured value of the different fertilizer sources used each year at the study site (granular ammoniacal N and urea; Weitzman et al., 2022). A portion of each fertilizer was ground into a homogenous powder and analyzed for δ^{15}N using a continuous-flow isotope ratio mass spectrometer (ISOPRIME 100; Elementar Americas Inc.) coupled to an elemental analyzer inlet (Vario ISOTOPE Cube; Elementar Americas Inc.). The average value was δ^{15}N = −0.7‰ ± 0.3‰. The end member for soil N value (δ^{15}N–NO$_3{}^-$) used in the mixing model was unique for each fertilizer signal period. The exact value of processed soil nitrate was unknown, so to be conservative, we used the δ^{15}N–NO$_3{}^-$ soil pore water values just prior to when δ^{15}N–NO$_3{}^-$ started decreasing and soil nitrate concentrations started increasing. We calculated the proportion attributed to fertilizer for each consecutive observation until δ^{15}N–NO$_3{}^-$ started increasing and applied those proportions to the leached volumes of nitrate. We included confidence intervals to communicate uncertainty associated with the calculations.

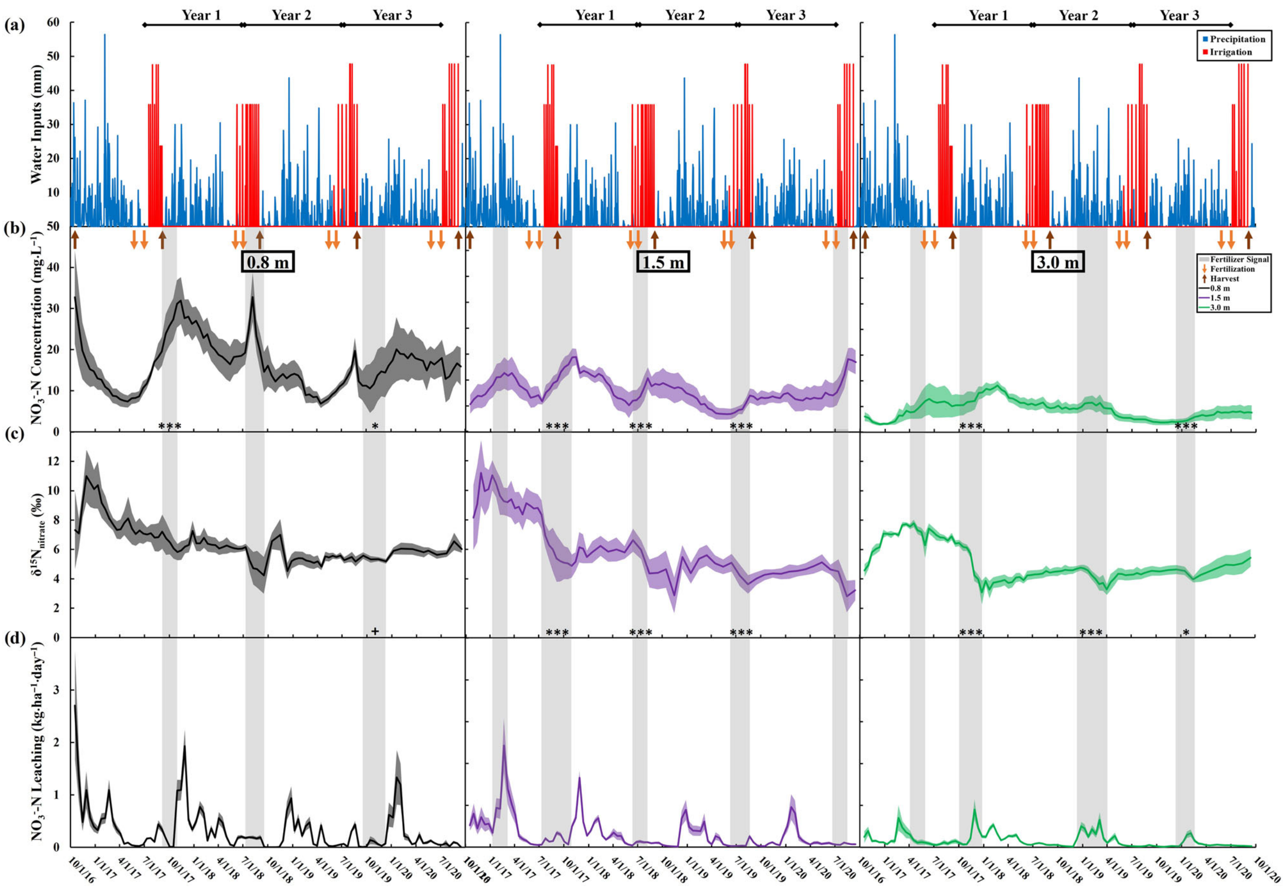

FIGURE 2 Fortnightly (a) water inputs from precipitation (blue lines) and irrigation (red lines) measured across the 4-year field study (with the three fertilizer years indicated); results from lysimeter samples: (b) mean nitrate (NO$_3^-$–N) concentrations; (c) mean d^{15}N–NO$_3^-$ values; and (d) nitrate (NO$_3^-$–N) leaching flux. In panels b–d, the three distinct soil depths are depicted vertically from left to right: 0.8 m (black lines), 1.5 m (purple lines), and 3.0 m (green lines). Corresponding shaded colors around each line represent the standard error of the mean for six replicate lysimeters, except at the 0.8-m depth during the last fertilizer year (July 2019 to June 2020) for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed). Vertical gray boxes running throughout each panel, b–d, correspond to fertilizer signal periods. Orange "down" arrows signify fertilization dates, and brown "up" arrows signify crop harvest dates. Statistically significant trends in NO$_3^-$–N concentrations (positive) and d^{15}N–NO$_3^-$ values (negative) during the fertilizer signal periods are represented as ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.05$, and †$p \leq 0.1$ in panels b and c.

3 | RESULTS

3.1 | Nitrate concentrations and nitrate isotopes over three fertilizer years

Soil solution nitrate concentrations and nitrate isotopes varied with depth and over time (Figure 2b,c). Nitrate concentrations were lowest just prior to fertilization at the start of the growing season, while δ^{15}N–NO$_3^-$ decreased over the study period. Values of δ^{15}N–NO$_3^-$ were highest in 2016 at the beginning of the study, following instrument installation, for the upper two depths (0.8 and 1.5 m), with maximum values of 11.0‰ and 11.2‰, respectively. After the first full growing season, δ^{15}N–NO$_3^-$ were lower and more stable over time, but still demonstrated distinct shifts in isotopic values. The anomalously high δ^{15}N–NO$_3^-$ values in 2016 were likely an artifact of soil disturbance from the installment of the soil monitoring equipment and the establishment of a new sweet corn crop planting at the site, and led us to the decision to report analyses and interpretation based on the three complete "fertilizer years" (signified at the top of Figures 2 and 4), spanning July 2017 through June 2020. For the fertilizer years, the highest δ^{15}N–NO$_3^-$ values across all three depths were found in the summer and early fall of Fertilizer Year 1, ranging from ∼7‰ to 8‰. The lowest δ^{15}N–NO$_3^-$ values over the same 3-year period were observed to be ∼3‰ for the two deeper depths, in the late fall of Fertilizer Year 2 for the 1.5-m depth and in winter of Fertilizer Year 1 for the 3.0-m depth. The lowest δ^{15}N–NO$_3^-$ values found at the 0.8-m depth were considerably higher, never dipping below 4.2‰, which was the minimum observed in the fall of Fertilizer Year 2. The median values of δ^{15}N–NO$_3^-$ over the three fertilizer years were distinct for each soil layer, showing a pattern in which values decreased with increasing depth, with 5.9‰, 5.1‰, and 4.4‰ for the 0.8-, 1.5-, and 3.0-m depths, respectively.

3.2 | Minimal evidence of denitrification

Denitrification would be associated with a decrease in nitrate concentrations and increasing $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$. We only saw indications of denitrification at the start of the study, soon after we installed the instruments within the soil (Figures 2 and S1). Initially, nitrate concentrations were very high at the 0.8-m depth, followed by a rapid decline in both concentration and our predicted leaching, while $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ increased to the highest values we measured during the 4 years of monitoring. We found a similar pattern at the 3-m depth but to a lesser degree. Interestingly at 1.5 m, the increase in $\delta^{15}N–NO_3^-$ directly after installation was associated with an increase in nitrate concentrations. After these initial periods that could indicate denitrification or other gaseous losses of N, possibly due to antecedent conditions at the field site, we did not see substantial increases in $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ associated with declining nitrate concentrations. In fact, $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ mostly stabilized (Figures 2 and S2) except for excursions where $\delta^{15}N–NO_3^-$ declined associated with increases in nitrogen concentrations, which were interpreted to indicate source changes, as described in the next section.

3.3 | Evidence and timing of fertilizer signal periods

Each year, we observed distinct periods when increasing nitrate concentrations (Figure 2b) corresponded with abrupt and distinct decreasing $\delta^{15}N–NO_3^-$ values (Figure 2c). These periods were evident for all three soil depths, but did not occur at the same time at each depth (gray bars in Figure 2b–d). Significant changes in slopes were observed during the majority of fertilizer signal periods in the two deeper lysimeter depths (1.5 and 3.0 m; Table 2); only one time period had a significant slope change in the shallow lysimeters (0.8 m). These shifts tended to occur after fertilization (indicated in Figure 2 with orange down arrows). Fertilizer applied to the fields had N isotopic values near zero ($\delta^{15}N = -0.7$‰), which is much lower than the measured range ($\delta^{15}N–NO_3^- = 2.9$‰–8.4‰) and median ($\delta^{15}N–NO_3^- = 5.2$‰) values for soil solution across all three soil depths over the three fertilizer years. Thus, when recent fertilizer mixes with nitrate already in the soil, $\delta^{15}N–NO_3^-$ values would shift closer to zero (Figure 2c) and nitrate concentrations would increase. We refer to these periods as fertilizer signal periods (gray bars in Figure 2).

TABLE 2 Results of Mann–Kendall trend analysis for nitrate concentration and $d^{15}N–NO_3^-$ values during the fertilizer signal periods and outside of the fertilizer signal periods (i.e., other flux periods) across the three fertilizer years at each of the three soil depths (0.8, 1.5, and 3.0 m).

Depth		Fertilizer signal period						Other flux periods					
		Year 1		Year 2		Year 3		Year 1		Year 2		Year 3	
		$[NO_3^-–N]$	$\delta^{15}N$	$[NO_3^-–N]$	$\delta^{15}N$	$[NO_3^-–N]$	$\delta^{15}N$	$[NO_3^-–N]$	$\delta^{15}N$	$[NO_3^-–N]$	$\delta^{15}N$	$[NO_3^-–N]$	$\delta^{15}N$
0.8 m	*p*-value	0.002	ns	ns	ns	0.022	0.073	0.001	0.008	ns	ns	<0.0001	ns
	Trend direction	⬆	–	–	–	⬆	⬇	⇩	⬇	–	–	⇩	–
1.5 m	*p*-value	0.001	0.008	0.005	0.007	<0.0001	0.002	0.002	0.017	0.001	ns	ns	0.001
	Trend direction	⬆	⬇	⬆	⬇	⬆	⬇	⇩	⇧	⇩	–	–	⇧
3.0 m	*p*-value	0.001	0.004	ns	0.008	<0.0001	0.018	0.001	0.000	0.006	<0.0001	0.017	0.001
	Trend direction	⬆	⬇	–	⬇	⬆	⬇	⇩	⇧	⇩	⇧	⬆	⇧

Note: Trends are based on six replicate lysimeters at each depth during each time period, except at the 0.8-m depth during the last fertilizer year for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed; see Section 2 and Weitzman et al. [2022]). Trend direction arrows are represented as follows: Solid black provides supporting evidence for existence of fertilizer signal periods, for example, a black up arrow represents a significant increase in $[NO_3^-–N]$ (positive trend) and a black down arrow represents a significant decrease in $\delta^{15}N$ (negative trend). White outlined in black depicts times in which fertilizer signal period trends were not evident, for example, a white down arrow represents a significant decrease in $[NO_3^-–N]$ (negative trend) and a white up arrow represents a significant increase in $\delta^{15}N$ (positive trend).
Abbreviations: $[NO_3^-–N]$, nitrate concentration; $\delta^{15}N$, $\delta^{15}N–NO_3^-$.

TABLE 3 Annual contributions from flux events outside of the fertilizer signal periods (i.e., other flux periods) and during fertilizer signal periods to the total amount of nitrate (NO_3^-–N) leached across the three fertilizer years at each of the three soil depths (0.8, 1.5, and 3.0 m) plus/minus one standard error, with contributing percentage in parentheses.

Depth	Total amount NO_3^-–N leached	Other flux periods (unknown mix of recent fertilizer + legacy N inputs)	Fertilizer signal periods	Fertilizer signal from “recent fertilizer N inputs”	Fertilizer signal from “legacy N inputs”
	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}
0.8 m	104 ± 23.0	89.9 ± 19.1 (86%)	13.9 ± 4.8 (13%)	6.6 ± 2.3 (6%)	7.2 ± 2.5 (7%)
1.5 m	87.4 ± 17.8	73.5 ± 10.9 (84%)	13.9 ± 7.3 (16%)	8.9 ± 5.4 (10%)	5.0 ± 2.2 (6%)
3.0 m	55.5 ± 16.5	26.8 ± 12.7 (48%)	28.7 ± 8.7 (52%)	22.7 ± 9.4 (41%)	6.0 ± 1.5 (11%)

Note: The average contributions of “recent fertilizer N inputs” versus “legacy N inputs” to fertilizer signal periods are also presented, with the percent contribution to the total amount of nitrate leached in parentheses. Annual averages (with standard error) are based on six replicate lysimeters at each depth across 3 years, except at the 0.8-m depth during the last fertilizer year for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed).

In the shallowest depth of 0.8 m, three major fertilizer signal periods occurred across the fertilizer years, each within 1–2 months of fertilizer application (Figure 2). The Mann–Kendall test showed that only the third instance of the fertilizer signal period at the 0.8-m depth had a trend in which nitrate concentrations were significantly increasing and $\delta^{15}N$–NO_3^- values were significantly decreasing (Table 2; Figure 2), likely due to greater spatial variability between lysimeters at this shallow depth. Over the three fertilizer years, three fertilizer signal periods (one in each year) were also identified at the 1.5-m depth (with two others falling outside the fertilizer years of interest), each showing the paired nitrate concentration–$\delta^{15}N$–NO_3^- value trend of interest to be statistically significant (Table 2), and each beginning as soon as 1–2 weeks after application of fertilizer N to the land surface (Figure 2). And, while a total of three fertilizer signal periods were similarly identified within the deepest soil depth of 3.0 m (with $\delta^{15}N$–NO_3^- being statistically significant for all three periods, and nitrate concentration being significant in two [Table 2]), their timing lagged behind those closer to the surface, not appearing until after the fall rains began, or 4–6 months following fertilizer additions (Figure 2).

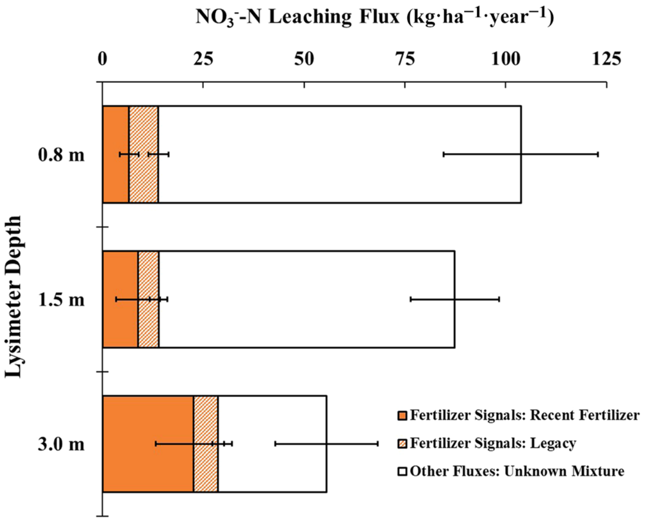

FIGURE 3 Annual nitrate (NO_3^-–N) leaching flux summarized by depth (0.8, 1.5, and 3.0 m) and N source (during and outside of fertilizer signal periods) across the field site. Average contributions of recent N fertilizer inputs (solid orange; left-most bar) and legacy N inputs (hatched orange; middle bar) are differentiated during fertilizer signal periods, while such differentiation cannot be ascertained for fluxes outside of the fertilizer signal periods (i.e., other fluxes; white, right-most bar). Annual averages (with standard error bars) are based on six replicate lysimeters at each depth across 3 years, except at the 0.8-m depth during the last fertilizer year for which only four replicate lysimeters were averaged (since results from the two East-positioned lysimeters were removed).

3.4 | Nitrate leaching during fertilizer signal periods

Nitrate leaching across the three fertilizer years at the study site was found to be variable among lysimeters at the same depth and across years (Weitzman et al., 2022). However, the average annual nitrate leaching across the three fertilizer years significantly decreased with depth—from ~104 kg N·ha^{-1}·year^{-1} near the surface at 0.8 m to ~56 kg N·ha^{-1}·year^{-1} in the deeper soil at 3.0 m (Weitzman et al., 2022; Table 3; Figure 3). Integrating across the fertilizer signal periods only (gray bars of Figure 2), the absolute amount of leached nitrate was similar across the three depths, ranging from ~14 to 29 kg N·ha^{-1}·year^{-1} (Table 3; Figures 2d and 3). However, the different timing of the fertilizer signal periods within each depth strongly impacted the proportion of fertilizer nitrate that contributed to the total nitrate flux from each soil layer. For instance, the fertilizer signal did not appear to reach the 3.0-m depth (gray bars of Figure 2) until after crop harvest (brown up arrows in Figure 2), months after it was initially applied at the surface, coinciding with larger nitrate fluxes driven by late fall/early winter precipitation (Figure 2d).

Large nitrate leaching events were noted for each depth when the fall rains began, but only at 3 m were such leaching periods associated with the fertilizer signal (decreased δ^{15}N–NO_3^- and increased nitrate concentrations). Thus, nitrate leached at the deepest depth of 3.0 m during fertilizer signal periods made up a much larger proportion of the total N leached at that depth (~52%) than compared to the two shallower depths of 0.8 and 1.5 m (~13% and 16% of total leached N, respectively), where most nitrate was lost outside of the fertilizer signal periods (Table 3; Figure 3).

A greater proportion of the nitrate leached from the upper, near-surface soil (0.8-m depth) was attributable to soil legacy N pools when the fertilizer signal was detected (~52%; Table 3; Figure 3). In contrast, newer fertilizer N inputs were more likely to move through the vadose zone, ultimately being leached at higher proportions in the deeper soils, making up ~64% and ~79% of the nitrate lost just during the fertilizer signal periods at 1.5 and 3.0 m, respectively. These values were derived by determining the proportion of recent N fertilizer (dark orange bars) that makes up the fertilizer signal periods (total of recent N fertilizer in dark orange and legacy N in light orange) (Figure 3). We estimated that 13.9 kg N·ha^{-1} was lost as nitrate during the fertilizer periods from the 0.8-m depth on average over the three fertilizer years for both N sources combined. However, we attributed 22.7 kg N·ha^{-1} solely to leaching from recent N fertilizer sources at the 3.0-m depth once the fall rains started (Table 3). We ascribe this larger flux of recent N fertilizer at deeper depths to our conservative approach to identifying fertilizer signal periods. While recent N fertilizer may have moved at other times, high variability in nitrate concentrations and δ^{15}N–NO_3^- values across the replicate lysimeters, especially at the 0.8- and 1.5-m depths (Table 2; Figure 2b,c), precluded us from confidently quantifying these fluxes. For this reason, nitrate leached outside of the fertilizer signal periods was likely a mixture that cannot be apportioned to specific sources, but we conservatively classified it all as legacy N. At the 3.0-m depth, the stability of the nitrate concentrations and δ^{15}N–NO_3^- values across the replicate lysimeters and over time increased greatly, which increased our confidence for predictions at this depth, as well for our estimate of a larger fertilizer N flux at this depth.

3.5 | Water stable isotopes within pore water

Precipitation and irrigation stable isotopes of water (including d-excess and δ^2H–H_2O) provided distinct source input signatures that were used to explore water mixing within the subsurface (Figure 4). Irrigation water isotopes were temporally stable with a δ^2H value ranging from −56.0‰ in 2017 to −59.2‰ in 2020 and characterized by a much lower d-excess value than precipitation, with values ranging from 5.64‰ in 2017 to 6.48‰ in 2020 (red points in Figure 4). Precipitation stable isotopes varied from event to event with cumulative, volume-weighted averages over the water year that tended to be lower than irrigation water averaging −65.9‰ in 2017 to −56.4‰ in 2020, and with d-excess values averaging 11.5‰ in 2017 to 12.9‰ in 2020 (blue points and lines in Figure 4).

Pore-water stable isotope values fluctuated between these two input endmembers and generally decreased in δ^2H–H_2O with depth, while increasing in d-excess. Values at the 0.8-m depth were more dynamic than deeper depths, with average d-excess ranging from 4.0‰ to 9.6‰ over the three fertilizer years, while average δ^2H–H_2O ranged from −69.3‰ to −53.2‰ (Figure 4a). This variation at 0.8 m was most pronounced in the first winter rainy season when over 1 m of precipitation fell with a particularly low δ^2H–H_2O; pore-water δ^2H–H_2O dropped from a high of −53.5‰ at the end of 2016 to a low of −69.3‰ at the beginning of the growing season, 3–4 months after the cumulative precipitation δ^2H–H_2O reached its lowest value for the rainy season. Interestingly, in the following years, pore water at 0.8 m was more stable and did not follow the precipitation input patterns. Instead, pore water at 0.8 m was similar to irrigation water both in δ^2H–H_2O and d-excess regardless of water inputs throughout the next couple of years. During the fertilizer signal periods (gray bars in Figure 4), water isotopic values showed the influence of evaporated irrigation water but did not show a shift in water mixing at the times of the fertilizer signals, indicating that shifts in water sources and water mixing were not the cause of the periods with a fertilization signal.

Pore-water isotopes varied less at the 1.5-m depth, with δ^2H–H_2O ranging from −65.6‰ to −56.2‰ and d-excess ranging from 5.2‰ to 11.3‰. The lowest δ^2H–H_2O was also reached around 3–4 months after the highly depleted precipitation inputs, but the values were not as low as they got at the 0.8-m depth. After July 2017, δ^2H–H_2O values slowly increased back up to the values of the irrigation input. The d-excess values of the fertilizer signal periods matched well with the signature of irrigation water (Figure 4a,b), showing signs of isotopic evaporative enrichment. This suggests that recent N additions transported in the two uppermost soil layers largely occurred during irrigation events, which also matched the timing of these periods. In contrast, the water isotope dynamics in the 3.0-m depth fell between the irrigation and the precipitation values, indicating mixing between these pools. The lowest δ^2H–H_2O values at 3.0 m occurred nearly a year after the low precipitation δ^2H–H_2O inputs and remained relatively stable and more isotopically depleted than inputs. The d-excess marker during the fertilizer signal periods, ranging from 6.8‰ to 10.5‰, represented more of an even mix between precipitation and irrigation water (Figure 4c). The timing of the fertilizer signal periods in the deepest depth lagged behind the appearance of the signals in the 0.8- and 1.5-m depths (Figure 4) and occurred with the fall/winter

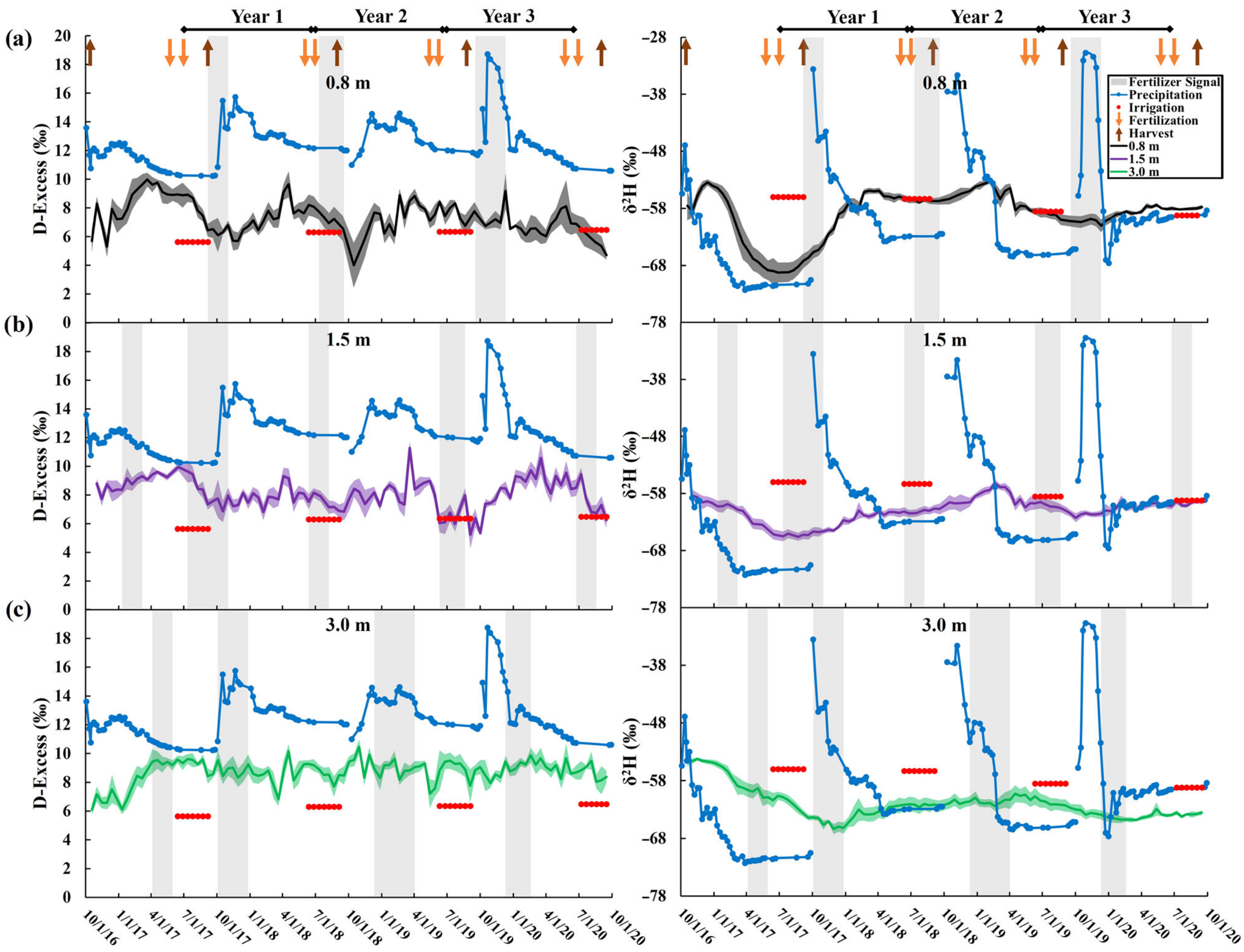

FIGURE 4 Fortnightly deuterium excess (d-excess) (left panel) and d^{2}H–H$_2$O (right panel) values measured in precipitation (blue dotted lines), irrigation (red dots), and soil lysimeter water (black, purple, and green lines) across the 4-year field study. Precipitation inputs (blue dotted lines) are the cumulative amount-weighted isotope values within a water year, while soil lysimeter water (black, purple, and green lines) represents mean values ($n = 6$ for each depth, except at the 0.8-m depth during the last fertilizer year, July 2019 to June 2020, when $n = 4$, since results from the two East-positioned lysimeters were removed). The three distinct soil depths are depicted from top to bottom: 0.8 m (black lines), 1.5 m (purple lines), and 3.0 m (green lines). Corresponding shaded colors around each line represent the standard error. Vertical gray boxes running throughout each panel, a–c, correspond to fertilizer signal periods. Orange "down" arrows signify fertilization dates, and brown "up" arrows signify crop harvest dates.

rains, further explaining its more mixed water signature. Precipitation over the three fertilizer years ranged from −66.4‰ to −60.3‰ (Figure 4c) and drove the movement of more concentrated nitrate to depth (as also evidenced by the peak in nitrate leaching fluxes [Figure 2d], coinciding with the timing of the fertilizer signal periods).

4 | DISCUSSION

Our findings illustrate distinct periods during which recently applied fertilizer can preferentially leach through the soil. The unique application of natural abundance stable isotopes of nitrate (δ^{15}N–NO$_3^-$), paired with a two-endmember isotopic mixing model, allowed us to distinguish these fertilizer signal periods (Figure 2) and further apportion the nitrate to either more recent fertilizer N applications or older, processed legacy soil N (Table 3). Outside of these distinct fertilizer signal periods, we cannot partition the N sources contributing to the nitrate flux (Figure 3). Nevertheless, these distinct periods with the fertilizer signal provide an initial insight into when recent fertilizer is moving within the soil profile, and which pools of N may be of most concern to groundwater contamination. Of the total N applied to the field averaged over the three fertilizer years, we estimate that 29% leached below 3.0 m, with 11% from recently applied fertilizer, while the remaining 18% was estimated to be from older, legacy N stored within the soil profile (Figure 5). Our estimate of fertilizer leaching was conservatively low because we assumed all nitrate fluxes outside the fertilizer signal periods were legacy N. This

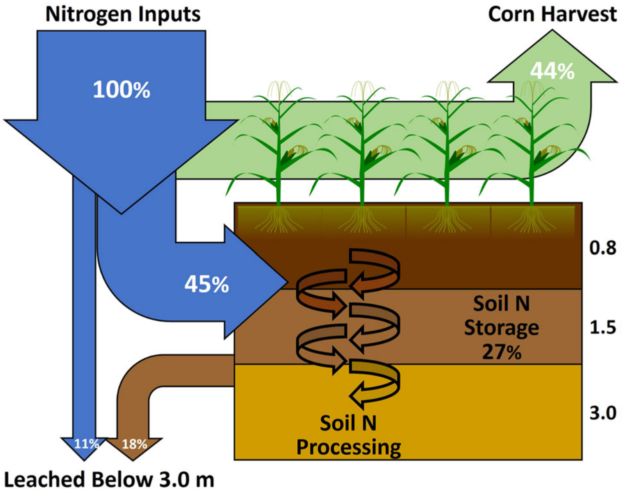

FIGURE 5 Fate of nitrogen inputs (i.e., fertilizer N + irrigation water N + atmospheric N deposition) at the field site. Fertilizer N was the largest input component (~80% of total N inputs) over the study period. Of the 29% that was leached below 3.0 m, ~11% was unaltered N fertilizer and ~18% was fertilizer N that processed through the vadose zone. Note that we apportioned all nitrate fluxes outside the fertilizer signal periods as legacy N that was stored and processed within the vadose zone (i.e., a portion of the soil N storage pool).

proportion of fertilizer inputs lost to groundwater is within the range of watershed export for agricultural areas within the nearby Calapooia River Basin (Lin et al., 2019), and a recent global review of ^{15}N tracer studies found a similar mean proportion of 30.5% of N applications unaccounted for in soils and corn crops in North American studies (Quan et al., 2021). Knowing when groundwater nitrate issues may be more linked to contemporary versus past practices could be important for assessing different management techniques without the possible confounding effects introduced by legacy N lag-times (Hamilton, 2012; Meals et al., 2010; Van Meter et al., 2016).

4.1 | Stable isotopes of δ^{15}N–NO_3^- and mixing models reveal sources of nitrate

Leaching studies that rely solely on tracking changes in nitrate concentrations over time cannot thoroughly assess the mechanisms controlling its movements. Nitrate isotopic data can help identify possible sources and/or transformations of N in the vadose zone (Böhlke & Denver, 1995; Kendall, 1998; Kendall & Aravena, 2000; Kendall et al., 2007; Kreitler, 1979; Mariotti et al., 1988; Pastén-Zapata et al., 2014). We found nitrate concentrations and leaching rates decreased with increasing soil depth (Figures 2 and 3), explored possible mechanisms that would explain this pattern, and concluded, via an N-budget approach in Weitzman et al. (2022) and this isotopic approach here, that the variation in leaching across depths and years was influenced most by the legacy N accumulation below the rooting zone.

Denitrification and ammonia volatilization can reduce nitrate leaching through the soil via the conversion of reactive N to gaseous forms. However, indications of such isotopically enriching processes were only found at the beginning of the study (Figure 2) with installation disturbance. Given the pH range of soil at the study site was near neutral, ammonia volatilization was likely not significant, as it tends to be promoted at pH >7 (Ernst & Massey, 1960; Fenn & Hossner, 1985; Martin & Chapman, 1951), suggesting denitrification played a bigger role during this installation time.

The extent of fractionation during mineralization (or ammonification) and nitrification, two soil processes that could explain the increase in nitrate concentrations and leaching we saw in our study, tends to be determined by the most rate-limiting step in the coupled transformation process (Kendall et al., 2007). The δ^{15}N–NO_3^- signatures of ammonium-based fertilizers and soil organic N overlap, making the contribution of nitrate from either pool challenging to resolve. Not surprisingly, previous studies have attributed decreases in δ^{15}N–NO_3^- values with increases in nitrate concentrations, like those identified here, as being due to nitrification stimulation following the application of ammonium-based fertilizers (Feigin et al., 1974) or ammonification of soil organic N followed by nitrification (Mengis et al., 2001; Sigler et al., 2022). At our study site, however, we propose that the times when nitrate concentrations increase but δ^{15}N–NO_3^- values decrease—what we call "fertilizer signal periods"—are a result of shifting of the primary source for nitrate from legacy N to mixing (Mayer et al., 2002) with newer, more isotopically depleted, fertilizer N.

Given neither nitrate concentrations nor N leaching rates were found to increase in Fertilizer Year 3, when application rates of ammonium-based fertilizer (as urea-N) were increased 25% above the calculated optimum based on a presidedress soil nitrate test, the field site was likely N limited. This suggests that any nitrification following fertilizer addition would have been complete and at such a rapid speed that net fractionation between pools would not be observed, and thus would not explain the decrease in δ^{15}N–NO_3^- values with increasing nitrate concentrations. Further supporting the idea that decreases in δ^{15}N–NO_3^- were caused by a source shift rather than fractionation changes in nitrification, the measured δ^{18}O–NO_3^- values remained steady during fertilizer signal periods (typically all below 0‰; Figure S1). They were also outside the range expected of nitrification processing in the system (+1.5‰ to +2.6‰) based on the assumption that oxygens from source water (δ^{18}O–H_2O; Figure S3) and atmospheric oxygen (δ^{18}O–O_2; assumed to be constant at +23.5‰) would be incorporated in a 2:1 ratio during nitrification (Amberger & Schmidt, 1987; Boshers et al., 2019; Snider et al., 2010; Veale et al., 2019). A change in nitrification fractionation would have shifted the isotopic values of $\delta^{18}O–NO_3^-$ closer to that of the soil water, but this was not the case. In addition, the timing of the fertilizer signal periods tended to occur shortly after fertilizer was applied to the fields, with the lag between application and appearance of the signal increasing with depth, as might be expected. These fertilizer signals generally occurred once a year, associated with N addition or with the onset of fall rains. This consistency across all years also increases our confidence that the identified signals are recently applied fertilizer moving through the vadose zone, with little processing, which is suggestive of a source change, rather than fractionation.

Moreover, values of $\delta^{15}N–NO_3^-$ in soil pore water were found to be the most negative at the deepest depth (Figure 2). This may appear to be counterintuitive to the notion that N deeper in the soil has undergone more transformations and therefore would be more enriched in $\delta^{15}N$ than material higher up in the soil profile. However, most studies have measured the $\delta^{15}N$ of soil organic matter (Baisden et al., 2002; Billy et al., 2010; Feigin et al., 1974; Nadelhoffer & Fry, 1988; Nadelhoffer et al., 1996), which is more representative of material that has undergone transformations, as opposed to soil pore water, which is what is actually moving through the vadose zone. When viewed in this light, our results strongly support the idea that fertilizer N is being flushed through the soil as nitrate, making its way to depth without further processing—thus, retaining its isotopically depleted $\delta^{15}N–NO_3^-$ signature.

As reasoned above, we present a conservative estimate concerning the amount of leached nitrate that can be attributable to recent N fertilizer flushing through the soil. We recognize that to properly measure the starting "effective" isotopic value of applied N fertilizer, one should collect samples following application, instead of simply measuring the average $\delta^{15}N$ of homogenized fertilizer (Kendall et al., 2007). Had we used such an approach, our estimated fertilizer end-member $\delta^{15}N$ value would have likely been higher (i.e., more enriched) due to rapid post-depositional N transformations. Those higher values would have led to a higher percentage of leached N being attributed to the fertilizer signal periods. We also did not try to account for any recent fertilizer outside of the periods when the fertilizer signals were easily identifiable, further suggesting that 11% of fertilizer applied to the field (Figure 5) is likely an underestimate of how much recent N fertilizer may be moving through the soil.

Older, legacy N appears to make up more of the leached nitrate in the upper soils during fertilizer flux periods; however, these periods had significantly less nitrate leaching compared to fluxes during other times at the 0.8-m depth (Table 3). This higher contribution of legacy N and higher variation between lysimeters in the upper layer contributed to our difficulty detecting significant trends when nitrate concentrations increased and $\delta^{15}N–NO_3^-$ decreased (Table 2). The fertilizer signal in the upper soils occurred during the growing season directly after fertilization, but the highest proportion of leaching occurred after harvest with the onset of rain. While there is likely some removal of recent fertilizer nitrate via microbial immobilization or root uptake near the soil surface, we suggest the reduction in nitrate leaching observed with depth was mostly from retention of processed, isotopically enriched N with higher $\delta^{15}N–NO_3^-$ between 0.8 and 3.0 m. This suggests that legacy N, regardless of form, is more readily released and bound within the bulk soil, leading to increased storage potential as it reaches the deeper soils. The upper soil layer showed the highest contribution of legacy N to fertilizer signal-driven leaching events, evidence that a portion of previously stored N may interact with the organic-rich bulk soil, leading to increased mineralization (i.e., remobilization) of older, legacy N. Cookson et al. (2000) found that N fertilizer could cause a priming effect, leading to increased mineralization of stored N and leaching outside the growing season. In contrast, newer fertilizer N inputs appear more likely to move through the vadose zone, ultimately being leached at higher proportions in the two deeper soil layers, making up ~64% and ~79% of the nitrate when we observe the fertilizer signal at 1.5 and 3.0 m, respectively (inferred from Table 3). When compared to remobilized legacy N, this suggests that N associated with recent fertilizer additions has a lower propensity for retention and thus is more available for immediate loss to the groundwater, possibly via preferential flow.

4.2 | Stable isotopes of $\delta^2H–H_2O$ reveal water flowpaths and the role of irrigation

When the water signatures of each depth were compared to the isotopic values measured in precipitation and irrigation water, a better understanding of the hydrology across the soil layers was captured. We cannot be certain whether the lysimeter water that was collected at each sampling site and time was drawn from the soil matrix or from a preferential flow path. However, we were most interested in the variability in the water isotopes of the soil water over time, which matches the variability we measured in the water isotopes of precipitation, and thus knowing which pool was sampled does not impact our line of interpretation. Water in the uppermost soil layer shows a strong irrigation signal, suggesting it plays an important role in transporting nitrate in recently applied fertilizer to the uppermost 0.8-m depth and the middle 1.5-m depth. During the growing season, transpiration and evaporation are taking place at the same time as irrigation. More transpiration during this time causes more loss of water at the soil surface, which is the management reason behind applying irrigation water to the field. Much of the applied irrigation water (only ~29% of the total water inputs to the field across the entirety of the field study) is thus likely evaporated or transpired by the planted crop, resulting in less irrigation water percolating to the deep soil, as corroborated by our results. Precipitation water, which is greatest during the fall and winter when plant roots are much less active, is thus more likely to move unimpeded to deeper depths (Brooks et al., 2010).

However, the delayed appearance of the fertilizer signal periods at the 0.8-m depth—from 1 to 2 months following N application—is likely due to more dynamic mixing of new fertilizer N inputs with more organic-rich topsoil and higher uptake by crop roots. Within the 1.5-m depth, on the other hand, fertilizer signal periods are evident within 1–2 weeks after the application of fertilizer N, potentially driven by preferential flow paths. The nitrate concentration for both the 0.8- and 1.5-m depths begin increasing around the same time, following new N additions, yet the shift in $\delta^{15}N–NO_3^-$ happens sooner at the 1.5-m depth, coinciding with the increase in nitrate—further evidence that preferential flow may impact water and recent fertilizer movement to the 1.5-m depth. In contrast to the upper two soil layers, large precipitation events in the fall and winter coincided with the fertilizer signal periods reaching the 3.0-m depth, likely causing newer nitrate additions to leach from the deepest depth through preferential pathways. Averaging across a range of crops in the southern Willamette Valley, most nitrate leaching occurred during the fall (60%) and winter (32%) (Compton et al., 2021). While legacy N was leaching through the 3.0-m depth, a greater proportion of the more recent fertilizer N was leached to this depth by the fall precipitation events, ultimately posing a more immediate threat to groundwater.

Interestingly, high temporal variability in the pore-water stable isotopes was only evident over the first year when over 1 m of isotopically depleted precipitation fell during the 2016–2017 winter. The lag in response to this precipitation varied with depth, with the upper layer responding the most in both magnitude and speed with only a 3- to 4-month lag from the precipitation. The pore water in the 1.5-m level showed a similar lag period, but the magnitude of the $\delta^2H–H_2O$ response was less. At the 3.0-m depth, the lag was nearly a year. However, after the first study year, $\delta^2H–H_2O$ values in soil pore water stayed relatively stable within each soil layer, yet decreased with depth (while d-excess increased). This indicates that irrigation water was the primary source to pore water for the shallower depths, while precipitation primarily influenced the deeper depths. Values of $\delta^2H–H_2O$ in local groundwater matched that of local precipitation with an average of −61.7‰ and d-excess of 8.4‰ during the study, suggesting it could possibly be influencing the $\delta^2H–H_2O$ values of the deepest depth (Hutchins et al., 2022). However, the average depth to the water table was 5.9 m and only approached the 3.0-m depth once during our experiment (on April 16, 2019) during extensive flooding of our study area by the Willamette River, after which the depth to the water table quickly returned to depths greater than 3.0 m. Interestingly, we saw no isotopic shift in any pore-water $\delta^2H–H_2O$ values following the flooding, event even though the Willamette River is isotopically depleted relative to the local precipitation and pore water measured during this experiment (averaging −76.5‰; Brooks et al., 2012). In addition, dynamics in the nitrate concentrations, δNO_3 values, and δH_2O values of the well water did not match that of the 3.0 lysimeters (Hutchins et al., 2022), so we concluded that groundwater (on average 3 m below the deepest lysimeter) was not a factor impacting the temporal patterns observed in this study.

4.3 | Minimal role of denitrification as a nitrate removal pathway

Dual stable isotopes of δNO_3^- in soil solution provided no evidence of denitrification as nitrate moves down through the soil at our field site after the initial installation disturbance period (Figure S2). The lack of a denitrification fractionation signal could possibly be due to the presence of hot spots and/or hot moments of denitrification (Harter et al., 2005; Weitzman, Groffman, et al., 2021), which completely consume nitrate, leaving no mass behind to impart a signal. However, this is unlikely at our study site where nitrate concentrations were always detectable in the lysimeter water. We previously found little isotopic evidence of denitrification in groundwater in a related study of 39 groundwater and drinking water wells in the Southern Willamette Valley Ground Water Management Area (SWV-GWMA) (Weitzman, Brooks, et al., 2021). And, while denitrification driven by hot spots and/or hot moments would not be easily identifiable with the use of stable isotopes, other studies provide corroborating evidence that such small area and brief periods of denitrification are largely absent in the region. For example, denitrification enzyme activity assays carried out on surface soils (0–15 cm) within the SWV-GWMA revealed low potential denitrification rates (Smith et al., 2018). These low rates suggest that denitrification is not a strong nitrate-loss pathway in the region due to microbial constraints (i.e., the activity of denitrifiers is low, even under optimal conditions), suggesting hot spots and hot moments of nitrate consumption are unlikely. These studies, along with the findings here from within the vadose zone of one site with high nitrate leaching, provide further evidence that denitrification is not an important process affecting nitrogen cycling in the agriculturally productive Willamette Valley of Oregon. Similarly, others have found a lack of evidence for isotope fractionation associated with denitrification in agricultural settings (Green et al., 2008; He et al., 2022; Spalding et al., 2019), questioning the reliance on denitrification to reduce nitrate loading to groundwater in some settings. More research may be needed to understand the factors influencing denitrification in vadose zone soils in regions with high nitrate leaching.

5 | CONCLUSIONS

Stable isotopes provide an effective means for better understanding the movement and processing of nitrate through the vadose zone. Our work shows that soil–water interactions (e.g., timing and spatial distribution; c.f. Brooks et al., 2010) drive vadose zone soil nitrate retention versus leaching. Specifically, we saw distinct annual signal periods that indicated that a portion of leached nitrate was from recent fertilizer applications. During these annual fertilizer signal periods, new additions of fertilizer N moved through the upper soil layers (0.8- and 1.5-m depths) via irrigation water during the growing season where it interacted with the bulk soil, potentially slowing immediate losses of nitrate. Given this, we were surprised to find periods of fertilizer N moving through the deep soil, especially since the average amount of nitrate leached during fertilizer events was similar across all three depths (average range 14–29 kg N·ha^{-1}·year^{-1}). Proportionally, however, newer fertilizer inputs made up the largest source to N leached during the fertilizer signal periods at the deepest depth (~52%), while contributing less than a fifth of the nitrate moving through the two shallower depths of 0.8 and 1.5 m (~13% and 16%, respectively), indicating a strong role for preferential flow to move recently applied fertilizer N from the surface to depth in soils. The findings here are especially valuable given nitrate leaching at the 3.0-m depth—deeper than most leaching studies include (Baram et al., 2016; Jankowski et al., 2018; Valkama et al., 2015)—was the one most influenced by the fertilizer-driven events, and with the lowest uncertainty. This residual fertilizer-associated N pushed to depth by fall and winter precipitation ultimately poses a more immediate threat to groundwater. In addition, denitrification was not evident across the soil depths, indicating that denitrification will not be an important pathway for reducing nitrate loading to groundwater. These results have important implications in terms of management, especially for local growers. Ultimately, improved nutrient management to avoid such fertilizer loss through the optimization of the amount and timing of fertilizer N additions might allow growers to improve crop N uptake and reduce deep soil leaching.

AUTHOR CONTRIBUTIONS

Julie N. Weitzman: Data curation; formal analysis; investigation; methodology; validation; visualization; writing—original draft; writing—review and editing. **J. Renée Brooks**: Conceptualization; data curation; funding acquisition; methodology; project administration; resources; supervision; validation; visualization; writing—review and editing. **Jana E. Compton**: Conceptualization; funding acquisition; methodology; project administration; resources; supervision; writing—review and editing. **Barton R. Faulkner**: Conceptualization; formal analysis; methodology; software; validation. **R. Edward Peachey**: Conceptualization; methodology; resources. **William D. Rugh**: Methodology; resources; supervision; validation. **Robert A. Coulombe**: Data curation; investigation; methodology; project administration. **Blake Hatteberg**: Data curation; investigation; methodology. **Stephen R. Hutchins**: Conceptualization; data curation; funding acquisition; investigation; methodology; project administration; resources; supervision; validation.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data associated with this study are openly available at https://doi.org/10.23719/1529554 and can be cited as

Weitzman et al. (2024), which is detailed in the reference list below.

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