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Nitrate–nitrogen and oxygen isotope ratios for identification of nitrate sources and dominant nitrogen cycle processes in a tile-drained dryland agricultural field

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ABSTRACT

Agricultural systems are a leading source of reactive nitrogen to aquatic and atmospheric ecosystems. In this study environmental $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ are used to identify the dominant nitrogen cycle processes and sources of NO_3^- leached from a tile-drained, dryland agricultural field. Tile-drain water discharge $\delta^{18}O_{nitrate}$ values suggest nitrification is the dominant soil nitrogen cycle process throughout the 5-year study period, because the expected $\delta^{18}O_{nitrate}$ from nitrification is indistinguishable from the measured value of $-1.3 \pm 1.5‰$. Given this there is no evidence that denitrification was occurring at a large enough scale to influence [NO_3^-]. Values for $\delta^{15}N_{nitrate}$ varied seasonally during the high-discharge season (January through May) and low-discharge season (June through December) with weighted means of $1.0 \pm 1.0‰$ and $4.7 \pm 2.3‰$ respectively. This suggests that during the high-discharge season NO_3^- originates from nitrification of NH_4^+ fertilizer, and during the low-discharge season NO_3^- originates from mineralized soil organic nitrogen. The estimated travel time through the soil for nitrified NH_4^+ fertilizer leached during the high-discharge season is less than 6 months, from fall fertilizer application to leaching through the tile-drain. This study suggests that understanding the hydrology of a region is necessary before dominant nitrogen cycling processes can be reliably determined.

1. Introduction

Nitrogen fertilizer leads to excess reactive nitrogen stimulating nitrogen cycle processes that transform and potentially release nitrogen from agricultural systems (Cey et al., 1999; Karr et al., 2001; Munoz et al., 2003; Deutsch et al., 2005). Processes of particular concern are nitrification and denitrification because of their potential to produce the greenhouse gases nitrous oxide (N_2O) and nitric oxide (NO), as well as controlling the abundances of ammonium (NH_4^+) and nitrate (NO_3^-) available for leaching to surface and groundwater systems. Most studies in agricultural systems account for nitrogen loss through nitrification and denitrification by assuming the rates are similar to previous field studies (Smith et al., 2000; Munoz et al., 2003; Ross et al., 2008) or that the rates are insignificant at the scale of the study (Soon and Clayton, 2003). Assumed rates can lead to misunderstanding of actual nitrogen cycle processes and pathways for nitrogen loss.

Developing a better understanding of nitrogen cycle processes and storage rates will lead to more precise nitrogen budgets and more efficient nitrogen management practices. The first step to achieve an accurate understanding of field-scale nitrogen cycling is to improve the understanding of nitrification and denitrification at these scales. In a dryland setting with strongly seasonal precipitation and temperature cycles, transitions between nitrification and denitrification regimes may be influenced by soil-vadose hydrologic dynamics. Prior to winter precipitation and the development of saturation, aerated profiles may promote nitrification. Later, saturated profiles may promote denitrification. These interactions of hydrologic and soil-biochemical processes could strongly affect the timing and rates of leaching losses of N as NO_3^-. Here we use nitrogen and oxygen isotopic compositions of NO_3^- to determine the seasonal timing of nitrification and denitrification, and how these processes influence the sources and fluxes of NO_3^- leached from a dryland agricultural field.

Natural abundance of N & O isotope ratios in NO_3^- ($\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$) have been shown to be useful tools to identify the sources of NO_3^- and dominant nitrogen cycle processes (Kendall et al., 1995; Lake et al., 2001; Robinson, 2001; Chang et al., 2002;

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McKinney et al., 2002; Vander Zaden et al., 2005; Kendall et al., 2007; Wankel et al., 2007; Wankel et al., 2009). Nitrate deposited in precipitation has $\delta^{18}O_{nitrate}$ values from +23‰ to +75‰ and $\delta^{15}N_{nitrate}$ values from −15‰ to +15‰ (Durka et al., 1994; Kendall et al., 1995; Oelmann et al., 2007). Nitrate originating from synthetic NH_4^+ fertilizer and mineralized soil organic nitrogen has $\delta^{18}O_{nitrate}$ values from −10‰ to +10‰ (Durka et al., 1994; Kendall et al., 1995), and $\delta^{15}N_{nitrate}$ values from −1.7‰ to +3.9‰ and +2‰ to +10‰; respectively (Vitoria et al., 2004; Kendall et al., 2007; Oelmann et al., 2007). Synthetic NO_3^- fertilizer $\delta^{18}O_{nitrate}$ ranges from +18‰ to +22‰ and $\delta^{15}N_{nitrate}$ from −1.7‰ to +3.9‰, similar to $\delta^{15}N_{nitrate}$ of nitrified NH_4^+ fertilizer (Vitoria et al., 2004; Kendall et al., 2007; Oelmann et al., 2007).

Dominant nitrogen cycle processes can also be distinguished through changes in NO_3^- concentration ($[NO_3^-]$) and $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$. Denitrification results in a fractionation ratio for $\delta^{15}N_{nitrate}$:$\delta^{18}O_{nitrate}$ of 1:1 to 2.1:1 while also decreasing $[NO_3^-]$ (Cey et al., 1999; Durka et al., 1994; Kendall et al., 1995; Davis et al., 2008). Nitrification does not discriminate against ^{18}O isotopes, so the $\delta^{18}O_{nitrate}$ is a combination of the ratios of $\delta^{18}O_{water}$ and $\delta^{18}O_{atmospheric\ O_2}$ (Kumar et al., 1983; Hollocher, 1984; Durka et al., 1994; Kendall et al., 1995).

The objectives of this study were to use $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ to identify the roles of nitrification and denitrification in NO_3^- production/consumption in a 12 ha field catchment, and to identify the source(s) of NO_3^- leached from this catchment via a tile drain. This study was conducted to test the following hypotheses: 1) the dominant source of nitrate in tile-drain discharge is synthetic nitrogen fertilizer applied in the fall prior to the onset of the precipitation season, 2) the dominant nitrogen cycle process during the low-discharge season (June through December) is nitrification, 3) the dominant nitrogen cycle process during the high-discharge season (January through May) is denitrification.

2. Methods and analysis

2.1. Study site

Research was conducted at the 12 ha tile-drained section (TD-12) of the Washington State University Cook Agronomy Farm (CAF) in the semiarid Palouse Basin of eastern Washington and northern Idaho (46°46′44″ N, 117°05′19″ W). Annual precipitation is 310–580 mm yr^{-1} with the majority occurring during the winter (Donaldson, 1980). Previous hydrologic investigations at the CAF and in the larger Missouri Flat Creek Watershed have shown that winter precipitation stimulated water movement in the soil at CAF and winter precipitation is the source water of stream flow for the Missouri Flat Creek Watershed throughout the year (Keller et al., 2008; Moravec et al., 2010). Mean annual temperatures range from a mean summer high of 27 °C to a mean winter low of −7 °C (Geyer et al., 1992). The topography consists of rolling hills with up to 30 m of relief in loess deposits that overly Columbia River Basalt flows (Treasher, 1925). The soils are silt loam Mollisols that are mapped as part of the Palouse–Thatuna Association soil series (USDA, 1978). The Cook Agronomy Farm is within the Missouri Flat Creek Watershed, which has a land use of >95% dryland agriculture with the remaining land use being residential farmhouses, horse pasture, and a gravel pit. Crops grown at the CAF consist of a rotation between winter wheat, spring wheat, and chickpeas. Fertilization rates at CAF range from 123 kg N ha^{-1} yr^{-1} to 215 kg N ha^{-1} yr^{-1} (Keller et al., 2008). The nitrogen is currently applied as an ammonium–nitrate–urea blend. Fertilization for the winter wheat occurs during the fall, and in the spring for the spring wheat and chickpeas. Soil organic nitrogen mineralization rates in the Palouse Region are reported to range from 4.5 kg N ha^{-1} yr^{-1} to 110 kg N ha^{-1} yr^{-1} (Fiez et al., 1994).

2.2. Sample collection

Samples were collected from the TD-12 outlet (April 2005–April 2010) and from a precipitation catch (April 2006–April 2010) above the TD-12 outlet in Nalgene® bottles that were previously acid washed with 10% HCl and rinsed three times each with deionized water and ultra-pure deionized water. TD-12 event samples were collected in 250 mL bottles at ~1 week intervals during the high-discharge season (January–May) and at 2–3 week intervals during the low-discharge season (June–December). Precipitation samples were collected in a 1000 mL bottle draining a tipping-bucket precipitation collector at the southwest corner of CAF. The tipping bucket was mounted on a post, with its top ~1 m above the soil surface and ~5 m from the TD-12 outlet. Precipitation samples were collected after the bottle had accumulated at least 100 mL of water, which could take <1 week during the winter and up to ~3 weeks during the summer. The longer sampling intervals during the summer occurred because of long periods without precipitation. The precipitation catch was kept as clean as possible and samples were collected after events to limit biological activity in the precipitation catch. TD-12 discharge was measured with a 1 L bucket (during low flow) or 18 L bucket (during high flow) and stopwatch to determine flow rates out of the tile-drain system. After collection, samples were stored in a cooler on ice and brought back to the Washington State University School of the Environment Vadose and Groundwater Hydrology Laboratory, the same day. Aliquots were vacuum filtered through 0.45 μm cellulose nitrate membrane filters; filtration was typically within 24 h and never exceeded 48 h. Field blanks of ultra pure deionized water were also filtered alongside samples and analyses for $[NO_3^-]$; field blank $[NO_3^-]$ never exceeded the detection limits. Samples not filtered the same day were stored in a refrigerator until filtration. After filtration two sample aliquots were stored in 25 mL Nalgene® bottles with foil lined caps and frozen until analysis for $[NO_3^-]$ and ^{15}N and ^{18}O isotopic composition of NO_3^-.

2.3. Chemical and isotope analysis

Samples were analyzed for $[NO_3^-]$ by Washington State University United States Department of Agriculture-Agricultural Research Service Laboratory (WSU USDA-ARS) by continuous flow analysis with Model RFA300, Alpkem/OI Analytical and were reported as mg N L^{-1}.

Nitrate $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ were measured using the denitrifier method of Sigman et al. (2001) and Casciotti et al. (2002), with the bacterial strain *Pseudomonas choloraphis subs. aureofacies* (ATCC no. 13985) at the Washington State University Stable Isotope Core Laboratory. Samples were injected into 20 mL glass vials that were previously inoculated with 2 mL of condensed bacterial cultures in growth media, and then purged with N_2 to achieve anoxic conditions. Samples were then incubated overnight to ensure the entire sample NO_3^- was converted to N_2O. Prior to analysis samples were injected with 10 N NaOH to lyse cell walls releasing trapped N_2O. $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ of the produced N_2O were then measured on a Thermo Finnigan Delta Plus XP mass spectrometer with a Thermo Finnigan Gas Bench II (Bremen, Germany) connected to a GC Pal (CTC Analytics, Zwingen, Switzerland) auto sampler using He as a carrier gas. The original Gas Bench II was modified slightly to include an initial dry ice + ethanol water trap and Ascarite + magnesium perchlorate trap to scrub CO_2 from the mixture. The sampling needle was