

Mineral Fertilizer and Manure Effects on Leached Inorganic Nitrogen, Nitrate Isotopic Composition, Phosphorus, and Dissolved Organic Carbon under Furrow Irrigation

R. D. Lentz* and G. A. Lehrs

Abstract

A better understanding of nutrient leaching in furrow irrigated agriculture is needed to optimize fertilizer use and avoid contamination of water supplies. In this field study (2003–2006), we measured deep percolation fluxes at 1.2-m depth and associated nutrient concentrations and mass losses from dairy manure nitrogen (N) or mineral N (urea, sodium nitrate [NaNO_3])–amended soils (372 kg available N ha^{-1} in 4 yr) and nonamended controls and determined the $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ isotope ratios in the leached nitrate. Flow-weighted concentration means for individual irrigations varied widely, from near zero to as much as 250 mg L^{-1} for $\text{NO}_3\text{-N}$, 480 $\mu\text{g L}^{-1}$ for dissolved reactive phosphorus (DRP), 43 mg L^{-1} for dissolved organic C (DOC), and 390 mg L^{-1} for chloride (Cl). Relative to other treatments, mineral fertilizer increased $\text{NO}_3\text{-N}$ concentrations 2.6- to 3-fold and Cl concentrations 2.6- to 3.6-fold in deep leachate, particularly when NaNO_3 was applied in 2004 and 2006, and produced maximum mean season-long $\text{NO}_3\text{-N}$ and Cl losses. Manure and control treatments produced similar leachate nutrient mass losses, and for some irrigation periods, mineral fertilizer produced 85 and 97% lesser DRP losses and two times greater Cl losses compared with manure and control treatments. Four-year cumulative losses among treatments differed only for Cl. Isotopic composition of deep-leached nitrate indicates that both transformation and biologic cycling of mineral and manure N are rapid in these soils, which, with percolation volume, influence the amounts of $\text{NO}_3\text{-N}$ and DOC leached. In light of the potential negative effects associated with either fertilizer type, and because even nonamended soils produced substantial amounts of leached $\text{NO}_3\text{-N}$ (69.5 kg $\text{ha}^{-1} \text{yr}^{-1}$), management must minimize percolation water losses to limit nutrient losses from these fertilized, furrow-irrigated soils.

Core Ideas

- Nutrient losses were more correlated with percolation water volume than nutrient concentration.
- Adsorption, precipitation, and cycling of manure nutrients limit their losses below 1.2-m depth.
- To limit nutrient losses in furrow irrigated soils, percolation water losses must be reduced.

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ON AVERAGE, only 40% of nitrogen (N) applied to the world's crops is incorporated into the harvested products. This low N use efficiency (NUE) produces excess soil reactive N, which, on leaching from soil as nitrate or escaping as a nitrogenous gas, adversely affects environmental and human health (Zhang et al., 2015). To remain sustainable and meet future global food needs, which are estimated to double between 2005 and 2050 (Tilman et al., 2011), agriculture must optimize NUE (Townsend and Howarth, 2010; Zhang et al., 2015).

Increasing fertilizer costs and the rapid growth of a regional dairy industry have resulted in increased dairy manure applications to farmlands in south-central Idaho (Lentz et al., 2018). Furrow irrigation can produce greater runoff, erosion, deep percolation, and associated nutrient losses compared with sprinklers (Flury et al., 1994; Ren et al., 1996; Wang et al., 1997; Al-Jamal et al., 2001; Spalding et al., 2001; Mack et al., 2005). Although furrow irrigation is increasingly being replaced by sprinkler irrigation there, nitrate concentrations in shallow groundwater in the region continue to increase (Lentz et al., 2018). Annual nitrate leaching losses from corn (*Zea mays* L.) crops in nonirrigated fields in Pennsylvania averaged 65 kg $\text{ha}^{-1} \text{yr}^{-1}$ (Toth et al., 2006), whereas those in furrow-irrigated corn in southern Idaho were reported to be 120 kg $\text{ha}^{-1} \text{yr}^{-1}$ (Lentz et al., 2001a).

Research comparing the influence of synthetic fertilizer and manure on nitrate leaching from amended soils has produced mixed results. In humid climates, dairy or poultry (liquid or solid) manure applications were reported to have either no effect or to increase N leaching relative to that of synthetic fertilizer applications (Bergström and Kirchmann, 1999; Ulén, 1999; Goulding et al., 2000; van Es et al., 2006; Toth et al., 2006). Conversely, when composted manure was applied in a number of US and international studies, nitrate N losses were reduced relative to those of synthetic fertilizer treatments (Leclerc et al., 1995; Maeda et al., 2003; Easton and Petrovic, 2004; Fan et al., 2017). Few mineral-versus-manure amendment comparisons have been reported for calcareous mediterranean or semiarid soils, particularly under furrow or other types of surface irrigation. A lysimeter study applied pig slurry or NH_4NO_3 treatments in spring with irrigation (Daudén et al., 2004). Nitrate loads in

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Abbreviations: DOC, dissolved organic carbon; DRP, dissolved reactive phosphorus; NUE, nitrogen use efficiency; VSMOW, Vienna Standard Mean Ocean Water.

drainage water of the NH_4NO_3 treatment exceeded those of the equivalent pig slurry treatment (Daudén et al., 2004). When the experiment was repeated in a surface-irrigated field, leached nitrate loads between equivalent NH_4NO_3 and pig slurry treatments did not differ (Daudén and Quilez, 2004). A more thorough understanding of mineral fertilizer and manure effects on nutrient leaching under furrow-irrigated crops is needed to better manage NUE for irrigated agriculture.

The amount and stable isotopic composition of the water ($^{18}\text{O}\text{-H}_2\text{O}$ and $^2\text{H}\text{-H}_2\text{O}$) and nitrate ($^{15}\text{N}\text{-NO}_3$ and $^{18}\text{O}\text{-NO}_3$) that leaches below the soil root zone can provide useful information about soil transport processes and potentially identify the source of the nitrate's N or the biogeochemical transformations influencing the added N (Kendall, 1998; Kellman and Hillaire-Marcel, 2003; Gazis and Feng, 2004; Rock et al., 2011; Elisante and Muzuka, 2016).

The objectives of this research were to measure deep percolation fluxes, nutrient concentrations, and nitrate isotope ratios beneath soils amended with dairy manure, with mineral N fertilizer, or without either. We hypothesized (i) that both amendments would lead to increased nitrate leaching relative to the unamended soil; (ii) that because of the P, organic C, and Cl included in the organic fertilizer, manure would increase deep leaching losses of these dissolved constituents relative to the other two treatments; and (iii) that effective, rapid solute leaching and bypass flow in soil under furrow irrigation would transport nitrate with an unaltered source isotopic signature to 1.2-m depth.

Materials and Methods

The experiment was part of an overarching study that also examined nutrient losses in runoff from furrow irrigation. The layout of the experiment, including a description of the cropping history, field operations, and irrigation procedures, was described in detail in an earlier paper (Lentz and Lehrs, 2010). In brief, experimental plots were established in fall 2002 on Portneuf silt loam (coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid) with 1.5% slopes near Kimberly, ID (42°31' N, 114° 22' W; elevation 1198 m). This area is within the Twin Falls Canal Company Irrigation Tract. The tract includes a system of tunnels and relief well and tile networks installed to alleviate localized high water tables caused by irrigation (Lentz et al., 2018). Portneuf is a deep soil formed

in silt loam and very fine sandy loam sediments. The surface soil is a silt loam, with 10 to 13 g kg^{-1} organic C, 5% calcium carbonate equivalent, and a pH of 7.7 (saturated paste). We aligned the experimental plots with previously installed soil water percolation samplers (Lentz et al., 2008). Plots were planted to silage corn in the first (2003) and second growing seasons and to barley (*Hordeum vulgare* L.) in the third and fourth growing seasons.

Experimental Design and Plots

The experimental design was a randomized complete block with three replicates. The three treatments included (i) dairy manure applied at locally typical rates (13 Mg ha^{-1} dry wt. in October 2002 and 34 Mg ha^{-1} dry wt. in March 2004), (ii) conventional mineral fertilizer, applied at a rate matching the N available from the manure amendment, and (iii) control (no amendments). The manure had been scraped from open pens and stockpiled and stored in uncovered, unconfined piles through the summer. Because of the large volume required, mixing the manure to make its composition uniform was not feasible. In light of this, and given the inherent variability in manure composition, we applied the manure based on its estimated available N, assuming that manure included 1.5% N, of which 40% was available in the subsequent growing season. Four to six samples of manure were collected from each block, composited, and the three composited samples frozen for later analysis. Manure composition and manure and mineral fertilizer applications are described in detail in Table 1.

Each experimental unit (i.e., plot) was 4 m wide by 57 m long and was separated from adjacent plots by a 1.3-m-wide buffer strip. Each plot included five planted rows of corn and four irrigation furrows (0.76-m spacing). Every other furrow was watered in a typical irrigation. During periods of exceptionally high evapotranspiration, however, all furrows were watered to maintain adequate soil moisture. The buffer strip included one irrigated furrow. We normally monitored and sampled runoff water from one furrow in each plot (see later discussion). However, on days when all four furrows per plot were irrigated, two furrows in each plot were monitored and the measurements taken were arithmetically averaged.

Individual plots were instrumented with three circular, continuous extraction soil water samplers, each of which collected percolation through an area of 314 cm^2 , placed at a depth of

Table 1. Crop grown and carbon, nitrogen, and phosphorus applied in manure and mineral fertilizer treatments in each of the 4 yr. No manure was applied in 2005 or 2006, but residual N mineralized from earlier applications was presumed available.

Year	Crop	Manure composition (total concentrations)					Date applied	Amounts applied in manure treatment				Amounts applied in mineral fertilizer treatment				
		Solids	C	N	P	C:N ratio		Bulk application rate	Total C	Total N	Total P	Estimated available N	Date applied	Form	C	N
		kg kg^{-1}	g kg^{-1}				Mg ha^{-1} (dry wt.)	kg ha^{-1}				kg ha^{-1}				
2003	Corn	0.56	302	18.6	7.8	16.2	10 Oct. 2002	13	3.92	242	102	78†	6 May 2003	Urea	34	78
2004	Corn	0.40	160	10.0	3.8	16.0	24 Mar. 2004	34	5.44	340	129	204†	12 May 2004	NaNO_3	–	195
2005	Barley	–	–	–	–	–	–	0	–	–	–	51‡	–	–	–	0
2006	Barley	–	–	–	–	–	–	0	–	–	–	33‡§	3 May 2006	NaNO_3	–	104

† Prior to total C, N analysis of manure samples, available N was estimated assuming bulk dry manure comprised 1.5% N, of which 40% was available in the subsequent growing season (A. Leytem, personal communication, 2003).

‡ Estimated N derived from residual mineralization of 2002 (fall) and 2004 (spring) manure applications (see Lentz and Lehrs, 2012).

§ Spring soil N in 0- to 60-cm soil layer provided 87 kg N ha^{-1} , in addition to the 33 kg N ha^{-1} mineralized from residual manure.

1.2 m, directly below one of the monitored furrows in each plot (Lentz and Kincaid, 2003). Each plot's three soil water samplers were spaced approximately 0.7 m apart and were located approximately midway down the furrow length, a location that receives near-average infiltrated irrigation water. Samplers were installed such that an undisturbed column of soil extended from within the sampler, through its open top, and up to the soil surface (Lentz and Kincaid, 2003). Thus, water flowing down macropores present in the undisturbed soil would be collected in the sampler, as would matrix-pore flow. The sampler's collection surface was horizontally oriented and subject to a continuous vacuum. The vacuum was adjusted for in situ soil matric potential to maintain parallel, vertical flow lines in the soil above and adjacent to the sampler. This design, which produced valid measures of soil water flux rates and leachate solute concentrations under continuous extraction, was described previously (Lentz and Kincaid, 2003; Lentz, 2006; Lentz and Lehrs, 2014), along with details of the vacuum extraction system and field installation.

Field Operations

After silage corn harvest in the fall of 2002, dairy cattle (*Bos* species) manure that had been stockpiled during summer was applied and immediately incorporated with a disk plow to 0.1-m depth in designated plots (Table 1). On 6 May 2003, urea fertilizer was applied with a drop spreader on designated plots and incorporated with a roller harrow. Silage corn was planted in 0.76-m rows on 15 May 2003, and V-shaped, 0.1-m-deep furrows were formed on 0.76-m centers as an integral part of the planting operation. After silage harvest in mid-September, the remaining corn stover (15- to 30-cm-tall stems with leaves) was incorporated by disking to 0.1 m. On 24 Mar. 2004, manure was again applied and incorporated into designated plots. The manure application rate was increased in 2004 (i) because we expected that the spring manure would contain less solids and have a higher C:N ratio (due to higher straw content) than the fall manure, and (ii) because the fall 2002 manure application was in the lower range of that typical for the area. Sodium nitrate fertilizer was applied on 12 May 2004 with a drop spreader to fertilizer plots (to match estimated N available from manure application) and incorporated using a roller harrow. The NaNO₃ fertilizer was derived from a Chilean source and had a unique nitrate isotopic signature ($\delta^{18}\text{O}-\text{NO}_3^- = 55\text{‰}$), which we used to track nitrate sources and leaching in the soils. Silage corn was planted on 13 May. Other field operations were the same in 2004 as in 2003. Standing corn silage yields were measured in both years from a mid-field location in each plot. Remaining corn was harvested for grain, and the standing residue was whipped and left on the plots.

To assess the residual influence of amendments on percolation losses, neither manure nor mineral fertilizer was applied for the 2005 growing season. Barley was planted in 0.07-m rows on 21 Mar. 2005, and furrows on 0.76-m centers were cut on 6 Apr. 2005. Barley was harvested on 8 Aug. 2005, and straw residue was burned. In 2006, only soils in fertilizer plots received amendments. Sodium nitrate was applied to designated fertilizer plots on 3 May 2006 (Table 1). Barley was planted on 21 Apr. 2006 and harvested 8 Aug. 2006.

Irrigation

The Snake River water used for irrigation had an average electrical conductivity of 0.04 S m⁻¹, had a sodium adsorption ratio of 0.6, and carried little sediment (<500 mg suspended solids L⁻¹). Seven 24-h irrigations on 14-d intervals were applied to plots each year beginning on 10 June 2003 and 15 June 2004. The barley crop received three irrigations in 2005 and two irrigations in 2006. We measured furrow inflow and runoff rates and runoff sediment concentrations during each irrigation. Inflows were metered into furrows under constant hydrostatic pressure, and flows were checked by measuring the time to fill a known volume. Outflow was measured using long-throated V-notch flumes. Sediment in runoff was measured by determining the volume of sediment that settled in a 1-L Imhoff cone in 0.5 h. Details of the protocol and calculations were reported in a previous paper (Lentz and Lehrs, 2010).

Sample Collection

During the irrigation season, percolation water volumes were measured and collected every 1 to 3 d, depending on sampler inflow rates. Water samples from each sampler in each plot were composited after collection and stored at 4°C. Percolation water collected from samplers contained no particulates. At the end of each week, or on the day before the next irrigation a 150-mL volume was collected from the thoroughly mixed composite. Of the sediment-free, 150-mL water sample, 20 mL was frozen in a scintillation vial for nitrate ¹⁵N and ¹⁸O isotope analysis and a 30 mL-portion was stored at 4°C for deuterium (²H) and ¹⁸O isotope analysis. The remainder was stabilized with a saturated H₃BO₃ solution (1 mL per 100 mL of sample) and stored at 4°C until analyzed. In addition, irrigation water inflows were sampled at 2- to 4-wk intervals during the growing season each year. These were analyzed in like manner to percolation samples.

Urea and NaNO₃ Effect on Stable Isotope Composition of Nitrate in Surface Soil

We amended Portneuf soil (0–15 cm) with urea, incubated the soil at 22°C for 48 h, and then measured the stable-isotope composition of soil nitrate. The incubation and extraction procedure used was that of Lentz and Lehrs's end-member-analysis (see Supplemental Material for more information), except that urea was applied at 5.6 kg N ha⁻¹ and the incubation time was 48 h. In addition, soil samples (0–15 cm) from the NaNO₃-amended field plots were collected 3 wk after the fertilizer was applied in 2004 and soil nitrate was extracted (50 g soil with 200 mL reverse-osmosis water was mixed on a reciprocating shaker for 30 min, followed by filtration [0.45 μm]). Nitrate solutions were analyzed for stable isotope composition as indicated below.

Sample Analysis

An automatic, colorimetric flow injection analyzer (Lachat Instruments) determined NO₃-N using cadmium reduction of NO₃ to NO₂ (QuikChem Method 10-107-04-1A) and Cl using the ferricyanide method (QuikChem Method 10-117-07-1-B; Lachat Instruments). The dissolved reactive phosphorus (DRP) in the samples was determined colorimetrically using the ascorbic acid method (Kuo, 1996, p. 908–909). The dissolved organic C (DOC; as nonpurgeable organic C) of water samples

was determined using a Shimadzu TOC-5050A (Shimadzu Scientific Instruments). The minimum detection limit was 10 $\mu\text{g L}^{-1}$ for $\text{NO}_3\text{-N}$ and DRP, 0.8 mg L^{-1} for Cl, and 50 $\mu\text{g L}^{-1}$ for DOC. Water samples were analyzed for $\text{NH}_4\text{-N}$, but as their mass losses were only 0.23% of those of $\text{NO}_3\text{-N}$, the $\text{NH}_4\text{-N}$ data were not reported.

Water samples were shipped frozen on dry ice to the Marine Chemistry and Geochemistry Laboratory at Woods Hole Oceanographic Institution (Woods Hole, MA) for nitrate isotope analysis. The laboratory used the microbial denitrifier method (McIlvin and Casciotti, 2011) and gas-source isotope ratio mass spectrometry (Finnigan Delta^{PLUS} XP) to measure $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ (Eq. [1] and [2]), where provisional standards reference atmospheric N_2 (AIR) scale for $\delta^{15}\text{N}$ and Vienna Standard Mean Ocean Water (VSMOW) scale for $\delta^{18}\text{O}$. Because the computed ratio is small, the value is multiplied by 1000 and reported in per mil (‰) units (Eq. [1] and [2]):

$$\delta^{15}\text{N-NO}_3 (\text{‰}) = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{AIR}}} - 1 \right] \times 1000 \quad [1]$$

$$\delta^{18}\text{O-NO}_3 (\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} - 1 \right] \times 1000 \quad [2]$$

where N and O are derived from the nitrate in the water. Measurement precision is 0.1 to 0.2‰ for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (McIlvin and Casciotti, 2011).

Samples were sent to the University of Arizona Environmental Isotope Laboratory, where they were analyzed for $\delta^{18}\text{O}$ in H_2O using a gas-source isotope ratio mass spectrometer (Finnigan Delta S). For oxygen, samples were equilibrated with CO_2 gas at approximately 15°C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW and Standard Light Antarctic Precipitation (SLAP):

$$\delta^{18}\text{O-H}_2\text{O} (\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} - 1 \right] \times 1000 \quad [3]$$

where O is derived from the sample water. Precision is 0.08‰ or better for $\delta^{18}\text{O}$ on the basis of repeated internal standards.

Due to expense, only a subset of all water samples was selected for isotope analysis. Approximately 110 of 222 inflow and percolation water samples in 2003 to 2005 were analyzed for nitrate isotopes ($\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$), and 74 of the 198 2003 and 2004 samples were analyzed for the water isotope ($\delta^{18}\text{O-H}_2\text{O}$).

Calculations and Statistical Analysis

Percolation and mass loss values were calculated as the arithmetic mean of the three samplers in each plot. Since irrigations were spaced 2 wk apart, the cumulative percolation and mass loss responses for a given irrigation were those that occurred in the following 14-d period. When calculating whole-field losses for components in percolation water, we assumed that the intercepted water at the sampler depth was representative of that in the entire field. Due to similarities in the pattern of results among irrigations and to reduce variability, responses in 2003 and 2004 were also grouped into four periods: (i) the first irrigation, (ii) early (irrigations 2 and 3), (iii) middle (irrigations 4 and 5), and (iv) late (irrigations 6 and 7).

Irrigation flow (nontransformed) and percolation water losses were examined using an analysis of variance (ANOVA)

repeated measures approach (PROC MIXED; SAS Institute, 2012), which accounted for correlations between a response variable's values measured in consecutive irrigations. The model included treatment, year, and irrigation as fixed effects and block with its associated interactions as random effects. Percolation constituent concentrations and mass losses were examined using the above ANOVA model with year, treatment, and irrigation (or period) as fixed effects. We also included a more powerful single-degree-of-freedom orthogonal contrast, which compared control and manure treatments as a group versus mineral fertilizer for each year and irrigation period (or irrigation for 2005–2006). Where needed, percolation volume and constituent concentration and mass loss responses were transformed using common log or square root to stabilize variances and improve normality. Means and 95% confidence intervals were back transformed to original units for reporting.

The influences of treatment on season-long percolation water and component mass losses were analyzed using an ANOVA model that included treatment as the fixed effect and year as the random effect, where responses were computed as across-block means. Analyses of season-long cumulative values did not require transformation of responses.

Percolation water concentrations were reported as flow-weighted means for each irrigation period; that is, mass losses from each percolation sampler were summed across sample periods within an irrigation, then divided by cumulative irrigation volume, and the plot response was the mean of the three collection flasks. Some plots produced no percolation in a given irrigation and were not included in the statistical analysis. Thus, treatment effects for some irrigations were not assessed because the data did not include full replication.

To analyze $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ composition in percolation water, we conducted an ANOVA using PROC MIXED (SAS Institute, 2012), where the treatment response variable was the mean for each block, with year and treatment as fixed effects and block as the random effect. A significance probability (*P*) of 0.10 was used in all the statistical analyses.

The position, alignment, and variance associated with percolation water $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values for different treatments were plotted for comparison. This was conveniently accomplished using a procedure involving the rotation of the data points with respect to the *X* and *Y* coordinate axis (see Supplemental Material for more information).

Results and Discussion

Furrow Inflows, Runoff, and Total Infiltration

Treatments did not influence irrigation responses for furrow inflow, runoff, infiltration, or percolation volume (Supplemental Table S1). Irrigations provided about 220 mm of water per set in 2003 to 2004 and 100 mm in 2005 to 2006 (Supplemental Table S2). Less irrigation water was applied for small grain crops in 2005 to 2006 than for corn in 2003 to 2004, but the fraction of total inflow water that infiltrated was less in the 2003 to 2004 crops (0.32 and 0.26) than in the 2005 to 2006 barley crops (0.79 and 0.53) (Supplemental Table S2). Flow resistance in the barley furrows was greater due to tillering, which increased furrow stream wetted perimeter and advance times and decreased flow velocity and maximum sediment concentration

(Trout, 1992; Trout et al., 1995). Furrow outflow rates ranged from 6.8 to 12.2 L min⁻¹.

Percolation Water

Percolation water volumes collected at 1.2-m depth, also called deep-leached water, is that which is effectively exiting the root zone. The measured percolation water in a given irrigation (i.e., in the 2 wk after the irrigation) varied widely during the season. Neither treatment nor any interaction involving treatment influenced percolation volumes, although the pattern of percolation water losses by irrigation varied depending on the year (Supplemental Table S1).

As expected, annual cumulative percolation was greater in years with more irrigations. Season-long cumulative percolation water losses ranged from 7 and 40 mm in 2005 and 2006 to 102 and 78 mm in 2003 and 2004 (Supplemental Table S2). Most percolation water losses occurred early in the growing season (2004–2006), which is typical of semiarid, irrigated soils (Rice et al., 1986; Willis et al., 1997). However, 2003 was the exception because most percolation losses occurred in the fall (Supplemental Table S2). The winter preceding the 2003 growing season was unusually dry with precipitation from November to February only 59% of normal (Supplemental Fig. S1), and hence the soil profile likely was not adequately recharged at the season's start. Furthermore, in 2003, the winter, spring, and summer were warmer than normal, which increased evaporation and particularly evapotranspiration. Percolation loss in 2005 for barley after corn totaled only 7 mm (Supplemental Table S2). This may be a consequence of the large corn residue mass that was tilled into the soils at the end of the 2004 growing season, which may have increased sorptivity and water holding capacity of the soil relative to other years. Overall, the soil annually lost an average of 57 mm water to drainage, or 17% of the total infiltrated water.

Measured irrigation percolation losses were highly variable in space and time owing to soil heterogeneity and temporal variations in water inputs (Strock et al., 2001). Percolation values measured in each plot's three samplers had a median CV of 85.4%. Hydraulic conductivity varies greatly, even across short distances, having been found to range widely, from 0.01 to >40 m h⁻¹ across a distance of <1 m (Deeks et al., 2007). Rapid conduction of water through macropores is a common feature in most soils (Flury et al., 1994), including Portneuf silt loam (Lentz et al., 2001b). Previous research at this site indicates that the transport times for water moving from furrow to 1.2-m depth fall into three main groups: 1 to 3 d, 7 d, and 14 d (Lentz et al., 2001b; unpublished data), which is likely associated with flow through macropores, mesopores, and micropores, respectively (Deeks et al., 2007).

Constituent Concentration and Mass Losses

Constituent concentrations for individual percolation water samples also ranged widely, from near zero to as much as 581 mg L⁻¹ for NO₃-N, 1750 µg L⁻¹ for DRP, 79 mg L⁻¹ for DOC, and 957 mg L⁻¹ for Cl (Supplemental Fig S2). Leachate concentrations also varied greatly among each plot's three samplers, with median CVs ranging from 82 to 100%. Preferential flow through macropores bypasses the soil matrix, which inhibits the transfer of nutrients from the soil solution and solids to percolating

waters, and vice versa (Flury et al., 1995). In our soils, concentrations of deep-leached NO₃-N, Cl, and DOC tended to be least during macropore flow and greatest during matrix pore flow, whereas the reverse was apparent for DRP, although DRP fluctuations tended to be relatively small (Lentz et al., 2001b; Lentz and Lehrs, 2014; unpublished data). Under matrix flow, constituent leaching becomes a function of the soil's constituent content, adsorption capacity and saturation, and microbial activity. Thus, leachate concentrations can differ extensively because individual samplers intercept widely varying amounts of macropore and matrix flow (Lentz et al., 2001b). Temporal variation in leachate concentrations occurs partly in response to varying water percolation rates and differences in the partitioning of water between macropore and matrix flows. Large variability observed for percolation rates and leachate concentrations, and hence leachate loads, reduced the power of statistical tests to distinguish treatment effects (thus lending support for our use of an α of 0.10 rather than 0.05).

Flow-weighted concentration means for irrigation periods varied less widely (Fig. 1 and Supplemental Fig. S3). The ANOVA contrasts indicated that flow-weighted means for measured constituent concentrations were influenced by treatments within specific irrigation periods. The mineral fertilizer increased NO₃-N concentrations in leachate to 2.6 to 3.0 times that of control and manure treatments as a group (i.e., mineral vs. the mean of control and manure) during the 2004 early-irrigation period (Fig. 1B) and irrigations 2 and 3 in 2006 (Supplemental Fig. S3B). Mineral fertilizer also (i) increased leachate DOC concentrations 2.1 times that of the control-manure group early (period) in 2004 and 1.5 times early in 2006 (Fig. 1F, Supplemental Fig. S3F) and (ii) increased leachate Cl concentrations 2.6 times late in 2003 and 3.6 times early in 2004 and 2006 relative to that of the control-manure group (Fig. 1G, 1H, Supplemental Fig. S3H). No treatment differences were found for 2005 flow-weighted mean concentrations (Supplemental Fig S3).

When constituent mass losses for individual irrigation responses were evaluated, neither treatment nor any treatment interactions were found to be significant, but irrigation and the year \times irrigation interaction was significant (Supplemental Table S1). Mean annual percolation volume and mass losses reported in Supplemental Table S3 show that (i) mean constituent losses under corn (2003–2004) were 3 to 14 times greater than those under barley (2005–2006) and (ii) constituent mass losses increased with increasing percolation volume. We confirmed the latter via Pearson correlation analyses, which showed a highly significant positive correlation between percolation volume and associated constituent mass losses ($P < 0.0001$, correlation = 0.46–0.89). Conversely, sample percolation volumes were uncorrelated with associated constituent concentrations, with the exception of DOC ($P = 0.07$, correlation = -0.18).

Treatment group differences (contrasts) for mass losses given on an irrigation-period basis were identified and plotted. The ANOVA contrasts indicated that the mineral fertilizer produced (i) less DRP losses than the grouped control and manure treatments during early and middle periods in 2003 (Fig. 2C), early in 2004 (Fig. 2D), and for irrigations 2 and 3 in 2006 (Supplemental Fig. S4D); (ii) less DOC losses during the middle period in 2003 (Fig. 2E); and (iii) greater Cl losses than the grouped control and manure treatments during the late period in 2003 (Fig. 2G).

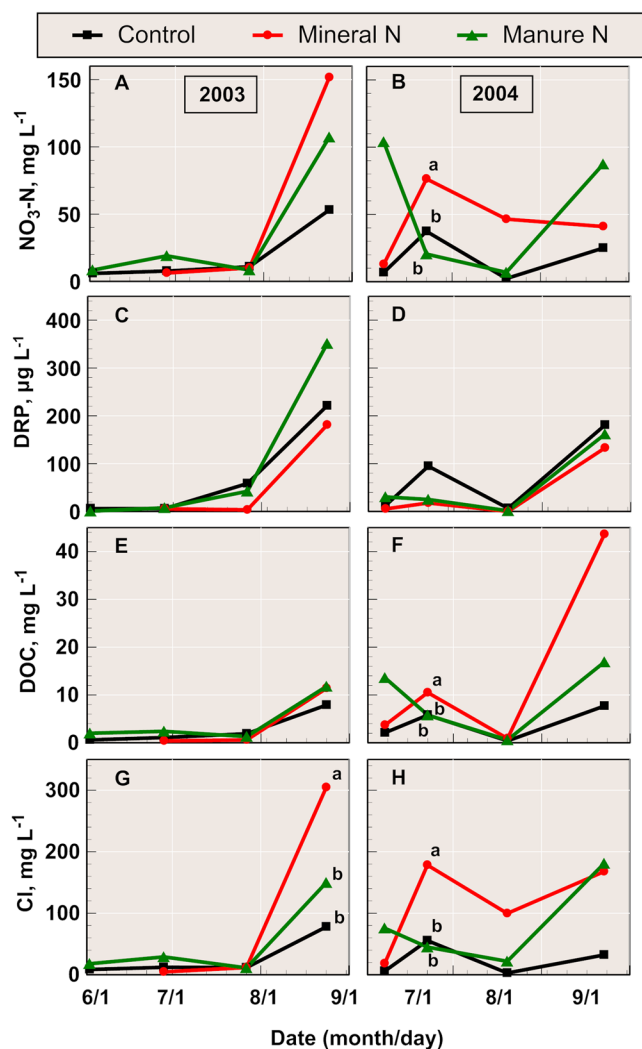


Fig. 1. Treatment flow-weighted mean percolation constituent concentrations for irrigation periods in 2003 and 2004. Treatment means for a given period are significantly different ($P \leq 0.1$) if labeled with different lowercase letters. DOC, dissolved organic C; DRP, dissolved reactive P.

When evaluated on a season-long basis, 4-yr average $\text{NO}_3\text{-N}$ mass losses for conventional mineral fertilizer were 1.5 times that of the control and 2.7 times that of manure, but these differences were not significant (Table 2). A similar pattern observed for Cl mass losses, however, was statistically significant; mineral fertilizer Cl losses were 2.9 times greater than those for manure (Table 2). Season-long DRP losses averaged 281 g ha^{-1} for the control, 122 g ha^{-1} for manure, and only 53 g ha^{-1} for conventional, but, as with $\text{NO}_3\text{-N}$, differences were not significant. Note that season-long DOC mass losses were similar among the three treatments ($\bar{x} = 8.3 \text{ kg ha}^{-1}$), although manure produced the quantitatively smallest mean DOC loss of the three.

Across all treatments, the $\text{NO}_3\text{-N}$ lost to percolation below the furrow-irrigated fields averaged $72 \text{ kg ha}^{-1} \text{ yr}^{-1}$. For a given irrigation period and year, however, $\text{NO}_3\text{-N}$ losses could be as little as $0.1 \text{ kg ha}^{-1} \text{ irrigation}^{-1}$ or as great as $53.2 \text{ kg ha}^{-1} \text{ irrigation}^{-1}$ (Fig. 2A, 2B, Supplemental Fig. S4A, S4B). Overall DRP lost in leachate was $152 \text{ g ha}^{-1} \text{ irrigation}^{-1}$ (Table 2), far lower than that of other measured constituents. For individual irrigation periods, DRP losses were as small as $0 \text{ g ha}^{-1} \text{ irrigation}^{-1}$ or as large as $116 \text{ g ha}^{-1} \text{ irrigation}^{-1}$ (Fig. 2C, 2D, Supplemental Fig.

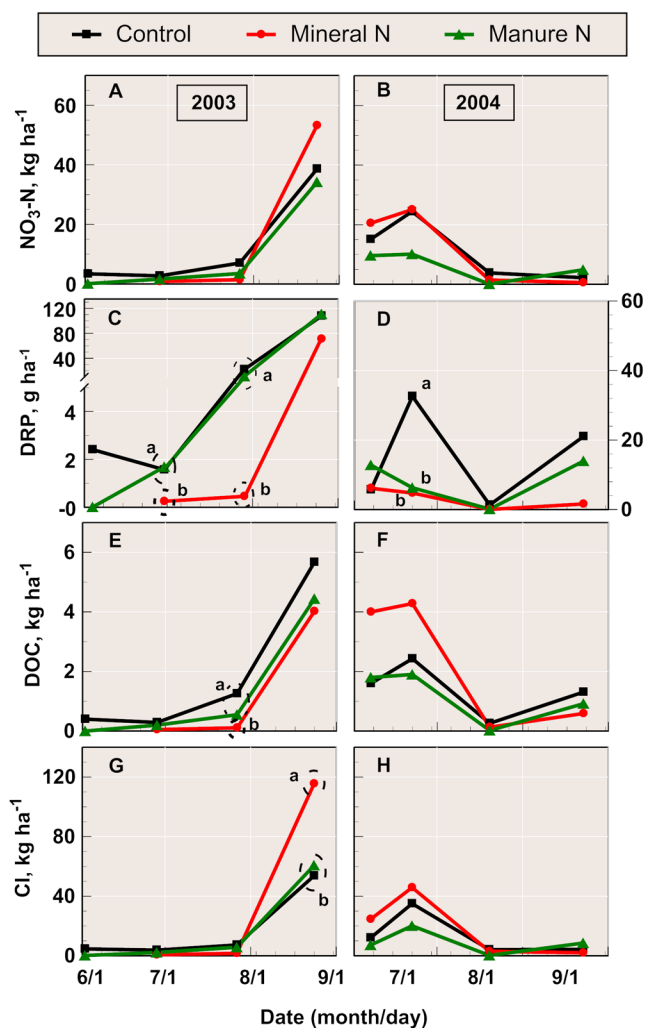


Fig. 2. Treatment percolation mass losses for irrigation periods in 2003 and 2004. Means of individual treatments, or treatment classes defined by dashed circles (contrasts), are significantly different if labeled with different lowercase letters. DOC, dissolved organic C; DRP, dissolved reactive P.

S4C, S4D). Similar great variability was noted for DOC and Cl constituents (Fig. 2E–H, Supplemental Fig. S4E–H).

Relative to other treatments, mineral fertilizer increased $\text{NO}_3\text{-N}$ and Cl concentrations 2.6 to 3.6 times in deep leachate (Fig. 1B, 1G, 1H, Supplemental Fig. S3B, S3H), particularly when NaNO_3 was applied in 2004 and 2006, and produced the greatest average season-long $\text{NO}_3\text{-N}$ and Cl losses (Table 2). Yet, these concentration increases did not produce associated increases in $\text{NO}_3\text{-N}$ and Cl mass losses (Fig. 2, Supplemental Fig. S4). In contrast, mineral fertilizer did not affect DRP concentrations in deep leachate yet decreased DRP mass losses during two irrigation periods in 2003 (Fig. 2C, 85 to 97% reduction) and two irrigations in 2006 (Supplemental Fig. S4D, 82 and 56% reduction) and produced the least mean season-long DRP losses (Table 2).

It is possible that some treatment effects listed in the previous paragraph resulted from soil spatial variability, which may have produced differing flow regimes among treatments. For example, the proportion of macropore relative to matrix flow contributions to mineral N water samplers may have been smaller than that in manure N plots, even though the total percolation flows

were similar (Supplemental Fig. S5). A greater fraction of matrix pore flow into mineral N water samplers could explain the relative greater NO₃-N and Cl concentrations and lesser DRP mass losses in the mineral N treatment, whereas the greater fraction of macropore flow into the manure N samplers may explain the relatively greater DRP losses there relative to mineral N (see discussion in “Percolation Water” section, above). Alternatively, the manure itself, through effects on macroporosity or soil water retention, may have increased the fraction of macropore flow in manure-amended than in mineral N plots. Preferential flow in the area's soils is affected by management. Lentz et al. (2001b) presented evidence indicating that macropore flow in Portneuf soils could be altered by amending surface soil with polyacrylamide. Likewise, the NaNO₃ fertilizer may have altered surface soil hydraulic properties via dispersion, increasing matrix flow relative to macropore flow in the mineral N treatment compared with the manure N treatment. Leachate concentrations and mass losses in control plots paralleled those of manure N plots, likely because (i) mean percolation volumes in controls in 2003 to 2005 were 1.5 to 3.9 times greater than average values for manure N and mineral N plots (Supplemental Fig. S5) and (ii) soil Olsen P values for control plots were relatively large (averaging 35 mg kg⁻¹ at 0- to 30-cm depth and 30 mg kg⁻¹ at 30 to 60 cm), which, when coupled with greater percolation rates, could support increased P losses.

In any case, results suggest that mineral N fertilizer amendments relative to manure or the control may have a greater potential to increase NO₃-N and Cl loads and decrease DRP loads to groundwater. Furthermore, results suggest that most of deep-leached NO₃-N is derived from organic N that was already incorporated into microbial and plant tissue and not from a pool of accumulated inorganic N. Thus, NO₃-N concentrations appear to be governed by mineralization-immobilization-nitrification rates. The isotopic data reported in a subsequent section support this view.

It is known that surface-applied manure increases DRP, DOC, NO₃-N, and Cl concentrations in leachate collected immediately below the soil plow layer compared with nonamended soils (Hannapel et al., 1964; Jensen et al., 2000; Gallet et al., 2003; Ziadat, 2009; Lentz, unpublished data, 2018). Yet in the current study, constituent concentrations in leachate collected at 1.2-m depth in manure-treated soils were equal to or less than those of control and mineral-N treatments (Fig. 1 and Supplemental

Fig. S3). What was the fate of large nutrient loads added to our manure-amended surface soils? In the water percolating through the soil matrix, a fraction of the DRP likely precipitated as Ca phosphates or was sorbed to amorphous and organically complexed Fe and Mn metals (Leytem and Westermann, 2003). The manure-derived DOC and NO₃-N leached from surface soil may have been (i) utilized as nutrient or energy sources by subsoil microorganisms, resulting in increased immobilization, or (ii) lost from the system via microsite denitrification or in the subsequent reduction of deep-leached NO₃-N (Choi et al., 2017). These processes ultimately reduced the N leaching coefficient (N leached/total N applied) for manure (158/596 = 0.3) relative to that of mineral fertilizer (430/391 = 1.1). The total applied N includes 14.2 kg N ha⁻¹ added in irrigation water.

Percolation Nitrate Isotope Composition

The δ¹⁵N-NO₃ and δ¹⁸O-NO₃ isotope composition of conventional and manure treatment percolation waters strongly overlap, and to a lesser degree the two fertilizer treatments also overlap data from the control (Supplemental Fig. S6). Three sample points from conventional and two from control treatments were isolated from the bulk of the data (see circled data in Supplemental Fig. S6). The outlying samples were collected in 2004 from only two samplers, one from each treatment. The relatively dilute NO₃-N (data not shown) and enriched δ¹⁵N-NO₃ content in these samples indicate they were subject to denitrification (Kendall, 1998). However, because the uncharacteristic results are confined to only two samplers and 5 of 110 percolation water samples analyzed, it is possible that they may be spurious, possibly caused by a failure in the specific samplers or collection circuits. In any case, the evidence indicates that denitrification is not a dominant biological process in these furrow-irrigated plots.

Because the δ¹⁵N-NO₃ and δ¹⁸O-NO₃ isotope ratios of conventional and manure percolation samples did not differ significantly (Supplemental Table S4), the two treatments were pooled in the subsequent analysis. The mineral and manure amendments as a group produced sample isotope compositions that were enriched in δ¹⁵N-NO₃ (8.2‰) relative to control (7.1‰) samples and enriched in δ¹⁸O-NO₃ (-4.4‰) relative to control (-7.2‰) samples (Supplemental Table S4). Only the δ¹⁸O-NO₃ ratio was influenced by year, such that the mean δ¹⁸O-NO₃ was about 1.6 times greater in 2004 than in 2003 and 2005 (Supplemental Table S4). The lack of treatment × year interaction indicates that

Table 2. Average season-long and 4-yr cumulative percolation volumes and associated mass losses of NO₃-N, dissolved reactive phosphorus (DRP), dissolved organic carbon (DOC), and Cl during the 4-yr study. The table includes P values from an analysis of variance for season-long treatment effects.

Source of variation	Percolation	NO ₃ -N	DRP	DOC	Cl
	P values				
Treatment	0.5140	0.1249	0.1563	0.5497	0.10
	Season-long losses				
	mm depth	kg ha ⁻¹	g ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹
Control	65.6	69.5	281	8.8	107 ab
Mineral N	58.0	107.5	53	9.2	256 a
Manure N	53.6	39.4	122	6.8	89 b
	Four-year cumulative losses				
Control	262	278	1125	35.0	426
Mineral N	232	430	215	36.7	1024
Manure N	214	158	487	27.1	355

relationships between mineral fertilizer and manure treatments did not change when manure application was altered from fall to spring and mineral fertilizer changed from urea to NaNO_3 (Supplemental Table S4).

Despite the isotopic differences among source and incubated soil NO_3^- , deep-leached nitrates from the mineral N and manure N amendments were isotopically similar (Fig. 3). Urea and NaNO_3 fertilizers have like $\delta^{15}\text{N}$ isotope ratios, $0.2 \pm 3.6\text{‰}$ (Michalski et al., 2015), whereas the $\delta^{18}\text{O}-\text{NO}_3^-$ ratio for nitrate derived from urea-N after 48 h in soil is $7.1 \pm 4.8\text{‰}$ versus $53.3 \pm 2.8\text{‰}$ for the Chilean NaNO_3 (Fig. 3A). Microbial nitrification of NH_4^+ from urea and manure N in the surface soil resets the $\delta^{18}\text{O}-\text{NO}_3^-$ ratio since the O typically is derived from two parts soil water ($\delta^{18}\text{O}$ of irrigation $\text{H}_2\text{O}-\text{O} = -16.5\text{‰}$) and one part soil O ($^{18}\text{O}-\text{O}_{\text{soil,air}} = +23\text{‰}$) (Hollocher, 1984; Kendall, 1998; McMahon and Böhlke, 2006; Nestler et al., 2011). Since the N from NaNO_3 is not nitrified, its $\delta^{18}\text{O}-\text{NO}_3^-$ ratio remains high after 3 wk in the soil (Fig. 3A). Presumably, a large fraction of the added NO_3^- is immobilized by heterotrophic microbes in the low- NH_4^+ soil environment (Burger and Jackson, 2003), followed by a series of ammonification–nitrification/immobilization cycles, which produce the observed shift in isotope ratios of deep-leached nitrate (Dittert et al., 1998; Somers and Savard, 2011; Craine et al., 2015). This suggests some nitrate was subject to transformation and cycling processes as it was translocated downward through the subsoil.

When the deep percolation water is compared with shallow and deep groundwater present beneath the Twin Falls Irrigation Tract (Fig. 3B), the $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ isotope composition of the different waters all fall on a line projecting from the relatively isotope-enriched percolation water, through the shallow groundwater sources (tunnel and tile waters), and terminating with the isotopically dilute deep groundwater. This implies that (i) little transformation occurs in the nitrate at depths below the root zone and (ii) changes in isotope composition below the root zone primarily result from dilution caused by mixing with deep water sources (Lentz and Lehrschr, unpublished data, 2018).

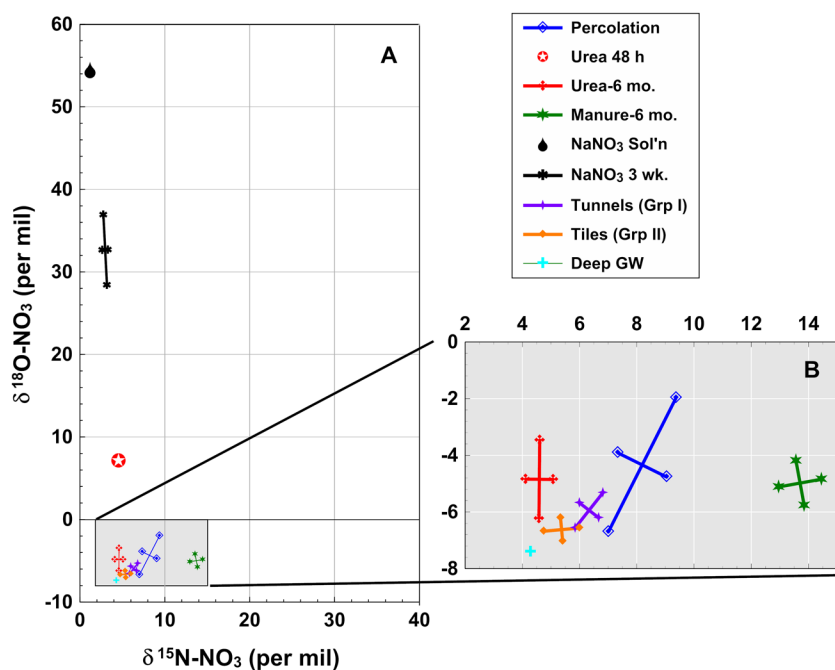


Fig. 3. Distribution of nitrate isotope compositions in water (i) from deep percolation beneath both mineral fertilizer or manure-amended soils; (ii) extracted from surface soils amended with urea or manure and incubated for 48 h or 6 mo (end-member analysis); (iii) extracted from field plot surface soils 3 wk after being amended with NaNO_3 ; (iv) from shallow groundwater sampled from tunnel drains and tile drain waters; and (v) deep groundwater (Deep GW). Data from parts ii and iv are from Lentz and Lehrschr (2018). The error bars are standard deviations obtained parallel and perpendicular to the direction of greatest variation for each data set.

Conclusions

1. Substantial soil spatial variability limited the power of statistical separations at the treatment level. For individual irrigations, however, differences between the mineral fertilizer and combined control and manure treatments (class comparisons) were found.
2. Deep leachate constituent concentrations and mass losses varied inversely on the whole, but differently for mineral fertilizer than for control and manure treatments. These findings support the supposition that the proportion of macropore relative to matrix-pore flow contributions differed between the two treatment classes, which may be attributed to amendment effects on soil structure or possibly to spatially variable soil properties among plots.
3. Leachate losses of DRP and DOC were equal or less from manure-amended than from nonamended soils for individual irrigations. This suggests that while there may be greater NO_3^- -N, DRP, and DOC losses from the surface soils of manure treatments relative to mineral or nonamended treatments, accompanying matrix-pore flux can facilitate adsorption, precipitation, and biological cycling of these nutrients, which limits their losses below 1.2-m depth.
4. The absence of an original N source–identifying isotopic signal in deep-leached NO_3^- indicates that (i) the N from the amendment is rapidly transformed through a repeated series of immobilization–mineralization cycles as it transits through the soil profile and/or (ii) the flux of the NO_3^- is slow; i.e., bypass or macropore flow is not transporting appreciable NO_3^- directly from surface soils to deeper depths.
5. Because leachate nutrient mass losses were positively correlated with percolation volume, but not nutrient concentrations, and because even unfertilized soils produced substantial amounts of mineralized and leached NO_3^- -N ($69.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$), it is clear that the key to limiting nutrient losses in these furrow-irrigated soils is to minimize percolation water losses.

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Supplemental Material

Additional detail on methods and data presented in Supplemental Tables S1 to S4 and Supplemental Fig. S1 to S6 are available online or can be obtained from the corresponding author.

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SUPPLEMENTAL MATERIAL

Mineral fertilizer and manure effects on leached inorganic N, nitrate isotopic composition, P, and DOC under furrow irrigation

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Supplemental Information (13 pages):

End-member Analysis (Incubation Method)

Determining Alignment and Variance Associated with Treatment $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ Values.

Tables S1 to S4

Figures S1 to S6

End Member Analysis.

A 0-30 cm depth sample of Portneuf silt loam was collected, ambient nitrate was removed by extraction with RO water, air dried, and sieved through a 2-mm screen. One of three amendment treatments was mixed with 125 g of soil: 1) 0.04 g total N as freeze-dried manure (where total manure N = 1.63% and assuming 40% of manure N is available, 6.74 g manure, dry wt.); 2) 0.04 g N as urea fertilizer (0.1 g); or 3) no amendment.

The treated soil was packed into 13-cm long by 4-cm diameter PVC cylinders with nylon cloth (50 μm mesh) bottoms in three lifts to achieve a dry bulk density of about 1.15 Mg m^{-3} . Extra soil columns prepared for each treatment were used to determine soil pore volumes and track soil $\text{NO}_3\text{-N}$ concentrations during incubation.

We wet the soil in each cylinder to 55% water filled pore space (WFPS) using RO water and incubated at 22°C . Soil water contents were adjusted to 55% WFPS weekly. All soil columns were leached after six months incubation, ensuring that the accumulated $\text{NO}_3\text{-N}$ included an ample proportion of input N that had cycled through the soil system. For leaching, RO water was applied to the column's nylon cloth shielded soil surface at a rate of 6.0 mL h^{-1} (4.8 mm h^{-1}) until one pore volume of soil percolate was collected from each soil column. Samples of the accumulated water were prepared for $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ analysis.

Determining Alignment and Variance Associated with Treatment $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ Values.

The alignment and variance associated with $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values from

tunnel drain waters and the end member series were plotted for comparison as follows. The $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values measured for each endmember experimental unit or tunnel water sample were plotted in treatment groups. An axial line intersecting the group's spatial mean and parallel to the long axis of each group's individual members was constructed, as was a second line (short axis) also intersecting the spatial mean but perpendicular to the first. We then obtained a measure of the spread among group's data points in the long- and short-axis directions. This was accomplished by rotating and aligning the X-Y coordinate axes with the group's long and short axis, transforming the group's point coordinate values relative to the new axes, then computing standard deviations for the transformed x and y coordinate values.

Table S1. The influence of fertilizer treatment, irrigation number, and year (2003 to 2006) on total irrigation water flux and cumulative percolation and dissolved constituent mass losses in two weeks following each irrigation.

Source of Variation	Irrigation water fluxes			Cumulative percolation losses in the two weeks following an irrigation				
	Total Inflow	Total Runoff	Total Infiltration	Percolation Volume	NO ₃ -N [†]	DRP [†]	DOC [†]	Cl [†]
Treatment (Trt)	ns [‡]	ns	ns	ns	ns	ns	ns	ns
Irrigation (Irr)	***	*	***	***	***	***	***	***
Year (Yr)	***	***	ns	ns	ns	ns	ns	ns
TRT * Irr	ns	ns	ns	ns	ns	ns	ns	ns
TRT * Yr	ns	ns	ns	ns	ns	ns	ns	ns
Irr * Yr	***	***	***	***	***	***	***	***
Trt * Irr * Yr	ns	ns	ns	ns	ns	ns	ns	ns

[†] Constituents in percolation water: NO₃-N, nitrate-N; DRP, dissolved-reactive P; DOC, dissolved organic C; Cl, chloride

[‡] ns=not significant

*, $P < 0.05$

**, $P < 0.01$

***, $P < 0.001$

Table S2. Cumulative inflow, runoff, net infiltration, and percolation values for each year and irrigation (averaged across treatments and replicates), given as mm water on the plot area.

Irrigation	Inflow		Runoff		Infiltration		Percolation		
	\bar{x}	SD [†]	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	
----- mm -----									
2003	1	250	7	158	15	92	11	1	2
	2	168	7	119	19	49	17	1	1
	3	221	5	148	9	73	9	2	3
	4	226	4	160	11	66	11	1	2
	5	220	3	135	17	86	16	9	7
	6	215	6	147	6	68	5	37	10
	7	220	10	163	11	57	13	50	9
	Cum.	1520	-	1032	-	488	-	102	-
2004	1	223	5	180	11	43	15	21	12
	2	220	4	172	25	48	28	31	10
	3	230	6	175	28	55	26	13	4
	4	227	4	162	21	65	23	2	2
	5	278	8	194	21	84	22	0	0
	6	222	8	160	23	62	18	4	4
	7	221	4	163	16	58	15	7	7
	Cum.	1621	-	1205	-	416	-	78	-
2005	1	100	5	18	14	82	15	5	3
	2	107	1	28	16	79	15	1	2
	3	34	1	5	3	30	3	1	2
	Cum.	242	-	61	-	191	-	7	-
2006	1	122	3	60	10	61	11	20	4
	2	126	3	55	6	71	4	15	4
	3 [‡]	-	-	-	-	-	-	5	2
	Cum.	249	-	125	-	132	-	40	-

[†] SD = standard deviation.

[‡] No third irrigation applied, but percolation volumes were collected in the period corresponding to what would have been the third irrigation.

Table S3. Overall mean annual cumulative percolation volume and mass losses of nitrate-N (NO₃-N), dissolved reactive phosphate (DRP), dissolved organic carbon (DOC), and chloride Cl. The analysis used transformed responses and means were back-transformed in the table.

Year	Volume	NO ₃ -N	DRP	DOC	Cl
	mm depth	kg ha ⁻¹	g ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹
2003	100 a	95 a	211 a	11 a	164 a
2004	54 ab	48 ab	54 ab	8.4 a	80 ab
2005	5 c	4.2 c	7.2 b	0.6 b	10 b
2006	21 bc	14 bc	20 b	4.2 ab	39 ab
Contrast					
2003, 2004 vs.	77 a	72 a	133 a	9.7 a	122 a
2005, 2006	13 b	9 b	14 b	2.4 b	25 b

Table S4. The influence of fertilizer treatment and year on the annual mean $\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$ isotope ratios in percolation water samples. Significance *P*-values resulting from analysis of variance and mean values.

	$\delta^{15}\text{N-NO}_3$	$\delta^{18}\text{O-NO}_3$
Source of Variation	----- P values -----	
Treatment (Trt)	**	***
Year	ns [†]	*
TRT * Year	ns	ns
<i>Contrasts</i>		
Control vs. Mineral+Manure N	**	**
Mineral N 2003 vs Mineral N 2004	0.06	**
Manure N 2003 vs Manure N 2004	ns	**
Isotope Ratio Means		
	----- ‰ (per mil) -----	
Control	7.1 b	-7.2 b
Mineral N	8.5 a	-3.4 a
Manure N	7.9 a	-5.4 a
2003	7.5 a	-6.3 b
2004	8.2 a	-3.9 a
2005	7.7 a	-5.9 b
Control	7.1 b	-7.2 b
Mineral+Manure N	8.2 a	-4.4 a
Mineral N. 2003	7.6 a	-5.7 b
Mineral N 2004	9.2 a	-1.5 a
Manure N 2003	7.8 a	-5.8 b
Manure N 2004	8.1 a	-3.7 a

[†] ns=not significant

*, *P*<0.05

**, *P*<0.01

***, *P*<0.001

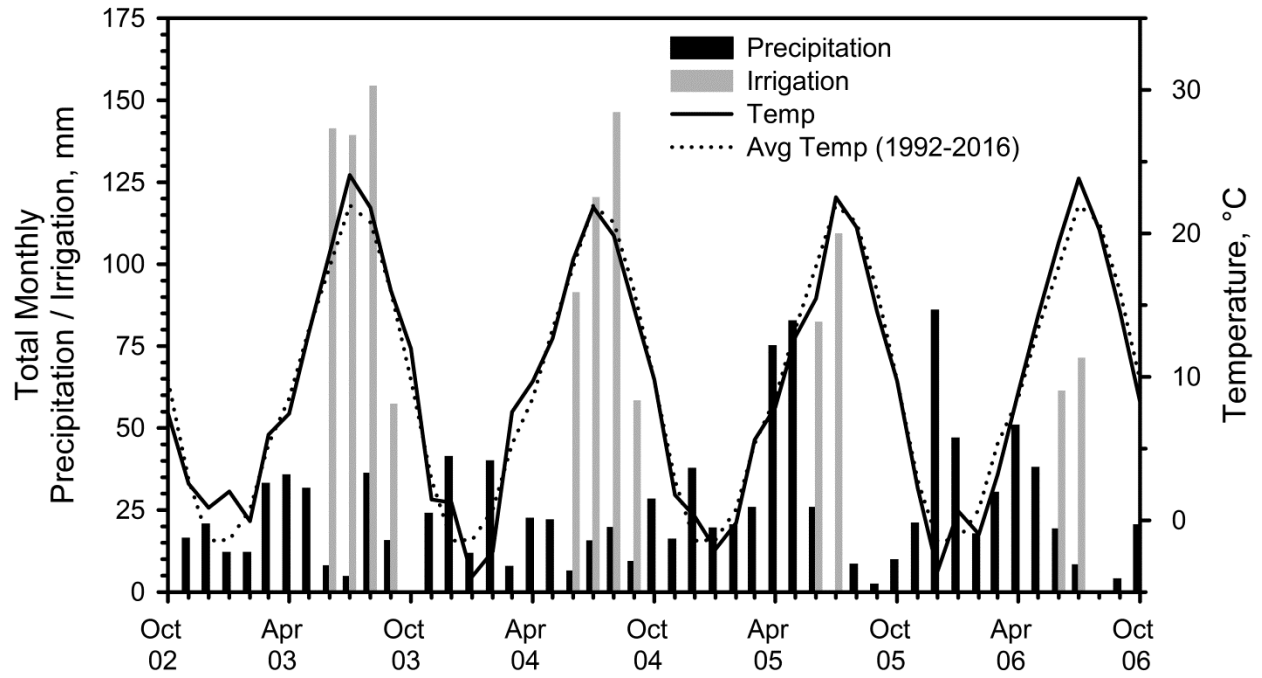


Fig. S1. Total monthly precipitation and irrigation inputs, and mean monthly and 1992-2016 average monthly air temperature at the study site from Oct. 2002 through Oct. 2006.

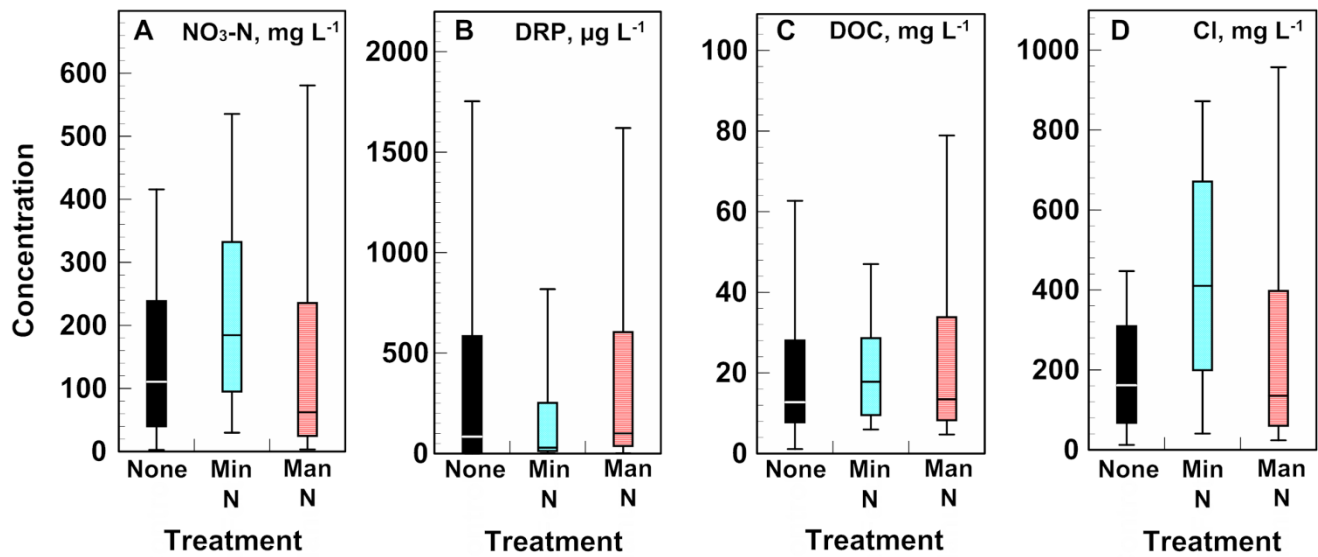


Fig. S2. Stem and whisker plots showing NO₃-N (A) , DRP (B) ,DOC (C), and Cl (D) concentrations in percolation water samples. Percentiles shown represent minimum and maximum values and 25, 50, and 75% percentiles.

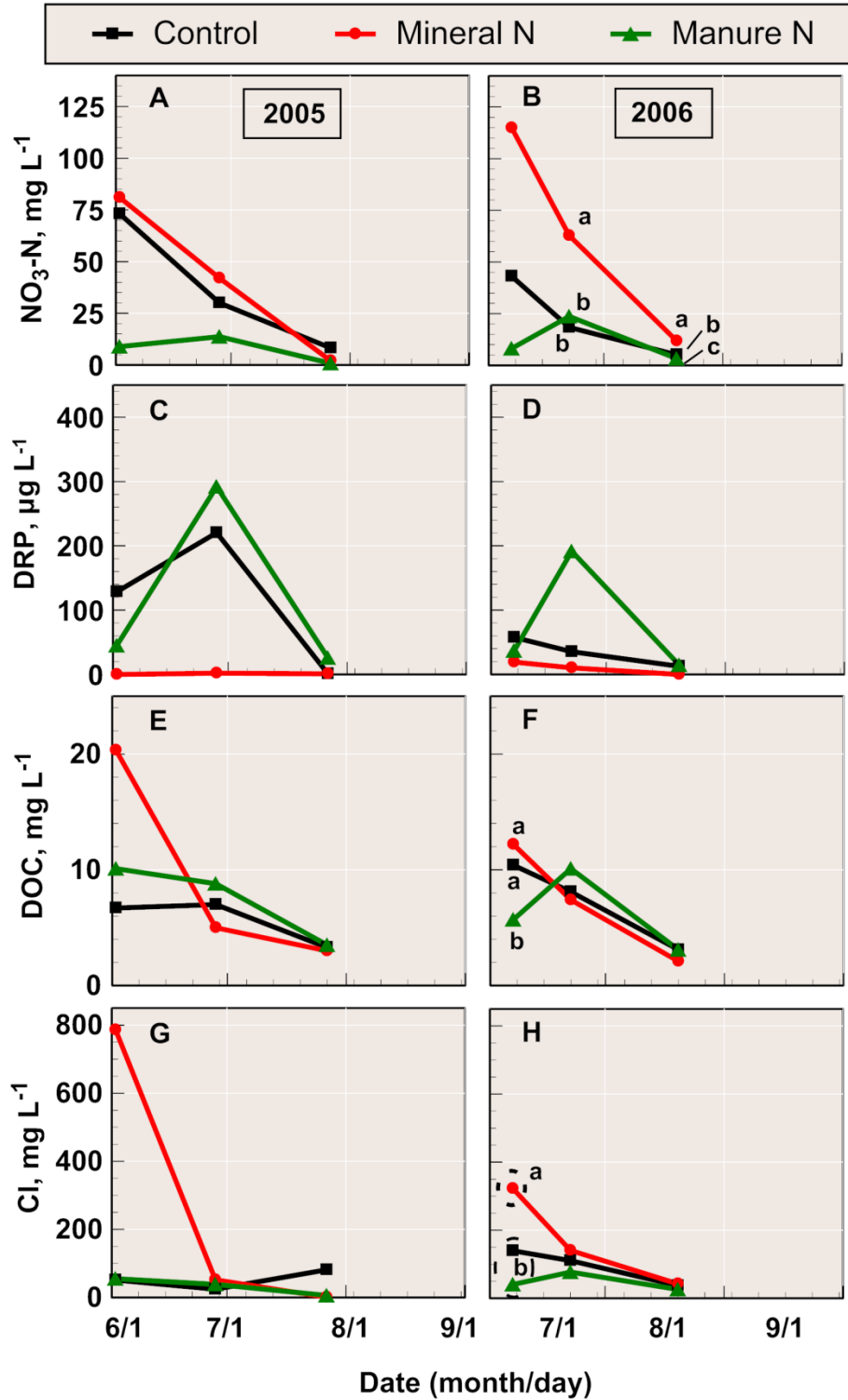


Fig. S3. Treatment flow-weighted mean percolation constituent concentrations for irrigations in 2005 and 2006. Absence of lowercase letters indicates nonsignificant difference among treatment means for a given irrigation.

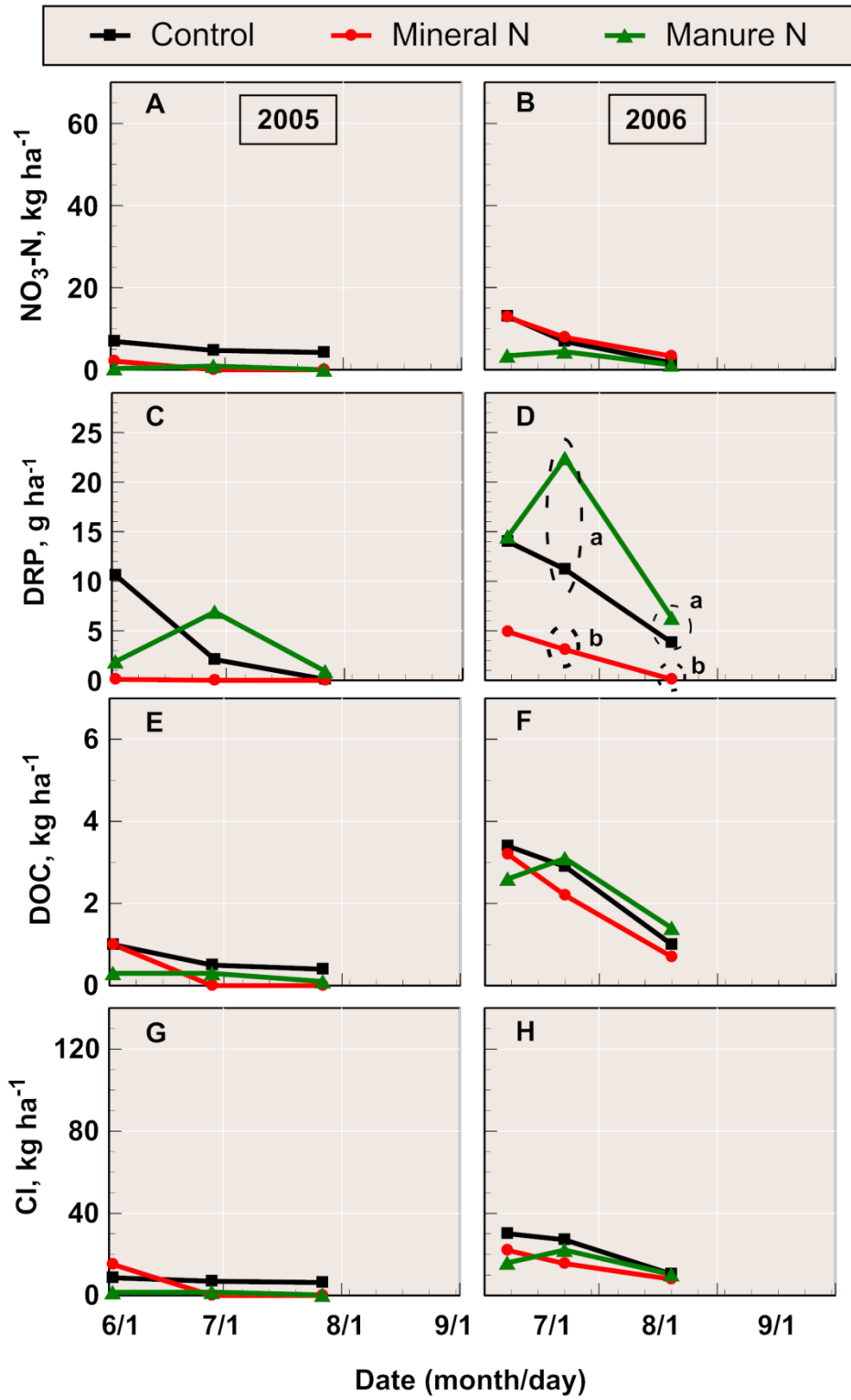


Fig. S4. Treatment percolation mass losses for irrigations in 2005 and 2006. Absence of lowercase letters indicates nonsignificant difference among treatment means for a given irrigation.

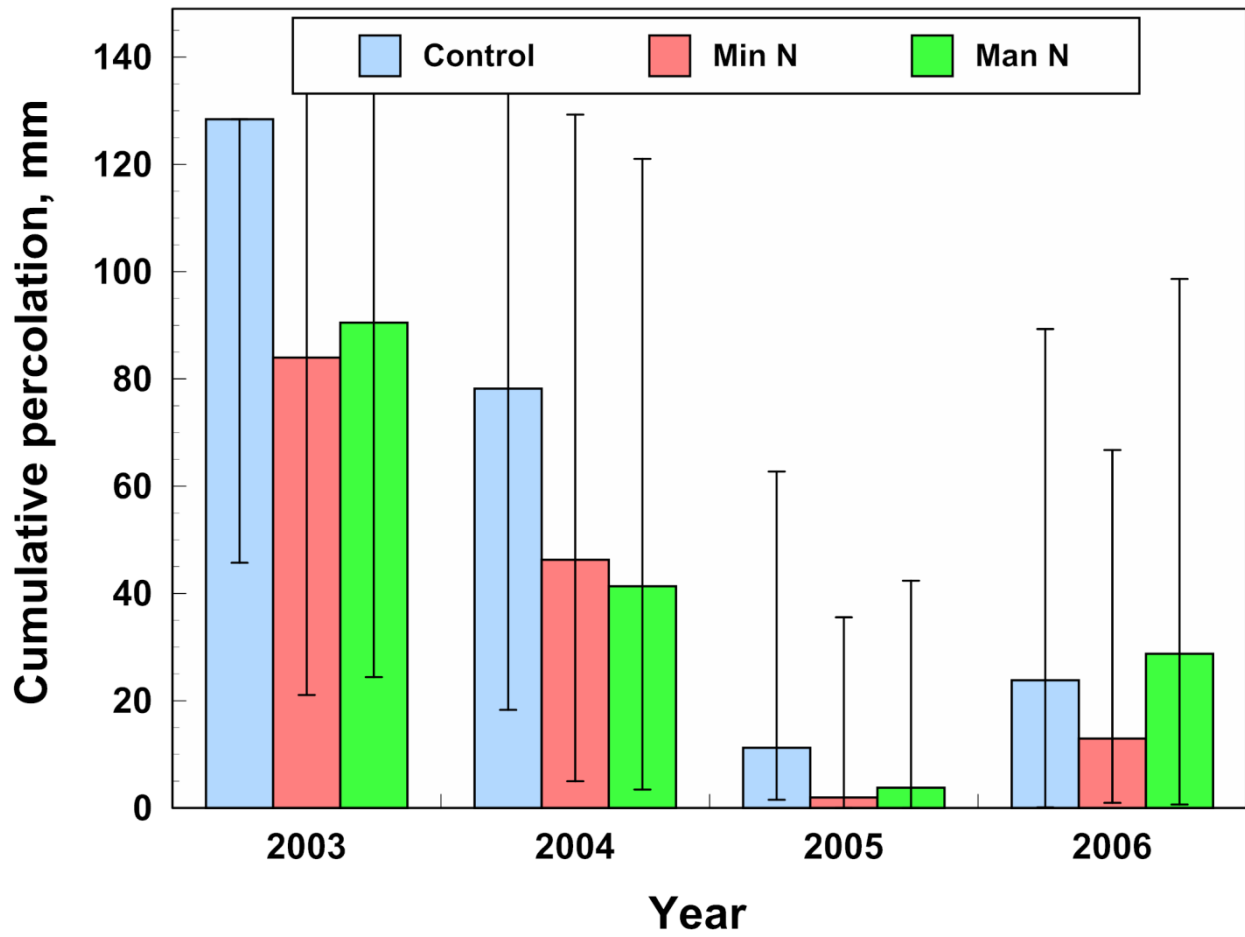


Fig. S5. Treatment cumulative annual percolation volume (mm). The error bars are confidence limits ($\alpha = 0.1$)

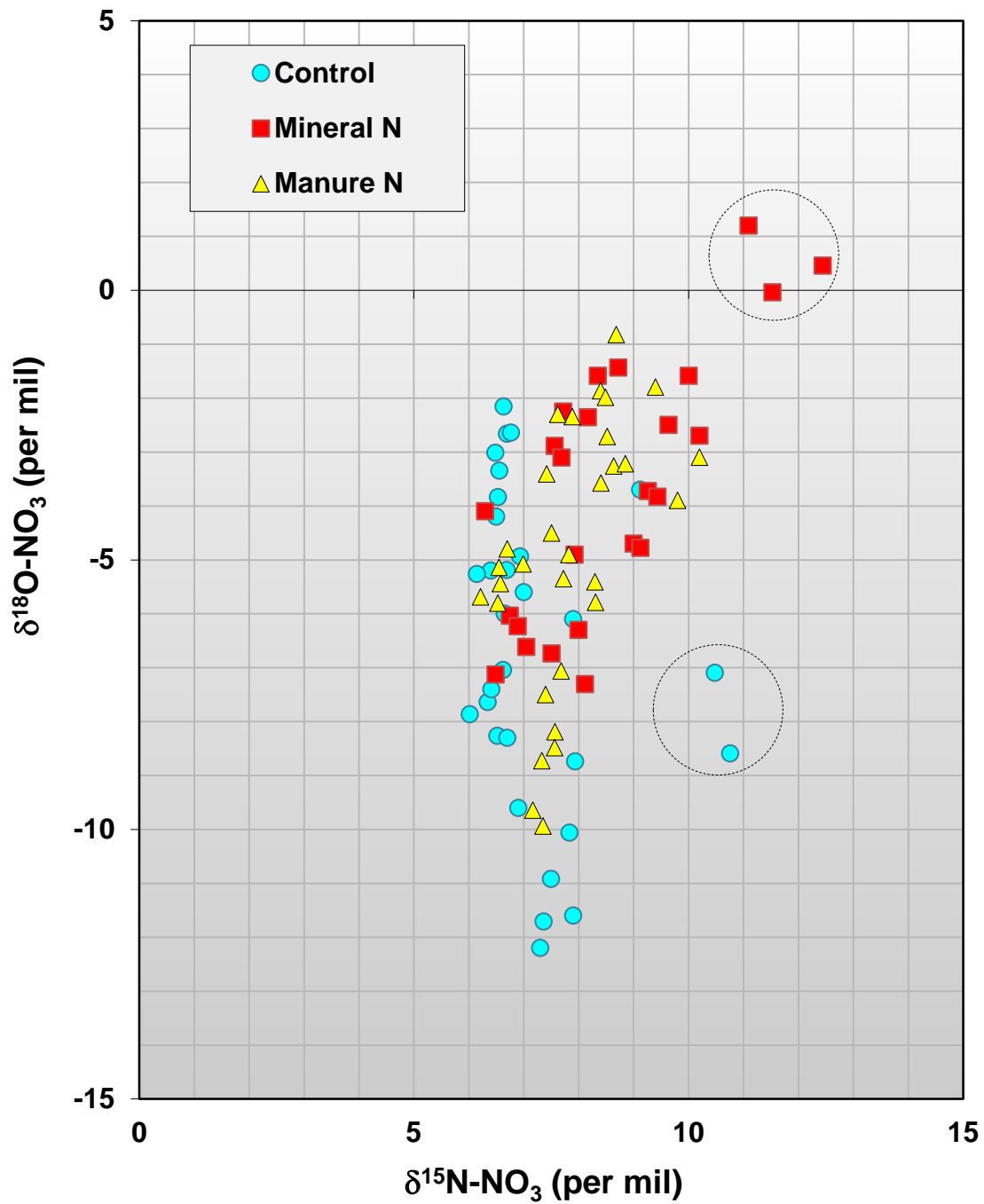


Fig S6. Percolation water nitrate isotope composition ($\delta^{18}\text{O-NO}_3$ vs. $\delta^{15}\text{N-NO}_3$) in samples collected in 2003, 2004, and 2005. Circled data points are from a single sampler in control and mineral fertilizer plots in 2004, which were atypical in that they showed evidence of denitrification.