doi:10.2489/jswc.2022.00155

Alfalfa reduces winter nitrate leaching relative to organic and conventional annual vegetable systems: Resin bag field measurements and modeling with HYDRUS-1D

E. Woodward, I. Raij-Hoffman, K. Scow, and N. Tautges

Abstract: Leaching of nitrate (NO_3^-) to groundwater is a major concern in California, where groundwater NO_3^- levels often exceed public safe drinking water thresholds. The state has enacted legislation to implement monitoring programs and management plans that will minimize future NO_3^- loadings to groundwater based on modeled NO_3^- leaching; however, a need remains for empirical NO_3^- leaching data and assessment of model suitability to specific systems. Moreover, debate remains around the ability of different management practices like cover cropping, replacement of chemicals with organic inputs, and cultivating perennials to reduce NO_3^- leaching in California's annual vegetable systems. We measured winter NO_3^- leaching over the wintery rainy season (October to March) within systems of the Century Experiment, a long-term cropping systems experiment in northern California evaluating effects of cover cropping, certified organic management, and alfalfa (*Medicago sativa* L.) incorporation in tomato (*Lycopersicon esculentum* Mill.)–maize (*Zea mays* L.) rotations. Anion exchange resin bags were installed at the bottom of the crop rooting zone (~65 cm) following tomato and prior to the onset of fall rains to adsorb leaching NO_3^- over the winter. Empirical resin bag NO_3^- leaching values were compared to modeled leaching results using HYDRUS-1D, which estimates water movement and reactive solute transport in soils. The rotation with alfalfa was the only system that reduced winter NO_3^- leaching (21.8 kg ha^{-1}), compared to conventional management (bare winter fallow after tomato) (47.1 kg ha^{-1}). Compared to conventional, certified organic management (44.7 kg ha^{-1}) and inclusion of a winter cover crop (58.2 kg ha^{-1}) had no significant impact on NO_3^- leaching. HYDRUS-1D model estimates for NO_3^- leaching were in good agreement with empirical field measurements in conventional and cover cropped systems, but less for certified organic and greater for the alfalfa systems. Results from this study show that perennial crops have potential to mitigate NO_3^- leaching losses across an agricultural landscape, and models like HYDRUS can provide useful estimates of NO_3^- leaching in some agricultural systems.

Key words: alfalfa—cover crops—HYDRUS-1D—nitrate leaching—resin bags

Nitrogen (N) in agronomic systems is essential for plant growth. The application of N fertilizer, either organic or inorganic, is often needed to meet crop N demands. In addition, the timing of N application and N availability with crop N demand is critical (Cassman et al. 2002; Sainju 2017). Asynchronous release of available N relative to crop N demand can result in reduced crop yields or excess N being lost from the system (Cassman et al. 2002; Gardner and Drinkwater 2009). One major loss pathway for soil N not taken up by the crop or immobilized by microorganisms is nitrate (NO_3^-) leaching. Leaching of NO_3^- from agronomic systems is an environmental and human health concern (Ward et al. 2005; Rosenstock et al. 2014). Drinking groundwater with high levels of NO_3^- can cause adverse human health effects, especially in infants under six months (Ward et al. 2005). With the Safe Drinking Water Act, the US Environmental Protection Agency (USEPA) established regulatory guidelines for NO_3^- in drinking water systems and set a maximum contaminant level (MCL) for NO_3^- as N in drinking water at 10 mg L^{-1} (USEPA 2018).

Leaching of NO_3^- to groundwater is a major concern in California (Harter et al. 2012; Viers et al. 2012; Rosenstock et al. 2014). Based on export markets across all commodities, California is the largest agricultural producer and exporter in the United States (CDFA 2018). High fertilizer inputs are often needed to achieve this level of production (Rosenstock et al. 2014). The most productive regions, such as the Central Coast and the Central Valley, are prone to greater amounts of NO_3^- leaching (Harter et al. 2012; Viers et al. 2012; Rosenstock et al. 2014), and groundwater NO_3^- levels often exceed regulatory levels (Harter et al. 2012). When fertilizer N is applied efficiently and doesn't exceed the plant's needs, then there is less accumulated N in the root zone available for leaching. In contrast, when applied fertilizer N exceeds the plant's needs, N can accumulate in the root zone and leach during irrigation or rainfall. State legislation like Senate Bill X2 1 (Perata) (Water Code Section 83002.5) has been developed to assess major sources of NO_3^- in California's drinking water and eventually implement monitoring programs and management plans to minimize future NO_3^- loadings to groundwater (Harter et al. 2012). However, the ability to estimate NO_3^- leaching from agricultural fields lags behind current legislative requirements for tracking NO_3^-, leading to grower confusion and scientific concern.

Even though NO_3^- leaching is a known challenge in California, field-level studies

Received October 14, 2021; Revised December 31, 2021; Accepted January 13, 2022.

Emily Woodward (corresponding author) was a project scientist when this work was conducted at the University of California, Davis in the Department of Land, Air, and Water Resources, Davis, California. **Iael Raij-Hoffman** is a postdoctoral scholar at the University of California, Davis in the Department of Land, Air, and Water Resources, Davis, California. **Kate Scow** is an emeritus professor at the University of California, Davis in the Department of Land, Air, and Water Resources, Davis, California. **Nicole Tautges** is an agroecologist at the Michael Fields Agricultural Institute, East Troy, Wisconsin.

that measure NO_3^- leaching, especially in dense agricultural areas, are sparse (Wyland and Jackson 1993; Wyland et al. 1996; Burger 2011; Baram et al. 2017). Quantifying NO_3^- concentrations in the soil solution, NO_3^- flux, and leaching below the root zone can be challenging and expensive. Traditional methods include a combination of lysimeters (drainage, pan, or suction), soil columns, and/or tracer studies (Weihermüller et al. 2007; Singh et al. 2017). These methods have known drawbacks: cost, disturbance during installation, aboveground instrumentation interfering with management, calibration, instrument maintenance, and/or type of output data (e.g., point in time concentrations versus cumulative flux) (Weihermüller et al. 2007; Singh et al. 2017).

One alternative to traditional techniques is the use of resin methods. Resins can act as cation or anion sinks in soil, capturing ions as soil water flows through the resin matrix (Qian and Schoenau 2002; Singh et al. 2017). Benefits of buried resin methods include the following: they are easy to implement, don't interfere with aboveground management, don't require an additional estimate of water flux either through field measurements or modeling, and are relatively inexpensive (Wyland and Jackson 1993; Qian and Schoenau 2002; Singh et al. 2017). However, buried resin methods are not without challenges. To avoid altered hydrologic conditions, there must be solid contact between the resin sampler and the surrounding soil, and it's important to consider textural discontinuities between the resin matrix and the surrounding soil (Schnabel 1983). Also, resin samplers capture passive, gravitational flow, but not diffusive flow (Binkley 1984).

Several studies have demonstrated the ability and effectiveness of resin-based methods to measure NO_3^- leaching in situ. Successful studies have been conducted with resin cores, membranes, and bag samplers (Wyland and Jackson 1993; Wyland et al. 1996; Pampolino et al. 2000; Finney et al. 2016; Grahmann et al. 2018; Kaye et al. 2019), and, in some cases, NO_3^- leaching data generated from resin methods were compared and validated against traditional methods (Wyland and Jackson 1993; Wyland et al. 1996; Pampolino et al. 2000; Susfalk and Johnson 2002). Cover crop effects on winter NO_3^- leaching in Salinas, California, were measured using resin bags, and field leaching estimates generated from the resin bag method were compared to measurements made with suction lysimeters (Wyland and Jackson 1993). Leaching estimates were similar between methods, and the mass of NO_3^- leached in the bare soil (9.87 mg NO_3-N bag^{-1}) was greater than the mass leached in soil planted with *Phacelia* (4.79 mg NO_3-N bag^{-1}) or Merced rye (*Secale*) cover crops (6.25 mg NO_3-N bag^{-1}). Another study compared the ability of resin capsules, suction cup lysimeters, and pan lysimeters to measure NO_3^- leaching via macropore flow (Pampolino et al. 2000). Methods were compared at a newly cultivated field site (onion [*Allium cepa* L.]) in one structured, clay-rich soil. Similar to pan lysimeters, the resin capsules were able to capture NO_3^- leached via macropore flow, and they were more effective at capturing leached NO_3^- than suction lysimeters. Grahmann et al. (2018) used a resin core method to measure cumulative NO_3^- flux in a maize (*Zea mays* L.)–wheat (*Triticum aestivum* L.) rotation with different tillage-straw treatments in northern Mexico. Leaching was higher in the maize (68 kg ha^{-1}) than wheat system (54 kg ha^{-1}), and leaching losses varied by tillage-straw treatments in the maize system only. Finally, in two recent studies, resin bags used to measure potentially leachable NO_3^- under different cover crop treatments in Pennsylvania showed that cover crops reduced NO_3^- leaching compared to bare winter fallow (Finney et al. 2016; Kaye et al. 2019). Mixtures of legumes and nonlegumes, even with a high seeding rate of the legume, only leached 2 to 5 kg ha^{-1} NO_3^- compared to fallow (94 kg ha^{-1}), and mixtures provided an apparent balance between NO_3^- retention and NO_3^- supply for the subsequent crop (Kaye et al. 2019).

Given the intensive time and labor requirements of performing field measurements of NO_3^- leaching, models are often seen as the future of NO_3^- measurement and monitoring. Soil geochemical models like HYDRUS, a modeling environment for saturated-unsaturated water flow and solute transport in porous media, have been used to estimate NO_3^- leaching (Šimůnek et al. 2016). The HYDRUS-1D environment models transport of solutes in liquid, and diffusion in the gaseous phase, considering coupled water, vapor, and energy transport. It also considers plant growth factors by including a sink term to account for water uptake by plants (Šimůnek et al. 2016). Investigating six models used to compare estimates of NO_3^- leaching with empirical measurements from soil columns, Al-Darby and Abdel-Nasser (2006) found that HYDRUS was one of two models that best predicted NO_3^- leaching. The HYDRUS-1D model, applied to irrigated agricultural systems to compare different fertilization and irrigation methods (Tafteh and Sepaskhah 2012), produced results similar to leaching estimates obtained by computing N mass balances and vadose zone soil water flow calculations (Baram et al. 2017). Nitrate leaching estimates by HYDRUS-1D were similar to in-field measurements using ion-exchange resin columns, supporting the use of ion exchange resin methods in conjunction with modeling to evaluate NO_3^- leaching among agricultural management systems (Desormeaux et al. 2019). More work is needed, however, to refine model agreement with empirically measured results, especially work focused on soil biologic activity.

The main objectives of this study were to (1) quantify and compare winter NO_3^- leaching in organic, conventional, conventional with winter cover crops, and alfalfa (*Medicago sativa* L.) cropping systems (maize–tomato [*Lycopersicon esculentum* Mill.]) at a long-term research site in California's Central Valley using resin bag methodology, and (2) assess the suitability of a numerical model to predict NO_3^- leaching under varying management systems and rainfall scenarios. We hypothesized that (1) adding winter cover crops will reduce winter NO_3^- leaching compared to conventional systems with bare winter fallow, and (2) estimates of NO_3^- leaching over the winter rainy season by HYDRUS-1D will be similar to empirical field observations.

Materials and Methods

Site Description. The experiment was conducted from October of 2018 to March of 2019 at the University of California Davis's Century Experiment at the Russell Ranch Sustainable Agriculture Facility. Individual plots (0.4 ha each) in the Century Experiment, a long-term cropping systems trial, represented four different agronomic systems: conventional (Conv) with chemical fertilizers and winter fallow; organic (Org + WCC), with compost fertility inputs and winter cover crops; hybrid defined as conventional with chemical inputs but also winter cover crops (Conv + WCC); and a six-year alfalfa-based system with conventional chemical management (Alf-Tom). All systems were initiated in 1994 and have been consistently managed in a two-year maize and processing tomato rotation, except for the alfalfa system. The alfalfa system was started in 2013, and it is a six-year rotation of tomato–maize–tomato–three-year-alfalfa (table 1). Tomatoes were planted in one row per bed on 1.5 m spacing, and maize was planted in a double-row per bed, with beds on 1.5 m spacings. In the alfalfa system, beds were knocked down with leveling tillage and alfalfa was established ("flat planted") on 20 cm rows.

All maize and tomato crops were irrigated during the summer season with subsurface drip irrigation, while alfalfa received flood irrigation during its growing season. The conventional and hybrid rotations both receive liquid urea chemical fertilizer at a rate of 200 kg ha^{-1} during the tomato phase (last application mid-July) and 235 kg ha^{-1} during the maize phase. The tomato–maize–tomato–three-year-alfalfa rotation receives chemical fertilizer during the maize–tomato phases (same rates as described above), but no fertilizer during the alfalfa phase. Guided by soil test results, crop managers decided that potassium (K) application to alfalfa was not necessary. Finally, the organic maize–tomato rotation received 9 t ha^{-1} of composted poultry manure (carbon [C]:N on average between 10:1 and 12:1) annually in the fall (October 24, 2018). The compost contains 225 kg N ha^{-1}, and 11% in inorganic forms. Additional details on the Century Experiment design and challenges associated with a long-term cropping systems study are described in Wolf et al. (2018) and Tautges and Scow (2020).

Plots sampled within the conventional, organic, and hybrid systems were rotating out of tomato (tomato harvested August of 2018), and plots sampled within the alfalfa system were rotating out of alfalfa. The alfalfa was terminated with a disk ripper, and residues were incorporated to a 38 cm depth in September of 2018. Plots are arranged in a randomized complete block design, with three blocks and one treatment replicate within each block (12 plots total) (see Wolf et al. [2018] for more details on the experimental layout of the Century Experiment).

While the resin bags were in the ground, plots were neither irrigated nor fertilized to remove the short-term impacts of specific practices. However, the organic and hybrid plots were planted with a winter cover crop mixture of legumes and grass, including faba bean (*Vicia faba* L.), oat (*Avena sativa*), and purple vetch (*Vicia benghalensis* L.). Cover crops were planted on November 5, 2018. On March 15, 2019, the cover crops were terminated, and residues were incorporated with two disk passes to a maximum depth of 25 cm. Figure 1 illustrates a complete timeline detailing all N input and output management during the study period.

Table 1

Management information for the four cropping systems studied at the Russell Ranch Sustainable Agriculture Facility.

Systems sampled	Fertilizer	Rotation	Crops
Alfalfa (Alf–Tom)	Chemical	6 y	Tom–Maize–Tom–Alf–Alf–Alf
Conventional (Conv)	Chemical	2 y	Tom–Maize
Hybrid (Conv + WCC)	Chemical + WCC	2 y	Tom–Maize
Organic (Org + WCC)	Compost + WCC	2 y	Tom–Maize

Notes: Alf = alfalfa. Tom = tomato. WCC = winter cover crops.

The soils on site are a Rincon silty clay loam (fine, smectitic, thermic Mollic Haploxeralfs) and a Yolo silt loam (fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvents). Soil texture and bulk density data are presented in the supplementary material (table S1), and there are two comprehensive soil property data sets available in the literature for this site (Wolf et al. 2018; Tautges et al. 2019). The temperature ranged from −1.2°C to 29°C and the total precipitation during the study period was 630 mm (UCD Weather & Climate Station 2019; figure 2).

Resin Bag Installation. Precipitation during the study period comprised most of the precipitation for the year, as the study took place in northern California, which is characterized by a Mediterranean climate with hot, dry summers and cool, wet winters; most precipitation falls between October and April. Ten resin bags were installed at each plot (120 bags total) during the week of October 23 to October 26, 2018, before the first rains of the winter rainy season. Resin bags were constructed (3.3 × 3.3 × 3.9 cm) of nylon stockings filled with 50 g of AMBERLITE PWA5 NO_3^- selective ion exchange resin (exchange capacity ≥ 1eq L^{-1}, equivalent to 3.3 g NO_3-N per bag assuming an efficiency of 65%). Before installation, resin bags were preconditioned according to the product data sheet by soaking for 20 minutes in 2 M sodium chloride (NaCl) and then triple rinsed with deionized (DI) water to remove excess brine. Bags were kept moist in sealed plastic bags to retain moisture until field installation. To install bags in the field, a 1 m deep trench was excavated by a trencher at an equivalent location within each plot, toward the side of the bed and away from the subsurface drip lines. A horizontal slit was drilled into an undisturbed side of the trench wall around 65 cm, and bags were packed tightly into the slit. Any spacing that remained in the slit was filled with soil, to ensure tight contact with bags and the undistributed soil profile. After installation, the trench was refilled.

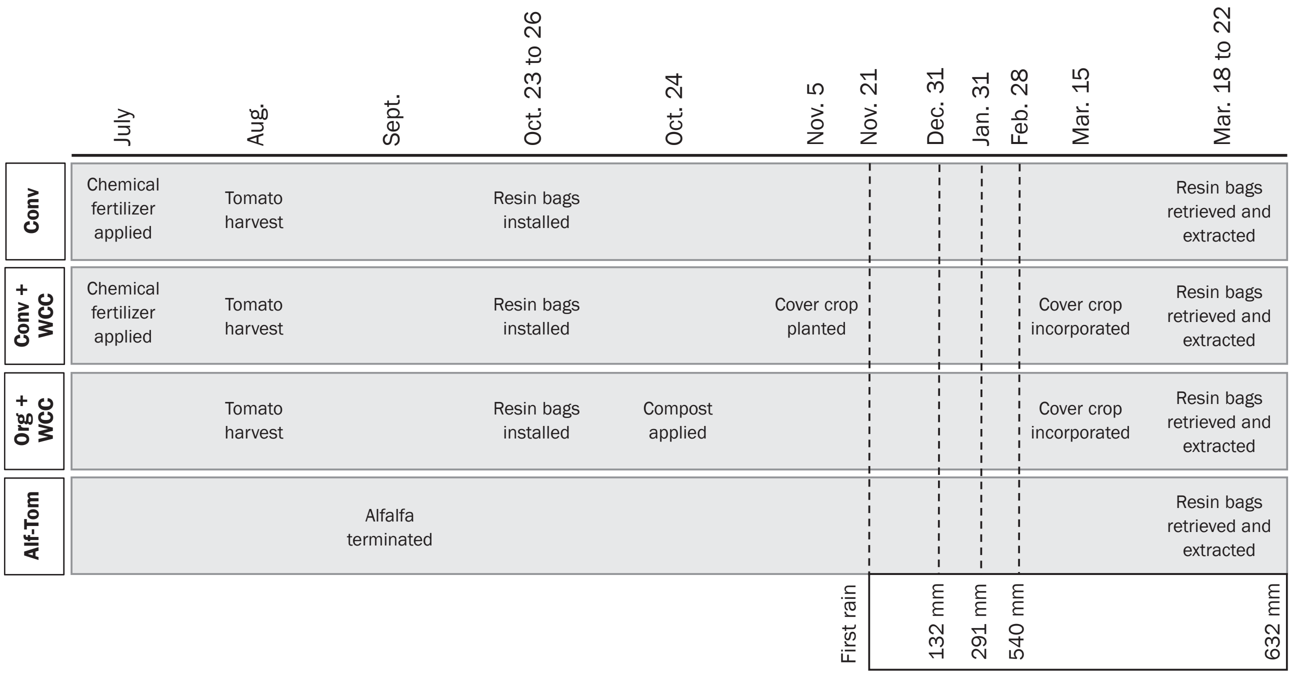
Resin Extraction and Analysis. Resin bags were removed from each plot the week of March 18 to March 22, 2019, at the end of the winter rainy season. All 10 bags were retrieved from each plot except at one conventional plot where only 9 bags were recovered. Bags were stored less than one week in a cold room (4°C) and then extracted with 2 M KCl. Six grams of resin were removed from each bag and extracted three separate times (1 h each) with 30 mL fresh KCl (1:5 resin to extractant ratio). Resin extracts were filtered and analyzed for NO_3^- using colorimetric and microplate methods based on the Greiss reaction (Sims et al. 1995; Doane and Horwath 2003). The three extracts from each bag were analyzed separately and the three masses were combined after analysis to calculate total mass extracted from the 6 g resin. Concentrations were back calculated to determine mass of NO_3^- per 50 g bag. This extraction method was tested in the lab prior to bag extraction to determine method efficiency testing at multiple concentrations and in triplicate. The total average recoveries were >93%; therefore, field data were not recovery corrected. As outlined in Kaye et al. (2019) and Finney et al. (2016), we calculated a NO_3^- leaching index value for each resin bag following equation 1:

$$PLN = (M_{\mathrm{NO3\text{-}N}} \div A_{RB}) \times 10, \tag{1}$$

where PLN is potentially leachable NO_3^- (kg ha^{-1}), $M_{\mathrm{NO3\text{-}N}}$ is the mass of NO_3^- for each

Figure 1

Timeline of nitrogen input and output management from July of 2018 to March of 2019 and resin bag installation and retrieval for each cropping system. Timeline also includes monthly rainfall accumulation data for the resin bag installation period.



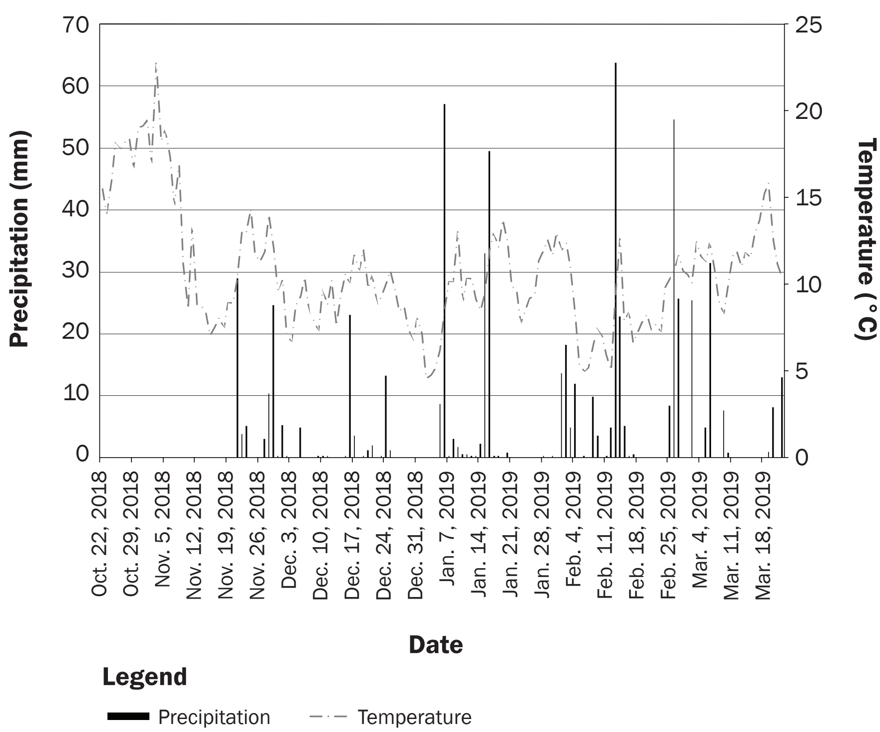
resin bag (g), and A_{RB} is the area of the resin bag (0.0076 m^2).

Soil Sampling and Analysis. Soils were sampled twice to determine changes in soil N: during resin bag installation and resin bag removal. Ten subsamples of soil from two depths, 0 to 30 cm and 30 to 60 cm, were taken from each plot during resin bag installation and retrieval. Soils were sampled in as close proximity to the bags as possible without disturbing the overlying soil profile. Subsamples were composited and transferred to a cold room (4°C) until extraction (within one week) and analysis. Soils were analyzed for microbial biomass N (MBN), NO_3^-, ammonium (NH_4^+), total N, total dissolved N (TDN), and gravimetric water content (GWC).

MBN was measured using a chloroform ($CHCl_3$) fumigation method (Brookes et al. 1985). In brief, 6 g soil was fumigated for 24 h with $CHCl_3$. After fumigation, soil was extracted for 1 h with 30 mL 0.5 M potassium sulfate (K_2SO_4). Fumigated soil extracts were filtered through Fisherbrand Q5 filter paper (Fisher Scientific, Hampton, New Hampshire). An unfumigated soil sample (6 g) was also extracted for 1 h with 30 mL 0.5 M K_2SO_4 and filtered through Fisherbrand Q5 filter paper. Aliquots of the

Figure 2

Daily total precipitation (mm) and daily average air temperature (°C) data for the study period (a) October 23, 2018, to (b) March 22, 2019.



fumigated and unfumigated extracts went through a persulfate oxidation (Cabrera and Beare 1993), and oxidized samples were analyzed using a combined spectrophotometric method described in Doane and Horwath (2003) and a microscale method found in Sims et al. (1995). The unfumigated sample that was extracted and oxidized was used to determine TDN. A correction factor, K_e = 0.68, was used to calculate final MBN concentrations (Horwath and Paul 1996).

To measure inorganic N (NO_3^--N and NH_4^+-N), 6 g soil was extracted for 1 h with 30 mL 0.5 M K_2SO_4 (1:5 soil mass to extractant volume ratio). Extracts were filtered and analyzed, again at a microscale level (Sims et al. 1995), for NH_4^+-N using a salicylate method (Verdouw et al. 1978), and for NO_3^--N using the spectrophotometric method described in Doane and Horwath (2003). GWC was measured at 105°C using standard soil analysis methods (Black 1965). Subsamples of the remaining soil were air dried and analyzed for total N using a standard combustion method on an ECS 4010 Costech Elemental Analyzer (Costech Analytical Technologies, Valenica, California).

Cover Crop Sampling and Analysis. Cover crop aboveground biomass was sampled in March before incorporation by harvesting two 2 m^2 quadrats per plot (east and west side of plot). Biomass was sorted fresh by species, including weeds, and then dried (60°C), weighed, and ground. Total C and N of incorporated aboveground biomass were determined using a dry combustion analysis on an ECS 4010 Costech Elemental Analyzer (Costech Analytical Technologies, Valencia, California).

HYDRUS Modeling Methodology: Parameters and Domain. The HYDRUS-1D software (Šimůnek et al. 2013) was used to simulate water flow and reactive N transport during the 151 days of the experiment in replicated field plots. Instead of using the common approach of performing one simulation for each treatment and heavily calibrating a number of parameters, we chose to simulate each replicated plot and compare simulation results as a range for each treatment. Such an approach acknowledges that model results are not absolute, and measured values are influenced by physical and chemical heterogeneity.

Variably saturated water flow was simulated following Richards' equation and using van Genuchten (1980)-Mualem (1976) hydraulic functions. One-dimensional simulations were chosen as no irrigation was applied during the simulated time period. Hydraulic parameters were obtained using Rosetta3 pedotransfer function (Zhang and Schaap 2017) from soil texture data and bulk density measured in each of the experimental plots at increasing intervals with depth (table S1). Reactive N transport was simulated as NH_4 and NO_3^- using the convection-dispersion equation. Ammonium was assumed to adsorb to the soil following a linear adsorption isotherm as defined in equation 2; k_s, the adsorption coefficient was set to 3.5 cm^3 g^{-1} (Hanson et al. 2006). Ammonium mineralization was described as a zero-order reaction in the top 30 cm of the soil profile, while nitrification was described as a first-order reaction throughout the entire profile where μ'_w is the first-order rate coefficient of nitrification and γ_w is the zero-order rate coefficient of mineralization (ML^{-3} T^{-1}). Nitrification, defined as a first-order reaction and therefore dependent on concentration, varied with depth due to spatial variation in NH_4 concentrations. Two distinctive zero-rate coefficients of mineralization were defined at 0 to 15 cm and 15 to 30 cm depth, assuming that organic N and C contents, as well as microbial activity, change with depth. A manual calibration was performed for both zero- and first-order rate coefficients of nitrification and mineralization by running 245 simulations for each plot with ranges of μ'_w = (0.001, 0.05, 0.1, 0.15, 0.2) and γ_w = (0.0001 to 0.0007 with 0.0001 increments). Manual calibration, as opposed to an automated inverse solution, was used to calibrate three plots of the same treatment simultaneously. Root-mean-square error (RMSE) as presented in equation 3 was calculated for final NO_3^- and NH_4 concentrations in the soil for each treatment, defined as mg cm^{-3} of soil, at the depths of 0 to 30 and 30 to 60 cm. The objective function was defined to minimize the RMSE for each treatment with a total of 12 data points each. Calibrated rate coefficients per treatment are summarized in table 2. Each set of calibrated coefficients was used in the three plots of each treatment:

$$s_k = k_s c_k \text{ , and} \tag{2}$$

$$RMSE = \sqrt{\frac{\sum_i^n (P_i - O_i)^2}{n}} \text{ ,} \tag{3}$$

where P_i are modeled NH_4-N and NO_3-N concentrations in the 0 to 30 and 30 to 60 cm intervals at the end of the simulations, and O_i are the respective measured values. n is the number of data points, in this case four for each plot.

Overall, a process-based modeling approach (Ramos et al. 2012) was used in this study. Therefore, there aren't calibration and validation periods. When possible, parameters were measured or taken from the literature, and results are presented as a probabilistic range instead of a single value. This is a novel and robust approach for a study like this one, when only one season was monitored. It might yield modeled results that are in less agreement with the measurements but with a higher certainty that the results are not biased by extensive calibration.

Nitrogen Uptake. Total N uptake (r_a) was calculated as the sum of total active ($a_{a,k}$) and passive ($p_{a,k}$) uptakes for NO_3^- and NH_4 (equation 4; Šimůnek and Hopmans 2009). Ammonium uptake was assumed to be only passive [$a_{a,k}(x,t)$ = 0 for k = ammonium]. Unlimited passive NH_4 or NO_3^- uptake was calculated following equation 5 where s is the transpiration or root water uptake and c is the NH_4 concentration in the soil pore water at every time node and time step. Active NO_3^- uptake is defined in equation 6 as the maximum value of either a potential NO_3^- uptake or the passive uptake. Potential NO_3^- uptake (r_p) is described using a logistic function with a maximum value equal to the total seasonal N uptake measured as total N in the cover crop biomass for the hybrid and organic treatments. If passive NO_3^- uptake is lower than the potential NO_3^- uptake then active uptake will take place following Michaelis-Menten kinetics as explained in Šimůnek et al. (2013) to fulfill potential NO_3^- uptake values. The Michaelis-Menten kinetic constant and minimum concentration for uptake were taken from Kage (1995) for faba bean and used for the mixed cover crops:

$$r_a(x,t) = \textstyle\sum_i^k p_{a,k}(x,t) + a_{a,k}(x,t) \text{ ,} \tag{4}$$

$$r_{p,k}(x,t) = s(x,t) \times c_k(x,t) \text{ , and} \tag{5}$$

$$r_{a,k}(x,t) = max[r_{p,k}(x,t) - p_{a,k}(x,t), 0] \text{ .} \tag{6}$$

Domain, Initial, and Boundary Conditions. A 2 m profile was defined with 201 equidistant nodes. Different soil layers were defined according to soil data in table S1. An observation node was defined at a depth of 60 cm and fluxes and concentrations were recorded. Relative root density was calculated from root biomass measurements at the end of the experiment sampled at intervals of 0 to 30, 30 to 60, and 60 to 100 cm. The top boundary of the domain was defined as a time variable atmospheric boundary condition, allowing for precipitation and potential evaporation and transpiration. The bottom boundary at 2 m was defined as free drainage.

Initial water content in each soil profile was imported from final water contents in preliminary simulations that ran from September 1 until October 22, the day before the experiment started. This was in order for the simulated profiles to be in hydraulic equilibrium on the first day of simulations. Initial soil potential conditions for preliminary simulations were set to field capacity because the fields were irrigated during the summer season. Atmospheric boundary conditions were set based on potential reference evapotranspiration (ET) from the nearest California Irrigation Management Information System (CIMIS) station (Davis, California) and no precipitation was measured during this time-frame. During the main simulations, precipitation data were obtained from the nearest CIMIS station as well as potential reference ET. A crop factor of 1.15 was used for the cover crops (Doorenbos and Pruitt 1977; Abraha and Savage 2008). During cover crop growth, all ET was assumed to be transpiration (uptake through the root distribution). Before seeding, after harvest and during the entire simulation when there were no cover crops, all ET was defined as evaporation. Treatments with no cover crops were left bare and any emerging weeds were sprayed with herbicide. Initial NO_3^- and NH_4 simulations were defined as the mass of solute per volume of soil as measured for 0 to 30 and 30 to 60 cm in each plot.

Rainfall Scenarios. Simulations with good agreement between modeled and measured NO_3^- leaching were used to study the effect of long-term rainfall patterns on NO_3^- leaching. The same simulation setup used for the winter of 2018 to 2019 was deployed in the winters of 1990 to 2018. Rainfall between October 23 and March 22 was summed for each season and then divided into three groups: wet, dry, and medium years. Wet and dry years were defined as those years with rainfall in the upper and lower 95% confidence interval, respectively. Medium years were assumed to be all seasons with rainfall rates in between.

Data Analysis. Data were analyzed using R software (version 3.5.0, R Core Team 2013). Soil inorganic N, NH_4^+, and NO_3^- were analyzed with mixed linear models, where system and date were treated as fixed effects and replicate was treated as a random effect. Soil moisture was included as a covariate in the inorganic N models to account for differences in soil water contents among systems. Soil total N, TDN, and MBN were analyzed with a linear mixed model with similar parameters, but soil organic matter was included as a covariate.

Leaching data were analyzed using a linear mixed model with system and date as fixed effects and block as a random effect. Leaching data were screened to check the assumptions of analysis of variance (ANOVA), and leaching data failed to meet assumptions due to a right-skewed distribution. Data were log-transformed (log base e) to meet ANOVA assumptions (Levene's test $p = 0.121$). Differences ($p < 0.05$) between treatments were evaluated using ANOVA and pairwise comparisons were compared using a Tukey Test. The leaching figure shows the back-transformed means with 95% confidence intervals, and the back transformed means are presented and discussed for each system. Modeling data were compared to the leaching data without transformation. For the cover crop species data, a *t*-test was used to determine differences in the percentage of each cover crop species, including weeds, between organic and hybrid systems ($p < 0.05$).

Modeled and observed data were compared using RMSE as defined in equation 3 and the Nash–Sutcliffe coefficient (NSE) as defined in equation 7:

$$NSE = 1 - \frac{\sum_i^n (P_i - O_i)^2}{\sum_i^n (O_i - O_{i,avg})^2}, \qquad (7)$$

where $O_{i,avg}$ is the mean of the observed concentrations.

Results and Discussion

Cover Crop Species and Nitrogen Uptake. Cover crop species establishment varied between the two systems, although identical seeding rates were used. In the organic system, the legumes (vetch and faba bean) comprised on average 26%, oat grass 56%, and weeds 18% of the species mixture. In the hybrid system, the mixture was made up of 79% legumes, 12% oat grass, and 9% weeds. The cover crop mixture contained more grass ($p < 0.001$) and less legume ($p < 0.001$) in the organic than hybrid system. The organic system also had a greater percentage of weeds of total biomass than the hybrid system ($p = 0.002$). Species establishment can have important implications for NO_3^- leaching in these systems because grasses are known to be better N scavengers than legumes (Thapa et al. 2018; Kaye et al. 2019). Biomass N contents also varied between the two systems; the average amount of N in cover crop biomass was 155 kg N ha^{-1} in the organic and 131 kg N ha^{-1} in the hybrid system.

Changes in Soil Nitrogen. Soil inorganic N levels between October and March were similar in the alfalfa, conventional, and organic systems, and decreased only in the hybrid system ($p = 0.037$; figure 3). Soil NH_4^+ levels increased across all systems between October and March ($p = 0.003$) but did not differ among systems in either October or March, implying that rates of organic matter N mineralization were similar among all systems. The most notable differ-

Table 2

Optimized nitrogen reaction chain parameters in HYDRUS simulations for each system. μ'_w is the first-order rate coefficient of nitrification and γ_w is the zero-order rate coefficient of mineralization (ML^{-3} T^{-1}).

Systems	μ'_w	γ_w 0 to 15 cm	γ_w 15 to 30 cm
Conventional (Conv)	0.05	0.0003	0.0004
Hybrid (Conv + WCC)	0.1	0.0002	0.0002
Organic (Org + WCC)	0.05	0.0004	0.0003
Alfalfa (Alf–Tom)	0.2	0.0004	0.0004

Notes: WCC = winter cover crops. Alf = alfalfa. Tom = tomato.

ences seen among systems were observed for soil NO_3^-, where levels decreased significantly between October and March, and there was a system by date interaction (p = 0.018). In October, soil NO_3^- levels were greatest in the hybrid system (28.6 mg kg^{-1}), followed by the organic (18.9 mg kg^{-1}) and conventional systems (16.8 mg kg^{-1}), which were similar, and lowest in the alfalfa system (14 mg kg^{-1}) (figure 3). In March, soil NO_3^- levels were lowest in the organic system (0.6 mg kg^{-1}), followed by the conventional (2.4 mg kg^{-1}) and hybrid systems (2.2 mg kg^{-1}), which were similar, and greatest in the alfalfa system (7.0 mg kg^{-1}) (figure 3).

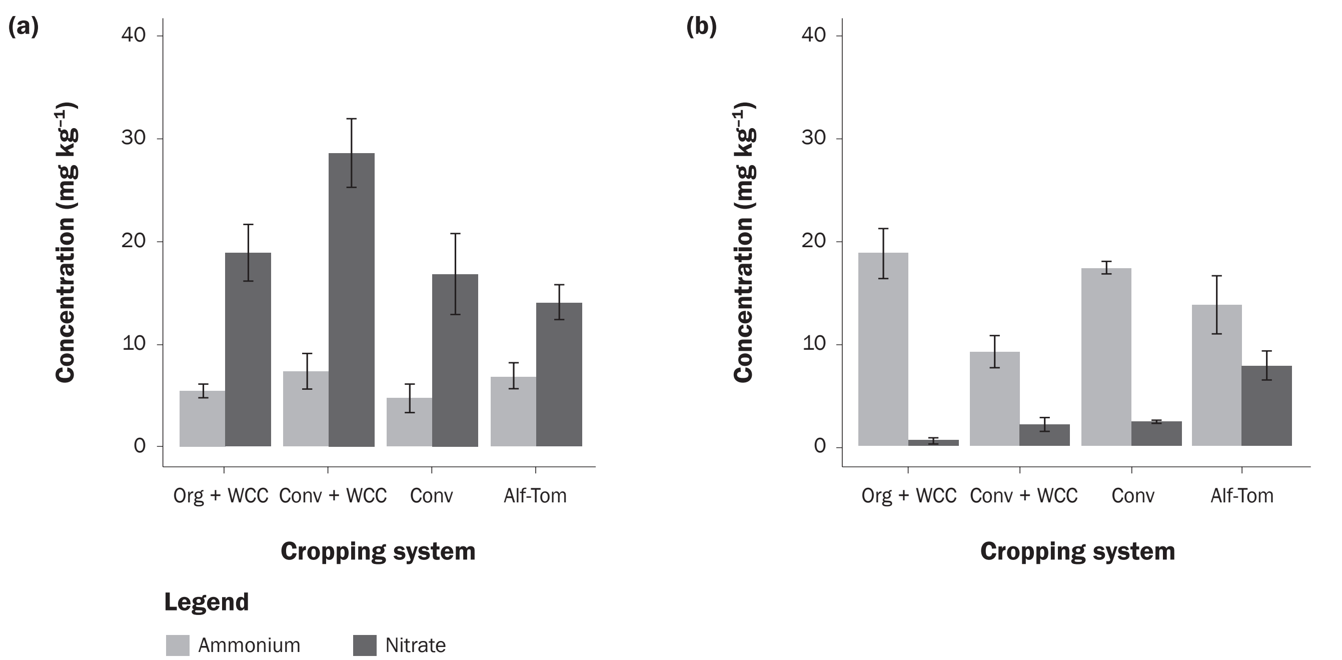
Soil MBN was similar between October and March and among systems on both dates. In March, there was slightly higher MBN in the hybrid system (33.9 mg kg^{-1}) compared to the other systems (21.7 to 24.6 mg kg^{-1}), and in October, there was slightly higher MBN in the alfalfa system (23.9 mg kg^{-1}) compared to the other systems (15.6 to 18.8 mg kg^{-1}); however, considerable variation in the microbial data precluded detection of statistical differences (table S3). TDN decreased by 55% across all systems from October to March (p = 0.001) but did not differ among systems (table 3). Across all systems, soil total N decreased by 12% from October to March ($p < 0.001$), and among systems, total N was greater in the organic than alfalfa, conventional, and hybrid systems (p = 0.001; table 3).

Nitrate Leaching in the Annual Systems. There were significant differences in NO_3^- leaching potential among the four cropping systems ($p < 0.001$). Less NO_3^- leaching was observed following alfalfa (21.8 kg ha^{-1}) compared to the conventional, hybrid, and organic systems (47.1, 58.2, and 44.7 kg ha^{-1}, respectively; figure 4). Nitrate leaching was similar among the conventional, hybrid, and organic systems. The amounts of leached N measured in this study are in general agreement with leaching amounts reported in other studies that utilized resin methods. Leaching measured with resin cores ranged from 46 to 82 kg ha^{-1} in a maize–wheat rotation with different tillage-straw treatments in northern Mexico, depending on the treatment and system (Grahmann et al. 2018), and ranged from 0.7 to 94 kg ha^{-1}, depending on the presence of cover crop and the mixture of cover crop species, in maize rotations in Pennsylvania (Kaye et al. 2019). At another site in California, Wyland and Jackson (1993) measured leaching (60 cm) under cover crop and fallow systems with values ranging from 4.79 to 9.87 mg bag^{-1} (20.8 to 42.9 kg ha^{-1}). Our mean leaching values by system ranged from 21.8 to 58.2 kg ha^{-1}. Leaching values in our study were in general agreement with resin based leaching values measured in Wyland and Jackson (1993).

One hypothesis of this study was that the addition of winter cover crops to the conventional system would mitigate NO_3^- leaching, but no reduction was observed relative to the conventional system with winter fallow. This was likely a result of the hybrid system's greater levels of soil inorganic N in October, primarily due to higher soil NO_3^- levels remaining after crop harvest (NH_4 levels were similar to the other systems). A majority of cover crop-N may have mineralized late in the season, leaving behind late residual N. The combination of cover crop-N plus chemical fertilizer N inputs to this system likely exceeded the N requirements of the tomato crop, resulting in a high end-of-season residual N pool that increased

Figure 3

Mean ammonium and nitrate levels (mg kg^{-1}) measured in soils (top 60 cm) sampled in (a) October of 2018 and (b) March of 2019 within each cropping system. Error bars depict standard error.



the risk of NO_3^- leaching. When legumes are added to a cropping system, farmers are usually encouraged to account for the legume N credit and reduce subsequent fertilizer rates. However, in the five years prior to this study within the Century Experiment, fertilizer rates were not reduced in the hybrid system relative to the conventional system without cover crops because historical crop yields in the hybrid system remained consistently lower than the conventional system (Li et al. 2019). Therefore, careful decisions were made amongst crop managers, farmer stakeholders, and researchers to maintain fertilizer N rates over time, even though cover crops can contribute N to the soil. The goal was to maximize the yield potential of crops in the hybrid system and avoid the risk of de-incentivizing winter cover crop adoption, especially considering their potential for decreasing N leaching and soil erosion. However, our leaching results in this study show how important it is to account for cover crop N and consequently reduce chemical N fertilizer applications (Li et al. 2019), as to decrease the high NO_3^- leaching potential observed in this study.

Interestingly, the organic system, which incorporates cover crops and composted poultry manure as fertility inputs, leached less NO_3^- (44.7 kg ha^{-1}) than the hybrid system (figure 4). The organic system also displayed lower inorganic N levels in October than the hybrid system, likely resulting in lower NO_3^- leaching potential. Given that <30% of the N content mineralizes from compost in one year (Lazicki et al. 2019), compost is likely to contribute less to the inorganic pool than chemical fertilizer in one year, and organic management may result in soils that better "retain" NO_3^- than conventional management with cover crops through the maintenance of a larger soil microbial biomass pool, which had been consistently observed in other studies in the organic compared to the hybrid system (Tautges and Scow 2020). However, in theory there are larger pools of potentially mineralizable N in compost and manure sources, and it's hard to control and predict the release of N from this pool (Basso and Ritchie 2005). Other studies have found that these biological N pools can lead to high levels of leaching in organic systems (Basso and Ritchie 2005; Kramer et al. 2006; Briggs 2008). In our study, the NO_3^- leaching levels were similar in the conventional and organic systems.

Another explanation for the leaching differences between the hybrid and organic systems could be the cover crop mixtures that established. There was a higher percentage of legumes in the hybrid system (79%) than in the organic system (20%) and a lower percentage of grasses in the hybrid system (12%) than in the organic system (56%). Many studies have shown that legumes are less effective at reducing NO_3^- leaching than grasses (Burger 2011; Thapa et al. 2018; Kaye et al. 2019). In fact, a previous NO_3^- leaching study conducted within the Century Experiment found that a triticale cover crop took up 15 times more soil NO_3^- than bell bean, and triticale plots had less winter NO_3^- leaching (0 to 0.7 kg NO_3^-–N) than both bell bean (0.8 to 1.8 kg NO_3^-–N) and fallow plots (0.8 to

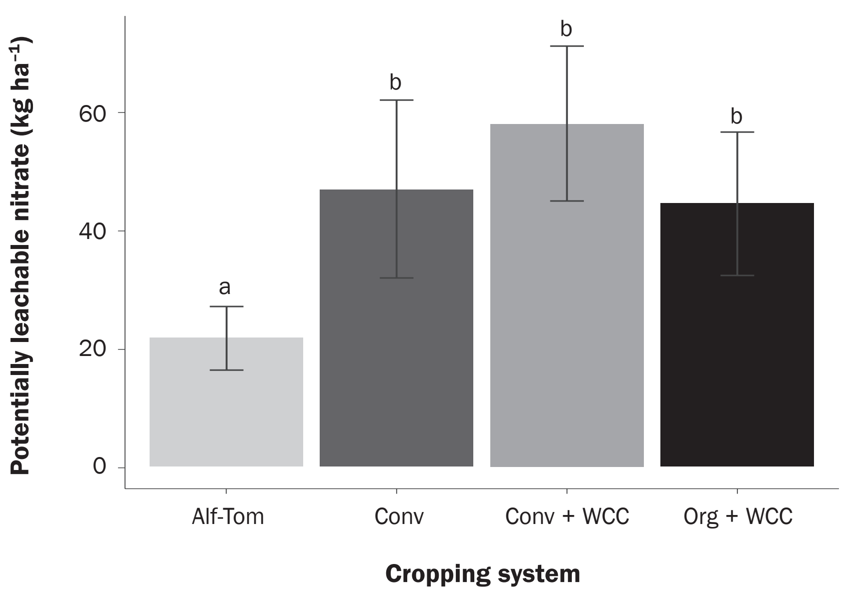
Table 3

Total dissolved nitrogen (TDN) and total N from soils collected in four tomato-based systems in October of 2018 and March of 2019, corresponding to the time of resin bag removal. se = standard error of the mean. Different letters depict statistically significant differences at α = 0.05.

	TDN (n = 3)		Total N (n = 3)	
System	**(mg kg^{-1})**	**se (mg kg^{-1})**	**(g kg^{-1})**	**se (g kg^{-1})**
October				
Alfalfa (Alf-Tom)	27.77a	1.97	1.000a	0.076
Conventional (Conv)	29.36a	9.12	0.983a	0.093
Hybrid (Conv + WCC)	45.60b	6.54	1.067a	0.033
Organic (Org + WCC)	44.20ab	7.10	1.283b	0.067
March				
Alfalfa (Alf-Tom)	11.29a	1.20	0.917ab	0.101
Conventional (Conv)	15.03b	0.96	0.883a	0.073
Hybrid (Conv + WCC)	21.98b	6.66	0.967a	0.017
Organic (Org + WCC)	18.34ab	10.05	1.070b	0.060

Figure 4

Mean potentially leachable nitrate (kg ha^{-1}) levels measured in each cropping system using the resin bag method. Error bars depict 95% confidence intervals.



10.4 kg NO_3^-–N) (Burger 2011). Our results suggest that conventional row crop farmers in the California Central Valley wishing to adopt winter cover cropping should employ grass mixes only, and avoid legume spp., to mitigate NO_3^- leaching potential. While cover cropping adoption is generally considered a conservation practice, if legumes are included, research delineating the N credit of the legumes, and adoption of subsequent reduced chemical fertilizer rates, will be very important. This research will help prevent consequent N pollution and preserve cover cropping's conservation advantages.

The above average precipitation (630 mm) that occurred during the study period, especially during the months of January and February (figures 1 and 2), could also explain why our cover crop systems were unable to reduce NO_3^- leaching. Based on historic rainfall records from 1901 to 2000, this amount exceeds average statewide precipitation by more than 100 mm, though, increasing frequency of flood conditions (and droughts) is highly likely as climate change effects progress in this region (NOAA 2019). Studies have shown that NO_3^- leaching is more likely and occurs at greater magnitudes during heavy rainfall periods, even when nonleguminous cover crops are planted (Thapa et al. 2018). This study showed that under these extreme conditions, our three-way winter cover crop mix was less effective at reducing leaching. However, considering the greater potential for NO_3^- leaching in the hybrid system, the fact that NO_3^- leaching was similar between the conventional and the hybrid systems implies that the addition of cover crops did somewhat increase N retention potential.

Nitrate Leaching in the Alfalfa System (Perennial and Annual Rotation). Even following alfalfa stand termination, the alfalfa system had the lowest amount of winter NO_3^- leached among the four systems (figure 4). Other studies have shown that NO_3^- leaching is reduced under living alfalfa stands (Mathers et al. 1975; Toth and Fox 1998; Basso and Ritchie 2005). For the three years prior to the resin bag installation, these plots were planted to alfalfa and no chemical fertilizer was applied, thus N inputs came solely from biological sources, including N fixation and mineralization of alfalfa biomass (mostly roots and some aboveground biomass left behind after removal) as well as other soil organic pools. This contrasts with the other three systems that received external fertilizer inputs each of the three years prior to the resin bag installation. In addition, cumulatively over the last three years, the tillage intensity was much lower in the alfalfa system than in the other three systems, and tillage intensity could influence microbial activity and the release of NO_3^-. Given alfalfa residue C:N ratios of 15:1 in the shoots and 20:1 in the roots, it was surprising that mineralization of alfalfa residues did not contribute to more NO_3^- leaching, considering that roughly 50% of N mineralization occurs in the winter and early spring periods in the region (Geisseler et al. 2019).

While this study failed to detect differences in soil MBN among the alfalfa, hybrid, and organic systems in this study, likely because of high variability, a remarkably similar study conducted by Song et al. (2021) did detect MBN differences between systems. Song et al. (2021) compared microbial nutrient pools between alfalfa, a sweet clover (*Melilotus*) cover crop, and winter fallow and observed significantly higher MBN in the alfalfa compared with the other nonperennial systems. The presence of a larger microbial community does not necessarily lead to higher N mineralization rates because soil microbial communities can differ significantly in N use efficiency (Zhang et al. 2019). Some microbial communities can take up and incorporate more N (into their bodies) and at higher ratios compared to N loss pathways (e.g., to leaching or denitrification) than other soil microbial communities. Indeed, a concurrent study within these systems of the Century Experiment that employed genomic and functional gene analysis methods to examine microbial communities among the alfalfa, hybrid, and organic systems, found that alfalfa, during its three-year growing period, recruited a microbial community with higher N use efficiency compared to the conventionally managed systems (Samaddar et al. 2021). Interestingly, the microbial pool's higher N use efficiency capacity carried over into the following year of the crop rotation (Samaddar et al. 2021). The findings from the Song et al. (2021) and Samaddar et al. (2021) studies may explain the alfalfa system's ability to limit NO_3^- leaching compared to the incorporation of winter cover crops. It could be the unique ability of a three-year alfalfa stand to facilitate a highly efficient soil microbial community that retains N in biological forms rather than inorganic forms susceptible to loss pathways. Apart from living plants themselves, understanding the ability of certain cropping systems to foster soil microbial communities that are directly capable of higher nutrient use efficiencies and that disfavor loss pathways could be enormously important in improving agriculture's environmental impacts and for preserving surface and groundwater quality. Our results point to a great need to link NO_3^- leaching measurements with the full biological N pathway, incorporating new methods and knowledge of soil microbial pool dynamics. However, these studies are logistically quite difficult, which is where models may become important.

Environmental Implication. Putting our results into an environmental context, we converted mean NO_3^- leaching (kg ha^{-1}) to concentrations (mg L^{-1}) using modeled leaching fluxes. Mean concentrations ranged from 5 mg L^{-1} in the alfalfa treatment to 11 mg L^{-1} in the conventional and organic treatments and 14 mg L^{-1} in the hybrid treatment. Leaching at our site exceeded the USEPA drinking water NO_3^- as N standard of 10 mg L^{-1} for all treatments except alfalfa. These data question the effectiveness of cover crops as a N leaching mitigation strategy. While such cover crops take up and remove mineral N from the soil, they also transpire soil water that otherwise would be flowing to the groundwater as recharge. Across California, NO_3^- leaching, derived primarily from agriculture, is an environmental concern because groundwater concentrations often exceed the USEPA MCL (Harter et al. 2012; Rosenstock et al. 2014). Because groundwater accounts for approximately 60% of California's drinking water (Rosenstock et al. 2014), it is imperative to protect the quality of these waters.

Numerical Modeling. Calibrated HYDRUS-1D estimates of final soil NO_3^- and NH_4 profile concentrations were in good agreement with measured values for all four cropping systems (NSE = 0.8 for total mineral N; figures 5 through 8 [b,c,and d]). Modeled and observed averaged total N uptake were in the same range for both treatments with cover crops (figures 6f and 7f). These results are as expected, as measured final N contents in cover crop biomass were used as potential N uptake and reassure that the model follows field behavior. Estimates of NO_3^- leaching by modeling and measurements were in agreement for the hybrid and conventional systems, when considering the standard deviations calculated for each system (from 3 simulations and 30 measured resin bags each). In the conventional system, leached N in the model averaged 103.7 ± 40.5 kg ha^{-1}, and measured leached N was 47.1 ± 39.5 kg ha^{-1} (figure 5e). In the hybrid system, the model estimated 62.6 ± 8.9 kg ha^{-1}, and measurement estimated 58.2 ± 35.1 kg ha^{-1} (figure 6e) of leached N.

However, in the organic system the model underestimated N leached compared to what was observed. Leached N estimated by the model was 7.1 ± 4.4 kg ha^{-1}, and by measurement was 44.7 ± 32.6 kg ha^{-1} (figure 7e). The observed differences could be due to the lack of accounting for compost application in the model as well as biologically fixed cover crop N. Some proportion of compost-N likely mineralized and leached during the winter rainy season. Also, larger pools of mineralizable N due to higher organic matter content in the organic system, as well as uncertainty related to the timing and rates of N release from these pools, likely contributed to the lack of reconciliation between methods. Organic material first-order mineralization processes and biologically fixed N should be included in HYDRUS simulations and similar models to improve N leaching predictions, particularly for alternative, nonchemical-N based systems (Matteau et al. 2019).

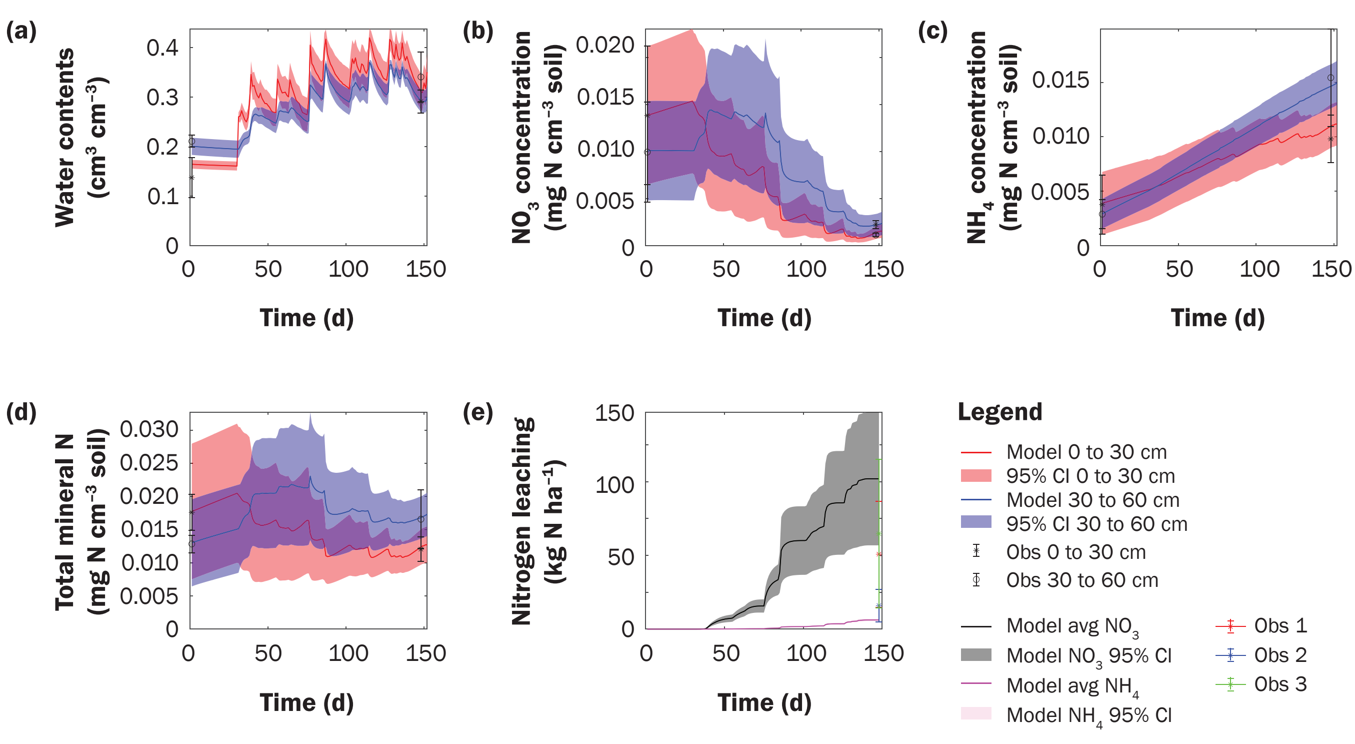
For the alfalfa–tomato system, the model predicted more than five times the N leached (116.3 ± 18 kg ha^{-1}) than what the measured data (21.8 ± 14.5 kg ha^{-1}) indicated (figure 8e). Incorporation of >4,000 kg ha^{-1} of high C:N biomass, in the form of alfalfa roots and crowns, likely resulted in high rates of microbial immobilization of soil NO_3^-, a process not simulated in the model, either residual or mineralized during the winter season. Toth and Fox (1998) also observed large reductions in NO_3^- leaching both during growth and after termination of alfalfa compared to maize. Microbial processes not considered in the model, such as perennial rhizosphere activity dynamics, N fixation, and first-order mineralization of organic amendments, may have had an important influence on winter NO_3^- leaching.

The process-based modeling approach used in this study yielded modeled results not biased by extensive calibration. These results emphasize that the HYDRUS model used in its general form gives reasonable results for systems that rely mainly on mineral fertilizers, but for systems relying on biological sources of N such as organic or in rotational alfalfa, N production models need to be added to the solute transport and flow models from HYDRUS.

Rainfall Scenarios. The models developed for NO_3^- leaching in the conventional and hybrid systems were in the one standard deviation range with measured NO_3^- leaching values and were therefore used to evaluate how differences in precipitation patterns over 29 precipitation seasons might affect winter leaching. We considered these

Figure 5

(a) Averaged water contents, (b) nitrate (NO_3^-) soil concentrations, (c) ammonium (NH_4^+) soil concentrations, and (d) total mineral nitrogen (N) at the 0 to 30 and 30 to 60 depths in the *conventional system*. (e) Modeled NO_3^- and NH_4^+ leaching and potential measured NO_3^- leaching. Lines are three plot averages and shaded areas represent 95% confidence intervals. Empirical in-field measurements are depicted as treatment means, except for (e) N leaching, where all three replicate measurements are shown.



results to reflect general trends and not absolute values, as these models have not been validated for multiple years.

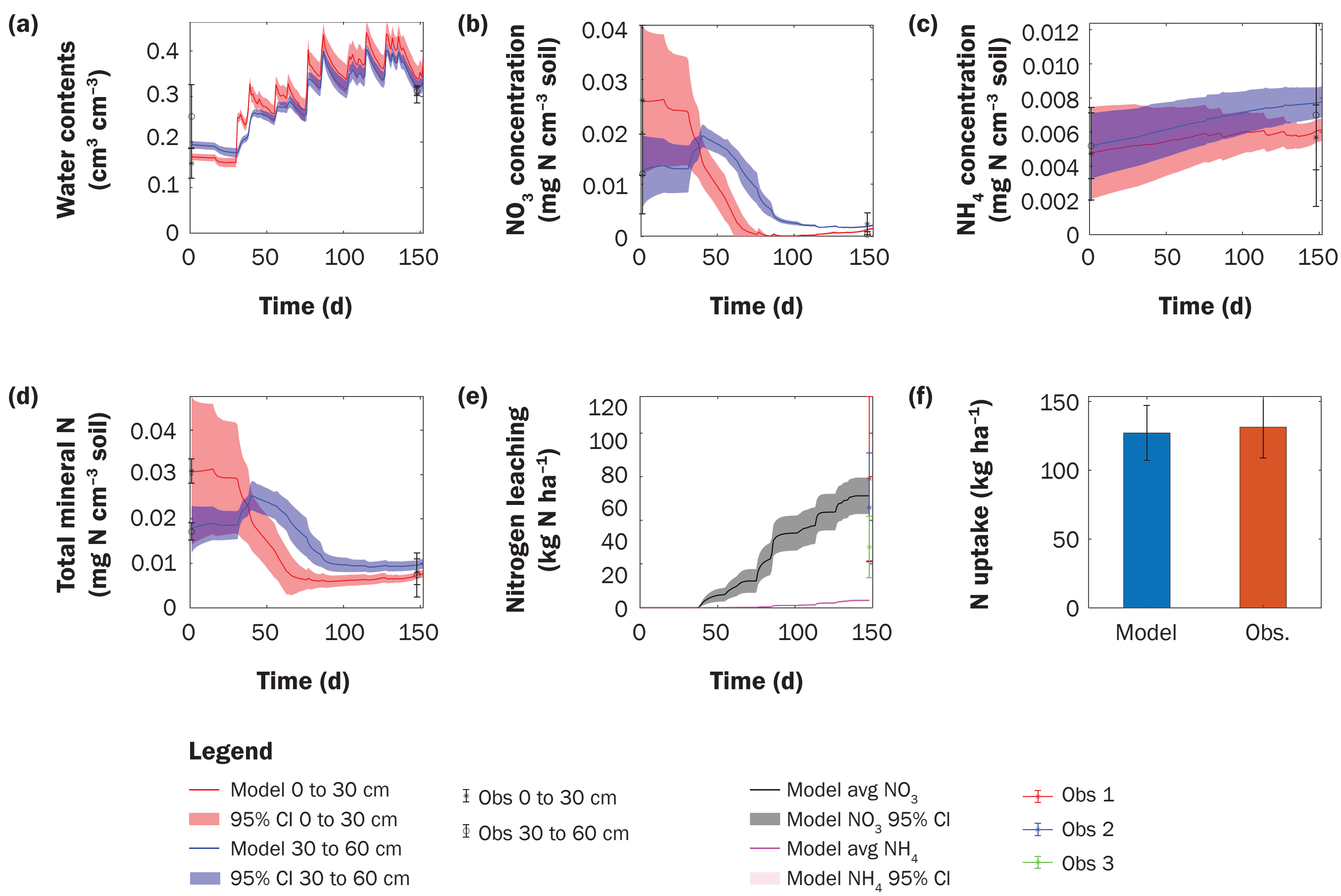
Simulations were divided into wet, dry, and medium years as defined in the methodology section. For both conventional and hybrid systems, wet years yielded higher N leaching than drier years (figure 9) even though NO_3^--N concentrations were lower in wet than dry years (figure 10). These results highlight the importance of winter aquifer recharge with low or N free water and the trade-off between lower N leaching with less water percolation, despite higher N concentrations in the leachate.

Resin Suitability and Considerations. There are some considerations that should be made when interpreting these leaching data. One consideration worth noting is that the resin bags were not installed below the entire cover crop rooting zone. However, from previous research, we know that the area above the resin bags encompassed most (>90%) of the effective rooting zone, therefore, it's likely that the leaching values reported are representative of actual field conditions. It's also important to consider the following assumptions that were made about the resin bags: (1) variability between resin measurements (within plot) can be justified by soil heterogeneity, roots, and biology; (2) resin bag dimensions were maintained throughout the study; (3) there were no hydrologic discontinuities created during bag installation; and (4) the bags were able to capture all the NO_3^- that passed through.

Nitrogen Budget. We measured many N pools and processes in our study including changes in soil TN, TDN, MBN, NO_3^-, and NH_4^+, cover crop N uptake, and N leaching, and could create a partial budget for our different systems. It was beyond the scope of our project to measure gaseous losses via N_2 and nitrous oxide (N_2O), ammonia (NH_3) volatilization, dissolved organic N leaching, and atmospheric N deposition (Sainju 2017; Gardner and Drinkwater 2009). Excluding

Figure 6

(a) Averaged water contents, (b) nitrate (NO_3^-) soil concentrations, (c) ammonium (NH_4^+) soil concentrations, and (d) total mineral nitrogen (N) at the 0 to 30 and 30 to 60 depths in the *hybrid system*. (e) Modeled NO_3^- and NH_4^+ leaching and potential measured NO_3^- leaching. Lines are three plot averages and shaded areas represent 95% confidence intervals. (f) Modeled and observed total N uptake in the winter cover crops, error bars depict one standard deviation. Empirical in-field measurements are depicted as treatment means, except for (e) N leaching, where all three replicate measurements are shown.



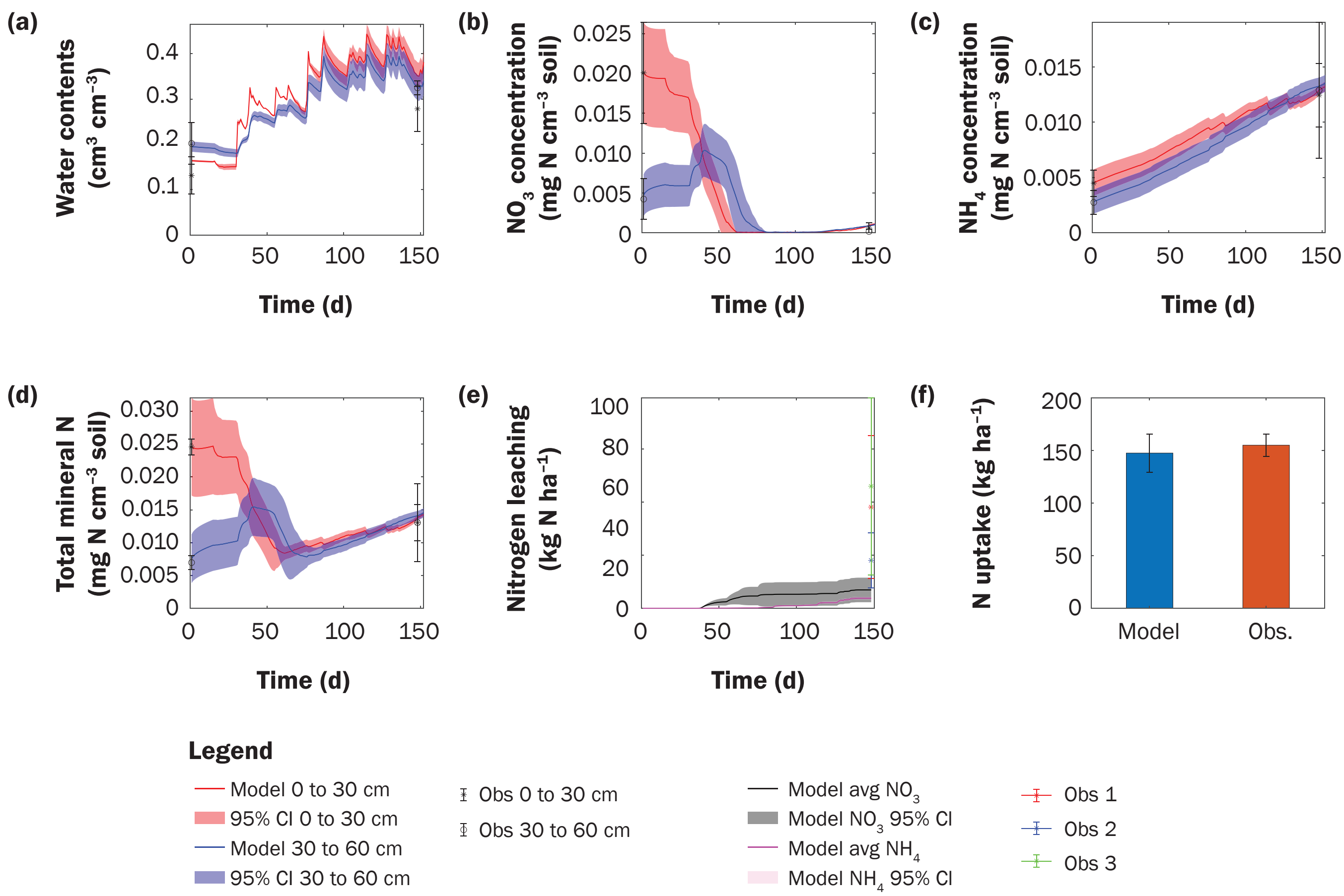
the N components that we did not measure, we were still able to account for between 84% and 93% of N in the systems. The largest amount of unaccounted N (16%) occurred in the organic system, which was smaller than the average 38% of unaccounted N found in a meta-analysis of studies using ^{15}N tracers to conduct field-scale mass balance N budgets (Gardner and Drinkwater 2009). Other possible losses of N in our study were gaseous losses of N_2 and N_2O and/or leaching losses via dissolved organic matter and dissolved organic N (Murphy et al. 2000; van Kessel et al. 2009).

Summary and Conclusions

Our leaching data revealed that perennial cropping with alfalfa was effective for reducing NO_3^- leaching, whereas replacement of chemical with organic fertilizers and/or a grass + legume cover crop mix had no effect. Alfalfa, even after termination, was able to significantly reduce NO_3^- leaching, likely because of alfalfa's transformative impact on soil microbial communities compared to annual systems (though much more research is needed in this area). Ion-exchange resin bags were a cost- and time-effective method for measuring NO_3^- leaching in our row crop systems, and this method would be easy to deploy on farms where more intensive instrumentation is impractical. HYDRUS-1D estimates of NO_3^- leaching losses were in agreement with in-field resin bag measurements under conventional production conditions where chemical fertilizers and winter fallow versus cover crops were used. However, in the system receiving compost as a soil amendment and in the alfalfa rotation, there was greater disagreement between model estimates and measurements of N leaching. Our results suggest that the model would be strengthened by incorporation of soil microbial processes, including first-order C and N mineralization and N fixation, that are not currently accounted for. Models that can better describe the roles soil microbes can

Figure 7

(a) Averaged water contents, (b) nitrate (NO_3^-) soil concentrations, (c) ammonium (NH_4^+) soil concentrations, and (d) total mineral nitrogen (N) at the 0 to 30 and 30 to 60 depths in the *organic system*. (e) Modeled NO_3^- and NH_4^+ leaching and potential measured NO_3^- leaching. Lines are three plot averages and shaded areas represent 95% confidence intervals. (f) Modeled and observed total N uptake in the winter cover crops, error bars depict one standard deviation. Empirical in-field measurements are depicted as treatment means, except for (e) N leaching, where all three replicate measurements are shown.



play in preventing nutrient losses would provide valuable and convincing evidence of the benefits of building and sustaining soil microbial communities and activity in agricultural soils (Matteau et al. 2019).

This study also highlighted the potential environmentally beneficial implications of including alfalfa in vegetable rotations, particularly after crops receiving high amounts of N fertilizers. Compared to other practices that have been suggested for mitigation of N pollution from agricultural systems, including cover cropping and replacement of chemical N fertility sources with organic sources like compost, alfalfa was the only practice that significantly reduced NO_3^- leaching in this study. Increased cultivation of alfalfa across the agricultural landscape, especially in areas highly susceptible to NO_3^- leaching like regions with sandy soils, high water tables, and close proximity to important sources of drinking water, could lead to significant gains in both prevention and mitigation of N pollution from agricultural nonpoint sources. However, action is needed to counteract the recent declines in alfalfa cultivation in the state of California and nationwide due to the poor economics often associated with alfalfa cropping. The decreased incidence of alfalfa on California's landscape may have already contributed to increases in NO_3^- leaching from agricultural systems that increasingly feature annual vegetable crops with high fertilizer N application rates. Greater financial incentives, offered either via the market through increases in alfalfa hay demand and price point, or via programs delivered by governmental and nonprofit organizations, are needed to increase farmer willingness and financial feasibility of alfalfa cultivation. While results from this study represent only one winter rainy season and an anomalous season at that, this study still provides useful data to guide N management in California vegetable cropping systems. To strengthen our findings, future work should focus on repeating this study over multiple years and crop phases. Our results also support recommendations to track soil N residual levels and adjust both cover crop mixes and N fertilizer rates accordingly. Proper tracking will help reduce residual soil N levels over the winter and limit N leaching and pollution from these systems.

Supplemental Material

The supplementary material for this article is available in the online journal at https://doi.org/10.2489/jswc.2022.00155.

Acknowledgements

We thank Israel Herrera and L. Loza Reyes at Russell Ranch Sustainable Agriculture Facility in University of California, Davis, for their valuable support in our field study. This publication was made possible by funding from the National Alfalfa & Forage Alliance (NAFA) and the USDA, National Institute of Food and Agriculture (NIFA) through Hatch Formula Funding CA 2122-H and multistate regional project W-2082. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the National Institute of Food and Agriculture (NIFA) or the United States Department of Agriculture (USDA).

Figure 8

(a) Averaged water contents, (b) nitrate (NO_3^-) soil concentrations, (c) ammonium (NH_4^+) soil concentrations, and (d) total mineral nitrogen (N) at the 0 to 30 and 30 to 60 depths in the *alfalfa-tomato system*. (e) Modeled NO_3^- and NH_4^+ leaching and potential measured NO_3^- leaching. Lines are three plot averages and shaded areas represent 95% confidence intervals. Empirical in-field measurements are depicted as treatment means, except for (e) N leaching, where all three replicate measurements are shown.

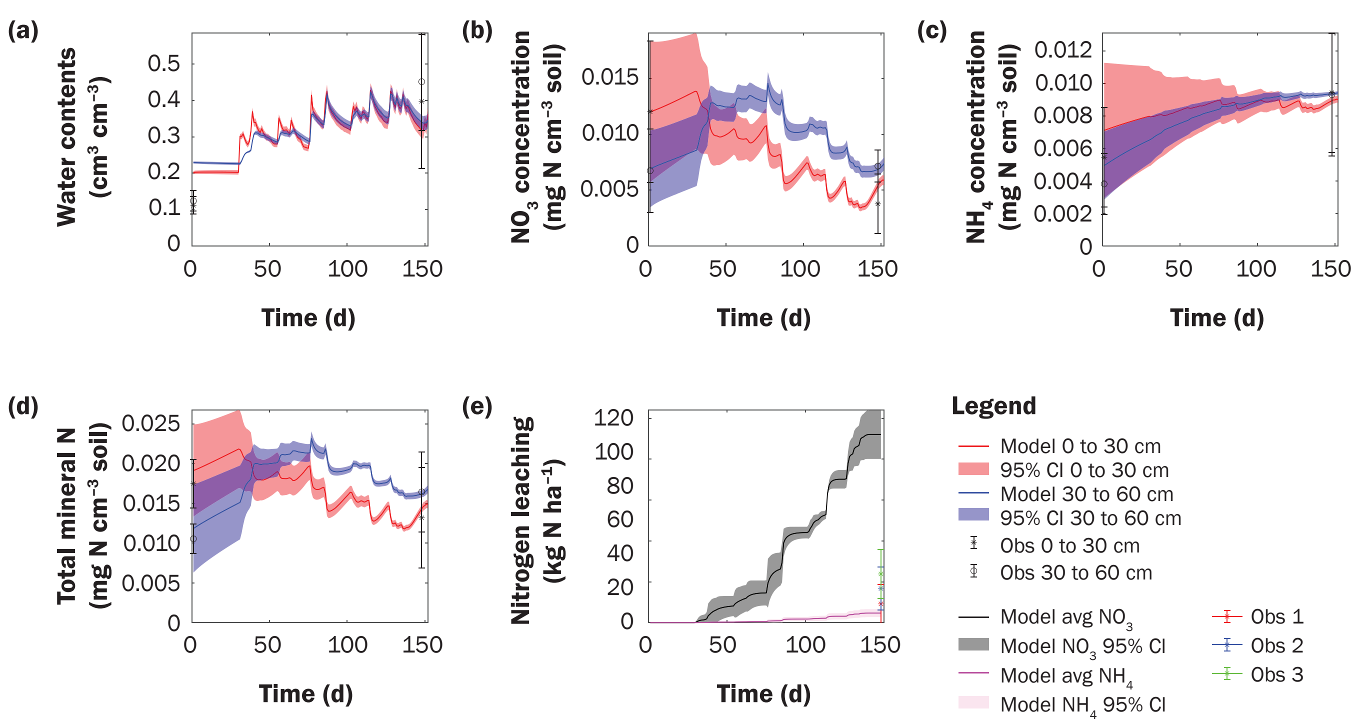


Figure 9
Nitrate (NO_3^--N) leaching averages and 95% confidence intervals in the (a) conventional and (b) hybrid treatments for 1990 through 2018. Results are divided into dry, wet, and average years.

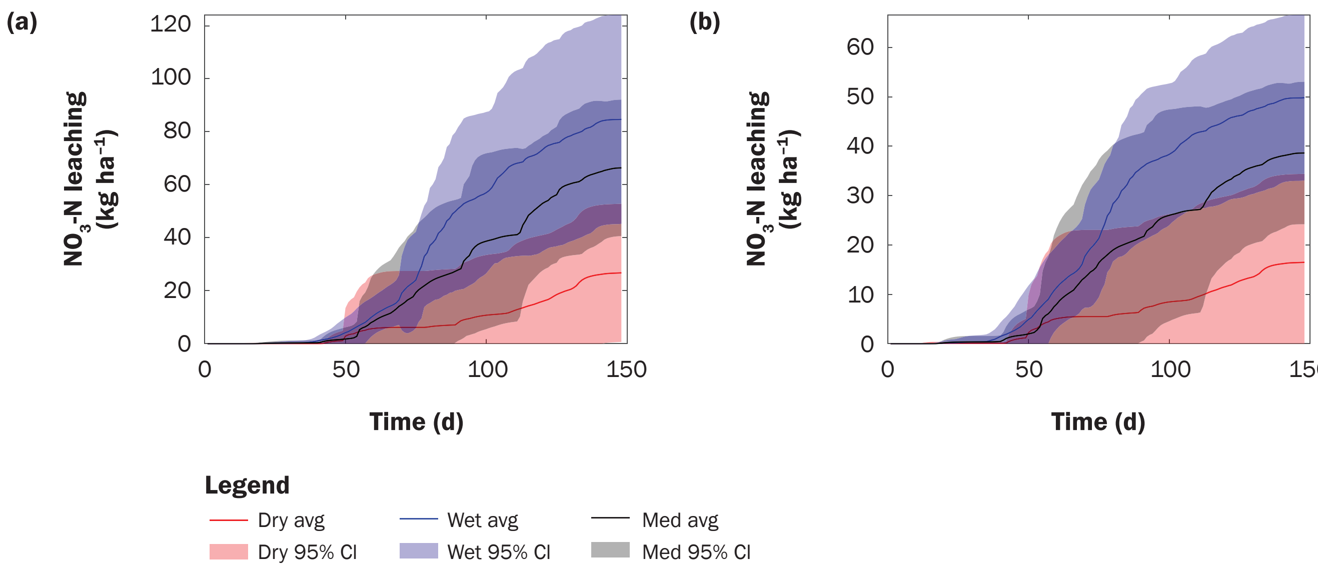
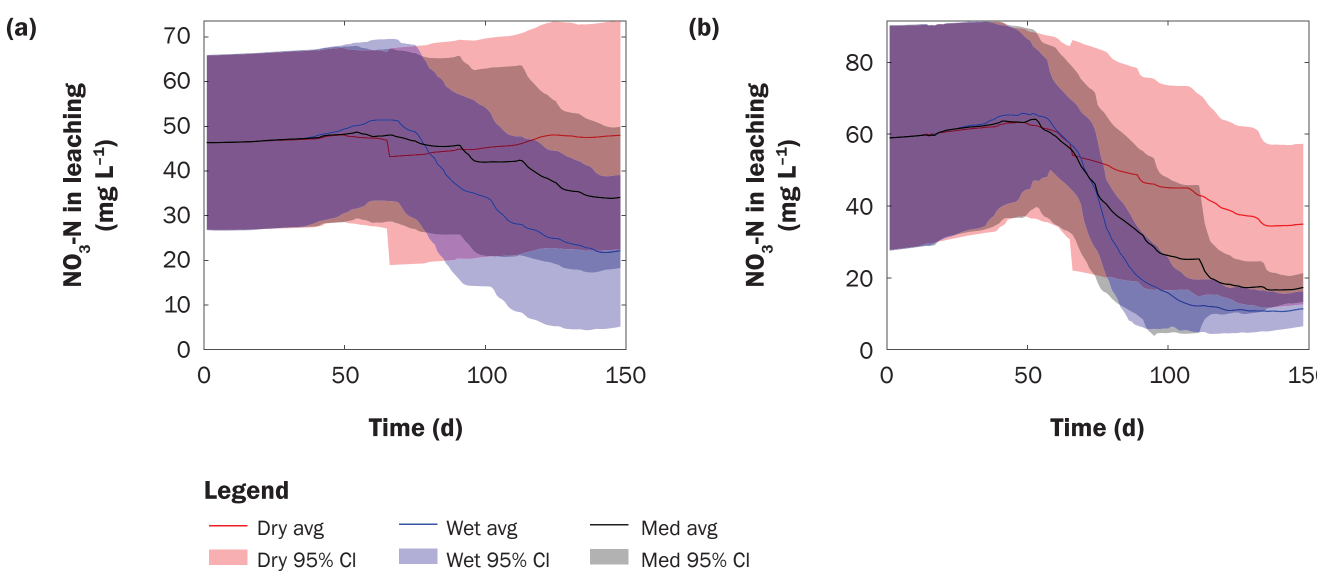


Figure 10
Nitrate (NO_3^--N) leaching concentration averages and 95% confidence intervals in the (a) conventional and (b) hybrid treatments. Results are divided into dry, wet, and average years.



References

Abraha, M.G., and M.J. Savage. 2008. The soil water balance of rainfed and irrigated oats, Italian rye grass and rye using the CropSyst model. Irrigation Science 26:203–212.

Al-Darby, A., and G. Abdel-Nasser. 2006. Nitrate leaching through unsaturated soil columns: Comparison between numerical and analytical solutions. Journal of Applied Sciences 6:735-743.

Baram, S., V. Couvreur, T. Harter, M. Read, P.H. Brown, M. Kandelous, D.R. Smart, and J.W. Hopmans. 2017. Estimating nitrate leaching to groundwater from orchards: Comparing crop nitrogen excess, deep vadose zone data-driven estimates, and HYDRUS modeling. Vadose Zone Journal 15:1-13.

Basso, B., and J.T. Ritchie. 2005. Impact of compost, manure, and inorganic fertilizer on nitrate leaching and yield for a 6-year maize-alfalfa rotation in Michigan. Agriculture, Ecosystems, and Environment 108:329-341.

Binkley, D. 1984. Ion exchange resin bags: Factors affecting estimates of nitrogen availability. Soil Science Society of America Journal 48:1181-1184.

Black, C.A. 1965. Methods of Soil Analysis: Part I, Physical and Mineralogical Properties. Madison, WI: American Society of Agronomy.

Briggs, S. 2008. Institute of Organic Training and Advice: Research Review: Nitrogen Supply and Management in Organic Farming. Institute of Organic Training and Advice.

Brookes, P.C., A. Landman, G. Pruden, and D.S. Jenkinson. 1985. Chloroform fumigation and the release of soil nitrogen: A rapid direct extraction method to measure microbial biomass nitrogen in soil. Soil Biology and Biochemistry 17:837-842.

Burger, M. 2011. Evaluation of winter cover crops to reduce nitrate leaching and increase yields in drip-irrigated tomato rotations. California Department of Food & Agriculture Specialty Crop Block Grant Program, 2011 Final Report No. 13. Sacramento, CA: California Department of Food & Agriculture. https://www.cdfa.ca.gov/Specialty_Crop_Competitiveness_Grants/FinalPerformanceReports.html.

Cabrera, M.L., and M.H. Beare. 1993. Alkaline persulfate oxidation for determining total nitrogen in microbial biomass extracts. Soil Science Society of America Journal 57:1007-1012.

Cassman, K.G., A.R. Dobermann, and D.T. Walters. 2002. Agroecosystems, nitrogen-use efficiency, and nitrogen management. Ambio 31:132-140.

CDFA (California Department of Food and Agriculture). 2018. California Agricultural Statistics Review. Sacramento, CA: California Department of Food and Agriculture. http://www.cdga.gov/statistics.

Desormeaux, A., M.D. Annable, D. Dobberfuhl, and J.W. Jawitz. 2019. In situ measurement of nitrate flux and attenuation using a soil passive flux meter. Journal of Environmental Quality 48:709-716.

Doane, T.A., and W.R. Horwath. 2003. Spectrophotometric determination of nitrate with a single reagent. Analytical Letters 36:2713-2722.

Doorenbos, J., and W.O. Pruitt. 1977. FAO irrigation and drainage paper. Crop water requirements. Rome: The Food and Agriculture Organization of the United Nations.

Finney, D.M., C.M. White, and J.P. Kaye. 2016. Biomass production and carbon/nitrogen ration influence on ecosystem services from cover crop mixtures. Agronomy Journal 108:39-52.

Gardner, J.B., and L.E. Drinkwater. 2009. The fate of nitrogen in grain cropping systems: A meta-analysis of ^{15}N field experiments. Ecological Applications 19:2167-2184.

Geisseler, D., K.S. Miller, B.J. Aegerter, N.E. Clark, and E.M. Miyao. 2019. Estimation of annual soil nitrogen mineralization rates using an organic-nitrogen budget approach. Soil Science Society of America Journal 83:1227-1235.

Grahmann, K., N. Verhulst, L.M. Palomino, W. Bischoff, B. Govaerts, and A. Buerkert. 2018. Ion exchange resin samplers to estimate nitrate leaching from a furrow irrigated wheat-maize cropping system under different tillage-straw systems. Soil and Tillage Research 175:91-100.

Hanson, B.R., J. Šimůnek, and J.W. Hopmans. 2006. Evaluation of urea-ammonium-nitrate fertigation with drip irrigation using numerical modeling. Agricultural Water Management 86:102–113.

Harter, T., J.R. Lund, J. Darby, G.E. Fogg, R. Howitt, K.K. Jessoe, G.S. Pettygrove, J.F. Quinn, and J.H. Viers. 2012. Addressing nitrate in California's drinking water with a focus on Tulare Lake Basin and Salinas Valley groundwater. Report for the State Water Resources Control Board Report to the Legislature. Davis, CA: Center for Watershed Sciences, University of California.

Horwath, W.R., and E.A. Paul. 1996. Microbial Biomass. *In* Methods of Soil Analysis, Part 2-Microbiological and Biochemical Properties, eds. R.W. Weaver, J.S. Angle, and P.S. Bottomley, 753-773. Madison, WI: Soil Science Society of America.

Kage, H. 1995. Interaction of nitrate uptake and nitrogen fixation in faba beans. Plant Soil 176:189–196.

Kaye, J., D. Finney, C. White, B. Bradley, M. Schipanski, M. Alonso-Ayuso, M. Hunter, M. Burgess, and C. Mejia. 2019. Managing nitrogen through cover crop species selection in the U.S. mid-Atlantic. PLoS ONE 14(4):e0215448.

Kramer, S.B., J.P. Reganold, J.D. Glover, B.J. Bohannan, and H.A. Mooney. 2006. Reduced nitrate leaching and enhanced denitrifier activity and efficiency in organically fertilized soils. Proceedings of the National Academy of Sciences 103:4522-4527.

Lazicki, P., D. Geisseler, and M. Lloyd. 2019. Nitrogen mineralization from organic amendments is variable but predictable. Journal of Environmental Quality 49:483-495.

Li, M., C.A. Peterson, N.E. Tautges, K.M. Scow, and A.C. Gaudin. 2019. Yields and resilience outcomes of organic, cover crop, and conventional practices in a Mediterranean climate. Scientific Reports 9(1):1-11.

Mathers, A.C., B.A. Stewart, and B. Blair. 1975. Nitrate-nitrogen removal from soil profiles by alfalfa. Journal of Environmental Quality 4(3):403-405.

Matteau, J.P., S.J. Gumiere, J. Gallichand, G. Létourneau, L. Khiari, M.O. Gasser, and A. Michaud. 2019. Coupling of a nitrate production model with HYDRUS to predict nitrate leaching. Agricultural Water Management 213:616–626.

Mualem, Y. 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. Water Resources Research 12:513–522.

Murphy, D.V., A.J. Macdonald, E.A. Stockdale, K.W.T. Goulding, S. Fortune, J.L. Gaunt, P.R. Poulton, J.A. Wakefield, C.P. Webster, and W.S. Wilmer. 2000. Soluble organic nitrogen in agricultural soils. Biology and Fertility of Soils 30:374-387.

NOAA (National Oceanic and Atmospheric Administration, National Centers for Environmental Information). 2019. Climate at a Glance: Statewide Time Series. Washington, DC: NOAA. https://www.ncdc.noaa.gov/cag/.

Pampolino, M.F., T. Urushiyama, and R. Hatano. 2000. Detection of nitrate leaching through bypass flow using pan lysimeter, suction cup, and resin capsule. Soil Science and Plant Nutrition 46:703-711.

Qian, P., and J.J. Schoenau. 2002. Practical applications of ion exchange resins in agricultural and environmental soil research. Canadian Journal of Soil Science 82:9-21.

R Core Team. 2013. R: A language and environment for statistical computing. Vienna: R Foundation for Statistical Computing. http://www.R-project.org.

Ramos, T.B., J. Šimůnek, M.C. Goncalves, J.C. Martins, A. Prazeres, and L.S. Pereira. 2012. Two-dimensional modeling of water and nitrogen fate from sweet sorghum irrigated with fresh and blended saline waters. Agricultural Water Management 111:87–104.

Rosenstock, T.S., D. Liptzin, K. Dzurella, A. Fryjoff-Hong, A. Hollander, V. Jensen, A. King, G. Kourakos, A. McNally, G.S. Pettygrove, J. Quinn, J.H. Viers, T.P. Tomich, and T. Harter. 2014. Agriculture's contribution to nitrate contamination of Californian groundwater (1945-2005). Journal of Environmental Quality 43:895-907.

Sainju, U.M. 2017. Determination of nitrogen balance in agroecosystems. MethodsX 4:199-208.

Samaddar, S., R. Schmidt, N.E. Tautges, K. Scow. 2021. Adding alfalfa to an annual crop rotation shifts the composition and functional responses of tomato rhizosphere microbial communities. Applied Soil Ecology 167:104102.

Schnabel, R.R. 1983. Measuring nitrogen leaching with ion exchange resin: A laboratory assessment. Soil Science Society of America Journal 47:1041-1042.

Sims, G.K., T.R. Ellsworth, R.L. and Mulvaney. 1995. Microscale determination of inorganic nitrogen in water and soil extracts. Communications in Soil Science and Plant Analysis 26:303-316.

Šimůnek, J., and J.W. Hopmans. 2009. Modeling compensated root water and nutrient uptake. Ecological Modelling 220:505–521.

Šimůnek, J., M. Šejna, H. Saito, M. Sakai, and M.T. van Genuchten. 2013. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Riverside, CA: University of California Riverside.

Šimůnek, J., M.T. van Genuchten, and M. Šejna. 2016. Recent developments and applications of the HYDRUS computer software packages. Vadose Zone Journal 15:1-25.

Singh, G., G. Kaur, K. Williard, J. Schoonover, and J. Kang. 2017. Monitoring of water and solute transport in the vadose zone: A review. Vadose Zone Journal 17:1-23.

Song, X., C. Fang, Z. Yuan, and F. Li. 2021. Long-term growth of alfalfa increased soil organic matter accumulation and nutrient mineralization in a semi-arid environment. Frontiers in Environmental Science 9:649346.

Susfalk, R.B., and D.W. Johnson. 2002. Ion exchange resin based soil solution lysimeters and snowmelt solution collectors. Communications in Soil Science and Plant Analysis 33:1261-1275.

Tafteh, A., and A.R. Sepaskhah. 2012. Application of HYDRUS-1D model for simulating water and nitrate leaching from continuous and alternate furrow irrigated rapeseed and maize fields. Agricultural Water Management 113:19-29.

Tautges, N.E., J.L. Chiartas, A.C.M. Gaudin, A.T. O'Green, I. Herrera, and K.M. Scow. 2019. Deep soil inventories reveal that impacts of cover crops and compost on soil carbon sequestration differ in surface and subsurface soils. Global Change Biology 25:3753-3766.

Tautges, N., and K. Scow. 2020. Chapter 3: Pursuing agroecosystem resilience in a long-term Mediterranean agricultural experiment. *In* Long-term Farming Systems Research, ed. G. Bhullar and A. Riar, 53-69. Amsterdam: Elsevier.

Thapa, R., S.B. Mirsky, and K.L. Tully. 2018. Cover crops reduce nitrate leaching in agroecosystems: A global meta-analysis. Journal of Environmental Quality 47:1400-1411.

Toth, J.D., and R.H. Fox. 1998. Nitrate loss from a corn-alfalfa rotation: Lysimeter measurement of nitrate leaching. Journal of Environmental Quality 27:1027-1033.

UCD Weather & Climate Stations (University of California Davis). 2019. Campbell Tract rainfall and air temperature. http://atm.ucdavis.edu/weather/uc-davis-weather-climate-station/.

USEPA (US Environmental Protection Agency). 2018. 2018 Edition of the drinking water standards and health advisories tables. Washington, DC: Office of Water, USEPA.

van Genuchten, M.T. 1980. A Closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44:892–898.

van Kessel, C., T. Clough, and J.W. van Groenigen. 2009. Dissolved organic nitrogen: An overlooked pathway of nitrogen loss from agricultural systems? Journal of Environmental Quality 38:393-401.

Verdouw, H., C.J.A. van Echteld, and E.M.J. Dekkers. 1978. Ammonia determination based on indophenol formation with sodium salicylate. Water Research 12:399-402.

Viers, J.H., D. Liptzin, T.S. Rosenstock, V.B. Jensen, A.D. Hollander, A. McNally, and A.M. King. 2012. Addressing nitrate in California's drinking water, with a focus on Tulare Lake Basin and Salinas Valley groundwater. Report for the State Water Resources Control Board Report to the Legislature. Davis, CA: Center for Watershed Sciences, University of California.

Ward, M.H., T.M. deKok, P. Levallois, J. Brender, G. Gulis, B.T. Nolan, and J. VanDerslice. 2005. Workgroup report: Drinking-water nitrate and health—Recent findings and research needs. Environmental Health Perspectives 113:1607-1614.

Weihermüller, L., J. Siemens, M. Deurer, S. Knoblauch, H. Rupp, A. Göttlein, and T. Pütz. 2007. In situ soil water extraction: A review. Journal of Environmental Quality 36:1735-1748.

Wolf, K.M., E.E. Torbert, D. Bryant, M. Burger, R.F. Denison, I. Herrera, J. Hopmans, W. Horwath, S. Kaffka, A.Y.Y. Kong, R.F. Norris, J. Six, T.P. Tomich, and K.M. Scow. 2018. The century experiment: The first twenty years of UC Davis' Mediterranean agroecological experiment. Ecology 99(2):503.

Wyland, L.J., and L.E. Jackson. 1993. Evaluating nitrate recovery by ion-exchange resin bags. Soil Science Society of America Journal 57:1208-1211.

Wyland, L.J., L.E. Jackson, W.E. Chaney, K. Klonsky, S.T. Koike, and B. Kimple. 1996. Winter cover crops in a vegetable cropping system: Impacts on nitrate leaching, soil water, crop yield, pests and management costs. Agriculture Ecosystems & Environment 59:1-17.

Zhang, Y., and M.G. Schaap. 2017. Weighted recalibration of the Rosetta pedotransfer model with improved estimates of hydraulic parameter distributions and summary statistics (Rosetta3). Journal of Hydrology 547(2017):39–53.

Zhang, S., Q. Zheng, L. Noll, Y. Hu, and W. Wanek. 2019. Environmental effects on soil microbial nitrogen use efficiency are controlled by allocation of organic nitrogen to microbial growth and regulate gross N mineralization. Soil Biology and Biochemistry 135:304-315.