

# Fertilizer Management Effects on Nitrate Leaching and Indirect Nitrous Oxide Emissions in Irrigated Potato Production

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Potato (*Solanum tuberosum* L.) is a N-intensive crop, with high potential for nitrate ( $\text{NO}_3^-$ ) leaching, which can contribute to both water contamination and indirect nitrous oxide ( $\text{N}_2\text{O}$ ) emissions. Two approaches that have been considered for reducing N losses include conventional split application (CSA) of soluble fertilizers and single application of polymer-coated urea (PCU). The objectives of this study were to: (i) compare  $\text{NO}_3^-$  leaching using CSA and two PCUs (PCU-1 and PCU-2), which differed in their polymer formulations, and (ii) use measured  $\text{NO}_3^-$  leaching rates and published emissions factors to estimate indirect  $\text{N}_2\text{O}$  emissions. Averaged over three growing seasons (2007–2009),  $\text{NO}_3^-$  leaching rates were not significantly different among the three fertilizer treatments. Using previously reported direct  $\text{N}_2\text{O}$  emissions data from the same experiment, total direct plus indirect growing season  $\text{N}_2\text{O}$  emissions with PCU-1 were estimated to be 30 to 40% less than with CSA. However, PCU-1 also resulted in greater residual soil N after harvest in 2007 and greater soil–water  $\text{NO}_3^-$  in the spring following the 2008 growing season. These results provide evidence that single PCU applications for irrigated potato production do not increase growing season  $\text{NO}_3^-$  leaching compared with multiple split applications of soluble fertilizers, but have the potential to increase N losses after the growing season and into the following year. Estimates of indirect  $\text{N}_2\text{O}$  emissions ranged from 0.8 to 64% of direct emissions, depending on what value was assumed for the emission factor describing off-site conversion of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ . Thus, our results also demonstrate how more robust models are needed to account for off-site conversion of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ , since current emission factor models have an enormous degree of uncertainty.

POTATO (*Solanum tuberosum* L.) is the fourth most consumed food crop in the world, after rice (*Oryza sativa* L.), wheat (*Triticum* L.), and corn (*Zea mays* L.), and is the leading vegetable crop in the United States, with an annual per capita consumption of 60 kg (ERS, 2010). Potato is also N intensive. In Minnesota, best management practices (BMPs) recommend fertilizer rates up to 285 kg N ha<sup>-1</sup>, depending on yield potential (Rosen and Bierman, 2008). Potato is commonly grown on coarse-textured soils requiring irrigation to maintain tuber size and quality (Shock et al., 2007). Irrigated potatoes concentrate 60 to 85% of their root mass within the top 30 cm of soil (Stalham and Allen, 2001; Leszczynski and Tanner, 1976) and are relatively inefficient in capturing fertilizer N. Errebhi et al. (1998) found that an irrigated potato crop recovered only 33 to 56% of the N that was applied. Thus, groundwater  $\text{NO}_3^-$  contamination originating from potato production is a concern (Kraft and Stites, 2003).

High rates of N fertilizer input also create the potential for elevated emissions of  $\text{N}_2\text{O}$ , which has a global warming potential 298 times greater than carbon dioxide and is the most important ozone-depleting anthropogenic emission (Forster et al., 2007; Ravishankara et al., 2009). Fertilizer N can be transformed to  $\text{N}_2\text{O}$  and be emitted directly from fertilized soil to the atmosphere (Venterea, 2007). Direct  $\text{N}_2\text{O}$  emissions in potato systems have been examined in several studies (Ruser et al., 2006; Vallejo et al., 2006; Burton et al., 2008; Haile-Mariam et al., 2008). In addition, so-called “indirect” emissions of  $\text{N}_2\text{O}$  can originate from other chemical forms of N that are lost from the fertilized field and subsequently transformed to  $\text{N}_2\text{O}$  in a receiving ecosystem. For example, the highly mobile  $\text{NO}_3^-$  ion can be transported to groundwater, aquatic, or estuarial ecosystems where it can be transformed and emitted as  $\text{N}_2\text{O}$  (von der Heide et al., 2009; Nevison, 2000; De Klein et al., 2006). Thus, the high  $\text{NO}_3^-$  leaching potential of irrigated potatoes represents a possible source of  $\text{N}_2\text{O}$  emissions that is not accounted for by in-field measurements of direct soil-to-atmosphere  $\text{N}_2\text{O}$  flux. The importance of indirect

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**Abbreviations:** AN, ammonium nitrate; AWC, available water capacity; BMPs, best management practices; CI, confidence interval; CSA, conventional split application; ET, evapotranspiration; DAP, diammonium phosphate; IPCC, Intergovernmental Panel on Climate Change; MJ, megajoules; PCU, polymer-coated urea; PVC, polyvinylchloride; RAWs, Remote Automated Weather Station; RCB, randomized complete block; UAN, urea ammonium nitrate.

N<sub>2</sub>O emissions on global and regional scales has been highlighted by Crutzen et al. (2008) and Beaulieu et al. (2011). However, there have been very few studies in potato (or other) cropping systems where both direct and indirect N<sub>2</sub>O emissions have been examined simultaneously.

Previous studies have shown that decreasing the proportion of fertilizer N applied at planting versus postemergence increases marketable tuber yields and also decreases NO<sub>3</sub><sup>-</sup> leaching (Errebhi et al., 1998), so multiple split applications of N fertilizer have been recommended as a BMP (Rosen and Bierman, 2008). Use of polymer-coated urea (PCU) products designed to release N slowly over the course of the growing season has also been proposed as a means of decreasing off-site N losses (Shaviv, 2000). While there are several commercially available PCU products having different formulations, there have been few side-by-side comparisons of different PCUs with respect to their agronomic or environmental impacts (Pack et al., 2006).

The primary objective of this study was to compare rates of NO<sub>3</sub><sup>-</sup> leaching in an irrigated potato cropping system managed for three consecutive growing seasons using different N management strategies, including conventional split application (CSA) and single preplant application of two different PCU types. A secondary objective was to use the measured NO<sub>3</sub><sup>-</sup> leaching rates to estimate indirect N<sub>2</sub>O emissions and then use direct N<sub>2</sub>O emissions from the same experiment previously reported by Hyatt et al. (2010) to estimate total (i.e., direct plus indirect) N<sub>2</sub>O emissions.

## Materials and Methods

### Site Description and Experimental Design

This study was performed at the University of Minnesota Sand Plain Research Farm in Becker, MN (45°23'21"N, 93°53'26"W). Soil at the site is a coarse-textured uniform Hubbard loamy sand (sandy, mixed, frigid, Typic Hapludoll) with sand, silt, and clay content of 820, 100, and 80 g kg<sup>-1</sup>, respectively. The site has a 30-yr average annual temperature and precipitation of 6.0°C and 745 mm, respectively (MRCC, 2010). A weather station (CR1000, Campbell Scientific, Inc, Logan, UT) was positioned onsite to measure air temperature, wind speed, relative humidity, and net solar radiation at 10-min intervals. To address gaps due to power interruptions, data from the National Interagency Fire Center Remote Automated Weather Station (RAWS) located approximately 20 km northeast of the site were used.

A different section of the farm was used for experimentation each year. Selected properties of soils sampled from each field in the spring before establishing treatments are shown in Table 1. The fields used for the 2007 and 2009 experiments were planted the previous year to nonfertilized rye (*Secale cereal* L.). The field used for the 2008 experiment was planted the previous year to rye followed by mustard (*Brassica* L. and *Sinapsis* L), which was fertilized on 17 Aug. 2007, with 38 kg N ha<sup>-1</sup> as ammonium nitrate (AN). Fields were not irrigated during either rye or mustard production. Rye grain was harvested in summer followed by a rye cover crop that was incorporated the

following spring before planting in 2007 and 2009; rye stover and the 2007 mustard crop were disk incorporated in October 2007. One week before planting in all years, 280 kg ha<sup>-1</sup> of potassium–magnesium sulfate and 280 kg ha<sup>-1</sup> of potassium chloride were broadcast and incorporated with a moldboard plow in all plots. During 26–29 Apr. of each year, plots were hand planted with five rows of Russet Burbank whole “B” seed potatoes, using 0.9-m row spacing and 0.3-m seed spacing. A starter fertilizer containing 45 kg N ha<sup>-1</sup> as diammonium phosphate (DAP), 0.6 kg B ha<sup>-1</sup>, 2.2 kg Zn ha<sup>-1</sup>, 34 kg Mg ha<sup>-1</sup>, and 67 kg S ha<sup>-1</sup> was added to all treatments, except for the control, which received the same formulation except with an equivalent amount of P as triple superphosphate instead of DAP. The starter was banded at planting 0.05 m below and 0.08 m from both sides of the row. The inner two rows of each plot were designated as “harvest rows,” wherein foot traffic and sampling were minimized.

Fertilizer treatments were established in a randomized complete block (RCB) design with three replications of each treatment (Table 2). Plots were 6.1 m long by 4.6 m wide. Treatments included a CSA, consisting of an initial application of granular urea that was surface banded on both sides of the row at plant emergence followed by either five (in 2007) or four (in 2008 and 2009) split applications of a mixture of 50% granular urea and 50% granular AN. The mixture was broadcast uniformly over the entire plot and watered in to simulate fertigation with 28% urea ammonium nitrate (UAN), consistent with recommended BMPs

**Table 1.** Selected chemical soil properties (means with standard errors,  $n = 2-5$ ). Samples were collected before establishing treatments in April of each year from the upper 0.15 m, except for inorganic N samples, which were collected from the upper 0.6 m.

	2007	2008	2009
pH (H <sub>2</sub> O)†	6.7 (0.04)	6.2 (0.1)	4.9 (0.03)
	g kg <sup>-1</sup>		
organic matter‡	15 (1)	20 (0.3)	24 (0.3)
	mg kg <sup>-1</sup>		
P§	32 (2)	32 (2)	23 (2)
K¶	88 (7)	110 (2)	66 (3)
Ca¶	720 (49)	810 (6)	335 (65)
Mg¶	140 (9)	140 (2)	40 (6)
SO <sub>4</sub> #	Not determined	2.0 (0)††	5.0 (1)
B‡‡	0.20 (0)††	0.21 (0.01)	0.28 (0.01)
Zn§§	0.67 (0.03)	0.70 (0)††	1.35 (0.05)
Fe§§	19 (0.7)	29 (0.2)	114 (10)
Cu§§	0.30 (0.04)	0.41 (0.01)	0.50 (0)††
Mn§§	4.9 (0.2)	7.2 (0.1)	37.6 (4.3)
NH <sub>4</sub> <sup>+</sup> -N¶¶	1.8 (0.1)	2.2 (0.2)	1.6 (0.1)
NO <sub>3</sub> <sup>-</sup> -N¶¶	1.5 (0.2)	2.4 (0.1)	1.4 (0.1)

† Determined in a 1:1 (by volume) soil:water mixture.

‡ Loss on ignition.

§ Bray extraction method.

¶ Extracted with ammonium acetate at pH 7, followed by analysis using inductively coupled plasma atomic emission spectroscopy (ICP–AES).

# Extracted with calcium phosphate, followed by precipitation with barium chloride and colorimetric analysis of the resultant turbidity.

†† All replicates had same result.

‡‡ Extracted with hot water followed by ICP–AES.

§§ Extracted with diethylenetriaminepentaacetic acid followed by ICP–AES.

¶¶ Extracted with potassium chloride followed by flow-through colorimetric analysis.

and grower practices in the area (Rosen and Bierman, 2008). The actual dates of postplant CSA fertilizer application each year are indicated in the results section. Two PCU treatments (PCU-1 and PCU-2) each employed single applications of two different PCU products, which were broadcast 0 to 6 d before planting and incorporated by disking within 24 h of application. The PCU-1 treatment used a product containing 42% N by weight manufactured by Shandong Kingenta Ecological Engineering Co. LTD (Linshu, Shandong Province, China). The PCU-2 treatment used a product (Environmentally Smart Nitrogen) containing 44% N by weight, manufactured by Agrium, Inc. (Calgary, AB, Canada). The PCU-1 product was obtained directly from the manufacturer. In 2007, PCU-2 was obtained from the manufacturer, whereas in 2008 and 2009 product was obtained from a local distributor. A nonfertilized control treatment was also examined. All treatments except the control received a total of 270 kg N ha<sup>-1</sup> of applied fertilizer over the entire growing season (Table 2), consistent with yield-based recommendations for this cropping system (Rosen and Bierman, 2008). Within 24 h of the initial postemergence application of urea to the CSA treatment (15–28 May of each year), hills were formed in all treatments. Hilling is a common practice in potato production to maintain tubers below the surface and prevent exposure to sunlight and desiccation. In 2008, equipment malfunction required all plots to be hilled a second time. Irrigation water was applied through an aluminum solid-set overhead sprinkler system. Irrigations were scheduled by the checkbook method as described in Wright (2002), which estimates daily evapotranspiration (ET) and soil water deficit. Irrigation amounts were calculated to replace soil water deficit and minimize drainage. Potato vine kill was achieved via flail mowing on 15–19 Sept. and tubers were mechanically harvested on 16–28 Sept. of each year. Tuber yields for this study were previously reported (Hyatt et al., 2010).

### Soil Water Nitrate Concentrations

Water samples from below the rooting zone were collected at a depth of 1.2 m using suction cup lysimeters. Each lysimeter consisted of a round-bottom, 100-kPa high-flow porous ceramic cup (60-mm length, 48-mm outside diam., 44-mm neck diam.) (Soilmoisture Equipment Corp., Santa Barbara, CA), affixed with epoxy to one end of a 1.3-m length of 48-mm (inside diam.) SDR-26 polyvinylchloride (PVC) pipe. The other end of the

pipe was fitted with a no. 10 black rubber stopper, through which two sections of 6.35-mm (outside diam.) polyethylene tubing were inserted. One section of tubing (the “vent tube”) extended inside the pipe to 0.1 m below the stopper and the other section (the “sample tube”) extended to 2 mm above the surface of the ceramic cup. On the outside of the PVC pipe, the sample and vent tubes were connected to tygon tubing (4.76-mm inside diam.), equipped with polypropylene ratcheting clamps (Halkey–Roberts Corp., St. Petersburg, FL). Before installation, lysimeters were prepared by submerging them in water and applying 40 kPa of suction with a hand pump (Soilmoisture Equipment Corp, Santa Barbara, CA) to allow water to be drawn into the ceramic cups.

After planting each year, a 1.3-m-deep hole was bored in each plot in the hill zone of a nonharvest row using an 83-mm diam. soil auger. Silica-flour slurry was poured into the borehole to a depth of approximately 0.1 m and lysimeters were inserted vertically, setting the cup into the slurry at a depth of 1.2 m. Soil removed from the borehole was returned and gently tamped, filling the gap between the lysimeter and the edge of the hole. Soil was replaced in reverse order of removal, paying attention to horizonation. At a depth of 0.15 m, a 10-mm-thick layer of powdered bentonite was evenly applied around the pipe to prevent preferential water flow. The remainder of the removed soil was placed over the bentonite until the hole was filled to a level consistent with the surrounding soil. After 24 h, water was drawn out of the lysimeters with the hand pump by opening both vent and sample tubes and applying suction to the sample tube. This initial volume of water was discarded. In preparation for the first and all subsequent samplings, the vent tube was clamped and a vacuum of 40 kPa was reapplied to the lysimeters through the sample tube, which was then also clamped. Lysimeter installation was completed during 5–20 May of each year.

Sample water was collected from lysimeters approximately once per week during all growing seasons, except 18 Jun–12 July 2008, and 1 July–16 July 2009, due to personnel limitations. Water samples were collected in 50-mL polypropylene vials by opening the vent and sample tubes and applying vacuum to the sample tube until all water was drawn out. Samples were collected on 30 dates in 2007, 19 dates in 2008, and 28 dates in 2009, with sample collection terminating during 12–25 Nov. of each year. All water was removed from the lysimeters before winter. Lysimeters were kept in the ground over winter (without suction) so that

additional samples could be collected during the following spring. However, in each spring except 2009, the majority of lysimeters failed to maintain suction or produce sufficient sample volume. Thus, spring data are reported only for 2009 (i.e., following the 2008 season). Samples of irrigation water were also collected approximately every four weeks. All water samples were capped and stored at –5°C until analysis for total nitrite (NO<sub>2</sub><sup>-</sup>) plus NO<sub>3</sub><sup>-</sup> using flow-through colorimetric analyzers (Wescan prototype, Carlson et al., 1990; or QuickChem 8500 with ASX 520 Series autosampler, Lachat Instruments, Milwaukee, WI; Wendt, 2003).

**Table 2. Nitrogen fertilizer applications for the conventional split application (CSA), two polymer-coated ureas (PCU-1 and PCU-2), and nonfertilized control treatments.**

Treatment	Preplanting	Planting†	Emergence‡	Postemergence§	Total
<b>2007</b>					
CSA	0	45	112	5 × 22.5	270
PCU-1	225	45	0	0	270
PCU-2	225	45	0	0	270
<b>2008, 2009</b>					
CSA	0	45	112	4 × 28	270
PCU-1	225	45	0	0	270
PCU-2	225	45	0	0	270
Control	0	0	0	0	0

† N source at planting is diammonium phosphate.

‡ Urea.

§ Urea and ammonium nitrate.

## Drainage and Nitrate Leaching

The volume of water moving below the root zone during each growing season was estimated using a water balance equation approach, which can be expressed as

$$(P + I) - (ET + D) = \Delta S \quad [1]$$

where  $P$  is precipitation,  $I$  is irrigation water applied,  $ET$  is evapotranspiration,  $D$  is drainage, and  $\Delta S$  is change in the soil water storage, with all terms expressed in  $\text{mm}^3 \text{H}_2\text{O mm}^{-2} \text{soil d}^{-1}$  (hereafter we abbreviate  $\text{mm}^3 \text{H}_2\text{O mm}^{-2} \text{soil}$  as  $\text{mm}$ ). Our application of the water balance approach to estimate drainage follows the same approach as in other studies (Errebhi et al., 1998; Waddell et al., 2000; Zvomuya et al., 2003; Wilson et al., 2010), i.e., we assumed that soil–water storage on a daily time step did not exceed the available water capacity (AWC) of the soil profile. Determination of  $P$  and  $I$  were made daily using an on-site National Weather Service catch can and gauge stick, and based on irrigation flow rate and duration of application, respectively. Daily  $ET$  was estimated using a semiempirical model described below. The value of AWC for the soil profile to a depth of 1.2 m was assumed to be 85.1 mm, based on data in the Sherburne County, MN Soil Survey (NRCS, 2002). The initial amount of water stored in the profile after ground thaw and before planting was assumed to be equivalent to AWC.

Evapotranspiration ( $\text{mm d}^{-1}$ ) was estimated on a daily basis using the Penman–Monteith equation (Allen et al., 1998):

$$ET = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)} \quad [2]$$

where  $R_n$  is net radiation at the crop surface ( $\text{megajoules [MJ] m}^{-2} \text{d}^{-1}$ ),  $G$  is the soil heat flux density ( $\text{MJ m}^{-2} \text{d}^{-1}$ ), which was assumed to be zero for daily calculations,  $T$  is the air temperature ( $^{\circ}\text{C}$ ) 2 m above the surface,  $u_2$  is the wind speed ( $\text{m s}^{-1}$ ) 2 m above the surface,  $e_s$  is the saturation vapor pressure (kPa),  $e_a$  is the actual vapor pressure (kPa),  $\Delta$  ( $\text{kPa}^{\circ}\text{C}^{-1}$ ) is the slope of the curve of saturation vapor pressure as a function of temperature, and  $\gamma$  is the psychrometric constant ( $0.065 \text{ kPa } ^{\circ}\text{C}^{-1}$ ). Values of  $T$  and  $u_2$  were measured with an on-site weather station from which the minimum, maximum, and average temperature, and average wind speed were determined at 10-min intervals. Relative humidity was also measured with the weather station at 10-min intervals. Values of  $e_s$  and  $e_a$  were estimated using appropriate equations given by Allen et al. (1998), also at 10-min intervals. Solar radiation was measured with a net radiometer attached to the on-site weather station. Periodic power failures in 2007 and 2008 necessitated using solar (shortwave) radiation collected via pyranometer at the Sherburne, MN RAWS station. These data were converted to net radiation ( $R_p$ ), using equations given by Allen et al. (1998). Since the  $ET$  values calculated using Eq. [2] are for a grass reference crop, these values were multiplied by a crop coefficient based on stage of growth in the potato crop to give daily  $ET$  estimates for potato using equations in Stegman et al. (1977) and Allen et al. (1998).

To determine daily rates of  $\text{NO}_3^-$  leaching ( $\text{kg N ha}^{-1} \text{d}^{-1}$ ), daily drainage rates were multiplied by daily  $\text{NO}_3^-$  concentrations, which were estimated based on linear interpolation

between  $\text{NO}_3^-$  concentrations measured in lysimeter samples (Errebhi et al., 1998). The amount of drainage and  $\text{NO}_3^-$  leaching induced by irrigation was determined by weighting each daily value by the ratio of irrigation to total water inputs for that day. Cumulative seasonal drainage and N leaching were determined by summing daily values.

## Residual Soil Nitrogen

After harvest each growing season (on 12 Oct. 2007, 19 Sept. 2008, and 20 Oct. 2009), four replicate soil cores were collected from each plot to a depth of 0.60 m, using a 22-mm ID manual soil core sampler. Cores from each plot were composited and extracted with 2 M KCl for determination of  $\text{NH}_4^+$  and  $\text{NO}_2^- + \text{NO}_3^-$  concentrations using flow-through colorimetric analysis per above. Soil extract concentrations ( $\mu\text{g N mL}^{-1}$ ) were converted to  $\text{kg N ha}^{-1}$ , using bulk density values determined from total dry mass and volume of the soil core samples.

## Data Analysis and Statistics

Indirect  $\text{N}_2\text{O}$  emissions were estimated by multiplying cumulative  $\text{NO}_3^-$  leaching values by an emission factor ( $\text{EF}_3$ ) published in the Intergovernmental Panel on Climate Change (IPCC) Guidelines for Greenhouse Gas Inventories (De Klein et al., 2006), which represent the percentage of leached  $\text{NO}_3^-$  that is subsequently converted to  $\text{N}_2\text{O}$  in surface or groundwater ecosystems after leaving the fertilized field. We compared indirect emission results obtained using the default  $\text{EF}_3$  value (0.75%) with results obtained using the lower (0.05%) and higher (2.5%) limits of the 95% confidence interval (CI) (De Klein et al., 2006). Indirect  $\text{N}_2\text{O}$  emissions estimates were added with cumulative seasonal direct  $\text{N}_2\text{O}$  emissions measured in the same treatments by Hyatt et al. (2010) to obtain total direct plus indirect  $\text{N}_2\text{O}$  emissions. Because direct  $\text{N}_2\text{O}$  emissions were not measured in the control treatment in 2007, total  $\text{N}_2\text{O}$  emissions were evaluated for the period 2007 to 2009 using only the three fertilized treatments.

Effects of fertilizer treatment on residual soil N,  $\text{NO}_3^-$  leaching, and  $\text{N}_2\text{O}$  emissions were determined using the Proc Mixed procedure in SAS for RCB split-plot design treating year as the main plot factor, fertilizer as the sub plot factor, and block as a random effect (SAS Institute, 2003; Littell et al., 2006). Effects of fertilizer treatment on lysimeter  $\text{NO}_3^-$  concentration were determined by repeated measures analysis using Proc Mixed in SAS with auto-regressive covariance structure. The Kenward–Roger correction for degrees of freedom in mixed models was applied and means comparisons were conducted using least squares means with pairwise error criteria of  $P < 0.05$ . Linear regression was done using the Proc Reg procedure in SAS.

## Results

### Climate and Drainage

Total precipitation during 1 May–30 Nov. during each of 2007, 2008, and 2009, was within 5% of normal (30-yr average) (Fig. 1a–c). However, monthly rainfall patterns varied considerably from long-term averages. Precipitation during July in all three years was 50 to 60% of average (data not shown). Lower than average rainfall was also recorded in June 2007 (28% of average), August 2008 (49%), May 2009 (25%), and September 2009 (12%). Rainfall during September 2007,

May 2008, and September 2008 was greater than normal (169, 156, and 169% of average, respectively). Irrigation amounted to 48, 39, and 45% of total water inputs during 1 May to 30 November in 2007, 2008, and 2009, respectively (Fig. 1a–c). Mean daily air temperature and radiation in 2007 (16.3°C and 10.8 MJ m<sup>-2</sup> d<sup>-1</sup>) were greater than in 2008 (14.0°C and 9.7 MJ m<sup>-2</sup> d<sup>-1</sup>) and 2009 (14.4°C and 8.6 MJ m<sup>-2</sup> d<sup>-1</sup>), primarily because of higher temperatures and radiation during May through June and October through November. These differences resulted in greater cumulative ET during 2007 (636 mm), compared with 2008 (571 mm) and 2009 (441 mm). Daily ET reached maximum values of 6.5 to 10 mm d<sup>-1</sup> in the first half of July and then decreased to <1 mm d<sup>-1</sup> by mid-September each season (data not shown). Total seasonal drainage amounted to 38, 43, and 53% of total water inputs in the 2007, 2008, and 2009 growing seasons, respectively, and was driven mainly by rainfall events. Estimated irrigation induced drainage accounted for 11%, 4.5%, and 19% of total water drainage in 2007, 2008, and 2009, respectively.

### Lysimeter Nitrate Concentrations

Irrigation water contained, on average, 7.0, 9.4, and 8.3 mg N L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup> in 2007, 2008, and 2009, respectively, which contributed 33 to 35 kg N ha<sup>-1</sup> each season in addition to fertilizer N inputs. Lysimeter NO<sub>3</sub><sup>-</sup> concentrations varied from <1 to >40 mg N L<sup>-1</sup> and peaked during June through August each year (Fig. 2). Control treatments also had NO<sub>3</sub><sup>-</sup> concentrations that were elevated above irrigation water concentrations on some sampling dates during these periods. Thus, some of the increase in lysimeter NO<sub>3</sub><sup>-</sup> concentrations was likely due to mineralization of soil organic N and/or leaching of inorganic N initially present in the soil profile before fertilizer application. Lysimeter NO<sub>3</sub><sup>-</sup> concentrations remained elevated above irrigation water concentration in the PCU-1 treatment in the spring following the 2008 growing season (Fig. 3). Averaged across all sampling dates within each sampling period, lysimeter NO<sub>3</sub><sup>-</sup> concentrations tended to be greater in the fertilized treatments compared with the control, although the differences were not always significant (Fig. 4). For the 2008 growing season, NO<sub>3</sub><sup>-</sup> concentrations in the CSA and PCU-1 treatments were greater than the control; during the spring following the 2008 growing season, the PCU-1 treatment had greater NO<sub>3</sub><sup>-</sup> concentrations than all other treatments; and in 2009, all fertilized treatments had greater lysimeter NO<sub>3</sub><sup>-</sup> concentrations than the control (Fig. 4).

### Nitrate Leaching

The magnitudes of individual daily NO<sub>3</sub><sup>-</sup> leaching events are illustrated as vertical bars in Fig. 2 (lower plates). The majority of the total seasonal cumulative leaching can be attributed to large drainage events occurring in June through August of each year. For example, a rainfall-induced 41-mm drainage event in mid-August 2007 (Fig. 1a) accounted for 16 to 26% of the total seasonal

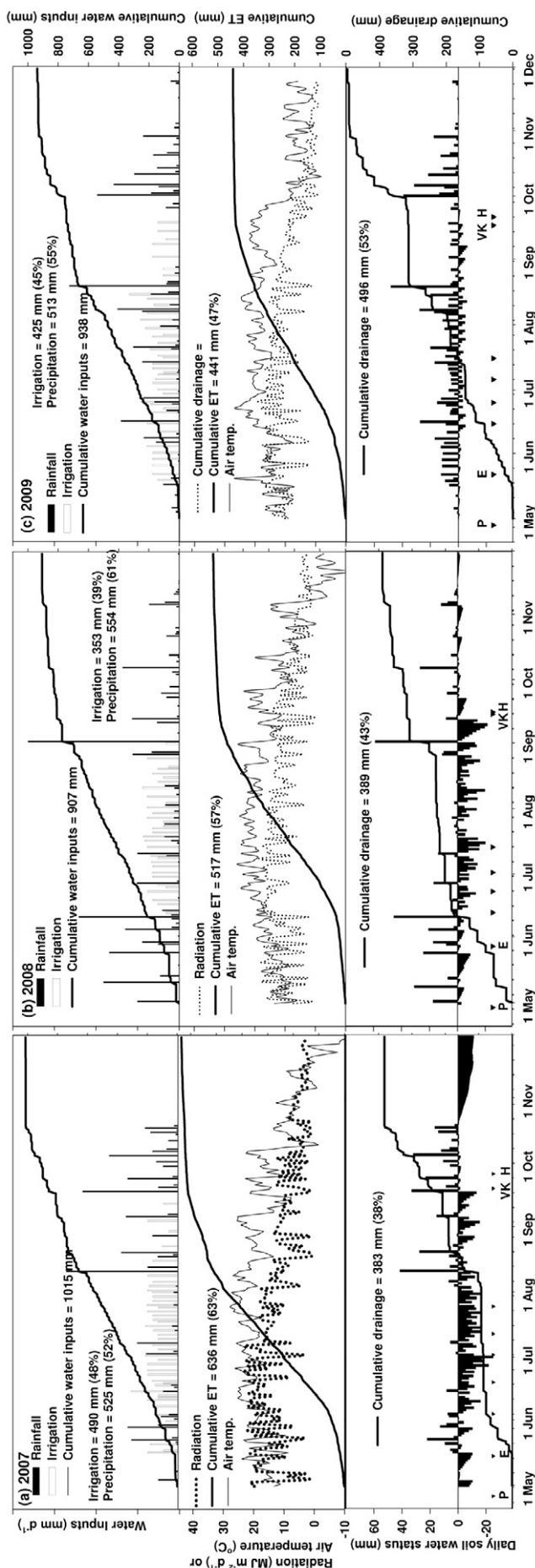


Fig. 1. Water inputs, meteorological variables, calculated evapotranspiration (ET), soil water status, and cumulative drainage in (a) 2007, (b) 2008, and (c) 2009. Arrows indicate dates of planting (P), vine kill (VK), harvest (H), and timing of fertilizer applications for the conventional split application treatment, occurring at emergence (E) and five times (in 2007) or four times (in 2008 and 2009) after emergence. Polymer-coated urea products were added in a single broadcast application 0 to 6 d before planting. Values in parentheses are percentages of total water inputs.

cumulative  $\text{NO}_3^-$  leaching in the three fertilized treatments (Fig. 2a). Similarly, in 2008, a rainfall-induced 45-mm drainage event in mid-June (Fig. 1b) accounted for 20 to 33% of seasonal cumulative  $\text{NO}_3^-$  leaching (Fig. 2b). Averaged across all years and treatments, irrigation-induced  $\text{NO}_3^-$  leaching accounted for 13% of total  $\text{NO}_3^-$  leaching, with no differences among treatments. Irrigation-induced  $\text{NO}_3^-$  leaching accounted for 18% of total  $\text{NO}_3^-$  leaching in 2009, which was significantly greater than in 2007 (8.7%) or 2008 (11.6%). Most of the irrigation-induced leaching in 2009 occurred during 22 July to 6 August, when only 16 mm of rainfall occurred compared with 76 mm of applied irrigation water, which accounted for 14% of total seasonal cumulative  $\text{NO}_3^-$  leaching. The greatest  $\text{NO}_3^-$  concentrations in 2007 occurred during periods of soil water deficit with minimal drainage (Fig. 2a). In contrast, in 2008 and 2009, more frequent and larger drainage events occurred during June through August when  $\text{NO}_3^-$  concentrations were elevated (Fig. 2b–c). Averaged across all treatments, cumulative  $\text{NO}_3^-$  leaching varied significantly by year, increasing in the order 2007 (8.2 kg N ha<sup>-1</sup>) < 2009 (20 kg N ha<sup>-1</sup>) < 2008 (28 kg N ha<sup>-1</sup>) (Fig. 5). In 2009, cumulative  $\text{NO}_3^-$  leaching in both the PCU-2 and CSA treatments were significantly greater than the control and PCU-1 treatment (Fig. 5c). Averaged across all three years, all three fertilized treatments had greater  $\text{NO}_3^-$  leaching than the control (Fig. 5d). For the entire study, growing season  $\text{NO}_3^-$  leaching averaged 21.1 kg N ha<sup>-1</sup> in the fertilized treatments (CSA, PCU-1, and PCU-2), compared with 12.2 kg N ha<sup>-1</sup> in the control.

### Residual Soil Nitrogen

The soil profile to the 0.6-m depth contained 15 to 35 kg N ha<sup>-1</sup> of residual  $\text{NH}_4^+$  and  $\text{NO}_3^-$  after harvest each year (Fig. 5). There was significantly more residual  $\text{NH}_4^+$  averaged across all treatments in 2008 (37 kg N ha<sup>-1</sup>), compared with 2007 (21 kg N ha<sup>-1</sup>) and 2009 (26 kg N ha<sup>-1</sup>). In direct contrast, there was less residual  $\text{NO}_3^-$  averaged across all treatments in 2008 (15 kg N ha<sup>-1</sup>), compared with 2007 (21 kg N ha<sup>-1</sup>) and 2009 (21 kg N ha<sup>-1</sup>). Amounts of residual  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were similar to each other in 2007 and 2009, whereas in 2008 residual  $\text{NH}_4^+$  was more than twice as great as  $\text{NO}_3^-$  (Fig. 5). After harvest in 2007, the soil profile in the PCU-1 treatment contained significantly more  $\text{NH}_4^+$  and  $\text{NO}_3^-$  than the other treatments (Fig. 5a). In contrast, in 2009 the PCU-1 treatment had less  $\text{NO}_3^-$  than the CSA or PCU-2 treatments (Fig. 5c). For the entire study, only the PCU-2 treatment had more  $\text{NO}_3^-$  than the control and residual  $\text{NH}_4^+$  did not vary by treatment (Fig. 5d).

### Indirect and Total Nitrous Oxide Emissions

Assuming the IPCC default emissions factor (EF<sub>2</sub>) of 0.75% for off-site conversion of leached  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ , cumulative  $\text{NO}_3^-$  leaching was equivalent to 0.11 to 0.24 kg  $\text{N}_2\text{O}$ -N ha<sup>-1</sup>, representing 11 to 19% of direct emissions (Fig. 6). Assuming EF<sub>5</sub> equal to the lower

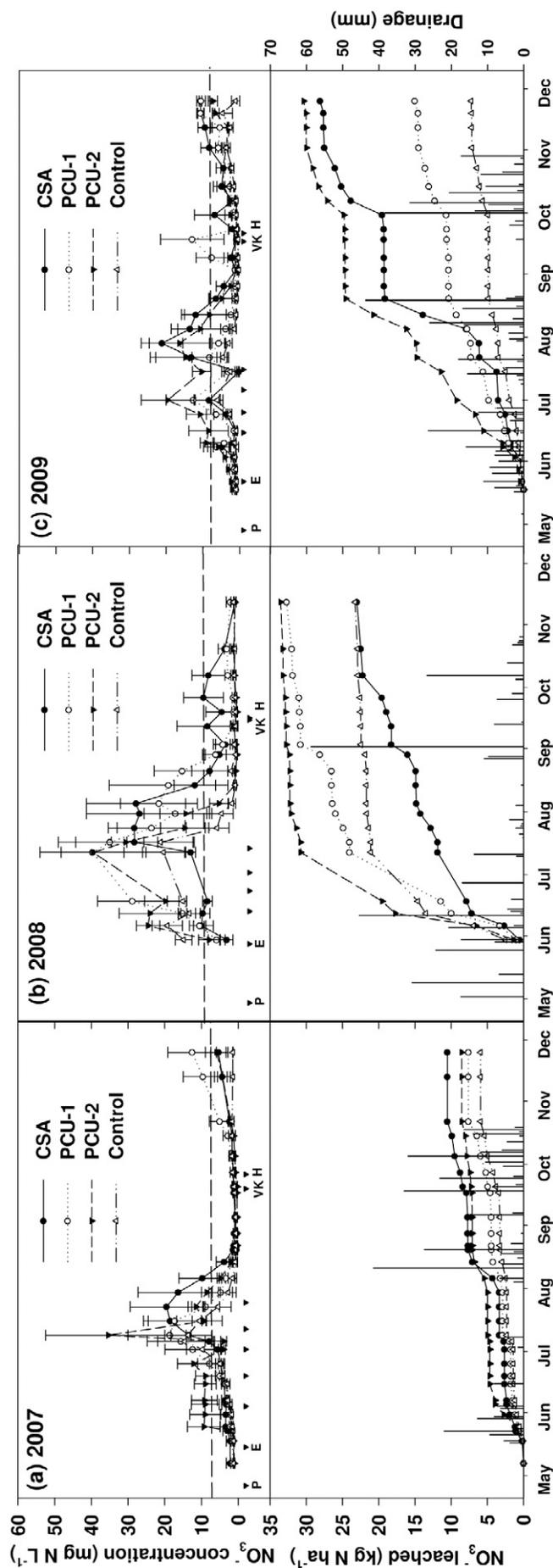


Fig. 2. Upper plates: Daily mean (and standard error) lysimeter  $\text{NO}_3^-$  concentrations in treatments receiving conventional split application (CSA), two different polymer-coated ureas (PCU-1 and PCU-2), and no fertilizer (control); and Lower plates: Mean cumulative  $\text{NO}_3^-$  leached (right-hand axis) and daily drainage events (left-hand axis), during: (a) 2007, (b) 2008, and (c) 2009. Arrows indicate same information as in Fig. 1. Horizontal dashed lines represent mean  $\text{NO}_3^-$  concentrations in irrigation water. Statistical comparisons for these data are shown in Fig. 4 and 5.

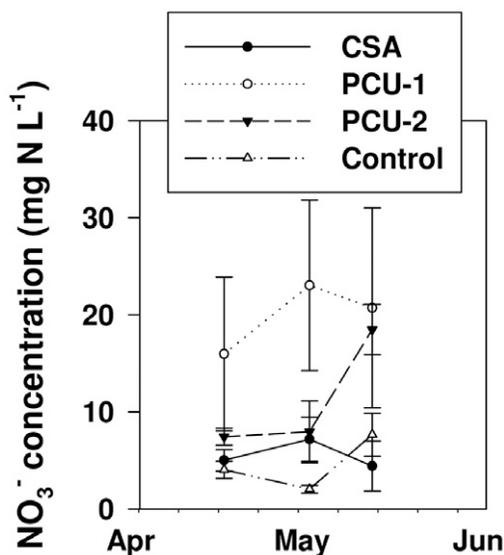


Fig. 3. Daily mean (and standard error) lysimeter NO<sub>3</sub><sup>-</sup> concentrations in treatments receiving conventional split application (CSA), two different polymer-coated ureas (PCU-1 and PCU-2), and no fertilizer (control) during spring of 2009.

(0.05%) and upper limits (2.5%) of the 95% CI, indirect N<sub>2</sub>O emissions represented 0.8 to 1.3% and 38 to 64% of direct N<sub>2</sub>O emissions, respectively. The PCU-1 treatment had significantly less total N<sub>2</sub>O emissions than the CSA treatment (Fig. 6). Assuming an EF<sub>5</sub> value of 2.5% resulted in greater statistical means separation compared with EF<sub>5</sub> values of 0.05% and 0.75%, such that the PCU-1 treatment also had lower total emissions than the PCU-2 treatment. This effect was due to the increasing influence of the indirect emissions contribution, which reflected the overall means in NO<sub>3</sub><sup>-</sup> leaching (Fig. 5d). Averaged across all fertilizer treatments, computed total growing season N<sub>2</sub>O emissions were greater in 2008 (1.9 kg N ha<sup>-1</sup>), compared with 2007 (0.8 kg N ha<sup>-1</sup>) or 2009 (1.1 kg N ha<sup>-1</sup>) (assuming EF<sub>5</sub> = 0.75%). Total emissions in 2007 and 2009 were not significantly different. When averaged across treatment replicates within each year, direct N<sub>2</sub>O emissions were weakly but positively correlated ( $r^2 = 0.35$ ,  $P = 0.056$ ) with cumulative NO<sub>3</sub><sup>-</sup> leaching amounts, with slope of 0.029 kg N<sub>2</sub>O-N kg<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N and intercept of 0.44 kg N<sub>2</sub>O-N ha<sup>-1</sup> (Fig. 7).

## Discussion

Polymer-coated urea products are designed to improve synchrony between soil-N availability and crop-N demand, without the need for multiple field operations. Some studies have shown potential for increased yields of irrigated potatoes using PCU versus multiple split applications, although yield improvements have not been consistently found (Wilson et al., 2010; Hyatt et al., 2010; Hopkins et al., 2008). The overall benefits of PCUs will depend on a cost-benefit analysis that accounts for (i) potential yield benefits, (ii) cost of the PCU product, (iii) cost of multiple versus single application, and (iv) environmental impacts. With

regard to NO<sub>3</sub><sup>-</sup> leaching, the overall results for the 3-yr study (Fig. 5d) show no clear differences between the CSA and either of the PCU treatments. With regard to N<sub>2</sub>O emissions, the current results show that after adding the contribution of NO<sub>3</sub><sup>-</sup>-leaching-derived indirect emissions, the PCU-1 treatment had lower total (direct plus indirect) emissions. Based on these results and since no yield benefits were found in the current experiment (Hyatt et al., 2010), the cost-benefit analysis in this case would involve comparing the increased PCU cost versus reduced cost of multiple applications and reduced N<sub>2</sub>O emissions.

However, additional results indicate that N<sub>2</sub>O emissions and NO<sub>3</sub><sup>-</sup> leaching occurring during the growing season may not fully account for the environmental impacts of the PCU-1 treatment. That is, greater residual soil-N levels in fall 2007 (Fig. 5a) and greater lysimeter NO<sub>3</sub><sup>-</sup> concentrations in spring 2009 (Fig. 3–4) observed in the PCU-1 treatment indicate the potential for increased NO<sub>3</sub><sup>-</sup> leaching and/or increased N<sub>2</sub>O emissions during late winter or early spring following the growing season. These results are consistent with an in situ incubation study reported by Hyatt et al. (2010), showing lower rates of N release with PCU-1 compared with PCU-2, which may have been due to the greater mass of polymer coating on the PCU-1 product (42% N) compared with PCU-2 (44% N). These conclusions are also similar to those of Zvomuya et al. (2003), who found that a polyolefin-based PCU had greater soil-water NO<sub>3</sub><sup>-</sup> concentrations the following spring compared with split urea applications. Together, these results indicate that an unintended consequence of some PCU products may be that delayed N release can result in N losses occurring after the growing season. Similar findings led Zvomuya et al. (2003) to recommend cover cropping following the use of PCUs. Another approach would be to evaluate lower N application rates with PCUs that release N more slowly. Since the PCU-1 treatment was able to generate the same tuber yields as the other treatments while also resulting in greater residual N, it is possible that a lower N application rate could have also generated the same yields, but this would require further studies to confirm.

While it would be valuable to have more definitive data regarding postseason N losses, determining these losses presents methodological challenges. While we attempted to more intensively measure NO<sub>3</sub><sup>-</sup> concentrations during the spring, our efforts were largely thwarted due to failure of most of the lysimeters to

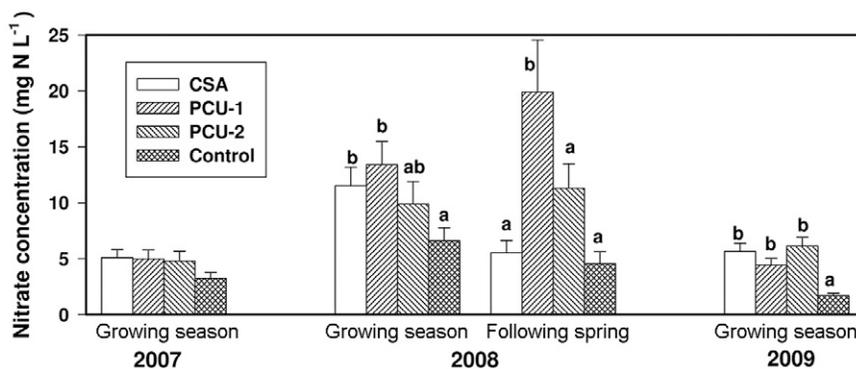


Fig. 4. Mean (and standard error) lysimeter nitrate (NO<sub>3</sub><sup>-</sup>) concentrations for 2007, 2008, spring 2009, and the 2009 growing season in plots fertilized using conventional split application (CSA), polymer-coated urea products (PCU-1 and PCU-2), and an unfertilized control. Within each time period, values having the same letter are not significantly different ( $P < 0.05$ ).

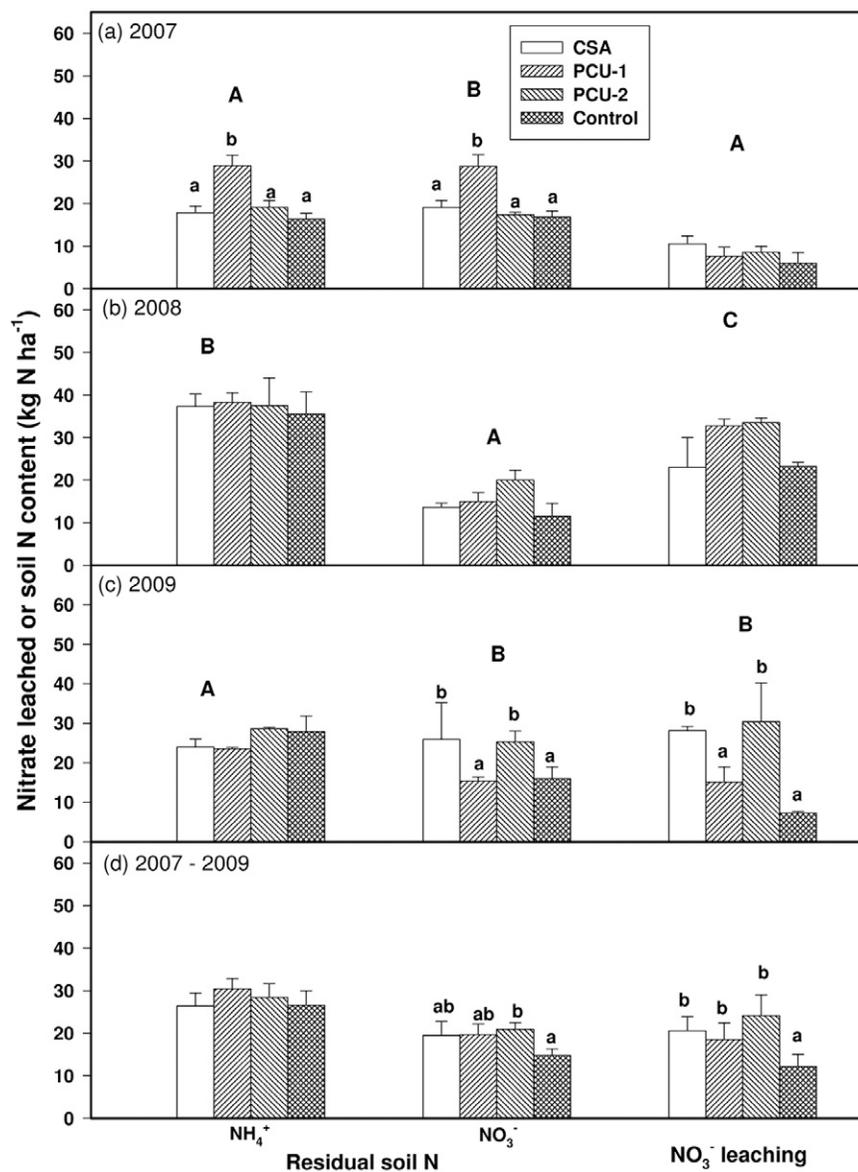


Fig. 5. Mean (and standard error) residual soil ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) after harvest and  $\text{NO}_3^-$  leaching amounts for: (a) 2007, (b) 2008, (c) 2009, and (d) 2007–2009, in plots fertilized using conventional split application (CSA), polymer-coated urea products (PCU–1 and PCU–2), and an unfertilized control. Within each time period and for each variable, values having the same lowercase letter are not significantly different by fertilizer treatment ( $P < 0.05$ ). For each variable, values having the same uppercase letter are not significantly different by year averaged across all fertilizer treatments ( $P < 0.05$ ).

generate samples in the spring. Another challenge would be to apply appropriate models that can account for ET during winter months under frozen soil conditions and/or with snowpack so that drainage and  $\text{NO}_3^-$  leaching rates during spring thaw can be estimated. Use of anion exchange resin boxes or strips (e.g., Ziadi et al., 2011) instead of lysimeters might alleviate these problems, but these techniques have their own limitations (Weihermüller et al., 2007). Determining residual soil-N content after harvest can be complicated by the possible presence of fertilizer prills still containing urea, which may not be detected by standard inorganic N analyses. And finally, measurement of direct  $\text{N}_2\text{O}$  emissions during spring thaw is also problematic due to temporal and spatial variability that may be even greater than encountered during the warmer months (Dörsch et al., 2004). Despite these challenges, because of its potential importance, we recommend

that additional research be directed to comparing the potential for postseason N losses among different PCU formulations.

Another issue requiring more study is determining optimal timing and placement of single PCU applications. Wilson et al. (2010) found that when one of the PCUs used in our study (PCU–2) was broadcast and incorporated before planting, there was increased  $\text{NO}_3^-$  leaching over 2 yr, compared with a CSA treatment, but no leaching differences were observed when PCU–2 was applied shortly after emergence. The current study used broadcast application with incorporation a few days before planting. We observed that  $\text{NO}_3^-$  leaching tended to increase more rapidly in the PCU–2 treatment, compared with the CSA treatment during the period of May through July in all three years (Fig. 2). This trend did not continue for the remainder of the year or result in significant differences in growing season cumulative leaching (Fig. 5). However, based on the early-season trends in our study and the findings of Wilson et al. (2010), a conservative recommendation would be application at emergence for PCUs with release characteristics like PCU–2. However, for a product with a lower apparent release rate such as PCU–1, even preplant application could increase the potential for the postseason N losses.

Site history appeared to be important in this study. We observed significantly greater  $\text{NO}_3^-$  leaching in 2008, compared with 2007 and 2009 averaged across all treatments. Also, leaching from the control treatment in 2008 was  $23.2 \text{ kg N ha}^{-1}$ , compared with  $<7.5 \text{ kg N ha}^{-1}$  in 2007 and 2009. These differences may have been due in part to the N fertilizer for the mustard crop that was applied in August 2007 to the field used in 2008. Levels of soil  $\text{NH}_4^+$  and  $\text{NO}_3^-$  present in the spring before establishing treatments were greater in 2008 than in 2007 or 2009 ( $P < 0.02$ ). Although the differences in concentration were relatively small ( $1.3\text{--}1.6 \text{ mg N kg}^{-1}$ ) (Table 1), across a depth of 0.6 m this is equivalent to 8 to  $10 \text{ kg N ha}^{-1}$ . There may have also been more mineralizable N in residue contributed by the rye + mustard crop in 2008, compared with the single unfertilized rye crop in 2007 and 2009.

Our estimates of total direct plus indirect  $\text{N}_2\text{O}$  emissions displayed the same pattern of differences in direct emissions previously reported for the same experiment (Hyatt et al., 2010), i.e., emissions from PCU–1 were less than CSA (Fig. 6). There is great uncertainty in our ability to predict off-site conversion of leached  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ , which is reflected in the wide 95% CI for  $\text{EF}_3$ , i.e., 0.05 to 2.5% (De Klein et al., 2006). This is also reflected in the wide range of our indirect emission

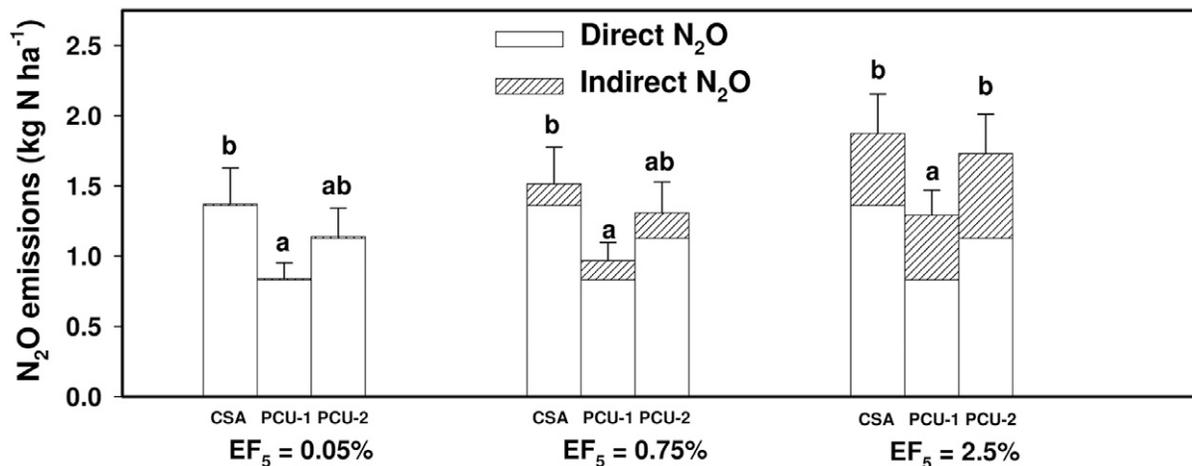


Fig. 6. Mean direct and indirect nitrous oxide ( $N_2O$ ) emissions estimated from  $NO_3^-$  leaching amounts averaged over 2007 to 2009, in plots fertilized using conventional split application (CSA) and two polymer-coated urea products (PCU-1 and PCU-2), assuming three different values of the  $NO_3^-$  to  $N_2O$  emission factor ( $EF_5 = 0.05\%$ ,  $0.75\%$  or  $2.5\%$ ). For each  $EF_5$  value, bars having the same letter are not significantly different ( $P < 0.05$ ). Error bars represent standard errors for total (direct plus indirect) emissions. Direct emissions data are from Hyatt et al. (2010).

estimates as a function of  $EF_5$ , with overall ranges of 0.01 to 0.8  $kg\ N\ ha^{-1}$  for indirect emissions and 0.8 to 64% for the ratio between indirect and direct emissions. We did not attempt to directly measure off-site conversion of leached  $NO_3^-$  to  $N_2O$ . This would entail tracing the transformation of  $NO_3^-$  to  $N_2O$  as it is transported below the root zone into the groundwater, and in the current case, most likely into the upper Mississippi River, which is located 2 km southwest of the field site. Recent studies using  $^{15}N$  tracer studies in streams and rivers have confirmed that emission factors can range from  $\leq 0.05\%$  to  $>2.5\%$  (e.g., Beaulieu et al., 2011) and that these values are influenced by multiple factors, including ambient levels of  $NO_3^-$ , dissolved oxygen, and organic matter, as well as stream geomorphology. Compared with direct measurement, a more practical method of constraining the appropriate  $EF_5$  value to use for any particular site would be the use of a more robust model that accounts for these factors, as well as the location of the site with respect to the receiving aquatic systems and intervening hydrology (Beaulieu et al., 2011). It should be pointed out that indirect  $N_2O$  emissions can also result from the off-site transport and subsequent transformation of gaseous emissions of ammonia and nitric oxide, which were not accounted for in the current study and involve similar levels of uncertainty as  $NO_3^-$ -derived indirect emissions (De Klein et al., 2006).

As far as we know, this is the first attempt to relate cumulative amounts of growing season  $NO_3^-$  leaching and direct  $N_2O$  emissions measured in the same experiment (Fig. 7). The positive correlation is consistent with the general idea that an increasing ratio between soil inorganic N availability or N inputs and crop-N uptake will increase off-site N losses. Similarly, studies have examined relationships between N surplus, defined as the difference between N inputs and N recovered in the crop, and found that N leaching and  $N_2O$  emissions

tend to increase with increasing N surplus (e.g., Oenema et al., 2005; Van Groenigen et al., 2010).

## Conclusions

The current results combined with previous studies provide strong evidence that single PCU applications for irrigated potato production do not increase growing season  $NO_3^-$  leaching, compared with multiple split applications of conventional soluble fertilizers. The study also shows that growing season total direct plus indirect  $N_2O$  emissions can be minimized with certain slow-release PCU products. On the other hand, consistent with Zvomuya et al. (2003), our results also suggest that these conclusions cannot necessarily be extended beyond the growing season. The potential for N losses occurring after the growing season and into the following year may be increased,

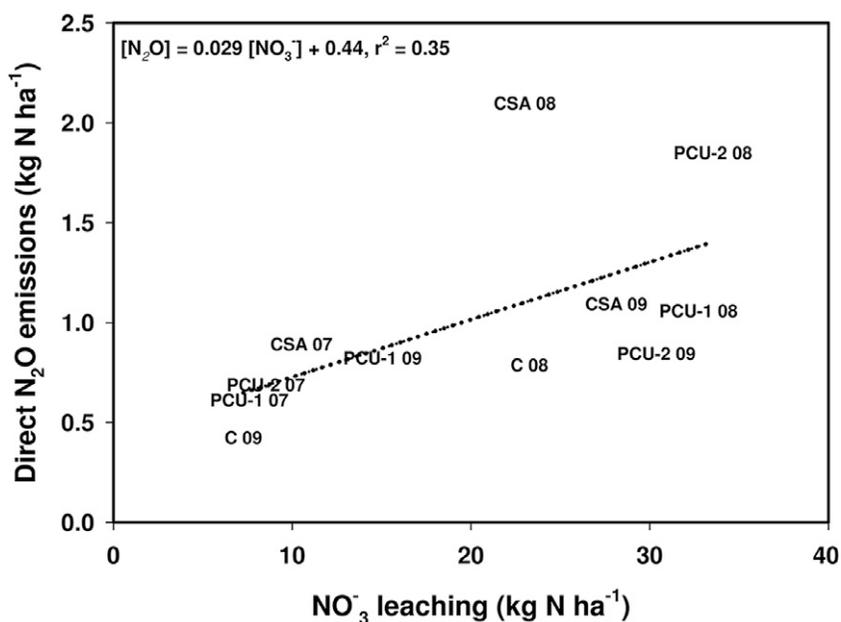


Fig. 7. Relationship between nitrate ( $NO_3^-$ ) leaching and direct nitrous oxide ( $N_2O$ ) emissions in plots fertilized using conventional split application (CSA), polymer-coated urea products (PCU-1 and PCU-2), and an unfertilized control (C). Values are treatment means for each of 2007 (07), 2008 (08), and 2009 (09). Direct emissions data are from Hyatt et al. (2010).

at least with some PCU products with slower release rates. Further study is needed in this regard. The results also demonstrate how more robust models are needed to account for off-site conversion of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ , since current emission factor models have an enormous degree of uncertainty.

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