



# Nitrous oxide (N<sub>2</sub>O) flux responds exponentially to nitrogen fertilizer in irrigated wheat in the Yaqui Valley, Mexico

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## ABSTRACT

The Yaqui Valley, one of Mexico's major breadbaskets, includes ~230,000 ha of cultivated, irrigated cropland, with two thirds of the area planted annually to spring wheat (*Triticum turgidum*). Nitrogen (N) fertilizer applications to wheat have doubled since the 1980s, and currently average around 300 kg N ha<sup>-1</sup>. Emissions of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas, increase following soil management activities, especially irrigation when N fertilizer is applied, and particularly when N fertilizer inputs exceed crop N requirements. Here we investigate trade-offs among N fertilizer inputs, spring wheat yields, and N<sub>2</sub>O emissions to inform management strategies that can mitigate N<sub>2</sub>O emissions without compromising yields, and link this to how farmers can generate carbon credits from N management to receive payment for more precise N use. We used static chambers to measure N<sub>2</sub>O fluxes from spring wheat at five N fertilizer rates (0, 80, 160, 240, and 280 kg N ha<sup>-1</sup>) during two growing seasons at CIMMYT in Ciudad Obregon, Sonora, Mexico. Average daily fluxes were between 1.9 ± 0.5 and 13.4 ± 2.8 g N<sub>2</sub>O-N ha<sup>-1</sup>, with lower emissions at N rates below those that maximized yield, and substantially higher emissions at N rates beyond maximum yield; this exponential response is consistent with crops in temperate regions. Results suggest that current average N fertilizer rates (300 kg N ha<sup>-1</sup>) are at least double economically optimum rates, resulting in low crop N use efficiency: 36–39% at higher N rates as compared to 50–57% for economically optimum rates. N fertilizer rate reductions to the economic optimum rates here (123 and 145 kg N ha<sup>-1</sup> in 2013 and 2014, respectively) could have avoided N<sub>2</sub>O emissions equivalent to 0.5 to 0.8 Mg CO<sub>2</sub>e ha<sup>-1</sup> yr<sup>-1</sup> or, regionally, 84–138 Gg CO<sub>2</sub>e yr<sup>-1</sup> without harming yields. Insofar as fertilizer use in Yaqui Valley is likely similar to high-productivity irrigated cereal systems elsewhere, our results provide evidence for a global triple-win scenario: large reductions in agricultural GHG emissions, increased farmer income, and continued high productivity.

## 1. Introduction

Nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas (GHG) that contributes to atmospheric warming and stratospheric ozone depletion (IPCC, 2007) is produced in soils mainly by microbial denitrification and nitrification (Panek et al., 2000; Robertson and Groffman, 2015). Agriculture contributes ~60% of global anthropogenic N<sub>2</sub>O emissions (Tian et al., 2016; Robertson, 2014), mostly due to the application of nitrogen (N) fertilizer to croplands (Syakila and Kroeze, 2011).

In Mexican agriculture N<sub>2</sub>O from cropped soils is the second largest source of GHG emissions (World Bank, 2015) and wheat (*Triticum* spp.) is one of the most important fertilized crops, grown on over half a

million hectares in Mexico in 2016, nearly a quarter as irrigated spring wheat grown in the semi-arid Yaqui Valley (SIAP, 2017). Yaqui Valley wheat yields are high, typically 5.2–7.0 Mg ha<sup>-1</sup> y<sup>-1</sup> (SAGARPA, 2016), with N fertilizer applications averaging ~300 kg N ha<sup>-1</sup> (Ortiz-Monasterio, 2017), a near doubling since the 1980s that coincides with adoption of the variety CIRNO C2008 with its high yields and low tolerance for N stress. High rates of fertilization can result in significant N losses to the environment via leaching, run-off, and N<sub>2</sub>O emissions (Matson et al., 1998; Riley et al., 2001; Beman et al., 2005; Ortiz-Monasterio and Raun, 2007) stemming from recoveries of only ~30% of fertilizer N in harvested grain (Raun and Johnson, 1999).

That N fertilizer rate is the best available single metric for predicting

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agricultural  $\text{N}_2\text{O}$  fluxes (Stehfest and Bouwman, 2006) suggests a potential for reducing fluxes by improving N fertilizer use efficiency (Eagle et al., 2012), and carbon credit organizations have expressed interest in using the carbon marketplace to pay farmers for more precise N management (Millar et al., 2010). The most accessible carbon credit programs for N management (Millar et al., 2012; 2013) use methodologies that incorporate emission-factor (EF)-based algorithms to estimate  $\text{N}_2\text{O}$  emissions reductions as a percentage of avoided N use. In the absence of regional experimental evidence, protocols default to the standard EF of 1% (de Klein et al., 2006) used in most national GHG inventories (Lokupitiya and Paustian, 2006). A 1% EF means that 1 kg of  $\text{N}_2\text{O}$ -N is emitted for every 100 kg of N fertilizer applied. Avoided  $\text{N}_2\text{O}$  emissions are then converted to units of avoided carbon dioxide equivalents ( $\text{CO}_2\text{e}$ ) based on  $\text{N}_2\text{O}$ 's global warming potential, about 300 times greater than  $\text{CO}_2$ 's (IPCC, 2007). Avoided  $\text{CO}_2\text{e}$  emissions can then be traded as carbon credits on environmental markets to generate income.

Recent evidence suggests that a 1% EF may underestimate emissions at fertilizer rates that exceed crop need (Hoben et al., 2011; Shcherbak et al., 2014), especially in high-productivity agriculture such as practiced in the Yaqui Valley. If so, then under a 1% EF scenario farmers would receive fewer credits than merited, reducing incentives for better N management and the environmental benefits that would accrue. However, there are no studies of  $\text{N}_2\text{O}$  response to added fertilizer N in semi-arid irrigated agriculture.

Our objectives here are 1) to investigate the trade-offs among N fertilizer input,  $\text{N}_2\text{O}$  emissions, and spring wheat yield in order to inform management strategies that can reduce  $\text{N}_2\text{O}$  emissions without compromising yields, and 2) to develop emission factor algorithms suitable for inclusion in  $\text{N}_2\text{O}$  mitigation protocols to help farmers use carbon markets to generate additional income from improved N management. More globally, we test the hypothesis that  $\text{N}_2\text{O}$  emissions response to fertilizer N is exponential in semi-arid, sub-tropical irrigated agriculture.

## 2. Materials and methods

### 2.1. Region

The Yaqui Valley is located in NW Mexico, on the west coast of Sonora, bounded on the west by the Gulf of California and on the east by the foothills of the Sierra Madre. Agroclimatic conditions are representative of regions in the developing world that produce 40% of the world's wheat (Pingali and Rajaram, 1999). The area comprises ~230,000 ha of irrigated cropland, predominantly spring wheat, with maize, safflower, chickpeas, vegetable crops, and cotton, among others, also grown. Wheat growing season (November to April) temperatures average 9.8 and 27.1 °C for night- and daytime, respectively. Soils in the valley are predominantly vertisols and aridisols, with elevations varying from 0 to 60 m asl (Ortiz-Monasterio and Raun, 2007).

### 2.2. Site and management

Experimental plots ( $3.2 \times 5.0$  m; each containing four planting beds) were established in Yaqui Valley at Campo Experimental Norman E. Borlaug (CENEB; Block 810), near Ciudad Obregon, Sonora, Mexico (27°N; 109°W, 40 m asl) using a randomized complete block design (eight treatments; six replications). Plots were planted to spring wheat (*T. turgidum* var. durum; cultivar CIRNO C-2008) during the 2012–2013 and 2013–2014 growing seasons. The soil is a coarse, sandy clay mixed montmorillonite classified as a Typic Calciorthid. Treatments were N fertilizer rates of 0, 40, 80, 120, 160, 200, 240, and 280 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Spring wheat was planted as two rows on top of each bed (26 cm apart) at a density of 120 kg seed ha<sup>-1</sup> using a Wintersteiger plot planter on 28 November 2012 and 13 December 2013 (within the recommended planting date range). Triple super phosphate (20 kg P ha<sup>-1</sup>) was

applied pre-planting and disk incorporated. N fertilizer (granular urea) was banded as a single dose by hand on the soil surface in each furrow after planting and immediately before furrow irrigation (29–30 November 2012, and 18–19 December 2013). Irrigation water was applied to the end of each furrow through the use of gated pipes, and was allowed to flow down the furrow and run out at the other end, until the top of the bed was fully wetted through capillarity. Unfertilized maize (grain and residue removed) was grown each year preceding the spring wheat as a catch crop for residual N. Herbicide (Starane Ultra; 0.4 L ha<sup>-1</sup> and Broclean; 2 L ha<sup>-1</sup>) was applied on 17 January 2014. No herbicide was applied in 2013; plots were field cultivated on 8 Jan 2013, and hoed throughout the crop cycle. Insecticide (Murala; 0.5 L ha<sup>-1</sup>, and Allectus; 0.2 L ha<sup>-1</sup>) was applied on 24 January and 18 February 2014, respectively. Fungicide (Folicur; 0.5 L) was applied on 21 February 2014. Grain was harvested on 22 April 2013 and 5 May 2014 from 4.8 m<sup>2</sup> in each plot using a Wintersteiger plot combine. Yields were estimated from grain weights at 12% moisture. Grain and straw N content were determined by Kjeldahl analysis. Meteorological data were collected using a Vantage Pro 2 Plus weather station system (Davis Instruments, Vernon Hills, IL).

### 2.3. Soil sampling

Soil samples (0–15 cm) were collected in bed and furrow positions on 45 and 49 occasions, respectively, during the 2012–2013 and 2013–2014 spring wheat growing seasons from five treatments (0, 80, 160, 240 and 280 kg N ha<sup>-1</sup>) in four replications (Blocks 1–4). Samples were immediately transferred to the laboratory at CENEB, weighed, dried for 48 h at 75 °C and weighed again to determine gravimetric soil moisture and soil water-filled pore space. Duplicate sub-samples (9 g each) of fresh soil were extracted with 1 M KCl (90 mL), shaken (1 min), stored (24 h at 21 °C), re-shaken (1 min), rested (60 min), then filtered (Whatman® 1 µm GF/B glass microfiber). An aliquot (8 mL) was transferred to a Corning® 15 mL clear polypropylene (PP) centrifuge tube, and frozen for transfer to Michigan State University's W.K. Kellogg Biological Station (KBS) for analysis of ammonium and nitrate in either a continuous flow analyzer (Flow Solution IV; OI Analytical, College Station, TX, U.S.A.) or a flow injector analyzer (Lachat QuikChem 8500 Series 2; Hach, Loveland, CO, U.S.A.). Instruments were cross-calibrated and seven calibration samples were analyzed twice per analytical run on each instrument along with multiple check standards.

### 2.4. Greenhouse gas sampling and analysis

Static chambers (Matson et al., 1996) were positioned at 5 cm depths in the furrow and bed areas of each plot from five treatments (0, 80, 160, 240 and 280 kg N ha<sup>-1</sup>) in four replications (Blocks 1–4). Gas fluxes were determined immediately prior to N fertilization (concurrent with furrow irrigation), on days 1, 2, and 3 after fertilization, on alternate days during the next two weeks, then twice weekly unless following a supplemental irrigation event (then on days 1, 2, 3, then as above) until harvest, for a total of 45 sampling events between 29 November 2012 and 23 April 2013, and a total of 44 sampling events between 13 December 2013 and 21 April 2014. In 2014, sampling continued once per month after harvest until September. Chamber headspace gas samples (10 mL) were collected via syringe four times at 10 min intervals from each chamber, transferred to storage vials (5.9 mL; Labco Ltd., Lampeter, UK) to over-pressure, and transported to KBS for analysis. Samples were analyzed for  $\text{N}_2\text{O}$  using gas chromatography with a 63Ni electron capture detector at 350 °C (Agilent Technologies 7890A, Santa Clara, CA, U.S.A.) coupled to a Gerstel MPS2XL auto-sampler (Mülheim An Der Ruhr, Germany). Seven calibration samples were analyzed four times, along with multiple blanks and check standards throughout each analytical run.

## 2.5. Flux calculation

Hourly fluxes of  $\text{N}_2\text{O}$  ( $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ ) were calculated from the linear relationship between  $\text{N}_2\text{O}$  concentration and chamber closure time (minutes), corrected for air temperature and air pressure (taken at site) and the ratio of chamber headspace volume to surface cover area, using the equation:

$$N_2O = (\alpha \times V \times W_A \times 60) / (A \times MV_{\text{corr}}) \quad (1)$$

where  $\alpha$  is the change in headspace concentration during the chamber closure period ( $\text{ppmv min}^{-1}$ ),  $V$  is the chamber headspace volume (L),  $W_A$  is the atomic mass of N in  $\text{N}_2\text{O}$  (28.0), 60 is the conversion from minutes to hours,  $A$  is the soil surface area covered by the chamber ( $\text{m}^2$ ), and  $MV_{\text{corr}}$  is the temperature and pressure corrected standard mole volume. Hourly fluxes were then converted to daily fluxes ( $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ). Daily fluxes from the 240 and 280  $\text{kg N ha}^{-1}$  treatments were averaged (hereafter referred to as 260  $\text{kg N ha}^{-1}$  w.r.t.  $\text{N}_2\text{O}$  fluxes) at the replicate level in each bed and furrow area to reduce the inherent high spatial variability of emissions associated with large N inputs (e.g., Parkin, 1987). Average daily fluxes from each plot were calculated by weighting the relative area occupied by the bed (0.325) and furrow (0.675) in each plot. Cumulative emissions over each growing season (133 days in 2012–2013 and 129 days in 2013–2014) were determined using linear interpolation between successive sampling days.

## 2.6. Emission reduction and emission factor (EF) calculations

Nitrous oxide emissions reduction values were calculated by subtracting cumulative growing season emissions of lower N application rates from cumulative growing season emissions of higher N application rates within the same block and growing season. This emissions difference was then divided by the difference in rate between the pairs to obtain eight emission reduction values (4 blocks  $\times$  2 site years) for each of the six reduction combinations (80-0, 160-0, 260-0, 160-80, 260-80, and 260–160  $\text{kg N ha}^{-1}$ ). A number of functions (e.g., linear and exponential) with various parameter combinations were tested to define the interpolation for these emissions reductions. Exponential emission rates (ER) for each N rate were represented as:  $ER = a e^{-bN}$  where ER is the emissions rate in  $\text{g N}_2\text{O-N}$  and  $N$  is the fertilizer N rate in  $\text{Mg-N}$ . Emission reductions equations  $(ER(N1) - ER(N2)) / (N1 - N2)$  in  $\text{g N}_2\text{O-N/Mg-N}$  where  $N1$  is the higher N rate and  $N2$  is lower N rate were converted to EF percentages:  $EF = a(e^{-bN1} - e^{-bN2}) / (N1 - N2)$ , and calculated when  $N2 = 0 \text{ kg N ha}^{-1}$  as  $EF = a(e^{-bN} - 1) / N$ .

## 2.7. Data analysis

Best fit response curves for  $\text{N}_2\text{O}$  flux as a function of N input,  $\text{N}_2\text{O}$  emission reduction values, and  $\text{N}_2\text{O}$  emissions factors as a function of N input were calculated using Mathematica (Version 10.0, Wolfram Research Inc., 2014). Within the framework of an RCBD, yield vs. N rate data were tested for significance using t Tests (LSD) in the GLM Procedure of SAS (SAS Institute Inc., Cary, NC, 2002–2008, Version 9.2). Economically optimum N fertilizer rate applications were determined as the  $R^2$  weighted mean of a number of yield functions, including quadratic, quadratic-plateau, and linear-plateau (IPNI 2013), using a historical crop grain to fertilizer N price ratio of 5.0 (Ortiz-Monasterio and Raun, 2007).

## 3. Results

### 3.1. Environmental variables

Total rainfall during the spring wheat growing season was 9 mm in 2012–2013 (145 days) and 20 mm in 2013–2014 (124 days); 19 mm fell as a single event on 9 March 2014 (Fig. 1). Rainfall during both growing

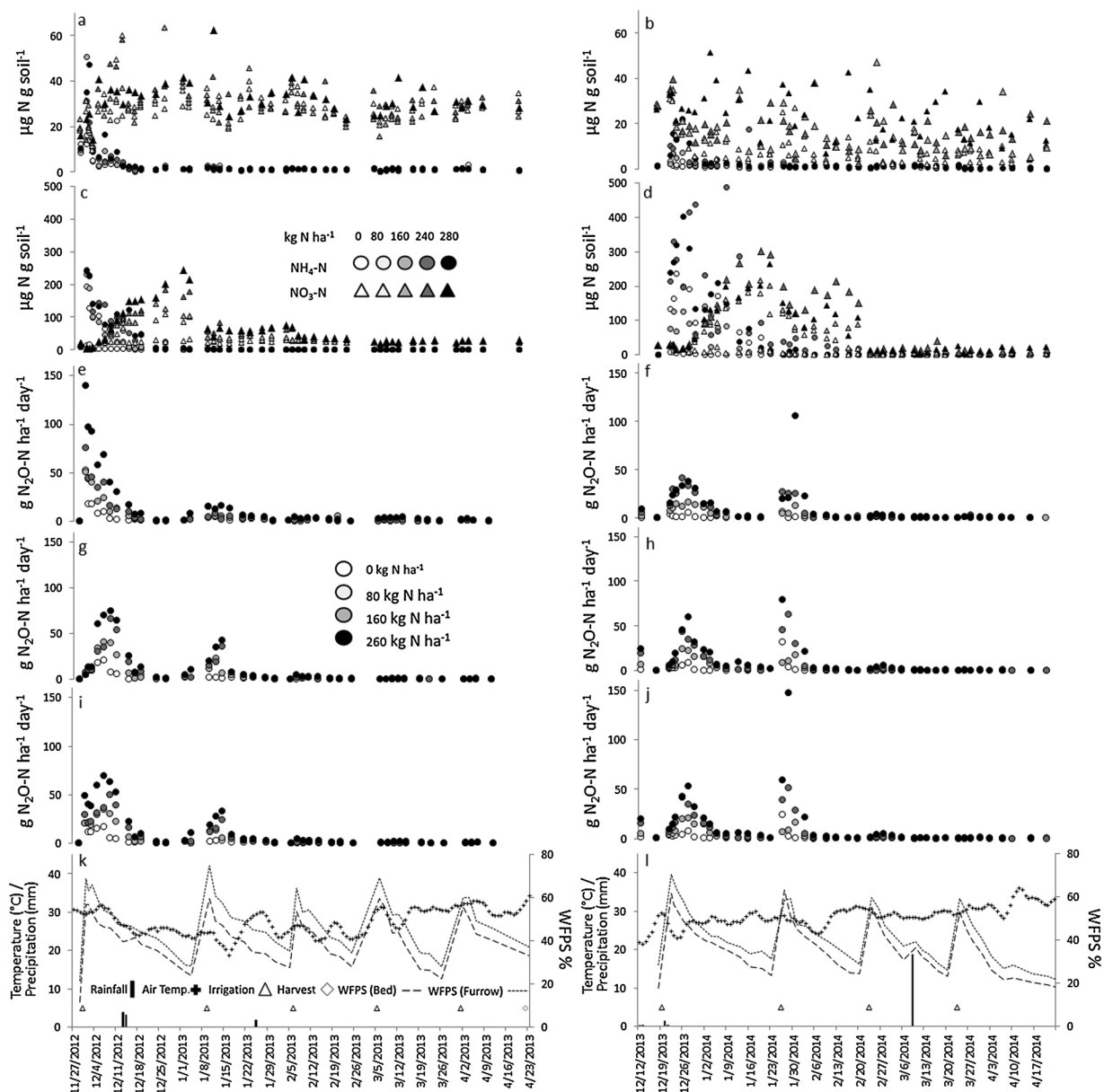
seasons was substantially lower than the 30 year prior (1982–2011) average (66 mm; Nov–April inclusive) and ranked 9th and 13th in lowest total rainfall during the growing season over this period. Rainfall between these two growing seasons (239 days) was 242 mm, close to the 30 year prior (1983–2012) average (302 mm; May–November inclusive). The average maximum air temperatures during the spring wheat growing seasons were 27.3 °C and 29.1 °C in 2012–2013 and 2013–2014, respectively; average minimums were 8.7 °C and 10.2 °C, respectively (Fig. 1). These temperatures were close to the 30 year prior average (28.1 °C and 10.9 °C for maximum and minimum air temperatures, respectively).

### 3.2. Daily and total $\text{N}_2\text{O}$ emissions

Daily  $\text{N}_2\text{O}$  fluxes increased rapidly from bed and furrow areas following N fertilizer application (banded in furrow immediately prior to initial irrigation) and the second irrigation event in both growing seasons (Fig. 1e–h). Three of the four highest daily fluxes over the experimental period (139.8, 96.8, and 92.8  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ , measured on 1, 2, and 3 December 2012, respectively) were from the bed area at 260  $\text{kg N ha}^{-1}$ , immediately following N fertilization and initial irrigation (30 November 2012). Daily fluxes in the bed and furrow areas then decreased rapidly to background levels ( $< 5 \text{ g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ) by  $\sim 3$  weeks after fertilization in both seasons, equivalent to phenological stage Z22 (Zadoks et al., 1974). A second  $\text{N}_2\text{O}$  pulse of  $\sim 1$ –2 weeks duration, typically smaller than the first pulse in the bed areas (but see peak on 31 Jan 2014 at 260  $\text{kg N ha}^{-1}$ ) and of similar magnitude in the furrow areas, followed the second irrigation event in both years (9 Jan 2013, and 26 Jan 2014), equivalent to phenological stage Z30–Z31. Subsequent irrigations between February and April in 2013 and 2014 did not result in substantial  $\text{N}_2\text{O}$  pulses. Average bed, furrow, and weighted daily emissions increased with increasing N fertilizer rate in both growing seasons; for example, weighted emissions ranged between  $1.9 \pm 0.5$  and  $13.4 \pm 2.8 \text{ g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$  at 0  $\text{kg N ha}^{-1}$  and 260  $\text{kg N ha}^{-1}$ , respectively, over the experimental period. Average total emissions (i.e., average of cumulative emissions over each wheat growing season) ranged from  $0.2 \pm 0.1$  to  $1.4 \pm 0.2 \text{ kg N}_2\text{O-N ha}^{-1}$  at 0  $\text{kg N ha}^{-1}$  and 260  $\text{kg N ha}^{-1}$ , respectively (Fig. 2). Average daily  $\text{N}_2\text{O}$  emissions were significantly ( $P < 0.05$ ) correlated with average concentrations of inorganic N ( $[\text{NH}_4^+ + \text{NO}_3^-]\text{-N}$ ), particularly  $\text{NH}_4^+\text{-N}$  in the furrow ( $R^2 = 0.98$ ) during both growing seasons.

### 3.3. Soil inorganic N and water content

Concentrations of inorganic N in the soil increased rapidly and immediately following N fertilization and irrigation events on 30 November 2012 and 19 December 2013 (Fig. 1a–d). For example, furrow (where urea fertilizer was banded) concentrations of  $\text{NH}_4^+\text{-N}$  increased more than 25 fold ( $9.3 \mu\text{g N g}^{-1}$  soil to  $240 \mu\text{g N g}^{-1}$  soil) at 280  $\text{kg N ha}^{-1}$  between 29 November and 1 December 2012, and increased from  $0.7 \mu\text{g N g}^{-1}$  soil to  $176 \mu\text{g N g}^{-1}$  soil at the same N rate between consecutive measurements on 18 and 22 December 2013, respectively, peaking at  $281 \mu\text{g N g}^{-1}$  soil on 28 December 2013, just before tillering. These very high concentrations were relatively short-lived;  $\text{NH}_4^+\text{-N}$  concentrations in all fertilized treatments in both years were back to baseline values ( $< 4 \mu\text{g N g}^{-1}$  soil) within 3–4 weeks of these peaks, at the beginning of stem elongation, except at 280  $\text{kg N ha}^{-1}$  in the second growing season, where concentrations  $> 7 \mu\text{g N g}^{-1}$  soil were observed for a further 3 weeks (Fig. 1d). Concentrations of  $\text{NO}_3^-\text{-N}$  started to increase about one week after fertilization, peaking  $\sim$  three weeks later; the highest concentration in each season in the furrow was measured on 2 January 2013 ( $203 \mu\text{g N g}^{-1}$  soil) and 20 January 2014 ( $252 \mu\text{g N g}^{-1}$  soil), respectively at 280  $\text{kg N ha}^{-1}$ , equivalent to mid to late tillering. A subsequent but less pronounced increase in  $\text{NO}_3^-\text{-N}$  concentrations occurred following the second irrigation event on 9 January 2013 and 26 January 2014, after



**Fig. 1.** Soil inorganic N concentrations ( $\mu\text{g N g}^{-1}$  soil; 0–15 cm; a–d), average daily  $\text{N}_2\text{O}$  emissions ( $\text{g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ ; e–j), daily rainfall (mm), maximum air temperature ( $^{\circ}\text{C}$ ), soil water-filled pore space (bed and furrow; %), irrigation dates, and harvest dates (k–l) during the 2012–2013 and 2013–2014 growing seasons at CENE (Block 810) in the Yaqui Valley. Soil inorganic N concentrations were measured from the 0, 80, 160, 240, and 280  $\text{kg N ha}^{-1}$  treatments in the bed (Lomo; a, b) and furrow (Fondo; c, d) positions. Average daily  $\text{N}_2\text{O}$  emissions were measured at 0, 80, 160, and 260 (average of 240 and 280  $\text{kg N ha}^{-1}$ ) treatments in the bed (Lomo; e, f) and furrow (Fondo; g, h) positions, and weighted based on relative area of the bed (0.325) and furrow (0.675) in each plot (i, j).

which concentrations slowly returned to baseline values  $\sim 3$  months after fertilization. Average concentrations of inorganic N during both seasons increased monotonically with increasing N fertilizer rate, particularly with furrow  $\text{NO}_3\text{-N}$  ( $P < 0.001$ ), and were higher ( $P < 0.001$ ) in the furrow area than in bed area in all treatments except for  $\text{NH}_4\text{-N}$  in the 0  $\text{kg N ha}^{-1}$  treatment. Soil water filled pore-space (WFPS) increased rapidly following all nine furrow irrigation events in both bed and furrow areas during the two growing seasons (Fig. 1k–l). Nitrogen rate had no measurable effect on soil WFPS during the experiment. Average WFPS across all N rate treatments and seasons was higher ( $P < 0.01$ ) in the furrow (44%) than in the bed (38%) areas.

### 3.4. Grain yields and economic N rates

Spring wheat grain yields were significantly higher in 2013 in all N rate treatments when compared to their counterparts in 2014

( $P < 0.001$ ). Differences in yield response to the same N rate between years were most pronounced in the lower N rate treatments and ranged between a 19% higher yield in the 280  $\text{kg N ha}^{-1}$  treatment to a 76% higher yield in the 0  $\text{kg N ha}^{-1}$  treatment. There were no statistically significant ( $P < 0.001$ ) increases in grain yield in our experimental N rate treatments after N fertilizer inputs reached 120  $\text{kg N ha}^{-1}$  and 200  $\text{kg N ha}^{-1}$  in 2013 and 2014, respectively (Fig. 3). Total N uptake in the grain over the two growing seasons ranged from 42  $\text{kg N ha}^{-1}$  in the 0  $\text{kg N ha}^{-1}$  treatment in 2014 to 172  $\text{kg N ha}^{-1}$  in the 280  $\text{kg N ha}^{-1}$  treatment in 2013, with average concentrations of N in the grain between 1.7 and 2.4%; increasing incrementally (but with reducing magnitude) with increasing fertilizer N rates. The N use efficiency of the crop (NUE) calculated as  $\text{NUE} = (N_{\text{gr}} - N_{\text{g0}})/N_{\text{rate}}$ , where  $N_{\text{gr}}$  is the total amount of N in the grain ( $\text{kg ha}^{-1}$ ) in a non-zero N rate treatment,  $N_{\text{g0}}$  is the total amount of N in the grain ( $\text{kg ha}^{-1}$ ) in the zero N rate treatment, and  $N_{\text{rate}}$  is the N rate of the treatment ( $\text{kg ha}^{-1}$ ),



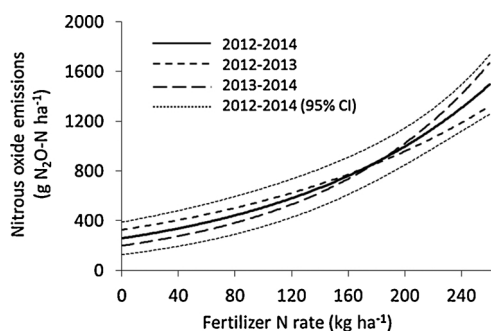


Fig. 2. Cumulative  $\text{N}_2\text{O}$  emissions response curves ( $\text{g N}_2\text{O-N ha}^{-1}$ ) in spring wheat (weighted average based on relative area of the bed [0.325] and furrow [0.675] in each plot) to increasing N fertilizer rate at CENEB (Block 810) in the Yaqui Valley in 2012–2013 (short dashed line), 2013–2014 (long dashed line), and averaged over 2012–2014 (solid line), along with  $\pm$  95% confidence intervals for 2012–2014 (dotted line). Equations for these and other response curves are presented in Table 1.

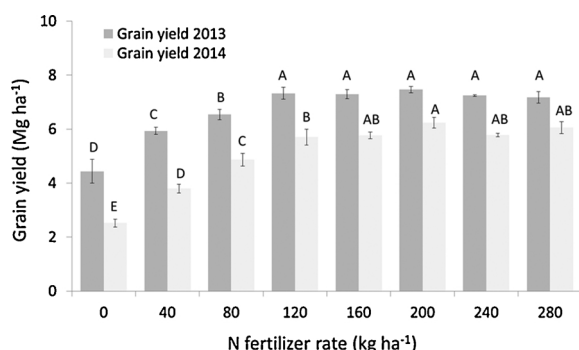


Fig. 3. Grain yield ( $\text{Mg ha}^{-1}$ ) of spring wheat in 2013 and 2014 at CENEB (Block 810) in the Yaqui Valley in response to increasing N rate (0, 40, 80, 120, 160, 200, 240, and 280  $\text{kg N ha}^{-1}$ ). Error bars are  $\pm$  one standard error of the mean. Significant differences ( $\alpha = 0.05$ ) between treatments in each year are represented by uppercase letters.

decreased with increasing N rate, averaging between 0.55–0.57, 0.49–0.50, and 0.36–0.39 in the 40–120  $\text{kg N ha}^{-1}$ , 160–200  $\text{kg N ha}^{-1}$ , and 240–280  $\text{kg N ha}^{-1}$  treatments, respectively across both years.

The most economic rate of N (MERN) for individual years was determined from the  $R^2$  weighted mean of a number of yield functions (IPNI, 2013) using an historical crop grain to fertilizer N price ratio of 5.0 (Ortiz-Monasterio and Raun, 2007). The MERN was 123 and 145  $\text{kg N ha}^{-1}$  in 2013 and 2014, respectively, with grain yields at these N rates of 7.28  $\text{Mg ha}^{-1}$  and 5.80  $\text{Mg ha}^{-1}$ , respectively.

### 3.5. Nitrous oxide response curves and emissions factors (EF)

Response curves for  $\text{N}_2\text{O}$  flux as a function of N input were generated for bed, furrow, and spatially weighted fluxes for each year and across both years (Table 1). Hereafter fluxes and emissions will refer to the spatially weighted values unless otherwise specified. The best-fit response curve for emissions over the experimental period was the exponential function:

$$\text{N}_2\text{O} = 258 \times \exp(0.0068 \times N) \quad (2)$$

where  $\text{N}_2\text{O}$  is total  $\text{N}_2\text{O}$  emissions, i.e., the average of the cumulative emissions over the two wheat growing seasons ( $\text{g N}_2\text{O-N ha}^{-1}$ ), and N is the N fertilizer rate ( $\text{kg N ha}^{-1}$ ).

## 4. Discussion

### 4.1. Nitrous oxide emissions

The range of average daily  $\text{N}_2\text{O}$  emissions measured from spring wheat (2 to 13  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ) along our N gradient (0–280  $\text{kg N ha}^{-1}$ ) is similar to those from other wheat N gradient studies, e.g., 1 to 13  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$  across 6 sites in Germany (0–400  $\text{kg N ha}^{-1}$ ; Lebender et al., 2014) and 2 to 6  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$  at a site in China (0–400  $\text{kg N ha}^{-1}$ ; Liu et al., 2012). Similar emissions ( $\leq 7 \text{ g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ) have also been observed from spring wheat (100  $\text{kg N ha}^{-1}$  fertilization; Lam et al., 2013) and winter wheat (100  $\text{kg N ha}^{-1}$ ; Barton et al., 2008) in semi-arid Australia. Our emissions are lower than those found for maize in the humid US Midwest (5 to 26  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ; Hoben et al., 2011) and spring barley in Canada (7 to 62  $\text{g N}_2\text{O-N ha}^{-1} \text{d}^{-1}$ ; Zebbarth et al., 2008) fertilized at N rates similar to our study. Our lower emissions may be due to higher NUEs in wheat at our site than for comparable N fertilizer rates in other grain crops, although this is not evident in large-scale studies (e.g., Cassman et al., 2002; Zhang et al., 2015), or larger losses of other N species at our site, such as nitrate (Riley et al., 2001), nitric oxide (Matson et al., 1998), or DON (Glibert et al., 2006). Also, soil WFPS values were high ( $> 60\%$ ) during periods following irrigation events, potentially favoring  $\text{N}_2$  rather than  $\text{N}_2\text{O}$  emissions as an end product of denitrification (e.g., Bouwman, 1998; Robertson and Groffman, 2015).

Soil inorganic N concentrations were strongly and positively related to  $\text{N}_2\text{O}$  emissions. The correlation between  $\text{NH}_4^+-\text{N}$  in the furrow and average daily  $\text{N}_2\text{O}$  emissions was particularly strong ( $R^2 = 0.98$ ), and especially so during the periods immediately following the first irrigation events in each year (Fig. 1). This is likely due to the formulation of N fertilizer and method of application. Granular urea, an ammonium-based fertilizer, was banded on the soil surface in the furrows immediately prior to the application of irrigation water. This likely resulted in the fast production and emission of  $\text{N}_2\text{O}$ , mirroring the immediate availability of the  $\text{NH}_4$  substrate in the furrow (Fig. 1c–d) and bed (Fig. 1a–b). Indeed, fluxes of  $\text{N}_2\text{O}$  from the bed were higher than from the furrow for  $\sim 1$  week after the first irrigation in late 2012 (Fig. 1e and g, respectively), suggesting a near immediate transport of the fertilizer in solution from the furrow to the bed, and more favorable conditions for  $\text{N}_2\text{O}$  production from nitrification (i.e., lower soil WFPS in the bed [46–57%] compared to the furrow [54–69%]; Fig. 1k). This  $\text{N}_2\text{O}$  pulse was not evident in late 2013.

In the second growing season, the first furrow irrigation (and N application) occurred six days after wheat planting in the bed (Dec 13 and 19, 2013, respectively), compared to one day after in the first growing season (Nov 28 and 29, 2012, respectively). Fluxes of  $\text{N}_2\text{O}$  were only measured once during the six day period in 2013 (Dec 18), and as such we may have missed higher  $\text{N}_2\text{O}$  fluxes due to soil disturbance from wheat planting; a pulse that would have been captured during 2012, but was not distinguishable due to its conflation with fluxes associated with N fertilization and irrigation immediately after planting. Concentrations of  $\text{NO}_3^--\text{N}$  increased as those of  $\text{NH}_4^+-\text{N}$  decreased between 1 and 3 weeks after urea fertilization, indicating that nitrification was occurring. This was most pronounced in the furrow in both years (Fig. 1c–d). A trend for higher concentrations of  $\text{NO}_3^--\text{N}$  at and immediately after the second irrigation in 2014, compared to 2013, likely accounts for the higher fluxes of  $\text{N}_2\text{O}$  during this time, particularly from the furrow, and suggests that denitrification may have been the predominant process of  $\text{N}_2\text{O}$  production at that time. Timing of irrigation events in conjunction with N fertilizer application should be further investigated as a means of reducing  $\text{N}_2\text{O}$  emissions and other N losses (Matson et al., 1998).

### 4.2. Nitrous oxide response curves and emissions factors

Emissions of  $\text{N}_2\text{O}$  responded strongly to fertilizer N. We found low

**Table 1**Equations and 95% Confidence Intervals (CI) for N<sub>2</sub>O emissions response curves, and N<sub>2</sub>O emissions factors (EF).

Calculation <sup>a</sup>	N <sub>2</sub> O emissions <sup>b</sup>	95% CI half-width for emissions	N <sub>2</sub> O emission factor (EF) <sup>c</sup>	95% CI half-width for EFs
1. Weighted 2013–14	$258 \times e^{(0.0068 \times N)}$	$2.04 \times \sqrt{[e^{(0.0135 \times N)} \times (4090 - 34 \times N + 0.075 \times N^2)]}$	$0.0258 \times (e^{(6.76 \times N)} - 1)/N$	$0.128 \times e^{(0.0012 \times N)}$
2. Weighted 2013	$327 \times e^{(0.0054 \times N)}$	$2.14 \times \sqrt{[e^{(0.0107 \times N)} \times (2648 - 22 \times N + 0.053 \times N^2)]}$	$0.0327 \times (e^{(5.38 \times N)} - 1)/N$	$0.333 \div e^{(0.0039 \times N)}$
3. Weighted 2014	$199 \times e^{(0.0082 \times N)}$	$2.14 \times \sqrt{[e^{(0.0163 \times N)} \times (10560 - 85 \times N + 0.182 \times N^2)]}$	$0.0199 \times (e^{(8.18 \times N)} - 1)/N$	$0.119 \times e^{(0.0038 \times N)}$
4. Bed 2013–14	$249 \times e^{(0.0061 \times N)}$	$2.04 \times \sqrt{[e^{(0.0122 \times N)} \times (2390 - 20 \times N + 0.046 \times N^2)]}$	$0.0249 \times (e^{(6.09 \times N)} - 1)/N$	$0.172 \times e^{(0.0012 \times N)}$
5. Bed 2013	$296 \times e^{(0.0059 \times N)}$	$2.14 \times \sqrt{[e^{(0.0118 \times N)} \times (2346 - 20 \times N + 0.045 \times N^2)]}$	$0.0296 \times (e^{(5.88 \times N)} - 1)/N$	$0.298 \div e^{(0.0036 \times N)}$
6. Bed 2014	$205 \times e^{(0.00632 \times N)}$	$2.14 \times \sqrt{[e^{(0.0126 \times N)} \times (5923 - 49 \times N + 0.112 \times N^2)]}$	$0.0205 \times (e^{(6.32 \times N)} - 1)/N$	$0.245 \div e^{(0.0008 \times N)}$
7. Furrow 2013–14	$263 \times e^{(0.00702 \times N)}$	$2.04 \times \sqrt{[e^{(0.0140 \times N)} \times (7881 - 65 \times N + 0.143 \times N^2)]}$	$0.0263 \times (e^{(7.02 \times N)} - 1)/N$	$0.133 \times e^{(0.0028 \times N)}$
8. Furrow 2013	$340 \times e^{(0.00517 \times N)}$	$2.14 \times \sqrt{[e^{(0.0103 \times N)} \times (3945 - 33 \times N + 0.080 \times N^2)]}$	$0.0340 \times (e^{(5.17 \times N)} - 1)/N$	$0.451 \div e^{(0.0047 \times N)}$
9. Furrow 2014	$196 \times e^{(0.00888 \times N)}$	$2.14 \times \sqrt{[e^{(0.0178 \times N)} \times (18084 - 145 \times N + 0.306 \times N^2)]}$	$0.0196 \times (e^{(8.88 \times N)} - 1)/N$	$0.129 \times e^{(0.0053 \times N)}$

<sup>a</sup> Plot area and year used in calculating N<sub>2</sub>O emissions and emissions factors. Weighted calculations use the relative area occupied by the bed (0.325) and furrow (0.675) in each plot. Bed and furrow refer to the calculations of emissions and emissions factors from the bed and furrow area, respectively.

<sup>b</sup> Nitrous oxide emissions (g N<sub>2</sub>O–N) per unit of N fertilizer applied (kg N).

<sup>c</sup> Nitrous oxide emissions factor (%) per unit of N fertilizer applied (kg N).

N<sub>2</sub>O emissions at 0 and 80 kg N ha<sup>−1</sup> fertilizer rates, corresponding to rates below the most economic rate of N (MERNs; 123 and 145 kg N ha<sup>−1</sup> for our site in 2013 and 2014, respectively), and increasing N<sub>2</sub>O emissions at N fertilization rates above the MERNs. Among a number of equation types tested, the best-fit N<sub>2</sub>O response curves to increasing N rate were all exponential functions (Table 1). This exponential increase was particularly evident in the 2013–2014 growing season where total weighted emissions were consecutively doubled and then trebled following incremental increases in N fertilizer rate from 0 to 80 kg N ha<sup>−1</sup> (149 vs. 279 g N<sub>2</sub>O–N ha<sup>−1</sup>) and 80 to 160 kg N ha<sup>−1</sup> (279 vs. 852 g N<sub>2</sub>O–N ha<sup>−1</sup>), respectively. This relationship suggests that competition between the requirements of the crop and soil heterotrophs for available N helps control the rate of N<sub>2</sub>O emissions; when crop N requirements were met by available soil N, additional N from the fertilizer was more readily available for microbes that produce N<sub>2</sub>O (e.g., Erickson et al., 2001). In 2013 and 2014, the maximum N uptake in the wheat (grain and straw) attributable to the N fertilizer input that year (i.e., N uptake in a non-zero N rate treatment minus N uptake in the zero N rate treatment) was ~ 140 kg N ha<sup>−1</sup>, similar to the MERNs, and suggesting that best economic rates and agronomic optimum rates were comparable.

This exponential N<sub>2</sub>O response in spring wheat is similar to findings in maize in the US Midwest (Hoben et al., 2011) and in Canadian wheat (Grant et al., 2006) and spring barley (Zebbarth et al., 2008), though differs from linear relationships found in Germany for wheat (Lebender et al., 2014). A recent meta-analysis of N gradient experiments determined that an exponential relationship best fit the N<sub>2</sub>O fertilizer response for grain crops globally (Shcherbak et al., 2014). Exponential N loss responses to increasing N fertilizer rate have also been shown for nitrate (Gehl et al., 2005; Hawkesford, 2014; Ruan et al., 2016) and nitric oxide (Zhou et al., 2015).

Emission factors (EFs) in our study ranged from 0.23% to 0.47% at 80 and 260 kg N ha<sup>−1</sup>, respectively, across both years. These EFs are higher than those found for rainfed (0.16% and 0.18% at 150 and 250 kg N ha<sup>−1</sup> inputs; Ding et al., 2007) and irrigated (0.09 to 0.15% at 120 and 400 kg N ha<sup>−1</sup> inputs; Liu et al., 2012) wheat crops in China, and for rainfed spring barley in Canada (0.11% and 0.21% at 75 and 150 kg N ha<sup>−1</sup>; Zebbarth et al., 2008), and much higher than those found for rainfed wheat crops in semi-arid Australia (0.02% at 100 kg N ha<sup>−1</sup>; Barton et al., 2008). Wheat EFs are typically lower than those for maize. For example, Hoben et al. (2011) calculated EF values of between 0.6 to 1.5% for N rates between 45 and 225 kg N ha<sup>−1</sup>, respectively, in the US Midwest. The change in emission factor ( $\Delta EF$ ; %) with increasing N input (kg N ha<sup>−1</sup>) in our study ( $25.8 \times (e^{(0.0068 \times N)} - 1)/N$ ) was very similar to  $\Delta EF$ s in US Midwest maize ( $67.1 \times (e^{(0.0067 \times N)} - 1)/N$ ;

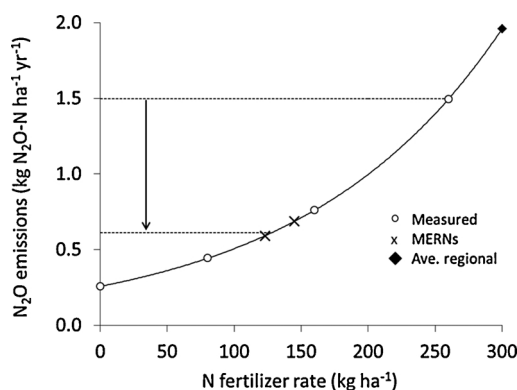
Millar et al., 2012, 2013) and upland grain crops globally ( $131 \times (e^{(0.0044 \times N)} - 1)/N$ ); following conversion from the quadratic form used in Shcherbak et al., 2014).

#### 4.3. Yield response

Spring wheat grain yields were significantly higher in 2013 in all N rate treatments when compared to their counterparts in 2014 (7.3 and 6.0 Mg ha<sup>−1</sup> in 2013 and 2014, respectively;  $P < 0.001$ ). Residual N in the soil prior to wheat planting, rainfall, and average daily temperatures in both crop years were similar (Fig. 1). Higher minimum (nighttime) temperatures have been shown to result in significant negative yield responses, equivalent to about a 10% yield reduction for every 1 °C increase in minimum temperature (Lobell et al., 2005; Lobell and Ortiz-Monasterio, 2007). Minimum temperatures during the second growing season in our study were higher than the first (10.2 °C and 8.7 °C, respectively), and can be considered equivalent to a 15% reduction in yield, compatible with the 21% observed. Our yields were in good agreement with the average wheat yields for the whole of Yaqui Valley (7.1 Mg ha<sup>−1</sup> and 6.2 Mg ha<sup>−1</sup> in 2013 and 2014, respectively).

Current regional average annual N fertilizer application to spring wheat in the Yaqui Valley (~ 300 kg N ha<sup>−1</sup>; Ortiz-Monasterio, 2017) is more than 2-fold greater than the MERNs for our site. The MERN value for our site in 2013 (123 kg N ha<sup>−1</sup>) was similar to the agronomic optimum for that year (120 kg N ha<sup>−1</sup>; i.e., the N rate above which grain yield showed no significant increase in our treatments), whereas in 2014 the MERN value (145 kg N ha<sup>−1</sup>) was lower than the agronomic optimum (200 kg N ha<sup>−1</sup>; Fig. 4). For durum wheat, grain quality is managed on the basis of the content of non-vitreous grains (e.g., yellow berry and black point). The threshold is typically 12% and local farmers associations typically use 10% as the limit of yellow berry. Grain quality in our study met this requirement at N fertilizer rates of between 120–130 kg N ha<sup>−1</sup> and 140–150 kg N ha<sup>−1</sup> in 2013 and 2014, respectively, coincident with the respective MERNs.

Our MERN values are lower than the N rate recommendation (167 kg N ha<sup>−1</sup>) estimated from on-farm trials using GreenSeeker™ NDVI (Normalized Difference Vegetation Index) technology (Ortiz-Monasterio and Raun, 2007). This may be due to management differences; in our study wheat was planted and then immediately irrigated and fertilized, whereas in the on-farm trials farmers planted wheat almost three weeks after irrigation. Evidence from <sup>15</sup>N studies suggests this latter practice may result in the loss of about 30% of the applied N (unpublished data). Our own and other studies (e.g., Matson et al., 1998; Ortiz-Monasterio and Raun, 2007) suggest that N fertilizer in the region is commonly over-applied to spring wheat from both economic



**Fig. 4.** N<sub>2</sub>O response curve (solid line) to increasing N fertilizer rate (0, 80, 160, and 260 kg N ha<sup>-1</sup>; open circles) averaged over two growing seasons (2012–2013 and 2013–2014) in spring wheat at CENEB (Block 810) in the Yaqui Valley. The best-fit curve ( $N_2O \text{ emissions} = 258 \cdot \exp^{(0.0068 \cdot N \text{ rate})}$ ) is the weighted average based on relative area of the bed (0.325) and furrow (0.675) in each plot. The most economic return to N (MERN) in 2013 (123 kg N ha<sup>-1</sup>) and 2014 (145 kg N ha<sup>-1</sup>) at the site (crosses), and the average reported regional (Yaqui Valley) N fertilizer rate (300 kg N ha<sup>-1</sup>; solid diamond) are shown on the response curve. The vertical downward pointing arrow depicts an example of one potential N<sub>2</sub>O mitigation scenario; a reduction from 260 kg N ha<sup>-1</sup> to the most economic return to nitrogen (MERN) rate in 2013 (123 kg N ha<sup>-1</sup>; mitigation = 0.88 kg N<sub>2</sub>O-N ha<sup>-1</sup>, equivalent to 0.44 Mg CO<sub>2</sub>e ha<sup>-1</sup>).

and agronomic standpoints. Despite the proven benefits of reducing N fertilizer rate (Matson et al., 1998), adoption of lower N input practices is not widespread in the region, although transfer of GreenSeeker™ technology by AOASS (Asociacion de Organismos de Agricultores del Sur de Sonora; <http://www.aoass.com/servicios.html#>), a farmer's association working in the Yaqui Valley, has been implemented on about 8000 ha of spring wheat.

#### 4.4. Regional N<sub>2</sub>O mitigation potential

Using the best-fit weighted average equation (Table 1; Eq. 1) over the two growing seasons (Fig. 4), and the area planted to wheat in 2014 (171,286 ha; 2013 not available), the annual potential for N<sub>2</sub>O emissions reductions from wheat based upon a reduction from 260 kg N ha<sup>-1</sup> to 123 kg N ha<sup>-1</sup> (the MERN in 2013) is 0.44 Mg CO<sub>2</sub>e ha<sup>-1</sup> yr<sup>-1</sup> or 75 Gg CO<sub>2</sub>e yr<sup>-1</sup> across the Yaqui Valley (Fig. 4). If we use the more conservative 167 kg N ha<sup>-1</sup> on-farm trial recommendation (Ortiz-Monasterio and Raun, 2007) as the lower N rate, then the reduction is 0.34 Mg CO<sub>2</sub>e ha<sup>-1</sup> yr<sup>-1</sup> or 58 Gg CO<sub>2</sub>e yr<sup>-1</sup> across the Yaqui Valley. Both of these mitigation rates are substantial.

By comparison, converting from conventional to no-till cultivation in the US has been estimated to sequester 0.34 Mg CO<sub>2</sub>e ha<sup>-1</sup> yr<sup>-1</sup> (West and Marland, 2002), and the total mitigation capacity (i.e., reduced Global Warming Impact [GWI]) based on reductions in emissions of the three major agricultural gases (N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>) for this conversion in humid US Midwest climates has been estimated as 0.69 Mg CO<sub>2</sub>e ha<sup>-1</sup> yr<sup>-1</sup> (Six et al., 2004). Much higher rates of N fertilizer application to spring wheat than those investigated here (up to 495 kg N ha<sup>-1</sup>) have recently been reported (personal communication: Ivan Ortiz-Monasterio); N rate reductions from these high levels would lead to much greater N<sub>2</sub>O mitigation than that noted here. Thus, even low to moderate adoption of reduced N rates could lead to substantial regional reductions in GHG emissions without harming yields and while improving economic returns.

#### 4.5. Carbon markets and farmer opportunities

Payments are available to farmers and other stakeholders for

implementing projects that reduce GHG emissions using mitigation protocols active on carbon markets (Davidson et al., 2014). To date, a number of protocols that focus on N<sub>2</sub>O mitigation in croplands are underpinned by empirical data collected from N gradient trials on commercial farms in the US Midwest (Millar et al., 2012, 2013). These protocols incorporate EF-based algorithms to estimate N<sub>2</sub>O emissions reductions on the basis of N fertilizer rate reductions, and are overseen by three voluntary carbon standard organizations: the Verified Carbon Standard (VCS; now renamed Verra; <http://verra.org/>) the American Carbon Registry (ACR; <https://americancarbonregistry.org/>), and the Climate Action Reserve (CAR; <http://www.climateactionreserve.org/>). Of these, ACR's protocol (Millar et al., 2012) currently allows the use of empirical data and new country or regional EFs to help develop projects. The current study offers the prospect of incorporating empirical data and EF-based algorithms from Yaqui Valley field trials into a straightforward N<sub>2</sub>O mitigation protocol. This and other opportunities, including the potential for combining GHG and nutrient credits (e.g., N<sub>2</sub>O emissions and nitrate leaching mitigation) derived from the same management practice change (i.e., N fertilizer rate reduction; Fox et al., 2011) should be further explored to help incentivize reduced N management practices in the Yaqui Valley and in semi-arid wheat crops globally.

## 5. Conclusions

Nitrous oxide emission response curves generated from N rate gradients in wheat outside temperate regions are rare, but essential to help better predict site- and region-specific N<sub>2</sub>O emissions in response to N additions for this globally important crop. Our results suggest that large reductions in N fertilizer rate could be adopted in irrigated spring wheat to substantially reduce N<sub>2</sub>O emissions in the Yaqui Valley, without harming grain yield or quality. Concomitant reductions in the loss of other potential N pollutants such as nitrate would also occur in these lower N environments. The N<sub>2</sub>O emission factor algorithms generated from our work can be readily integrated into current N<sub>2</sub>O mitigation protocols in carbon market organizations to help incentivize GHG mitigation and provide farmers with payments for doing so. Overall, our results emphasize the environmental and economic advantages of reducing N fertilizer additions to row-crop agriculture where N is supplied in excess of crop N requirements.

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