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How Do Variable Fertilizer and Irrigation Treatments Impact Greenhouse Gas Fluxes from an Aridland Agroecosystem?

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Abstract: Greenhouse gas (GHG) emissions from agriculture are significant contributors to global change. We experimentally manipulated biogeochemical control points of irrigation and nitrogen (N) to examine management strategies that could impact GHG flux, i.e., carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) and soil physiochemical changes over a growing season in an arid New Mexico sorghum (*Sorghum bicolor* (L.) Moench) cropping system. Sorghum is water and N efficient and amenable to environmental stress. Interrogating how crop systems perform in intense heat, aridity and ultraviolet stress of the southwestern US climate can inform future management in areas that produce more food currently, but that will undergo these stresses in the near future. Water was applied at regionally typical rates, or at ~30% below those rates. Timing N to plant needs may reduce N loss and N₂O emissions, and we tested this hypothesis by adding equal amounts of fertilizer to all plots, with half receiving all fertilizer at planting versus plots fertilized at 50:50 planting and 30 days post-planting. Gas flux from soil was analyzed via FTIR. More biomass was harvested from the fully irrigated plots; N timing did not significantly affect biomass. Soil pH fluctuated throughout the season in response to both treatments. Carbon dioxide emissions significantly increased in fully irrigated plots through time. Methane uptake was depressed by full irrigation. Nitrous oxide flux was lower in split N plots, but N₂O emissions were not impacted by reduced irrigation. These results suggest that arid adapted crops can maintain economically feasible yield, and biogeochemical monitoring within a growing season can help manage for GHG flux.

Keywords: agroecology; control points; carbon dioxide; methane; nitrous oxide; sorghum

1. Introduction

Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) induce atmospheric warming, and the flux of these gases between soils and the atmosphere is controlled by biological interactions with chemical inputs and physical alterations to soil [1–4]. Greenhouse gas (GHG) fluxes can also be indicators of soil C cycling and nitrogen fertilizer use efficiency [5,6]. Thus, understanding how land management decisions control GHG emissions is critical toward developing climate-responsible and efficient agrosystems.

Gas fluxes between soil and the atmosphere are highly spatially and temporally heterogeneous; gas fluxes peak at “hot spots” during “hot moments” [7]. A recent synthesis re-characterized this spatial and temporal variability across biogeochemical fluxes as control points on ecosystem fluxes, and expanded the concept to include the degrees of intensity for describing disproportionately important points in space and time for biogeochemical processes [8]. The control point concept is particularly relevant in agroecosystems, because major controls on gas flux such as substrate availability for C and N transformations and water are actively regulated. However, soil texture can lead to small-scale heterogeneity that promotes variation in soil-atmosphere exchange even in seemingly uniform fields [9,10]. A challenge is to understand tiers of control, and the hierarchy of interactions in soil leading to controls on other control points. For example, N fertilizer may lower bulk soil pH [11]. However, irrigation could have a counter-balancing effect if

it leads to nitrate (NO_3^-) leaching or if the water source is alkaline [12]. Fertilizer and irrigation timing are critical in controlling soil electrical conductivity (EC), which has a complicated relationship with crop nutrition, soil moisture and soil salinity [13]. Management efforts to abate GHG emissions will be improved with a better understanding of ultimate and proximate biogeochemical control points, especially those antagonistic to each other. While precision agriculture techniques that deliver water and nutrients show promise in increasing crop system efficiency, these technologies may be cost prohibitive to deploy at the scales needed for our current agricultural needs [14,15]. A potential management solution may be to maneuver control points; altered timing of fertilizer application such as splitting N applications in agricultural systems may act as a governor on the large fluxes of NO_3^- and N_2O expected under bare soil conditions prior to plants entering a phase of rapid growth and N uptake [16]. Nitrogen application timing is especially important in irrigated systems, where it can potentially be coupled with water application to reduce GHG emissions.

In the United States, research attention to greenhouse gas abatement is dominated by studies in the rain-fed Midwestern states [17]. Semi-arid cultivated land in the southwestern United States (SWUSA) is responsible for far less food and forage production than the Midwest, but climate extremes faced by these landscapes offer a natural experiment to test hypotheses about managing agricultural systems under increasing temperatures and greater precipitation variability due to anthropogenic climate change [18,19]. The SWUSA currently experiences conditions that are similar to projected future conditions across a much wider swath of the food producing Grain Belt [20,21]). Sorghum (*Sorghum bicolor* L. Moench) is a model crop for testing system-level effects of water and N manipulations [20,21]. Given the plant's ability to withstand water stress, salinity and relatively high N use efficiency compared to other grain crops, sorghum can tolerate stresses common to the SWUSA [22,23].

Sorghum's drought tolerance offers an opportunity to attempt conservation irrigation that relies more on irrigation timing than quantity. There is some empirical evidence that splitting N applications in sorghum increases yield [24]. Since soil water and available N are strong predictors of GHG flux, we tested if strategies to maneuver biogeochemical control points (less water but at the right time; timing N additions to plant phenology) maintain economically feasible harvested biomass and reduce agricultural GHG emissions.

Sorghum may tolerate drier conditions under a conservative watering schedule, which may also lower heterotrophic microbial activity and therefore CO_2 and N_2O emissions. Drier, aerobic conditions favor CH_4 oxidation [25], except in the case of abundant soil ammonium (NH_4^+) which interferes with microbial CH_4 uptake [26]. Wetter soils with excess N are expected to emit more N_2O , but anaerobic denitrification pathways are physiologically slow; the residence time of soil moisture in an arid climate may not be sufficient to maintain denitrifying conditions, especially if warm soil conditions accelerate plant uptake of N and water. Different crop plants likely respond to water stress and N application timing differently, i.e., root exploration for resource acquisition versus rapid biomass production, and the interaction of plants in the soil environment will alter GHG flux by providing different microbial resources in the form of root exudate C or rhizosphere habitat [27–29].

To address the utility of using a biogeochemical control point framework in GHG abatement, we designed a field experiment that controlled N timing, quantity of irrigation water applied, and included three phenologically distinct sorghum cultivars. This experiment was carried out in a semi-arid part of the SWUSA to provide field data over a growing season that is representative of climate likely to be experienced in the future across the US Great Plains grain producing regions.

2. Materials and Methods

2.1. Field Experiment

The study was conducted in 2017 at New Mexico State University's Los Lunas Agricultural Science Center (34.77 N, 106.76 W; elevation 1241 m). The study site had been in alfalfa (*Medicago sativa* L.) production for the previous 7 seasons. A series of tillage events were used to prepare the field for sorghum, and effects of those practices on pre-plant trace gas flux and soil C have been documented [4]. Soils are Gila clay-loam (superactive, thermic Typic Torrifuvent). During the growing season, 61.2 mm precipitation was measured.

2.2. Planting and management

Sorghum was planted on May 23, 2017 with three replicate plots of three varieties of sorghum, giving 9 plots per irrigation/N application timing section. Replicate plots consisted of 4 rows (6.1 m long, 0.3 m wide with 0.6 m row spacing) of the same variety. Planted varieties were 'Silage Master' [30], a short-statured variety, SP3902, and a photoperiod sensitive ethanol feedstock variety, SP1615 [31]. The three cultivars were selected based on their morphological and phenological differences documented over a series of previous sorghum trials conducted at the

Los Lunas site. Individual plots consisted of four planted rows of each variety.

2.3. Water applications

Irrigation water was applied into furrows between plants by piping water from canals connected to the Rio Grande. Since the field had been laser-leveled prior to planting, this method of flood irrigation offers control on lateral flow of water at the level of crop rows. Thus, the conservation irrigation sub-field remained un-watered even when the full irrigation field was watered. The experiment was split into two sections (hereafter "full irrigation" and "conservation irrigation") with perimeters ~25 m apart to separate irrigation treatments. On May 25, 886 m³ of water was applied across all plots. After plant emergence, the full irrigation treatment received 614, 467, 406, and 519 m³ water applications on June 22, July 12, July 25 and September 5, respectively. Conservation irrigation plots were watered on two of those dates, July 12 and September 5, with applications of 526 and 699 m³ water.

2.4. Nitrogen application timing

Base fertilizer was applied on May 20, 2017 as granular urea ammonium-nitrate (UAN; 44.8 kg N), 22.4 kg P and 22.4 kg K · ha⁻¹. Both full irrigated and conservation sub-fields were fertilized at the same rate over the course of the season, but divided into 2 sections that were fertilized with different application schedules. One section received inorganic N fertilizer (UAN 33-0-0 via broadcast) one week after planting ("single N"), and the other section was broadcast fertilized with 50% of the total application at that time, and the remaining 50%, 30 days after the first application ("split N"). All N applications totaled 168 kg N · ha⁻¹.

2.5. Gas flux measurements

Gas measurements were performed with a Gasmeter DX-4040 Fourier Transform Infrared

Gas analyzer [32]. We focused on measuring the fluxes of CO₂, CH₄ and N₂O. The instrument provides gas concentration, from which gas fluxes were calculated by converting gas concentration to molar mass, correcting by chamber volume, and then determining changes in molar mass of gases as a function of the time of sample measurement.

Samples were collected from static chambers affixed to 20.3 cm diameter collars placed ~10 cm in the ground ~2 hours before gas sampling. We chose the interspace be-

tween the first and second row of each plot to install chambers, thus placing static chambers 3 m away from each other from one plot to the next on the east to west field axis, and ~6 m away from other chambers on the field's north to south axis. Three height measurements were taken from the soil surface to the top of the chamber, which were averaged to determine the volume of chambers and for flux calculations. Collar rims ranged between 10 and 13 cm above the soil surface. Collars were not left in the field due to ongoing management such as weeding, and flood irrigation as practiced at the farm would shift collars. We re-installed collars on sampling dates by hammering collars with a mallet to ensure a seal with the soil was made and cracks that would release gas from the chamber were avoided. A PVC cap fitted with quick-connect hose attached to the Gasmeter was placed over the collar for measurements. Chambers were ~4 L in volume, and while the volume of each chamber slightly varied due to the height of the cap protruding from the soil, this was accounted for in each measurement as described above. Measurements began each sampling date around 0800. We alternated starting points for measurements each date to minimize effects of temperature change throughout the day.

2.6. Gas flux calculations and data QA/QC

The Gasmeter FTIR instrument provides concentration data that must be converted to molar mass of each gas species and consider the time of measurement and size of the chamber to arrive at a flux of mass of gas per area per unit time. Pressure and temperature are incorporated into the concentration calculation via FTIR, and volume of the chamber was determined empirically, thus only the molar mass needs to be converted and corrected by the R term in the ideal gas law, from which a flux is calculated from the difference in gas quantity over the duration of the measurement. The data logging system within Gasmeter provides a time signature that accounts for duration. After fluxes were calculated, we used CO₂ fluxes for QA/QC, as these were consistently the most linear. Samples with fluxes that met the threshold of an r^2 value >0.90 of CO₂ increase regressed against time of were assumed acceptable for other gasses. We removed samples from the data set that failed to meet this criterion ($n = 62$ of 435 total flux calculations).

2.7. Soil physio-chemical analysis

Soil pH was determined at the time of gas analysis by taking a ~10 g sample from the top

5 cm of soil immediately after flux measurements. The pH was measured in laboratory the same day from field-wet soil with a 1:1 soil to DI water ratio following orbitally shaking for 30 minutes. Soil moisture content, temperature and EC were measured every 5 minutes of the experiment with Decagon GS-3 probes installed prior to the experiment at 20 cm depths [33]. Point measurements at the time of gas sampling were taken for moisture, temperature and EC using a GS-3 probe attached to a Decagon Pro-check handheld data display.

Nitrate and NH₄⁺ were determined colorimetrically following 1.0 M KCl extractions [34,35]. Samples were pipetted into 96-well plates and soil N concentration was determined with a Tecan Infinite Pro 200 spectrophotometer [36].

2.8. Biomass sampling

Above ground biomass was sampled by collecting all plant material within a 4 m x 0.5 m strip from the middle two rows of experimental plots. Total fresh mass of these sample was weighed in the field. Two to three whole plants were ground in the field with a mulch-shredder. Sub-samples were dried at 60 °C for 72 hours to determine moisture content at harvest. Biomass is reported on a dry mass per area basis.

2.9. Statistical analysis

Harvested biomass and mineral N data from soils collected post-harvest were analyzed with a 3-way ANOVA model, using sorghum genotype, water treatment and N application as fixed effects. Time-series growing season data (GHG fluxes and pH) were analyzed with repeated measures ANOVA, employing the 'REML' function in R and the MANOVA option in JMP [37] and using sorghum genotype, water treatment and nitrogen application strategy as fixed effects, with sample date as a random effect [38]. Absent any significant genotype effects on GHG flux or pH, we reduced the model to a 2-way repeated measures design. Satterthwaite's method was employed for pair-wise comparisons.

3. Results

3.1. Soil response to water and N timing

Soil moisture was substantially lower in plots with split N application compared to single N in the conservation irrigation plots, but this pattern abated after the second irrigation application (Figure 1a). Fully irrigated plots displayed a similar pattern of moisture increase and draw-down following irrigation events, but there was less moisture in split N plots relative to single N plots (Figure 1b). Soil temperature temporal trends were similar among treatments (Figure 2).

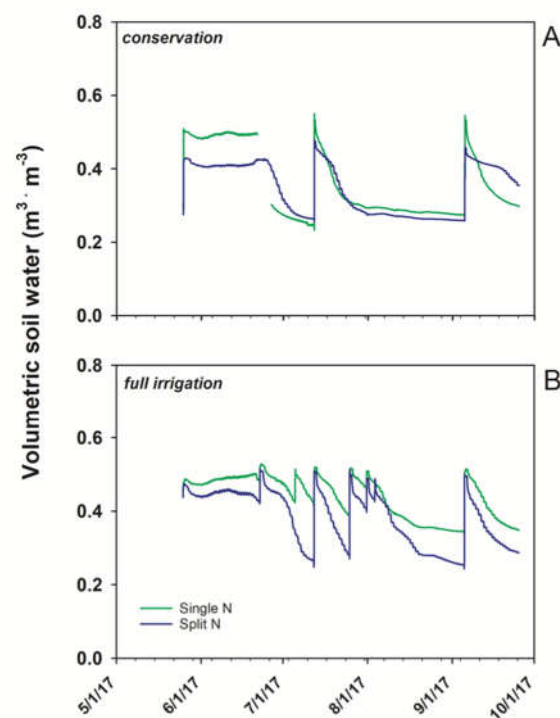


Figure 1. Soil moisture in sorghum fields under A) 30% less irrigation and B) full irrigation. Colored lines indicate fertilizer additions entirely at planting or split between 2 applications.

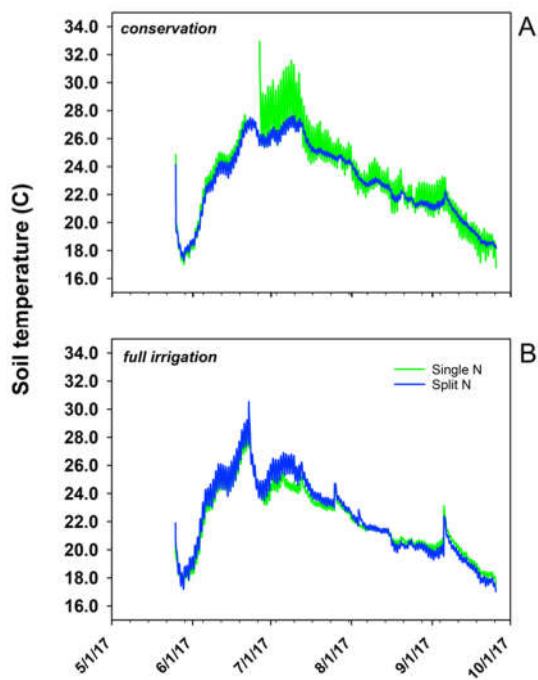


Figure 2. Soil temperature in sorghum fields under A) 30% less irrigation and B) full irrigation. Colored lines indicate fertilizer additions entirely at planting or split between 2 applications. .

Maximum values for soil EC were 1.4 dS . m-1 in both the fully irrigated and conservation irrigation plots following irrigation events (Figure 3). However, the maximum values were observed under split N application in the conservation plots but single N application in fully irrigated plots (Figure 3). Minimum EC values were lower in conservation irrigation plots (~ 0.2 dS . m-1) compared to fully irrigated plots (~ 0.5 dS . m-1).

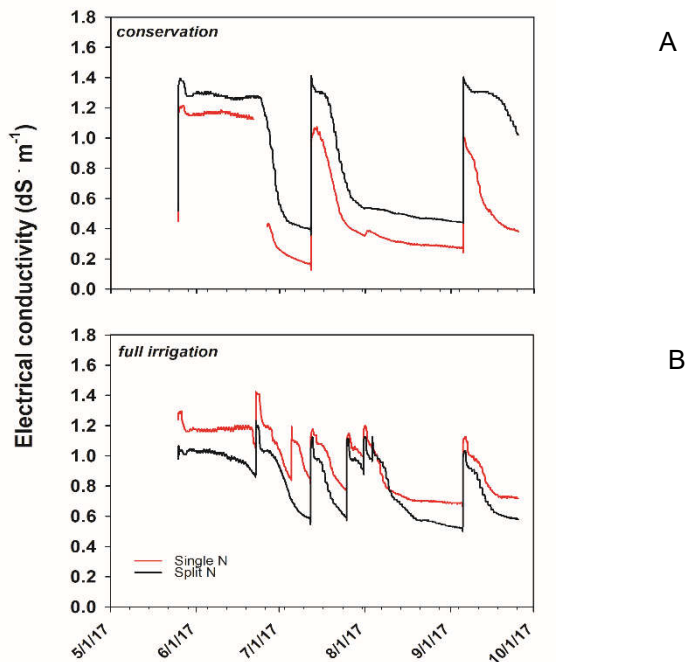


Figure 3. Soil temperature in sorghum fields under A) 30% less irrigation and B) full irrigation. Colored lines indicate fertilizer additions entirely at planting or split between 2 applications.

Soil pH varied considerably between sample dates (Figure 4). Values dropped in all plots the week following the first irrigation, but this pattern was more pronounced in the fully irrigated plots. For the remainder of the experiment, fluctuations in soil pH were relatively consistent among the irrigation and N application treatments, and subsequent watering did not impact pH. Values of soil pH at the end of the growing season (mean pH = 8.49, SD = 0.14 across treatments) were appreciably higher than at planting (mean pH = 7.07, SD = 0.17 across treatments).

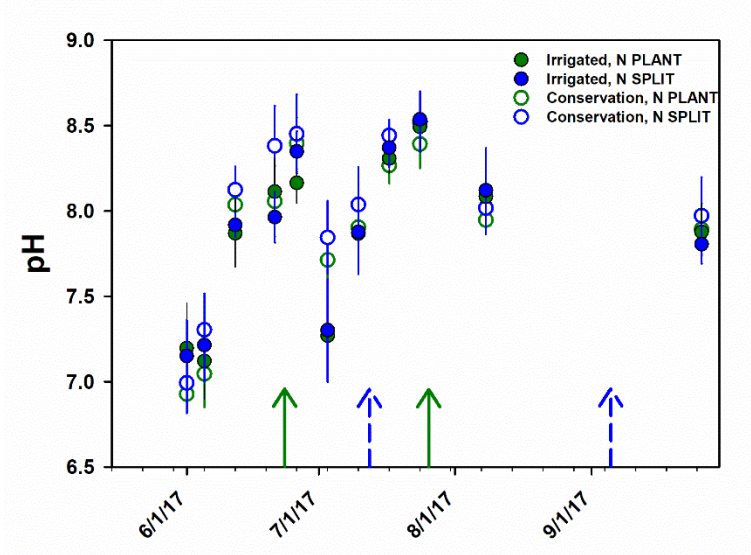


Figure 4. Soil pH in sorghum fields under 30% less irrigation and full irrigation. Closed symbols indicate fertilizer additions entirely at planting; open circles denote N fertilization split between 2 applications. .

3.2. Soil N at harvest

There were not significant differences among water or N treatments in soil NH_4^+ or NO_3^- at time of harvest ($P > 0.10$ for all comparisons and interactions). However, conservation irrigation with single N resulted in the lowest variation of NH_4^+ , while the same irrigation treatment resulted in the lowest variation of NO_3^- in plots receiving split N (Figure 5).

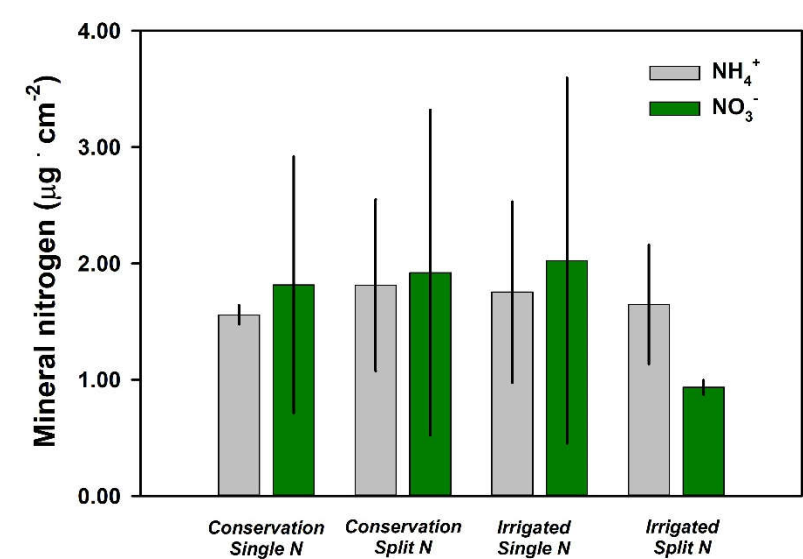


Figure 5. Soil mineral nitrogen ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$) in sorghum fields under 30% less irrigation and full irrigation, and with N fertilizer applied once at the start of the growing season or split into two applications. Grey bars denote ammonium, green bars denote nitrate, error bars are ± 1 SD.

3.3. Harvested biomass

Significant genotype effects were observed for harvested biomass. Sorghum SP1615, a photoperiod sensitive variety, was the highest producing variety in all treatments (Figure 6; 1-way ANOVA, $F_{1,34} = 8.11$, $P < 0.01$). A greater quantity of biomass was harvested from fully irrigated plots compared to conservation irrigation plots (Figure 6; 1-way ANOVA, $F_{1,34} = 12.09$, $P < 0.01$). Nitrogen timing did not significantly affect sorghum harvested biomass when genotypes and both irrigation treatments were pooled (1-way ANOVA, $F_{1,34} = 0.11$, $P = 0.74$).

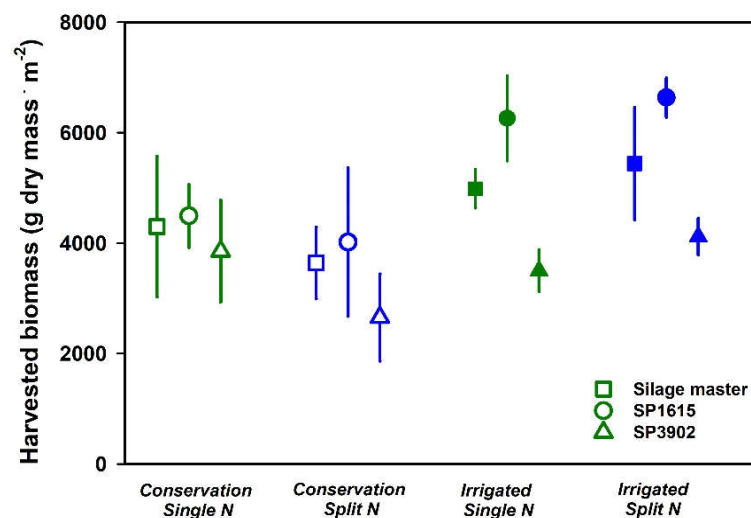


Figure 6. Soil mineral nitrogen ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$) in sorghum fields under 30% less irrigation and full irrigation, and with N fertilizer applied once at the start of the growing season or split into two applications. Grey bars denote ammonium, green bars denote nitrate, error bars are ± 1 SD. .

3.4. GHG flux

There was a significant effect of sample date on soil respiration (R_s) (CO_2 flux; $F_{11,16} = 57.17$, $P < 0.001$), and a significant effect of the irrigation treatment on R_s (Figure 7; $F_{11,16} = 3.59$, $P = 0.01$). Respiration was significantly higher on fully irrigated plots compared to conservation irrigation (Figure 6; $t = 2.94$, $P = 0.003$). We also observed a significant interaction whereby fully irrigated plots containing genotype SP3902 produced the highest CO_2 emissions over the course of the growing season. Carbon dioxide emissions were higher on plots that had single N application, for either irrigation treatment ($t = -1.99$, $P = 0.04$).

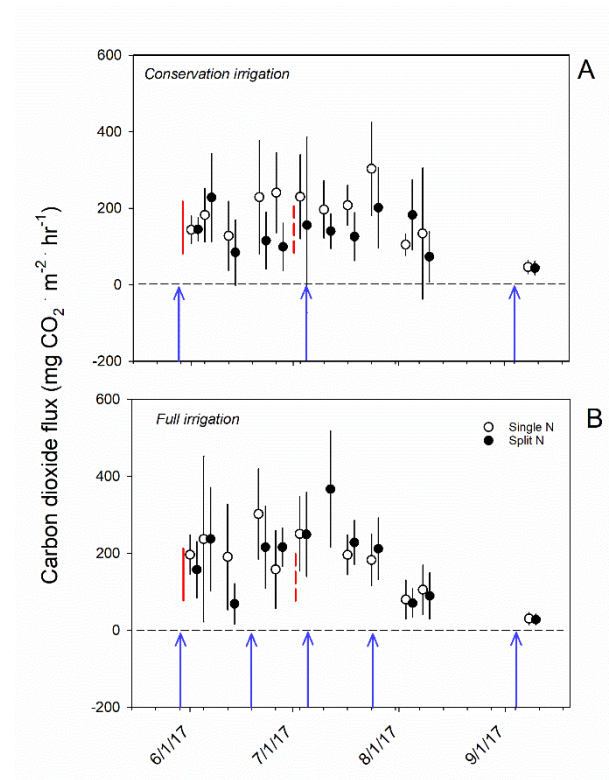


Figure 7. Soil respiration (CO_2 flux) from a sorghum field under A) 30% less irrigation and B) full irrigation, and with N fertilizer applied once at the start of the growing season or split between two applications. Red vertical lines denote when fertilizer was applied (second application timing for split = dashed line). Blue arrows denote irrigation events. Values are $\text{mg CO}_2 \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$, mean flux per treatment per sample date ± 1 SD.

Methane flux varied over time ($F_{11,16} = 2.59$, $P < 0.05$). There was a significant interaction between water inputs and sample date, with the highest emissions occurring on fully irrigated plots ($F_{11,16} = 2.92$, $P < 0.01$). Methane uptake was observed on several dates across all treatments, but was most pronounced in the conservation irrigation, particularly on 7/17/2017, a date associated with net CH_4 emissions in the fully irrigated plots (Figure 8). There were no single-factor or interactive effects of N application timing on CH_4 flux.

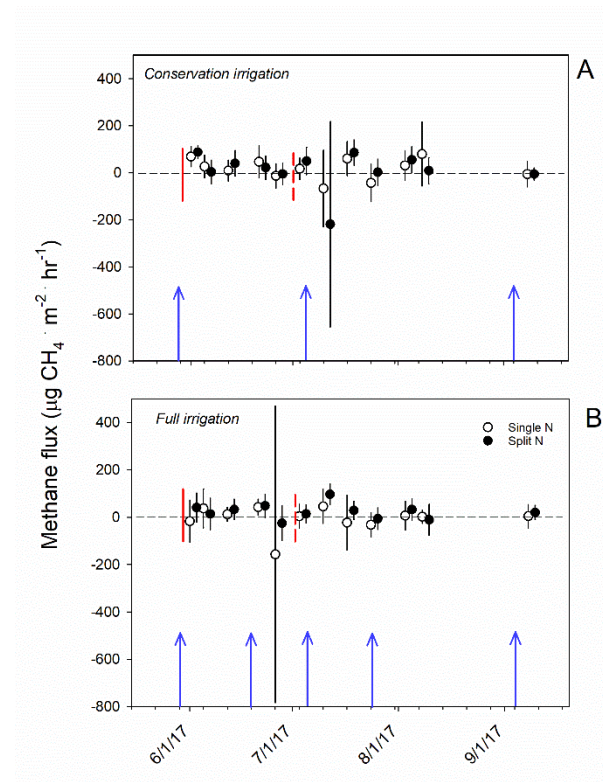


Figure 8. Soil methane (CH_4) flux from a sorghum field under A) 30% less irrigation and B) full irrigation, and with N fertilizer applied once at the start of the growing season or split between two applications. Red vertical lines denote when fertilizer was applied (second application timing for split = dashed line). Blue arrows denote irrigation events. Values are $\mu\text{g CH}_4 \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$, mean flux per treatment per sample date ± 1 SD.

Nitrous oxide emissions were significantly higher in plots receiving single N application compared to split N application for both conservation and irrigated treatments over the duration of the experiment ($F_{11,16} = 2.50$, $P < 0.05$; Fig. 9). Single N plots that were fully irrigated presented the highest N_2O emissions early in the growing season, while single N conservation irrigation treatments showed N_2O peaks 3 weeks after the last watering event (Figure 9). There were no single-factor or interactive effects of irrigation amount through time on N_2O flux.

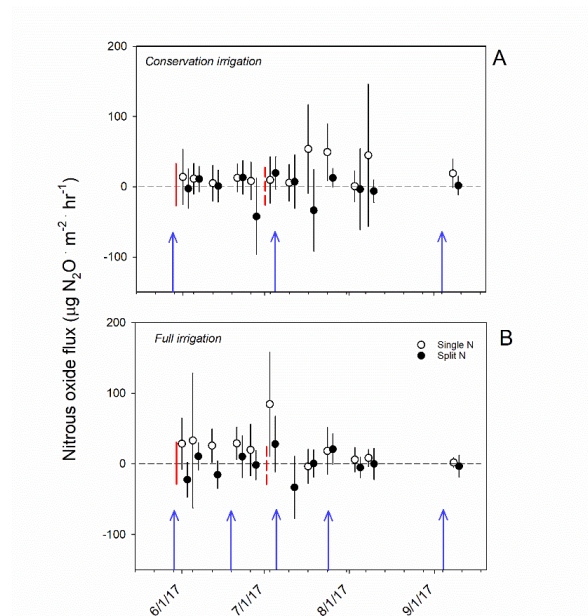


Figure 9. Soil nitrous oxide (N_2O) flux from a sorghum field under A) 30% less irrigation and B) full irrigation, and with N fertilizer applied once at the start of the growing season or split between two applications. Red vertical lines denote when fertilizer was applied (second application timing for split = dashed line). Blue arrows denote irrigation events. Values are $\mu\text{g N}_2\text{O} \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$, mean flux per treatment per sample date ± 1 SD.

4. Discussion

Understanding agro-ecosystem GHG flux at regional scales and over multiple seasons is critical to properly model climate, and those efforts must start with detailed knowledge of within-season gas flux and nutrient dynamics. Our observed differences in soil water as a consequence of irrigation were expected. Less clear are the differences in soil pH, which varied considerably over the season. We have two hypotheses for this phenomenon that are unfortunately untestable with the data at hand. First, irrigation water from the Rio Grande can vary based on the discharge source. It is possible that even though water was

Being extracted and applied from diversion channels connected to the Rio Grande, discrete irrigation events were from different sources. Secondly, because these soils are well-buffered, potentially different water sources interact with other plant/soil chemical variables like root exudates and available N fertilizer. Future work should consider performing chemical analysis on irrigated water, especially if it is applied multiple times in a season. Anecdotally, we have water data taken over a time series from a single flood irrigation event applied to a pecan (*Carya illinoensis*) orchard ~50 km south of the Los Lunas farm, and noted that over the course of 8 hours of continuous discharge both salinity and pH varied appreciably (~5% for EC and 0.1-0.6 pH units; Duval, unpublished data 2019).

Differences in harvested biomass were expected based on prior knowledge of the sorghum genotypes grown in the experiment. Root inputs can be implicated in changes to R_s because field measurements of CO_2 flux do not discriminate between heterotrophic and autotrophic CO_2 production, and both are likely dynamic. Prior work in our group has shown a nearly 1:1 correlation between above and belowground biomass in greenhouse-grown sorghum. Ergo, we assume that varieties exhibiting greater above ground biomass have greater root production, root exudate production and R_s . With respect to in-season differences among treatments, irrigation pulses correspond with increased CO_2 flux, albeit with some lag (Figure 7). The overall difference in CO_2 emissions related to N treatment are most pronounced early in the growing season, where most dates show higher R_s under the single N application. Higher soil N availability early in plant growth

could have resulted in less root production, and the higher emissions of CO₂ would likely be from heterotrophic microbes (Figure 7).

The heterogeneity of soil physical structure is important for gas diffusion and regulating microbial activity via substrate and habitat availability [39]. It is therefore expected that gas fluxes vary spatially, evidenced here by the large range of gas fluxes measured within treatments for given sample days (Figures 7-9). Given the high clay content of these soils, extended drying cycles following irrigation creates more heterogeneous physical habitat for microbes via cracking and aggregate cementation. However, we observed rates of R_s from the drier soil on the same order as the fully irrigated plots, suggesting that microbial activity was not hindered in the conservation irrigation plots (Figure 7). In both the set of fully irrigated plots as well as the conservation irrigation plots, following irrigation events, soil moisture and EC demonstrated an appreciably faster return to pre-irrigation levels in split N plots (Figure 1, Figure 3). Soil temperature changes followed similar patterns, but in the lower biomass conservation plots there was higher daily variation, likely related to plant growth differences in plots and the creation of shade conditions in plots with larger plants that lessened solar inputs directly to the surface.

The small amounts of CH₄ production did not follow a predictable pattern related to irrigation timing or N additions, but the high clay content of these soils could reduce CH₄ diffusivity even under anoxic conditions that favor methanogenesis, but due to limited porosity, CH₄ flux to the atmosphere could appear to be more consistent than physiological processes generating CH₄ [39]. Likely, the reasonably high moisture content of soils do not oxidize enough CH₄ to be a large sink, nor do they remain in anoxic conditions long enough to be CH₄ sources.

Nitrous oxide measured in this study was likely the result of both nitrification and denitrification pathways. However, increased N₂O emissions early in the growing season under the single N treatment support the hypothesis that N₂O losses are greater when providing N substrate for denitrifying microbes early in the growing season when plants are in nascent stages of development. We acknowledge that nitrification could be a mechanism for N₂O efflux as the water content of soils was often below 60%, which would create oxic microsites for nitrifying bacteria to convert the applied NH₄⁺ fertilizer to NO₃⁻ with some losses as N₂O [40]. The temporary drop in pH after fertilization in July (Figure 4) is suggestive of some N₂O loss via nitrification (Figure 9). However, it is more difficult to explain why the single N application would result in late growing season N₂O emission spikes in the conservation irrigation treatment (Figure 9a). A possibility is that if there was a lower growth rate of sorghum in those plots early in the season, significant residual N would remain in the soil, creating a lag between the last irrigation event and the observed N₂O pulses related to slow gas diffusion in these soils. However, we cannot dismiss that given the large variability in that treatment group (lower water, single N) micro-climate or soil heterogeneity is driving that result with a mix of microbial nitrification and denitrification activity, as well as abiotic pathways such as N loss via ammonia (NH₃) volatilization in these high pH soils.

It is difficult to scale from the molecular and cellular scales at which biogenic GHG flux occur to the global impact that these gases have on Earth's climate [41,42]. However, studies such as ours provide a potential link between understanding how field-scale management decisions about water and N additions affect field-scale GHG flux.

This study considered timing of fertilization and quantity of water as biogeochemical control points [8], and what we know about GHG formation in soil fits well into this concept. Our observations here show how moisture, temperature, EC and pH are dynamic under different GHG management/abatement strategies, while appreciating that isolating specific instances of biogenic and abiotic gas production remains a challenge [4].

Author Contributions: Conceptualization, B.D.D. and M.A.M.; methodology, B.D.D. and J.M.; validation, B.D.D.; formal analysis, B.D.D. and J.M.; investigation, B.D.D.; resources, B.D.D. and M.A.M.; data curation, B.D.D. and J.M.; writing—original draft preparation B.D.D.; writing—review and editing, B.D.D., J.M. and M.A.M.; visualization, B.D.D.; supervision, M.A.M.; project

administration, B.D.D.; funding acquisition, B.D.D. All authors have read and agreed to the published version of the manuscript.

Funding: This project was funded as part of a DOE ARPA-e grant.

Data Availability Statement: In this section, please provide details regarding where data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study. Please refer to suggested Data Availability Statements in section “MDPI Research Data Policies” at <https://www.mdpi.com/ethics>. If the study did not report any data, you might add “Not applicable” here.

Acknowledgments: Sincere thanks to Dr. David Hanson, Angelica Cave, Heather Curtsinger, Aubrey Hands, Sam Hoffman, Eleanor House and Sara Watson. Special thanks to MAC and Don Gustavo the Falcon.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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