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Short communication

# Net fluxes of $CO_2$, but not $N_2O$ or $CH_4$, are affected following agronomic-scale additions of urea to prairie and arable soils

Rebecca L. Phillips [a,*], Frances Podrebarac [b]

[a] USDA Agricultural Research Service, 1701 10th Avenue SW, Box 459, Mandan, ND 58554, United States
[b] North Dakota State University, Fargo, ND 58105, United States

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ABSTRACT

While experimental addition of nitrogen (N) tends to enhance soil fluxes of carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$), it is not known if lower and agronomic-scale additions of urea-N applied also enhance trace gas fluxes, particularly for semi-arid agricultural lands in the northern plains. We aimed to test if this were true at agronomic rates [low (11 kg N $ha^{-1}$), moderate (56 kg N $ha^{-1}$), and high (112 kg N $ha^{-1}$)] for central North Dakota arable and prairie soils using intact soil cores to minimize disturbance and simulate field conditions. Additions of urea to cores incubated at 21 °C and 57% water-filled pore space enhanced fluxes of $CO_2$ but not $CH_4$ and $N_2O$. At low, moderate, and high urea-N, $CO_2$ fluxes were significantly greater than control but not fluxes of $CH_4$ and $N_2O$. The increases in $CO_2$ emission with rate of urea-N application indicate that agronomic-scale N inputs may stimulate microbial carbon cycling in these soils, and that the contribution of $CO_2$ to net greenhouse gas source strength following fertilization of semi-arid agroecosystems may at times be greater than contributions by $N_2O$ and $CH_4$.

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Nitrogen addition to prairie soils (450 kg N $ha^{-1}$) and irrigated arable soils (134–220 kg N $ha^{-1}$) tends to enhance net fluxes of carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) (Mosier et al., 1991, 2006). However, agronomic-scale N additions common to dryland agricultural production in semi-arid regions of the northern US are much lower, and data are lacking to indicate how these soils respond to relatively lower doses of N. Most of the agricultural land in the northern Great Plains that is located west of the Missouri River is semi-arid, where yields are strongly correlated with rainfall. As such, yield goals for semi-arid and dryland crops are lower than in irrigated or more mesic regions, so N inputs are lower. Previously, we observed that $N_2O$ fluxes for dryland crops fertilized with urea at 60 kg N $ha^{-1}$ were similar to native prairie (Phillips et al., 2009), which prompted us to question if agronomic levels of N addition were high enough to stimulate fluxes of all the three gases ($CO_2$, $CH_4$, and $N_2O$). We postulated that agronomic-scale doses of urea-N (11, 56, 112 kg N $ha^{-1}$) may preferentially stimulate the cycling of carbon by heterotrophs, but these doses may not be high enough to also stimulate emissions of $N_2O$ by autotrophs. For $CH_4$, we postulated that arable soil methanotrophs were adapted to regular additions of N; therefore, $CH_4$ fluxes would not be affected by N at these doses. As a first step towards teasing out effects of agronomic N addition on trace gas exchange, we needed to know how different doses of N influenced fluxes for dryland agricultural soils. We tested how low (11 kg N $ha^{-1}$), moderate (56 kg N $ha^{-1}$), and high (112 kg N $ha^{-1}$) doses of urea influenced net fluxes of $CO_2$, $N_2O$, and $CH_4$. Since soil physical conditions (e.g. pH, soil moisture, temperature, and disturbance) influence trace gas fluxes, we used intact soil cores to minimize soil disturbance and to control environmental conditions. We aimed to simulate field conditions as closely as possible by (a) minimizing the time the cores were kept in the laboratory, (b) keeping soil moisture near field observations, (c) collecting short-term (1 h) fluxes comparable to surface flux measurements in the field, (d) maintaining soil structure, and (e) applying agronomic doses of urea. To further simulate conditions common to agricultural production in the northern Great Plains, where urea is commonly applied following harvest and before freeze-up, we used soil cores collected in autumn from recently harvested maize (*Zea mays* L.).

Samples were collected from arable and prairie sites that were similar with respect to soil series and topography (Phillips et al., 2009) near Mandan, ND, USA (46°46′N and 100°55′W). Soils are classified as Temvik-Wilton silt loam [FAO: Calic Siltic Chernozems; USDA: fine-silty, mixed, superactive, frigid typic, and Pachic Haplustolls (Soil Survey Staff, 2008)]. The prairie site was historically grazed and hayed with no history of tillage. It is densely

* Corresponding author. Tel.: +1 701 667 3002.
*E-mail address:* rebecca.phillips@ars.usda.gov (R.L. Phillips).

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covered by grasses [*Bromus inermis* (L.) and *Poa pretensis* (L.)] and has remained undisturbed since 2005. The arable site has been managed for annual grain production for over 50 years but has not been tilled since 1992. Granular urea is broadcast (approximately 50 kg N $ha^{-1}$) each spring prior to planting. Soil properties measured in spring 2008 indicated that C, N, and pH were 42.0 g $kg^{-1}$, 3.8 g $kg^{-1}$, and 6.2, respectively, for prairie and 24.0 g $kg^{-1}$, 2.3 g $kg^{-1}$, and 5.7, respectively, for arable soils (Phillips et al., 2009).

We designed an experiment to test for the effect of land use (arable vs. prairie) and N addition (0, 11, 56, 112 kg N $ha^{-1}$) on fluxes of $CO_2$, $N_2O$, and $CH_4$ using intact soil cores. Four (5.5 cm dia.) soil cores (one for each N treatment), excluding surface litter, were collected to a 15 cm depth from five randomly selected points within each land use using a tractor press with plastic sleeves and then stored at 4 °C. A total of 40 samples were collected near the end of October 2008, when vegetation was senescent and daily air temperature ranged from −3 to 9 °C. The following day, cores were placed in 1-L jars fitted with Swagelok O-seal fittings. Granular urea was dissolved in DIW and slowly delivered in 10-mL aliquots to the surface and allowed to infiltrate each core. We targeted a 60% water-filled pore space (WFPS) because (a) autotrophic nitrifying organisms contribute most (80%) of the total $N_2O$ emitted at this WFPS (Bateman and Baggs, 2005) and (b) field WFPS never exceeded 60%, based on three years of weekly measurements (M. Liebig, unpublished data, 2008). Cores were vented and allowed to equilibrate for 24 h at 21 °C in the dark. Short-term (1 h) core incubations were performed at initial headspace concentrations of approximately 2, 360, and 0.3 μL $L^{-1}$ $CH_4$, $CO_2$, and $N_2O$, respectively. We used short-term incubations to more closely simulate fluxes measured at the soil surface, which are collected over a short (<1 h) time course in the field (Phillips et al., 2009). Headspace samples (15 mL) were removed every 0.33 h and replaced with 15 mL of ultrapure $N_2$ to maintain pressure equilibrium (Phillips et al., 2001a,b; Phillips, 2007). Sample aliquots were immediately injected into 12-mL exetainers (Labco Unlimited, Buckinghamshire, UK) and analyzed within 24 h for $CO_2$, $N_2O$, and $CH_4$ with a Varian Model 3800 Gas Chromatograph and Combi-Pal autosampler (see Phillips et al., 2009 for details). We did not find headspace concentration changes in autoclaved cores, indicating that gas exchange was biologically mediated. Cores previously incubated with 50 Pa difluoromethane (Miller et al., 1998; Phillips et al., 2001a,b) indicated that $CH_4$ was not produced at the 0–15 cm depth when methanotrophy was inhibited (data not shown), so reported rates of net $CH_4$ flux were equivalent to rates of gross $CH_4$ consumption (Phillips et al., 2001a,b).

We tested for the effect of land use and N addition on the time-linear change in headspace concentration for each gas separately using a Proc GLM analysis of variance (SAS Institute, Cary, NC). Fluxes are reported as pg ($N_2O$), ng ($CH_4$), and μg ($CO_2$) $g^{-1}$ dry weight (dw) $h^{-1}$. Negative values represent a net reduction in headspace concentration, while positive values represent a net increase in headspace concentration during the time course. This experiment was designed to test for effects of N addition at similar soil water contents. Small differences in %WFPS among cores could affect fluxes; consequently, we measured %WFPS for each core and included %WFPS as a covariate in the statistical model. Overall mean (±1 SD) of %WFPS for all soils was 57.2 ± 9.1%. All interactions were tested; if interactions were not significant, they were dropped from the model.

Addition of urea-N at 11, 56, and 112 kg N $ha^{-1}$ enhanced net flux of $CO_2$ (Fig. 1c), but not $CH_4$ (Fig. 1a) or $N_2O$ (Fig. 1b). Average $N_2O$ flux for arable soil (29.1 ± 60.2 pg $N_2O$ g $dw^{-1}$ $h^{-1}$) was positive, while average $N_2O$ flux for prairie soil (−18.8 ± 21.9 pg $N_2O$ g $dw^{-1}$ $h^{-1}$) was negative. Our arable soil $N_2O$ fluxes were similar to undisturbed soil experiments by Bateman and Baggs (2005), which averaged 24 and 52 pg $N_2O$ g $dw^{-1}$ $h^{-1}$ when incubated at 50% and 60% WFPS, respectively. Our flux data were considerably lower than $N_2O$ flux for arable cores collected from the mesic Red River Valley (RRV) of the North, where cores were incubated at 40% WFPS and −2.5 °C (Phillips, 2007). In this case, average $N_2O$ flux was 327 ± 98 pg $N_2O$ g $dw^{-1}$ $h^{-1}$; however, higher soil organic matter, clay content, inorganic N, cation exchange capacity, and pH likely contributed to greater $N_2O$ fluxes (Phillips, 2007).

While N addition and land use did not significantly alter $N_2O$ (Table 1), arable soil $N_2O$ flux tended to be greater at the 112 kg N

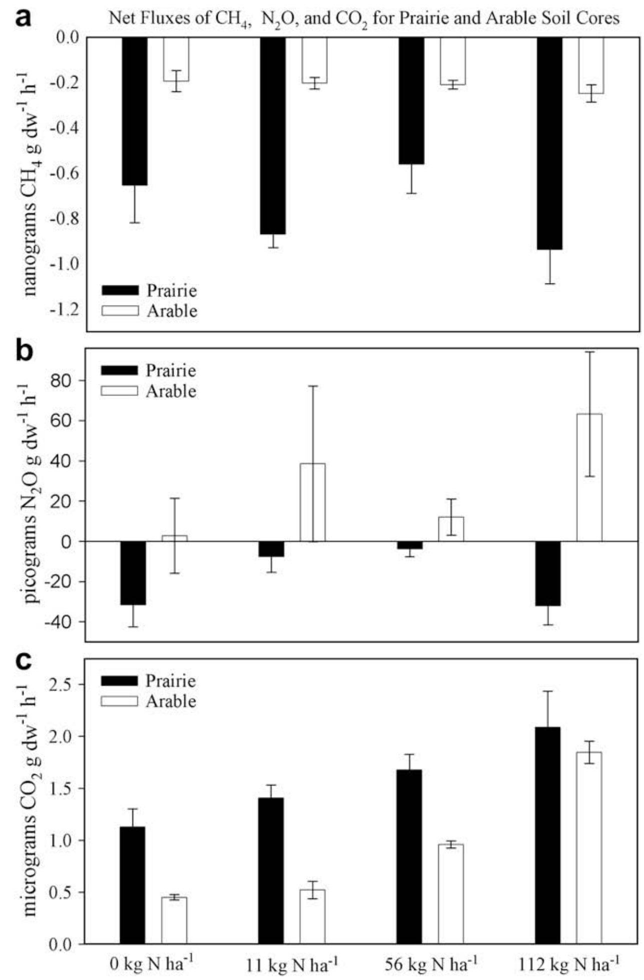


**Fig. 1.** Mean (±SD) fluxes by level of N addition for soil cores collected from arable and native prairie sites: (a) $CH_4$; (b) $N_2O$; and (c) $CO_2$.

**Table 1**
Results of the analyses of variance evaluated for each biogenic trace gas separately.

| Variable | Model $R^2$ | Source | DF | Mean square | $F$ | Pr > F |
|---|---|---|---|---|---|---|
| ng $CH_4$ g $dw^{-1}$ $h^{-1}$ | 0.6114 | Nitrogen | 3 | 0.0052 | 0.09 | 0.9630 |
| | | Land use | 1 | 0.7219 | 12.92 | 0.0010 |
| | | %WFPS | 1 | 0.0327 | 0.58 | 0.4499 |
| μg $CO_2$ g $dw^{-1}$ $h^{-1}$ | 0.8593 | Nitrogen | 3 | 3.3828 | 48.48 | <0.0001 |
| | | Land use | 1 | 1.1891 | 17.04 | 0.0002 |
| | | %WFPS | 1 | 0.0073 | 0.11 | 0.7477 |
| pg $N_2O$ g $dw^{-1}$ $h^{-1}$ | 0.3599 | Nitrogen | 3 | 2482.17 | 1.31 | 0.2886 |
| | | Land use | 1 | 1478.51 | 0.78 | 0.3841 |
| | | %WFPS | 1 | 3735.43 | 1.96 | 0.1701 |

$ha^{-1}$ dose (Fig. 1b), suggesting that $N_2O$ fluxes could potentially be stimulated at this dose. The lack of an $N_2O$-response for either land use may have resulted from competition between heterotrophic and autotrophic nitrifying organisms for available soil N (Gerards et al., 1998). These laboratory results are in alignment with field data, indicating that these agronomic doses of N may not stimulate microbial processes that produce $N_2O$ (e.g. nitrification) in the short term. Studies by Maag and Vinther (1996) and Bateman and Baggs (2005) demonstrate that $N_2O$ flux is linearly related to nitrification rate and that most of the $N_2O$ produced at this %WFPS is the result of autotrophic nitrification. We suspect that heterotrophic processes such as mineralization, rather than autotrophic respiration, were stimulated by urea-N but further investigation is needed to determine microbial processes governing $N_2O$ fluxes when urea is added.

Agronomic urea additions did not alter net fluxes of $CH_4$ (Fig. 1a), although average (±1 SD) flux for prairie soil (–0.76 ± 0.31 ng $CH_4$ g $dw^{-1}$ $h^{-1}$) was 3.5 times greater than $CH_4$ consumption for arable soil (–0.21 ± 0.07 ng $CH_4$ g $dw^{-1}$ $h^{-1}$). Average arable $CH_4$ flux reported here is similar to average $CH_4$ flux (0.24 ± 0.09 ng $CH_4$ g $dw^{-1}$ $h^{-1}$) reported for pine forest soil (Phillips et al., 2001a,b). These agronomic N inputs may not have been high enough to increase net flux of $CH_4$ (Whalen, 2000) and may reflect microbial adaptation to fertilization. Differences between land uses (Table 1) likely reflect historical effects of cultivation disturbance on methanotrophic activity (Ojima et al., 1993; Hütsch, 2001).

Agronomic urea additions increased net fluxes of $CO_2$ for both land uses (Fig. 1c; Table 1). Addition of 112 kg N $ha^{-1}$ nearly doubled prairie $CO_2$ flux (from 1.2 to 2.1 μg $CO_2$ g $dw^{-1}$ $h^{-1}$) and more than tripled arable $CO_2$ flux from (0.5 to 1.8 μg $CO_2$ g $dw^{-1}$ $h^{-1}$). Others have reported that soils in unmanaged ecosystems respond to N addition with short-term acceleration of carbon (C) mineralization (Craine et al., 2001; Waldrop et al., 2004; Zeglin et al., 2007), and this response is often attenuated by the longer-term decline in easily decomposable C substrates (Sinsabaugh et al., 2008; Treseder, 2008). We expect arable soils to be more depauperate in easily decomposable C substrates, compared to native prairie. As such, arable soil response to N addition may decline more quickly than prairie soil over time, but this needs to be tested with extended incubations.

This dose–response experiment suggests the microbial response to agronomic additions of urea may not necessarily result in greater fluxes of $N_2O$ and $CH_4$ for semi-arid agroecosystems but may instead result in greater fluxes of $CO_2$. Mean flux for $N_2O$ at the high N rate was six orders of magnitude lower than mean flux for $CO_2$, and the contribution of $N_2O$ to arable soil greenhouse gas source strength was <2%. These data are preliminary, but they suggest that urea application may increase microbial metabolism of soil carbon for enhanced soil respiration. As such, potential effects of urea fertilization on soil $CO_2$ emissions should be considered when evaluating management effects on the greenhouse gas source strength for arable and prairie agroecosystems. We suggest that additional work is needed to determine (a) how urea alters nitrification, mineralization, and trace gas fluxes, (b) how urea-N is partitioned among soil organisms to support C and N cycling activities, and (c) if there is a temporal decoupling between mineralization and nitrification that affects fluxes of $N_2O$. Linking agronomic N additions to microbial transformation processes that affect trace gas fluxes may help constrain the greenhouse gas source strength for semi-arid agroecosystems in the northern plains.

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