Nitrite-Driven Nitrous Oxide Production Under Aerobic Soil Conditions: Kinetics and Biochemical Controls

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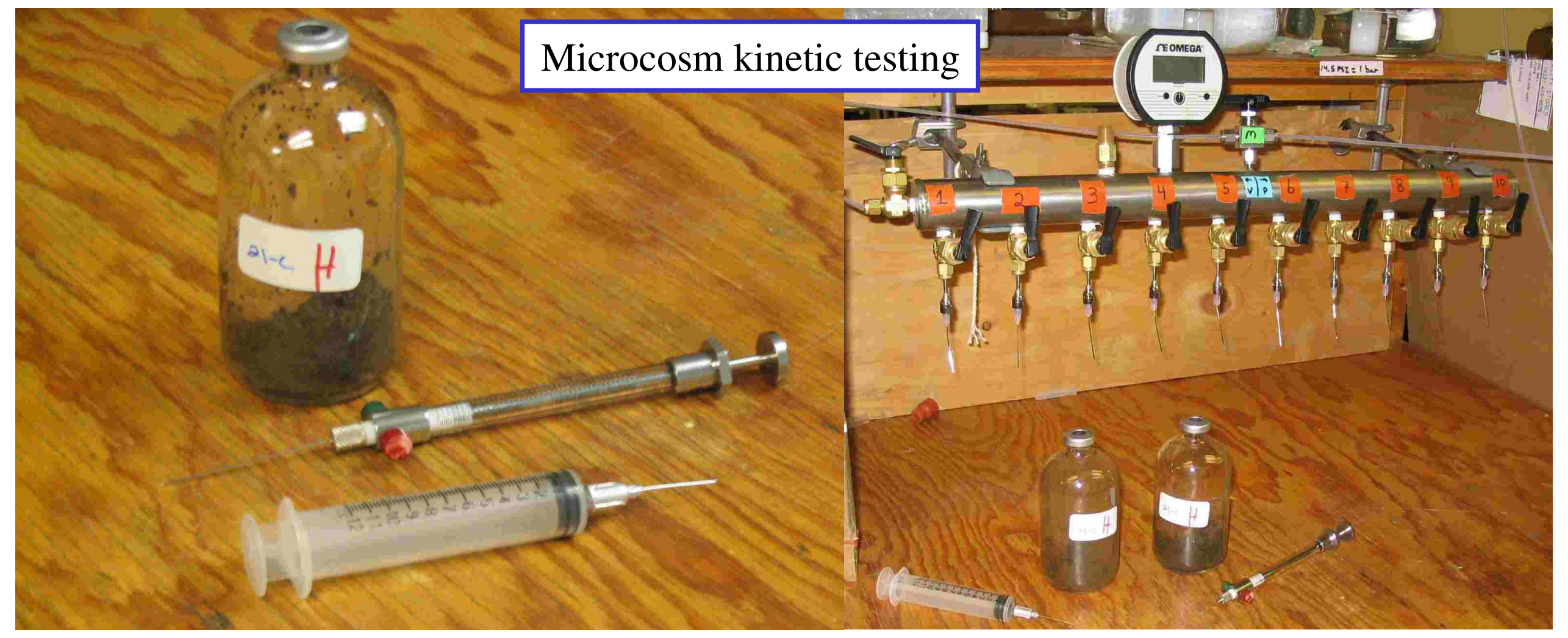
BACKGROUND

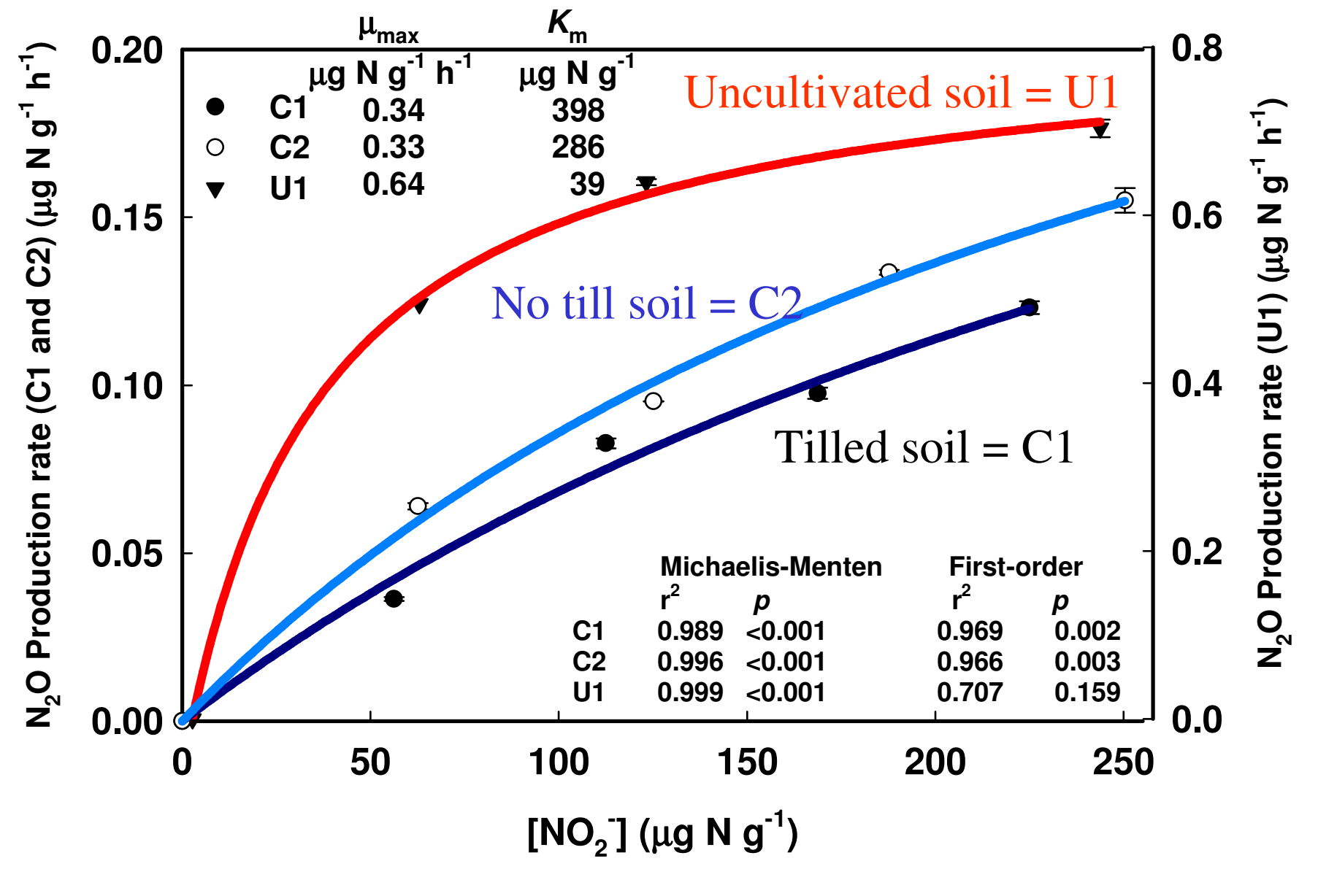
- **Understanding controls over N_2O production is required for developing effective mitigation strategies and for improving emissions assessments.**
- **N_2O production via denitrification is well-studied, but there is much less understanding of N_2O emitted under highly aerobic conditions.**
- **"Nitrifier denitrification" has been identified in pure culture and in soils; ammonia-oxidizing autotrophic bacteria reduce nitrite (NO_2^-) to N_2O in the presence of O_2. "Chemodenitrification" of NO_2^- to N_2O has also been observed. However, the kinetics of these process in soils have not been studied.**
- **How important are these sources of N_2O and what are their primary controls?**



OBJECTIVES AND METHODS

1. **We measured rates of N_2O production as a function of NO_2^- levels in soils from tilled and untilled agricultural fields and uncultivated fields in southeastern Minnesota in aerobic laboratory microcosms.**
2. **We confirmed that the incubation conditions did not support either NO_3^- reduction (i.e., denitrification) or the reduction of N_2O itself.**
3. **We quantified the contribution of abiotic versus biological NO_2^--reduction to the overall rate of N_2O production under fully aerobic conditions.**
4. **We measured the sensitivity of NO_2^- and NO_3^- -driven N_2O production to headspace O_2 concentration over the range of < 0.1 % to 100 %.**
5. **We measured the temperature sensitivity of NO_2^- -driven N_2O production at headspace O_2 concentrations of 5% and 20%.**
6. **We used the measured kinetic parameters in a simplified model of N_2O emissions in order to estimate the potential importance at the field scale.**

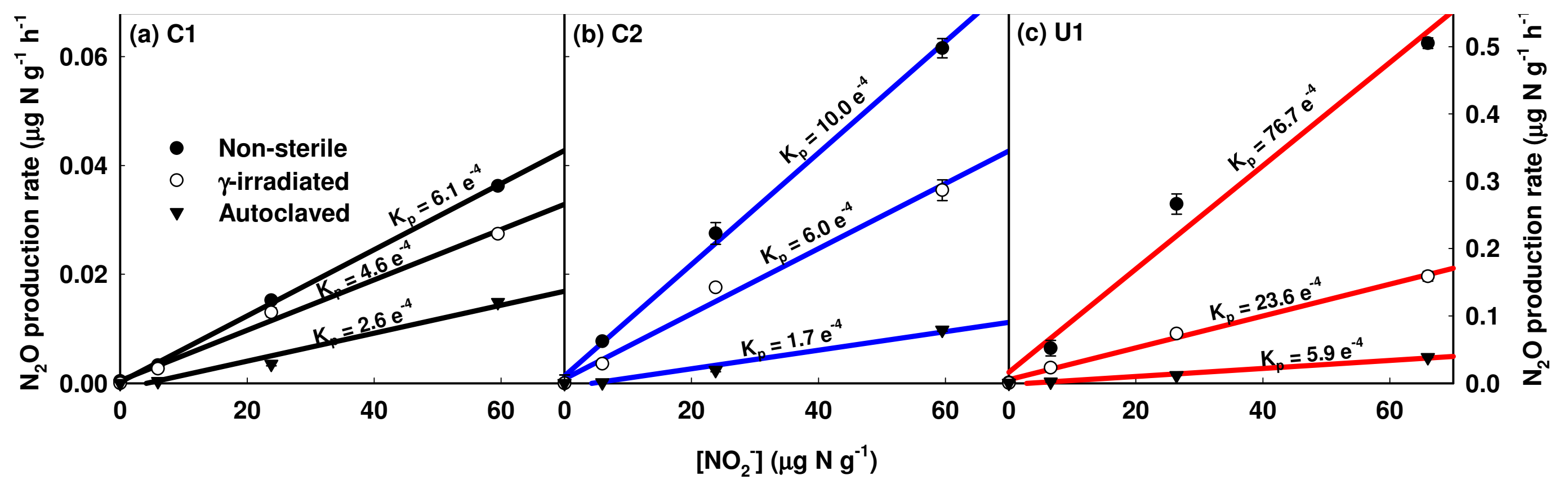
Fig 1. Kinetic response to high-level NO_2^- addition



- **The response to NO_2^- addition over the range of 50 – 250 ug NO_2^- -N/g followed a Michaelis-Menten function in all three soils :**

$$P_{N_2O} = \left(\frac{\mu_{\max}[NO_2^-]}{K_m + [NO_2^-]} \right) \qquad (1)$$

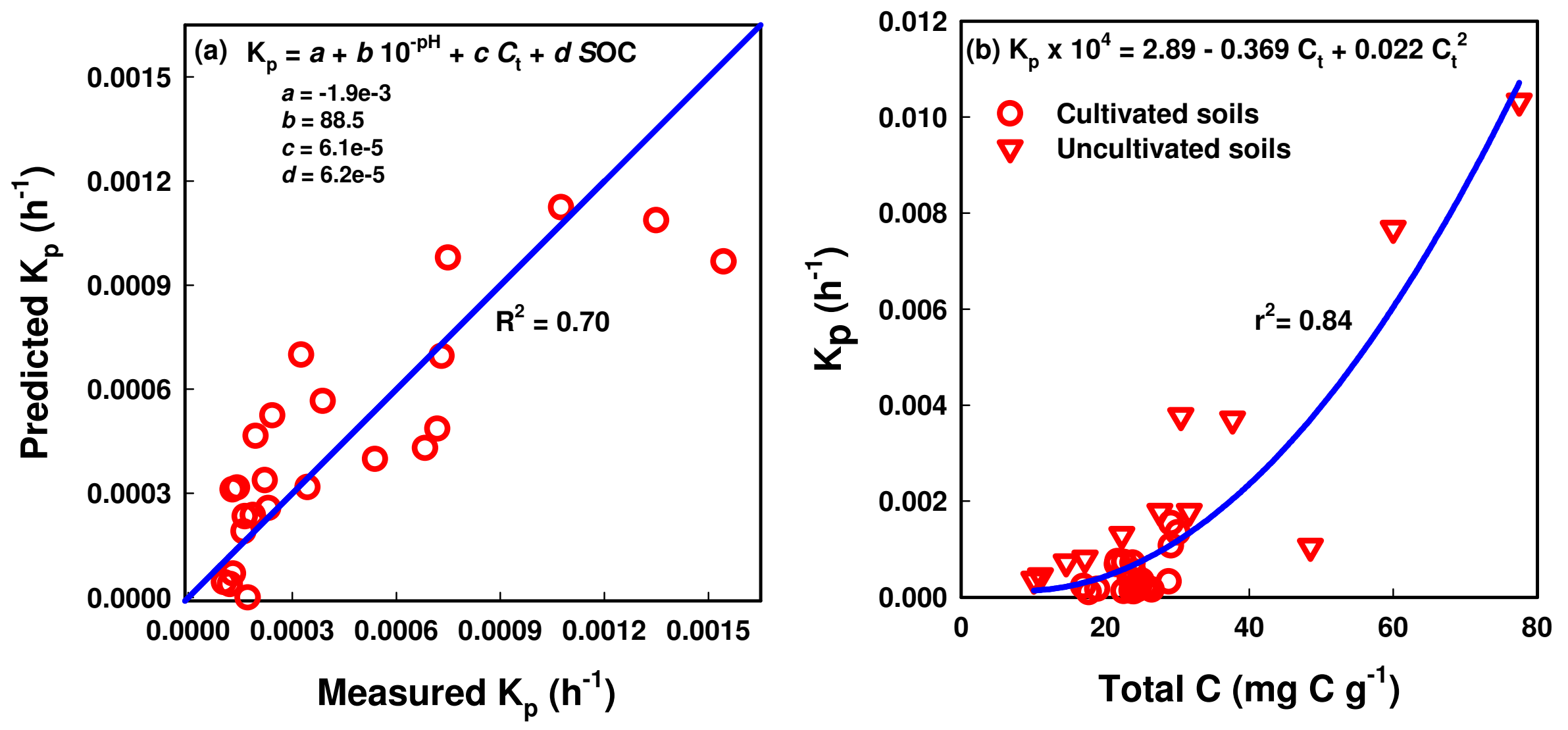
Fig 2. Kinetic response to low-level NO_2^- addition



- **The response to NO_2^- addition over the range of 5 – 50 ug NO_2^- -N/g was linear and could be described by: $P_{N2O} = K_p[NO_2^-]$ where K_p is a first-order production rate coefficient.**

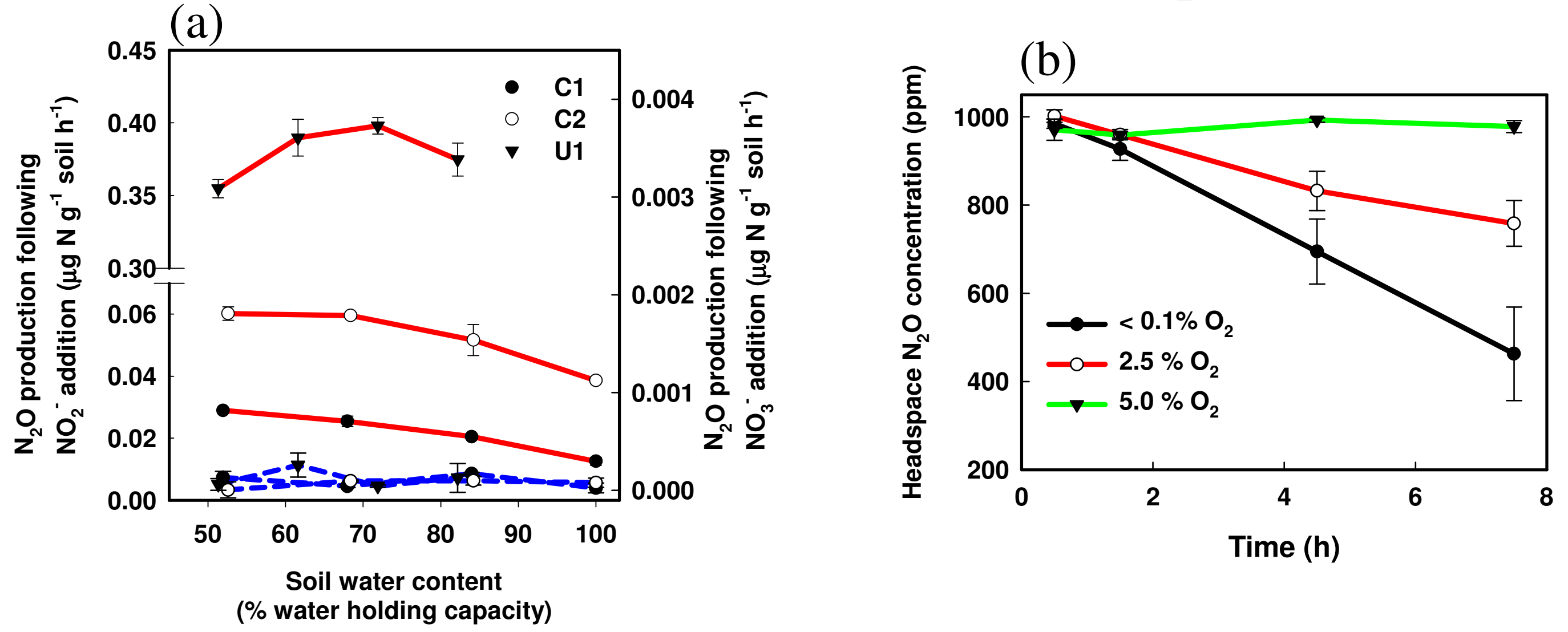
K_p values in γ-irradiated soils were 25, 40, and 69 % lower than in non-sterile soil for C1, C2, and U1, respectively (Fig. 2). Thus, abiotic reactions accounted for 31 – 75 % of total N_2O production in incubations done at ambient O_2.

Fig 3. Soil controls over production rate coefficient, K_p



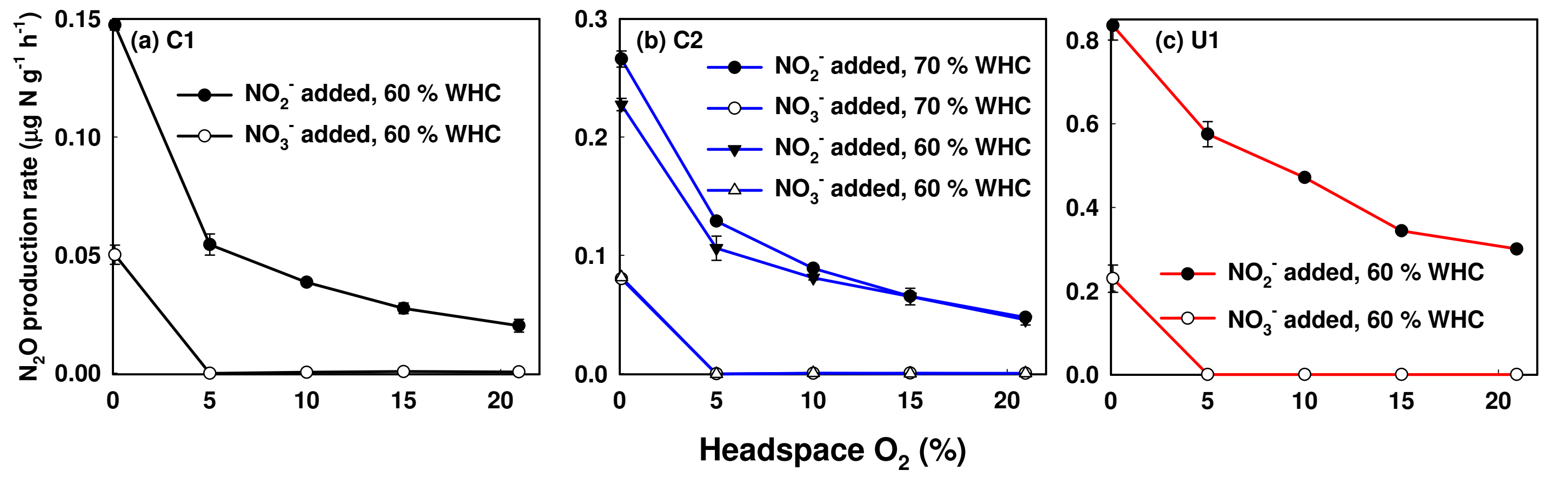
The rate coefficient K_p was correlated with pH, 10^{-pH}, soluble organic C (SOC), total C & total N. A multiple regression model explained 70 % of the variance within the cultivated soils (Fig. 3a). A single-factor model explained 84 % of the overall variance as a function of total C (Fig. 3b). Positive correlations with 10^{-pH} and total C are also consistent with a substantial abiotic component based on the work of Stevenson (1970) who showed that reactions involving soil organic matter are promoted at lower pH.

Fig 4. Confirmation of absence of denitrification and N_2O reduction



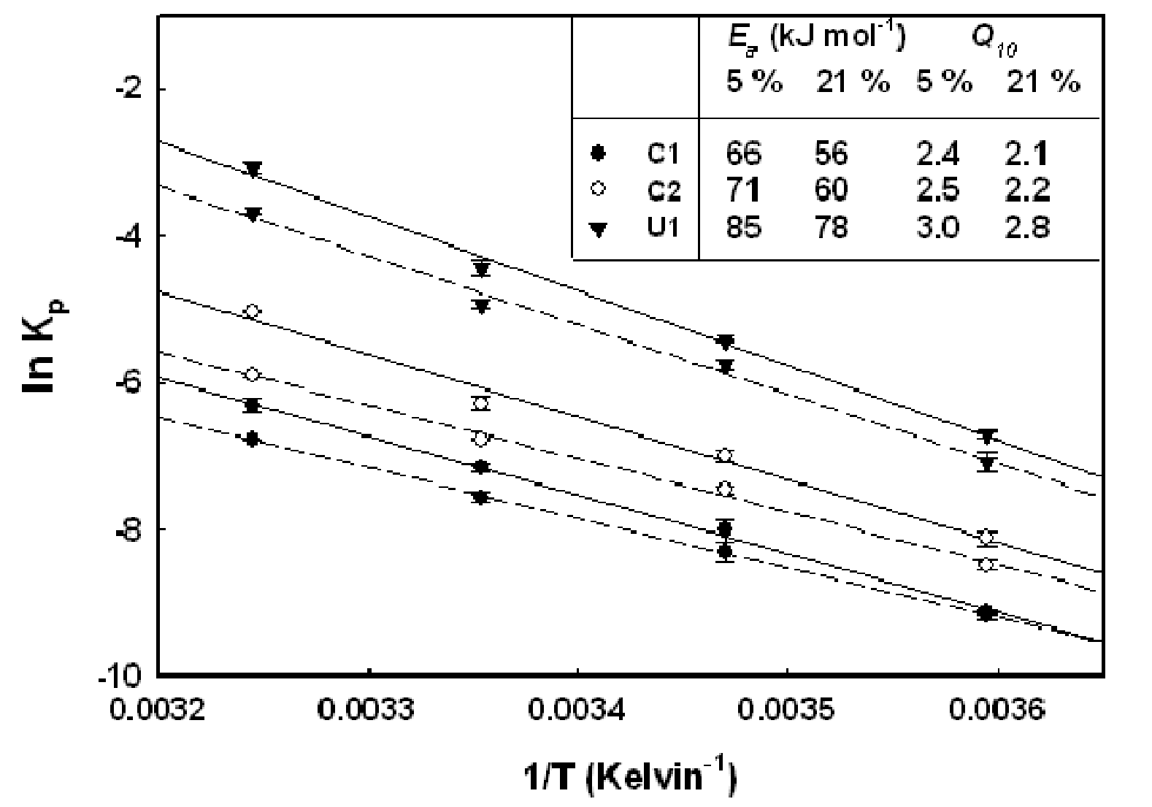
Rates of aerobic N_2O produced following addition of 60 μg NO_3^--N g^{-1} were < 1 % of rates observed following addition of the same amount of NO_2^- (Fig. 4a). N_2O was readily produced in anaerobic incubations using sub-samples amended with NO_3^- and glucose. In microcosms using three cultivated soils at 80 % of WHC, N_2O consumption increased as headspace O_2 levels decreased below 5 % (Fig. 4b). There was no evidence of N_2O consumption at 5 % O_2.

Fig 5. Response to headspace O_2 concentration



NO_2^--amended soils displayed increased N_2O production as O_2 decreased from 21 to < 0.1 % (Fig. 5). In contrast, NO_3^--amended soils showed no response to varying O_2 except at < 0.1 %. Rates of N_2O produced in NO_2^--amended soils incubated at 100 % O_2 were significantly lower ($p < 0.05$) than soils incubated at ambient O_2 (data not shown). There was no response to O_2 in NO_2^--amended sterilized soils (data not shown) suggesting that the above response was entirely due to nitrifier denitrification activity.

Fig 6. Response to temperature and headspace O_2 concentration



Temperature responses at both 5 and 21 % O_2 were well-described ($r^2 \geq 0.99$) by the Arrhenius equation (Fig. 6). Q_{10} factors were also calculated from the data at 25 and 35 °C. A pattern of higher activation energy (E_a) and Q_{10} factor (i.e., greater temperature sensitivity) at the lower O_2 level was consistent across soils. The higher activation energies observed at 5 % compared to 21 % imply a greater temperature sensitivity of the biological than the chemical reduction process, since a greater proportion of the total production can be attributed to biotic than abiotic processes at lower O_2 (see above result).

Model extrapolations

The rate coefficients were applied in a simplified N_2O emissions model. Assuming steady-state and uniform conditions and the absence N_2O consumption, the equation governing N_2O transport is:

$$-D_p \frac{d^2[N_2O]}{\partial z^2} = \rho\, P_{N_2O} \qquad (2)$$

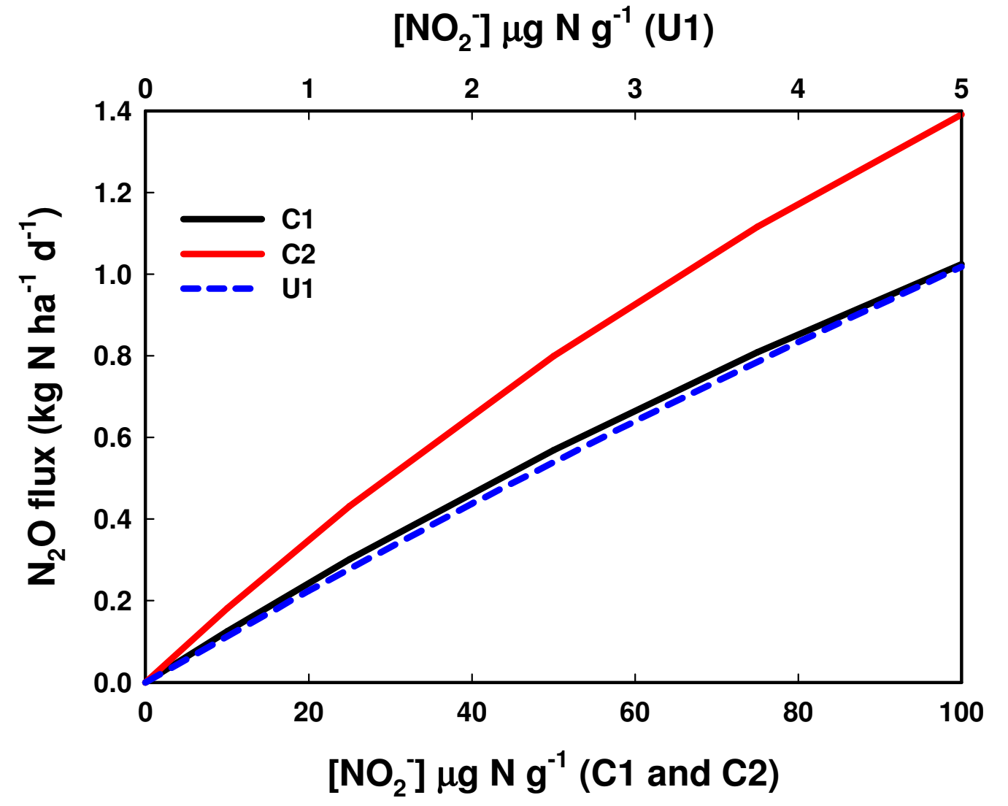
where D_p is the soil-gas diffusion coefficient, ρ is bulk density, and z is depth. Eq. [1] can be integrated to determine the N_2O concentration gradient at the soil surface and then combined with Fick's equation to yield an expression for the N_2O flux that is independent of D_p:

$$F_{N_2O} = \rho \int_{z_a}^{z_b} P_{N_2O}\, dz \qquad (3)$$

Eq. [3] assumes that there is a gas-impermeable (no-flux) boundary at some depth and that N_2O production occurs in a vertical band of thickness (z_b - z_a). The measured Michaelis-Menten kinetic parameters (Fig. 1, Eq. [1]) were used in Eq. [3], assuming a 5-cm band of NO_2^-, yielding:

$$F_{N_2O} = L\, \rho \left(\frac{\mu_{\max}[NO_2^-]}{K_m + [NO_2^-]} \right) \qquad (4)$$

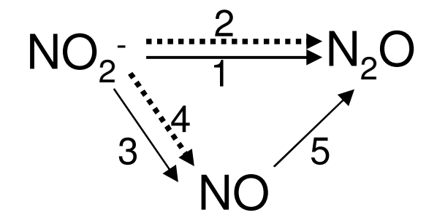
Fig 7. Model extrapolations of kinetic parameters



Eq. [4] predicts N_2O fluxes of 1.0 and 1.4 kg N ha^{-1} d^{-1} in soils C1 and C2, respectively, at $[NO_2^-]$ = 100 μg N g^{-1}, and a flux of 1.0 kg N ha^{-1} d^{-1} in soil U1 at $[NO_2^-]$ = 5 μg N g^{-1} (Fig. 7). This range agrees closely with N_2O fluxes in anhydrous ammonia-fertilized fields (e.g., Venterea and Rolston, 2000), and is comparable to fluxes attributed to denitrification (Riley and Matson, 2000; Li et al., 1992).

CONCLUSIONS

1. **Major processes found to be generating N_2O in the presence of NO_2^- and O_2 were: (1) direct biological reduction, (2) direct abiotic reduction, (3) biological reduction to NO and (4) abiotic reduction to NO, with (3) and (4) each followed by (5) biological NO reduction.**



2. **The data shown here suggest that field and lab observations showing a response of N_2O fluxes to O_2 may sometimes be misinterpreted as indicative of NO_3^- denitrification, when in fact nitrifier denitrification may be at play.**
3. **Steady-state model simulations predict that NO_2^- levels often found after fertilizer applications have the potential to generate substantial N_2O fluxes even at ambient O_2. This potential derives in part from the production of N_2O under conditions not favorable for N_2O reduction, in contrast to N_2O generated from NO_3^- reduction.**
4. **The potential importance of NO_2^--driven reactions in generating N_2O emissions appears to be high given the widespread use of anhydrous ammonia and urea, the two fertilizers having the greatest potential for promoting NO_2^- accumulation. Urea and anhydrous ammonia together account for 80 % of total fertilizer N applied worldwide (IFA, 2006).**
5. **The role of organic matter in promoting NO_2^--driven reactions shown here suggests that agricultural management practices designed to increase soil C storage may have unintended consequences that could counteract greenhouse gas benefits.**

Reference: Venterea, R.T. 2007. Nitrite-driven nitrous oxide production under aerobic soil conditions: Kinetics and biochemical controls. Global change biol. 13, 1798–1809.