Effects of soil moisture, physical, and chemical characteristics on abiotic nitric oxide production

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Abstract

The objective of this study was to examine the effect of soil water content, and other physical and chemical factors, on the abiotic component of nitric oxide (NO) production in laboratory studies using soils from agricultural fields in Minnesota, California, and Connecticut. In all soils, gross NO production decreased with increasing gravimetric water content (θ) in nitrite (NO_2^-)-amended sterilized soils. The rate coefficient describing nitrous acid (HNO_2)-mediated NO production (k_p) also decreased with increasing θ in both gamma-irradiated and autoclaved soils. Significant correlations were found between ln k_p and several soil properties including: content of silt, clay, total carbon, total N, and extractable iron, and an estimate of the cation exchange capacity of the clay fraction. Multiple regression models incorporating these variables explained 85–93% of the variance in ln k_p. The relationships obtained suggest that the mechanism of abiotic NO production is primarily mediated at the soil solution–surface interface. These findings provide consistent evidence of a previously unrecognized mechanism by which soil water content can affect NO production by mediating a chemical process. Application of a dynamic process model indicated that the simulated variation in NO emissions as a consequence of this effect is comparable to the variation observed in previous studies of NO emissions. Comparison of soils from two different long-term tillage studies also indicated that reduced pH in no-till systems may lead to greater NO emissions for a given level of NO_2^- accumulation. Overall, these results suggest that current views of controls over N oxide gas emissions may need to be revised to include abiotic reactions, in addition to microbial and physical processes, as yet another category of factors that is highly sensitive to soil water content.

Introduction

The production of nitric oxide (NO) gas within agricultural soil can lead to significant losses of fertilizer nitrogen (N) and may also have several different environmental impacts. Once emitted to the atmosphere, NO is rapidly oxidized to nitrogen dioxide (NO_2). The NO_x gases (NO and NO_2) together with organic radical species regulate the photochemical production of tropospheric ozone (O_3) (Crutzen 1979). Because O_3 production in rural areas tends to be limited by NO_x concentrations, soil NO emissions may exert significant control over local O_3 levels (NRC 1992; Stohl et al. 1996). Plant damage from O_3 is responsible for more than $2 billion y^{-1} in crop losses in the U.S.A. (Delucchi et al. 1996), and there is increasing concern regarding violations of O_3 air quality standards in rural areas (Saylor et al. 1998). Tropospheric O_3 is also recognized as a

greenhouse gas, although its contribution to global warming is difficult to estimate due to its large regional and temporal variation (Prather et al. 1995; Mickley et al. 2001). The eventual oxidation of NO_x gases to nitric acid (HNO_3) in the atmosphere contributes to downwind deposition of N and acidity (Crutzen 1979). Within the soil profile, the oxidation of NO may contribute to the production and subsequent leaching of nitrate (NO_3^-) (Venterea and Rolston 2002; Venterea et al. 2004). The potent greenhouse gas nitrous oxide (N_2O) may be produced within the soil via NO reduction or via the reduction of NO_3^- arising from NO oxidation (Conrad 1995).

Measurements of NO emissions from agricultural soils have been reported across a range of edaphic, climatic, and agronomic conditions. One consistent finding has been the high variability of NO emissions, both spatially and temporally. For example, Veldkamp and Keller's (1997) review of 23 field studies indicated that total growing-season NO emissions ranged widely, representing from < 0.01 to $> 10\%$ of fertilizer N inputs. This high variability, both within and across sites, combined with the large number of variables that may potentially influence NO emissions, has made the prediction of NO losses from agricultural systems a very uncertain endeavor. Another consistent finding has been that NO emissions tend to decrease with increasing soil water content. This trend has generally been attributed to (i) various microbiological responses to decreased oxygen (O_2) availability, and/or (ii) decreased gas diffusivity resulting from increased soil water content (e.g., Davidson 1993; Hutchinson and Davidson 1993; McTaggart et al. 2002).

The aim of the current study was to examine the influence of soil moisture, and other physical and chemical factors, on the production of NO via abiotic reactions involving HNO_2. This source of NO (Figure 1), which has been recognized for several decades (Allison 1963; Stevenson et al. 1970; Van Cleemput and Baert 1976; Venterea and Rolston 2000a, b, c), is actually the result of a sequence of biological and chemical reactions. The process is initiated by the biological generation of NO_2^- via nitrification and/or denitrification. Nitrite is then protonated to form HNO_2, to an extent that depends on the pH, followed by the aqueous disproportionation of HNO_2 and other possible chemical reactions of HNO_2 with soil
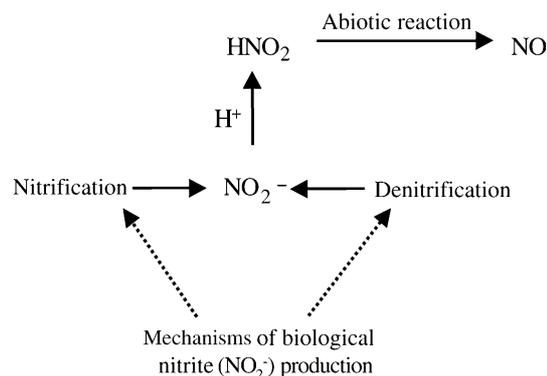

Figure 1. Illustration of the biotic/abiotic sequence of reactions leading to nitrous acid (HNO_2)-mediated nitric oxide (NO) production. The current study examines only the abiotic component.

organic and/or mineral constituents leading to NO production. In the current study, we examined NO production in sterilized soils from eight agricultural fields in Minnesota, California, and Connecticut in laboratory experiments following the addition of NO_2^- at varying soil water content. We also measured a range of soil properties in an effort to develop useful empirical relationships describing differences in rates of abiotic NO production within and among soils.

Materials and methods

Soils and site information

Basic taxonomic, textural, and agronomic information regarding each soil are provided in Table 1. Soils from California (CA) were selected to represent a range of clay and organic matter representative of agricultural soils in the Sacramento valley. Soils from Minnesota (MN) and Connecticut (CT) were collected from tilled and non-tilled fields in long-term tillage management experiments. The MN tillage experiment has been maintained since 1991 at the University of Minnesota Agriculture Experiment Station in Rosemount, MN (Hansmeyer et al. 1997). Samples for the current study were obtained from moldboard plowing and no till treatments within a continuous corn cropping system. The CT tillage experiment is located at the University of Connecticut Research Farm in Storrs, CT (Hooker et al. 2005). This

Table 1. Properties of soils used in laboratory experiments.

	California soils				Minnesota soils		Connecticut soils	
Series	Lang	Reiff	Columbia	Yolo	Waukegon	Waukegon	Paxton	Paxton
USDA textural class	Loamy sand	Sandy loam	Loam	Silt loam	Silt loam	Silt loam	Loam	Loam
USDA taxonomic class	Psammaquent	Xerofluvent	Xerofluvent	Xerorthent	Hapludoll	Hapludoll	Dystrudept	Hapludoll
Recent use	Alfalfa/Tomato	Corn/Tomato	Tomato	Row crops	Corn/Soybean	Corn/Soybean	Corn	Corn
Tillage	Conventional	Conventional	Conventional	Conventional	Conventional	No-till	Conventional	No-till
Sand ($g\ kg^{-1}$)	740	620	510	360	150	150	480	480
Silt ($g\ kg^{-1}$)	220	280	380	460	600	610	400	400
Clay ($g\ kg^{-1}$)	40	100	110	180	250	240	130	120
Total C ($g\ kg^{-1}$)	3.2	8.8	11	14	25	29	30	40
Total N ($g\ kg^{-1}$)	0.30	0.50	1.3	1.0	2.1	2.5	2.3	3.0
pH (1:1 M KCl)	5.6	6.5	5.3	6.3	5.7	5.3	4.9	4.6
CEC[a] ($meq\ kg^{-1}$)	70	170	120	230	205	214	122	145
Mn[b] ($mg\ kg^{-1}$)	28	40	53	56	25	47	9.3	15
Fe[b] ($mg\ kg^{-1}$)	21	13	96	11	53	75	32	55
Cu[b] ($mg\ kg^{-1}$)	1.6	2.2	3.8	5.2	0.76	0.82	0.59	0.75

[a] Cation exchange capacity, ammonium acetate extraction.
[b] DTPA (diethylene triamine pentaacetic acid) extraction.

study was initiated in 1972 and compares mold-board plowing with no tillage under continuous corn, with and without above-ground corn stover removal. Samples for the current study were obtained from the moldboard plowing and no till treatments, each with stover-return. For each CA soil, a single composite was generated by combining 10 individual samples taken at random locations from the upper 10 cm across fields measuring 1–3 ha. For each MN soil, a single composite was generated by combining six individual samples taken at random locations from the upper 10 cm within three replicate plots (each plot = 0.20 ha). For each CT soil, a single composite was generated by combining nine individual samples taken at random locations from the upper 15 cm within three replicate plots (each plot = 0.026 ha). Soils were air dried, sieved to 2 mm, and stored in sealed plastic bags.

Portions of each composite were treated with 3 Mrad of gamma radiation at Phoenix Memorial Laboratories, Ann Arbor, MI. Separate portions were preincubated and then autoclaved at 120 °C for 30 min followed by an additional 48 h of incubation and a second autoclaving for 1 h. The gamma-irradiated soils were used for the majority of the experiments and for the data analysis, because this method of sterilization causes less severe alteration of chemical and physical properties compared to autoclaving (Wolf and Skipper 1994). Because there is some evidence that gamma radiation of soils may not completely inactivate extracellular enzymes (Cawse and Cornfield 1971), the autoclaved soils were tested in order to confirm that the general pattern of abiotic NO production observed in the irradiated soils occurred in the absence of extra-cellular enzyme activity.

Abiotic NO production

Subsamples of each sterilized soil composite were amended with varying volumes of deionized water containing varying concentrations of potassium nitrite. For each soil, 4 or 5 levels of gravimetric water content (θ) were tested. At each θ level, 3 levels of NO_2^- were added equivalent to approximately 0, 1, and 2 $\mu g\ N\ g^{-1}$ soil above the background (post-sterilization) soil NO_2^- concentration, which varied from 0.03 to 0.35 $\mu g\ N\ g^{-1}$. Solutions were mixed manually with soil for 1–3 min using a stainless steel spatula, and then immediately transferred to a glass (250 ml) or acrylic (450 ml) NO production measurement chamber (Venterea and Rolston 2000a). Soil inside the reaction chamber was then continuously flushed with humidified air, which flowed to a chemiluminescent NO_x analyzer (Model 270B, Sievers Instruments, Boulder, CO, or Model LMA-3D, Unisearch Associates, Ontario, Canada[1])

[1]Mention of product names is for the convenience of the reader and implies no endorsement on the part of the authors, their respective institutions, or the USDA.

The net NO production rate (P_{net}, μg N g^{-1} h^{-1}) was calculated from:

$$P_{net} = \frac{q}{m}(NO_e - NO_i), \qquad (1)$$

where q is the air flow rate (0.03–0.06 m^3 h^{-1}), m is the dry soil mass (2–20 g), and NO_i and NO_e are the chamber influent and effluent concentrations (μg N m^{-3}), respectively. Valves installed on the flow lines allowed for rapid switching between measurement of NO_i and NO_e. The NO_e concentration vs. time data were output to a data acquisition system for real-time viewing. Once each effluent signal stabilized (after 5–20 min), the NO_e value was recorded. Values of P_{net} were obtained at multiple inlet NO concentrations for each sample by blending the chamber influent air with varying amounts of NO standard gas (balance N$_2$) using mass flowmeters. The gross NO production rate (P_g) was then obtained from the y-intercept resulting from linear regression of P_{net} vs. NO_e by assuming first-order NO consumption kinetics as described by:

$$P_{net} = P_g - k_c NO_e, \qquad (2)$$

where k_c is the NO consumption rate coefficient (m^3 h^{-1} g^{-1}) as previously described (Remde et al. 1989; Venterea and Rolston 2000a). Because NO consumption rates in these sterilized soils were low in relation to NO production rates, we found that the final term in Equation (2) was always < 5% of P_{net} values measured using NO-free chamber inlet air. Therefore, P_g could be estimated with < 5% error by measuring P_{net} using NO-free chamber inlet air.

Immediately following each P_{net} measurement, the soil was mixed with 2 N KCl solution adjusted to pH 8.0, extracted for 15 min on a reciprocating shaker, and centrifuged at 6000 rpm for 15 min (Stevens and Laughlin 1995). Soil:solution ratios of approximately 1:10 were used for the majority of extractions, except when low-level (ambient) NO_2^- concentrations were expected, in which cases higher ratios (~1:1) were used. Resulting supernatant was stored at 4 °C for 1–24 h, at which time the extract was analyzed for total $NO_2^- + HNO_2$ using the modified Griess–Ilosvay method (Keeney and Nelson 1982; Venterea and Rolston 2000a). Separate subsamples of each composite were mixed with an equal mass of 1 N KCl solution, stirred manually, and allowed to settle for 1 h before removal of supernatant for soil pH (pH$_s$) measurement. This method of pH$_s$

measurement was found to be less variable than using 0.01 M CaCl$_2$ as the extracting solution (Venterea and Rolston 2000a). The above procedures were conducted at laboratory temperatures (23–25 °C). In addition, the procedures were repeated using the Columbia loam from California in a temperature-controlled room at 20, 30, and 35 °C in order to examine the effect of temperature on NO production.

The HNO$_2$ concentration was calculated from the measured pH$_s$, total $NO_2^- + HNO_2$ concentrations, and the acid dissociation constant for HNO$_2$ (pK_a = 3.3) (Van Cleemput and Samater 1996) according to

$$[HNO_2] = \frac{[H^+][NO_2^- + HNO_2]_{total}}{[H^+] + 10^{-pK_a}}, \qquad (3)$$

where the hydrogen ion activity [H$^+$] is estimated from 10^{-pH_s}, as previously described (Venterea and Rolston 2000a). As noted by Venterea and Rolston (2000a), the above expression for HNO$_2$ concentration is operationally defined, since pH$_s$ is itself operationally defined and can vary considerably depending on the type of solution and the solution–soil ratio used (Sumner 1994; Nilsson et al. 1995). For each soil at each θ, the rate coefficient (k_p) describing HNO$_2$-mediated NO production was obtained by linear regression of P_g vs. HNO$_2$ concentration, i.e.,

$$P_g = k_p[HNO_2] \qquad (4)$$

according to (Venterea and Rolston 2000a, b, 2002; Venterea et al. 2003). Strictly, k_p has units of (μg NO-N) (μg HNO$_2$-N)$^{-1}$ (h^{-1}), but here for the sake of simplicity we cancel the mass terms and express the units as h^{-1}. Since k_p is a derivative of HNO$_2$ and pH$_s$, it is also operationally defined. Values of k_p were calculated in the current study in order to examine how NO production per unit HNO$_2$ changed with respect to (i) soil water content within each soil, (ii) temperature and soil water content in the Columbia soil, and (iii) other physical and chemical soil properties across soils.

If ln k_p is linearly related to the absolute temperature, the apparent activation energy (E_a) for the NO producing reaction at each θ level can be calculated using the Arrhenius relation

$$\ln k_p = A_o - \left(\frac{E_a}{R}\right)T^{-1}, \qquad (5)$$

where A_o represents the collision number, R is the universal gas constant (8.3144 J K^{-1} mol^{-1}), and T is the absolute temperature (K^{-1}) (Pauling 1970). The term in parentheses represents the slope of the regression line of ln k_p vs. K^{-1}, so that E_a can be calculated from $E_a = -$ slope·R.

Other soil analysis

Particle size (texture), total carbon (C) total N, cation exchange capacity (CEC), and extractable manganese (Mn), iron (Fe), and copper (Cu) were determined on irradiated composite samples. Total C and N analyses were performed using combustion with thermal conductivity detection (Carlo Erba NA 1500) of finely milled samples. CEC was determined using the ammonium acetate method (Sumner and Miller 1996). Extractable Mn, Fe, and Cu levels were selected for measurement based on previous studies that have suggested these metals may have a possible role in mediating abiotic NO production (Nelson 1982). Since the primary objective of the current study was to develop potentially useful empirical relationships, the diethylene-triamine-pentaacetic acid (DTPA) extraction method, which is commonly used as an index of plant-available trace metal concentrations, was used for Mn, Fe, and Cu (Loeppert and Inskeep 1996).

Modeling

Results of the current study were used in a previously developed model describing N oxide gas transport and transformation following ammonium (NH$_4^+$) fertilizer application (Venterea and Rolston 2000c, 2002). The model was used to simulate soil-to-air NO emissions resulting from abiotic production of NO as a function of water-filled pore space (WFPS), in a Yolo silt loam. The model describes (i) both steps of nitrification using Monod kinetics, (ii) pH dynamics in response to nitrification, (iii) HNO$_2$-mediated NO production, (iv) NO consumption, and (v) diffusive transport of dissolved and gaseous inorganic N species. All parameters used in the current simulations were identical to those used for the Case 1 simulations in Venterea and Rolston

(2000c), except those listed in Table 2. Initial conditions consisted of a fertilizer rate of 100 kg NH$_4^+$-N ha^{-1} applied in a 5-cm thick band at varying depths. The finite difference model used a soil depth (z) grid of 1 mm over a total depth of 20 cm, and a time step of approximately 1.1 s. Soil water content, temperature (25 °C), and dry bulk density (1.2 g cm^{-3}) were assumed constant over time and depth during each 20-day simulation. While the assumption of fixed soil water content and temperature for 20 days is certainly not realistic, these parameters were kept constant in each simulation so that the effect of varying soil water content could be examined more easily. Surface NO flux was calculated at each time step using Fick's equation and the gradient calculated from the simulated NO concentration at the 1 mm depth and the assumed atmospheric NO concentration of 1 ppb. Total emissions over 20 days were integrated by summing the fluxes calculated at each time step. Further model details are given in Venterea and Rolston (2000c).

Results

Water content effects

In all soils tested, the gross NO production rate decreased with increasing θ following amendment with NO$_2^-$ (Figure 2). At each θ level, NO

Table 2. Key parameters used in model simulations.

Parameter (units)	Value
NO production rate coefficient (k_p) (h^{-1})	exp (3.97–16.6θ)[a]
NO consumption rate coefficient (k_c) (cm^3 g^{-1} h^{-1})	16.2[b]
NH$_4^+$ liquid–solid partitioning coefficient (cm^3 g^{-1})	3.59[c]
Initial soil pH (−)	6.3
pH buffering capacity (μg H$^+$ g^{-1} pH^{-1})	23.5[d]
Inhibition factor, NO$_2^-$ oxidation (−)	6.5[e]

[a]Relationship derived from current data.
[b]Measured data for Yolo silt loam (Venterea and Rolston, 2000a). No change in k_c was observed with water content in current study in non-sterilized soils.
[c]Measured data for Yolo silt loam (Venterea, unpublished data).
[d]Calculated from total C, clay, and silt content using relationships in Curtin et al. (1996).
[e]Assumed based on model-data comparisons in Venterea and Rolston (2000c).

production increased with increasing NO_2^- concentration over the range of approximately 0–2 μg N g^{-1}. The rate coefficient describing HNO_2-mediated NO production (k_p) also decreased with increasing θ in both gamma-irradiated and autoclaved soils (Figure 3). Natural logarithm (ln)-transformed k_p values were negatively correlated with θ for each soil (Table 3). Autoclaved soils displayed higher rates of NO production at a given θ and HNO_2 level than the respective irradiated soils as reflected in the higher k_p values (Figure 3b).

Differences among soils

Within each group of soils, the highest NO production at a given θ and NO_2^- level was displayed by the soil with the lowest pH (Figure 2), as expected for processes driven by HNO_2. In the CA soils, the Columbia loam soil (pH 5.3) displayed the highest NO production across the full range of θ, while the Reiff sandy loam (pH 6.5) displayed the lowest NO production. The untilled plots in MN and CT (pH 5.3 and 4.6, respectively) had

higher NO production than the respective tilled plots (pH 5.7 and 4.9, respectively). The trends in NO production with pH did not hold across groups, i.e., the Waukegon silt loam from MN (pH 5.7) displayed much higher NO production than the Lang loamy sand from CA (pH 5.6).

Since all soils were not tested at the same θ levels, data in Figure 3 were used to estimate, by interpolation and extrapolation, k_p values for each soil at $\theta = 0.10$, 0.15, 0.20, and 0.25 g H_2O g^{-1}. Because k_p values were log-normally distributed, single-factor regression analyses were performed using ln k_p vs. soil physical and chemical properties. Significant positive correlations were found between ln k_p and silt and clay content across all θ values (Table 4). Positive correlations were found with total C, total N, and DPTA-extractable Fe at certain θ levels. Significant negative correlations were found with sand content across all θ levels. The bulk soil CEC and clay contents were used to estimate CEC of the clay fraction (CEC_{cf}) for each soil. A strong negative correlation was found between ln k_p and CEC_{cf} (Table 4). Multiple regression models incorporating θ, CEC_{cf}, Fe,
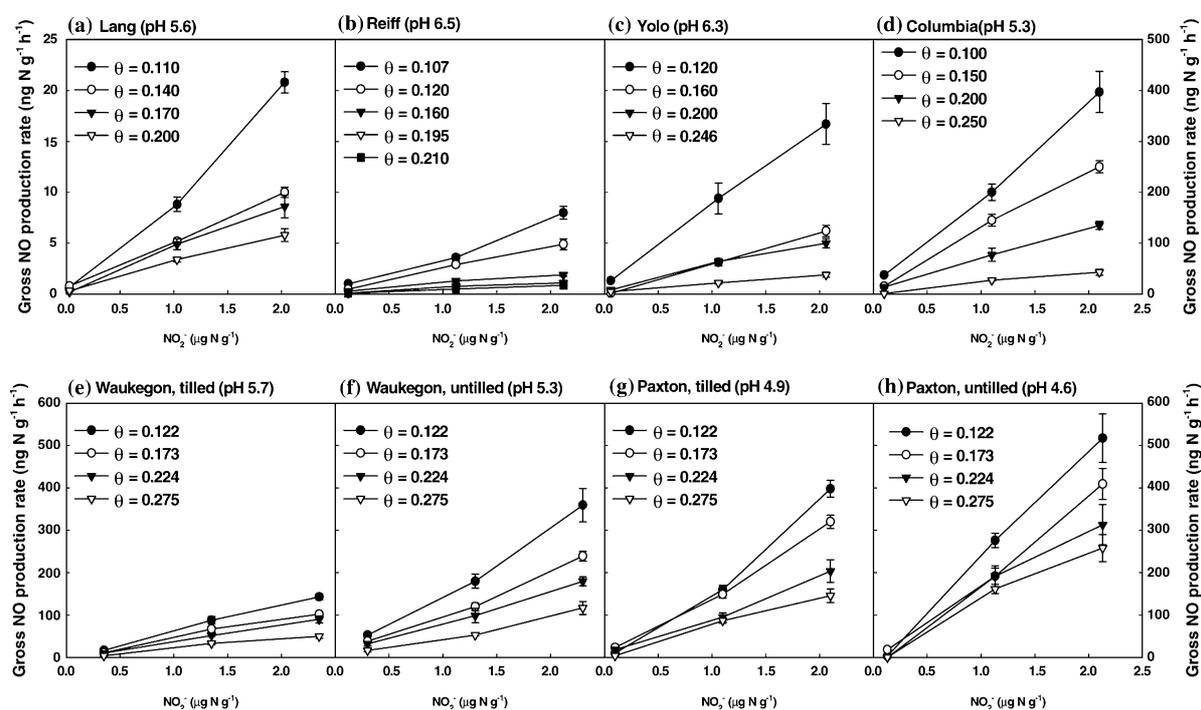

Figure 2. Gross NO production rate (P_g) at varying soil water content (θ) and soil nitrite (NO_2^-) concentration in gamma-irradiated soils sampled from agricultural fields in California (a–d), Minnesota (e, f), and Connecticut (g, h) (mean ± standard error, $n = 2$). Note: In upper plates, left-hand vertical axis scale applies to (a–c), and right-hand vertical axis scale applies to (d).
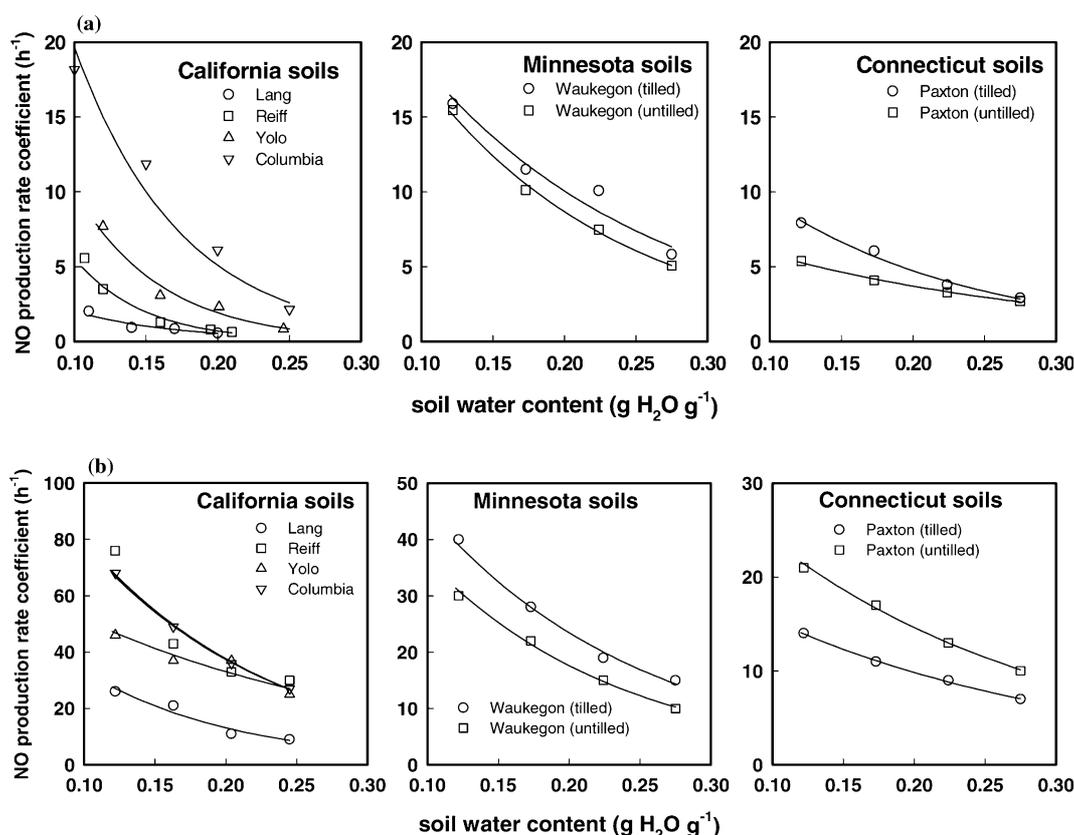
Figure 3. NO production rate coefficient (k_p) at varying soil water content (θ) in (a) gamma-irradiated soils and (b) autoclaved soils sampled from agricultural fields in California, Minnesota, and Connecticut. Regression lines for ln k_p vs. θ are shown. Further information regarding regression lines is given in Table 3.

Table 3. Relationships between NO production rate coefficient (k_p) and soil water content (θ) in gamma-irradiated and autoclaved soils sampled from agricultural fields in California, Minnesota, and Connecticut.

Soil	Irradiated[a]			Autoclaved[a]		
	r^2	a	b	r^2	a	b
Lang	0.91*	2.02	13.3	0.95*	4.44	9.34
Reiff	0.98**	3.78	20.7	0.89*	5.11	7.45
Columbia	0.96*	4.47	14.2	0.99***	5.13	7.51
Yolo	0.97*	3.97	16.6	0.86	4.39	4.46
Waukegon (tilled)	0.94*	3.54	6.16	0.99***	4.46	6.53
Waukegon (untilled)	0.99**	3.59	7.15	0.99***	4.31	7.21
Paxton (tilled)	0.99**	2.92	6.83	0.99***	3.18	4.47
Paxton (untilled)	0.99**	2.21	4.50	0.99***	3.66	4.89

[a]Coefficient of determination (r^2) values and regression parameters (a and b) are shown for linear model in the form: ln $k_p = a - b\theta$. Exponential regression lines are plotted in Figure 3.
*Significant at the 0.05 probability level; **Significant at the 0.01 probability level; ***Significant at the 0.001 probability level.

clay, total C content, and the product $\theta \cdot CEC_{cf}$ as independent variables explained 85–93% of the variance in ln k_p (Figure 4).

Variation with temperature and water content

In the Columbia loam soil tested at 20, 25, 30, and 35 °C, gross NO production rates increased with increasing temperature at each θ and NO_2^- level, as indicated in the Arrhenius plot of ln k_p vs. the reciprocal of the absolute temperature (K^{-1}) (Figure 5). The E_a values ranged from 66–69 kJ mol^{-1}. Analysis of covariance indicated that the E_a values at each level did not vary significantly ($P > 0.25$). Assuming that the Arrhenius relations in Figure 5 hold for the Columbia loam, calculations using Equations (4 and 5) indicate that at a soil NO_2^- concentration of 1 μg N g^{-1} with T varying over 20–35 °C and θ varying over 0.05–0.20 g H$_2$O g^{-1}, abiotic NO production
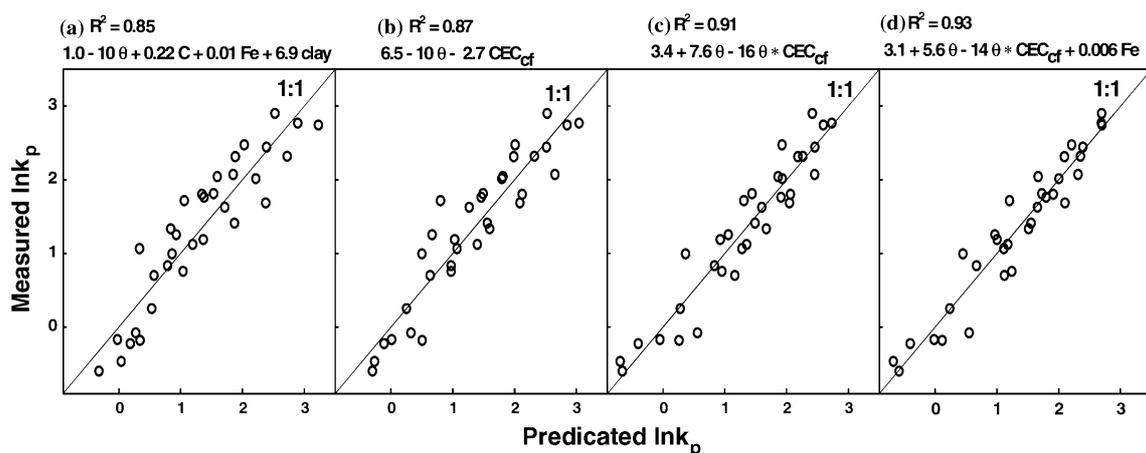
Figure 4. Results of multiple regression analysis describing ln-transformed NO production rate coefficient (k_p) as function of different combinations of soil physical and chemical properties: gravimetric soil water content (θ, g H_2O g^{-1}), total C (%), DPTA-extractable iron concentration (Fe, μg g^{-1}), clay content (%), and calculated cation exchange capacity of clay fraction (CEC$_{cf}$, meq g^{-1} clay). Coefficients of multiple determination (r^2) and variable coefficients are shown for each model. $P < 0.001$, $n = 33$.

would be expected to vary by a factor of approximately 25, ranging from a lower limit of 33 ng N g^{-1} h^{-1} (at $T = 20$ °C, $\theta = 0.20$) to 810 ng N g^{-1} h^{-1} (at $T = 35$ °C, $\theta = 0.05$).

Process modeling

The simulated inorganic N dynamics in the Yolo silt loam (Figure 6a) displayed a transient accumulation of NO_2^-, with a peak concentration of

Table 4. Single-factor correlation results of ln k_p vs. soil physical and chemical factors at varying soil water content (θ, g H_2O g^{-1}).

Factor	r^a at θ of			
	0.10	0.15	0.20	0.25
Sand content	−0.80*	−0.82*	−0.82*	−0.83*
Silt content	0.81*	0.84**	0.85**	0.85**
Clay content	0.78*	0.76*	0.75*	0.77*
Total C	0.40	0.62	0.71*	0.84**
Total N	0.43	0.68	0.77*	0.87**
pH	−0.03	−0.38	−0.49	−0.59
CEC	0.63	0.46	0.41	0.46
CEC$_{cf}$	−0.81*	−0.96***	−0.98***	−0.98***
Mn	0.39	0.11	−0.03	−0.15
Fe	0.63	0.75*	0.74*	0.65
Cu	0.12	−0.11	−0.23	−0.32

[a]Pearson product–moment correlation coefficient.
*Significant at the 0.05 probability level; **Significant at the 0.01 probability level; ***Significant at the 0.001 probability level.

1.4 μg N g^{-1} in the center of the 5-cm thick fertilizer band occurring 6 days after fertilizer application. The simulated soil-to-air flux of NO deriving from abiotic HNO_2-mediated NO production was highly sensitive to WFPS and fertilizer application depth (Figures 6b, c). Simulated total NO emissions decreased substantially as WFPS increased from 21 to 63%. The extent of this decrease ranged from 85% for surface application (0–5 cm) to >97% for applications at or below 3–8 cm. As a percentage of the applied fertilizer N (100 kg N ha^{-1}), total simulated NO emissions ranged from 1.7 to 11% for surface application and 0.05–1.9% for application at 5–10 cm.

Discussion

Water content effects on chemical source of NO

While the effects of soil water content on both biological and physical processes mediating NO emissions have been implicated in previous studies (e.g., Davidson 1993; Hutchinson et al. 1993; Bollman and Conrad 1998), the current results show that a strictly chemical component of NO production is also highly sensitive to water content. This particular effect, while generally consistent with the well-known 'hole-in-the-pipe' model of N trace gas emissions (Davidson and Verchot 2000), has not previously been shown or
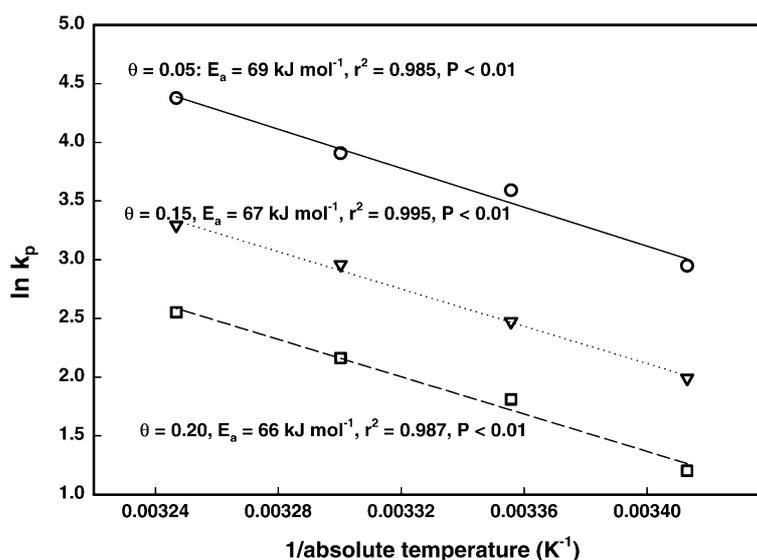
Figure 5. Arrhenius plots of ln-transformed NO production rate coefficient (k_p) vs. reciprocal of absolute temperature at gravimetric soil water content (θ) values of 0.05, 0.15, and 0.20 g H_2O g^{-1} using Columbia loam. Activation energies (E_a) calculated using Equation (5) are shown for each water content.

considered in interpreting data from field and laboratory studies. Most microbiological effects that have been examined are also expected to produce higher NO emissions with decreasing water content, at least to the point where low water content begins to limit nitrification rates (Davidson 1993). At higher water content, nitrification rates tend to be inhibited due to oxygen limitation, and presumably nitrification-derived NO production is also diminished (Hutchinson et al. 1993; Bollmann and Conrad 1998). While denitrifying sources of NO may increase with water content, reductive microbial consumption of NO also increases, and gaseous diffusion of NO decreases resulting in greater residence times in the soil with increasing water content (Hutchinson and Davidson 1993). The net result of these biological and physical processes has generally been greatly reduced rates of NO emissions to the atmosphere as water-filled pore space increases above 50–60%.

While it is not possible to determine the relative importance of these various effects of water content on NO emissions in a general sense, the current findings allow for estimation of the magnitude of the specific effect of water content on abiotic NO production. Gross NO production decreased by 50–89% in the various irradiated soils as θ increased over the range of 0.10–0.28 g H_2O g^{-1}.

The kinetic data also indicate that the simultaneous variation in water content and temperature can result in at least a 25-fold variation in gross NO production derived from abiotic sources. The dynamic simulations indicate that water content effects on abiotic sources, assuming constant temperature and modest levels of NO_2^- accumulation (< 2 μg N g^{-1}), can result in variations in NO emissions ranging from 0.05 to 11% of fertilizer application rates, which is very similar to the range reported in Veldkamp and Keller's (1997) review of field studies. Thus, these findings do suggest that water content effects on abiotic production kinetics may represent a significant underlying cause of the variation in NO emissions with changing water content observed in previous studies.

Implications for fertilizer N management

The most direct and practical implication of the current data is that, when using fertilizers which tend to cause elevated accumulations of NO_2^-, such as anhydrous ammonia (Chalk et al. 1975; Venterea and Rolston 2000b) and urea (Christianson et al. 1979; Riley et al. 2001), the maintenance of moderate-to-high water contents during the first 6–12 days following fertilizer application may greatly reduce NO emissions. In
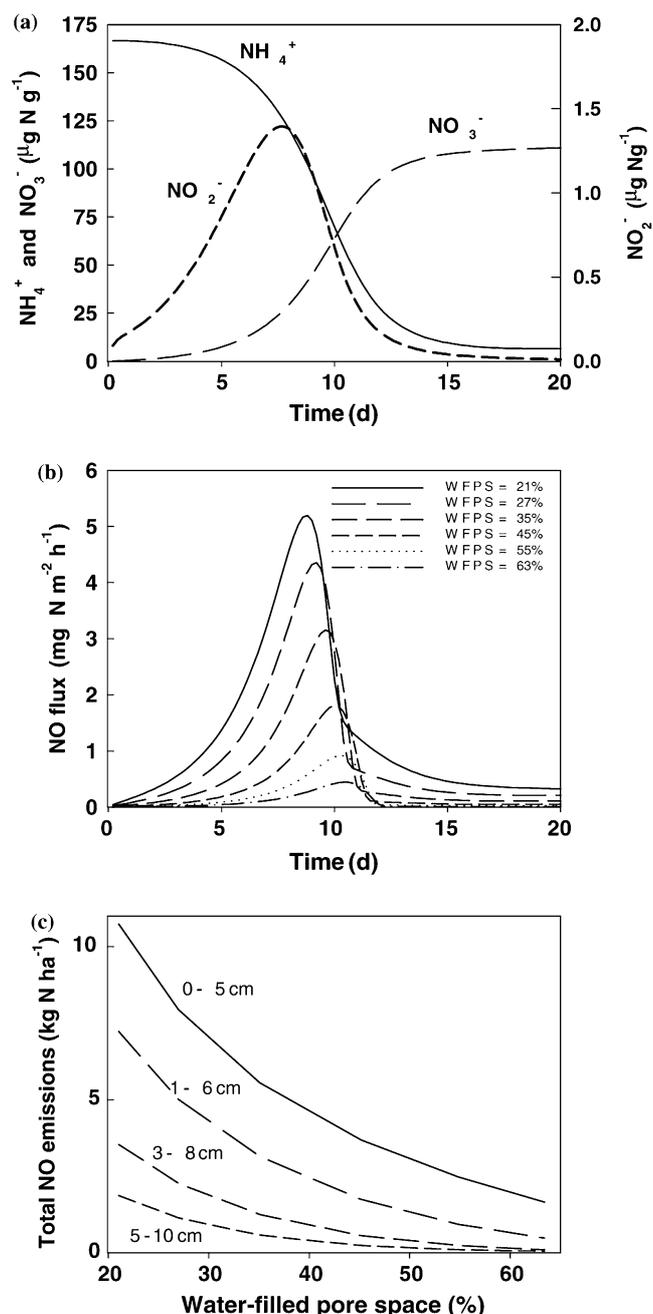
Figure 6. Simulated (a) inorganic N dynamics at center of 5-cm thick fertilizer band, (b) NO flux dynamics at varying water-filled pore space (WFPS) assuming 1–6 cm fertilizer application depth, and (c) total integrated NO emissions over 20 days as function of WFPS and varying application depths, following the application of 100 kg N ha^{-1} of NH_4^+-N fertilizer to Yolo silt loam as NH_4^+, using the parameters in Table 2.

addition, management of soil pH, which is not frequently considered in this context, may also be effective in minimizing HNO_2-mediated NO production. The overall cost-effectiveness of these

practices is currently impossible to assess, since the impact of fertilizer-induced NO emissions on local O_3 formation, and its subsequent impacts on crop losses and air quality, has not been quantitatively

assessed. Another implication of these data is that reduced tillage practices may have the unintended consequence of promoting NO losses due to reduced soil pH in the upper 10 cm of soil, which presumably results from reduced mixing of plant residues and NH_4^+ fertilizers with underlying soil. It is not known if other factors such as differential NO consumption or NO_2^- dynamics in tilled vs. non-tilled soils may counteract this pH effect.

Mechanisms

The current data support the hypothesis that the abiotic source of NO production is the result of reactions occurring primarily at the interface of the soil surface and soil solution. Our fundamental understanding of the structure and composition of the soil matrix suggests that the main effect, i.e., increased NO production at decreased gravimetric water content, arises primarily from two factors: (i) the increasing importance of the soil–water interface with decreasing water content, i.e., the increasing ratio of interfacial area to soil solution volume with decreasing θ, combined with (ii) the surficial nature of soil acidity, i.e., the importance of mineral and organic colloids as sources of exchangeable and non-exchangeable soil acidity (McBride 1994).

For a given NO_2^- concentration on a per mass soil basis, as θ decreases, the bulk solution-phase NO_2^- concentration will increase in proportion to the decrease in θ. Thus, assuming well-mixed conditions, the mass of NO_2^- per mass soil that is in proximity to acidic surfaces will increase with decreasing θ. This would be expected to promote greater formation of HNO_2 via

$$H^+ + NO_2^- \rightarrow HNO_2 \qquad (6)$$

and subsequently greater NO production per mass soil due to the aqueous-phase disproportionation of HNO_2 (Van Cleemput and Baert 1976) given by

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \qquad (7)$$

The kinetics of this surface-mediated process as a function of soil water content are fundamentally different than that of a process that proceeds in bulk solution. When the reactant concentration per mass soil is kept constant over varying water

content, the reactant concentration in bulk solution will vary inversely in proportion to the water content. For process kinetics that are first-order with respect to bulk solution concentrations, as the reactant concentration increases with decreasing θ, the rate per volume of solution will also increase in direct proportion to the increasing concentration. However, the decreased volume of solution will exactly compensate for the increased rate per volume solution, resulting in no change in the rate expressed per mass soil. For a solution-based rate that is less than first-order, the rate per mass soil would decrease with decreasing θ. In the surface-mediated case described above, the rate per mass soil instead increases because the interfacial area does not decrease in proportion to the decrease in θ. Since a greater total surface area per unit of soil would allow for more surface–solution interaction, the positive correlations between k_p values and clay content observed (Table 4; Figure 4a) are consistent with the hypothesis that the reactions controlling abiotic NO production are primarily surface-mediated.

Our estimate of clay fraction CEC (CEC_{cf}) is almost certainly subject to considerable error for at least two reasons: (i) the varying contributions of soil organic matter to bulk soil CEC which are not considered in our calculations (Sparks 2003), and (ii) the ammonium acetate method for determining bulk soil CEC tends to overestimate the actual CEC for soils with pH < 7 (Sumner and Miller 1996). Thus, the strong and highly significant negative correlations between CEC_{cf} and $\ln k_p$ ($r^2 > 0.90$ and $P < 0.001$, except at the lowest θ level, Table 4), are somewhat surprising but, nonetheless, compelling. This correlation lends additional support to a surface-mediated reaction mechanism. That is, as the negative surface charge density of soil colloids increases, the relative density of cations and exclusion of anions at the soil–solution interface would be expected to increase (Sparks 2003). Thus, for any given concentration of NO_2^- in bulk solution, a higher CEC_{cf} would seem to promote less interaction of NO_2^- with surficial sources of acidity resulting in less HNO_2 formation and less NO production at a given level of θ, NO_2^-, and pH.

The occurrence of the product $\theta \cdot CEC_{cf}$ as a highly significant ($P < 0.0001$) factor in multiple regression models (Figure 4c, d) suggests an interaction between θ and CEC_{cf} in regulating

ln k_p. Consistent with this finding, single-factor regression analyses (Table 4) indicate that the slope of ln k_p vs. CEC_{cf} is increasingly negative with increasing θ. While a mechanistic explanation of this effect is not immediately clear, it appears that the inhibition of HNO_2 formation by increasing surface charge density is stronger at higher water content.
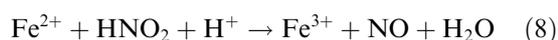
The current findings suggest that our previously derived method (Venterea and Rolston 2000a) of calculating soil HNO_2 concentration [Equation (3)] is overly simplistic from a mechanistic standpoint. This formulation is based on acid dissociation as would occur in a well-mixed aqueous solution, and therefore does not account for the pore-scale spatial distribution of H^+ sources that is expected in soil. This is particularly true because of our use of 1 M KCl for determining soil pH, which is more efficient than other extractants in accounting for both exchangeable (surficial) and active (solution-phase) acidity (McBride 1994). However, while this index of HNO_2 may not accurately represent bulk solution concentration, it may be a decent measure of the potential maximum HNO_2 concentration deriving from all sources of acidity that is available for participating in the reaction shown in Equation (7). Thus, while Equations (3 and 4) may imply that solution-phase HNO_2 concentration is the single factor controlling the NO production rate, and that k_p is simply a constant of proportionality, the current findings suggest that other factors including at least water content, clay content, and surface charge density, are embedded within k_p and serve to regulate the active amount of HNO_2 that is available for producing NO.

The magnitude of the activation energy obtained here (~ 67 kJ mol^{-1}; Figure 5) provides further support for a surface-mediated mechanism, since this value is within the range expected for surface-mediated processes (Sparks 2003). The apparent independence of the activation energy from soil water content further implies that the fundamental nature of the reaction is not altered with water content.

The positive correlations between ln k_p and total C and DTPA-Fe in both simple (Table 4) and multiple regression models (Figures 4a, d) imply that there may be additional sources of NO other than that indicated by Equation (7), and

therefore that additional factors may be embedded within the k_p term in Equation (4). According to Stevenson (1994), NO can be formed directly by the reaction of HNO_2 with enolic functional groups of soil organic matter, although evidence for this mechanism is not cited by Stevenson (1994). Soil organic matter also contributes to surficial acidity, and therefore total C may in part be correlated with k_p for reasons discussed above.

The production of NO via the reduction of HNO_2 by ferrous iron in soils according to

$$Fe^{2+} + HNO_2 + H^+ \rightarrow Fe^{3+} + NO + H_2O \quad (8)$$

was proposed by Wullstein and Gilmour (1966). Nelson and Bremner (1970) subsequently raised doubts about the feasibility of this reaction occurring in well-drained soils. Whether sufficient quantities of Fe^{2+} to promote Equation (8) could exist in previously air-dried, sterile soils under aerobic conditions is not known. The measure of Fe availability used here (DPTA-extractable) is known to correlate mainly with non-crystalline 'active' iron oxide minerals with high surface area, but also, at lower pH, with organically bound Fe (including possibly Fe^{2+}) (Loeppert and Inskeep 1996). Thus, whether the correlations between k_p and DTPA-extractable Fe found here indicate the role of Equation (8), or instead the role of amorphous Fe as an additional source of surficial acidity (McBride 1994), or perhaps indicate a correlation with certain types of surface-active organic C, are questions for further study. In the current study, we found no significant correlation between DTPA-extractable Fe and total organic C ($P = 0.32$; $r^2 = 0.16$).

The main effect of soil water content shown here, since it relies upon a source of NO_2^-, will also be subject to the constraints imposed by water content on nitrification rates and possibly other microbiological processes. More specifically, it is the relative activity of the NH_4^+ - and NO_2^- oxidizing nitrifiers which controls the accumulation NO_2^- (Morrill and Dawson 1967; Venterea and Rolston 2000c). Therefore, the differential effect of water content on this pair of biological processes will greatly influence how the water content effect on the abiotic component is actually expressed in a live soil. There is no information currently available to our knowledge regarding water content effects on NO_2^- accumulation in fertilized soils.

Conclusions

Our findings provide support for a mechanism by which soil water content can affect the production of NO that involves a strictly chemical process, apart from previously demonstrated effects on microbiological and physical processes. The variation in NO emissions as a consequence of this effect appears to be significant and comparable to that observed in many studies. The data also seem to be consistent in supporting a mechanism of abiotic production that is primarily surface mediated, and therefore controlled not only by water content but also by other properties including the content of clay, organic matter, Fe, and the surface charge density. Thus, another implication of these findings is that Equations (3 and 4) are an oversimplification of the abiotic processes regulating gross NO production on a mechanistic level. Nonetheless, for modeling purposes, the use of Equation (4) – with k_p modified using the relationships obtained here (Table 3; Figure 4; Equation (5)) – may in fact be very efficient. Future comparisons of this modeling approach to actual data, including field emissions data, will provide one test of the usefulness of the relationships developed. An additional challenge of improving mechanistic models of NO dynamics in soils will be to incorporate the kinetics of abiotic production with those of microbial sources (Conrad 1995; Beaumont et al. 2002).

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