



1 Effects of soil moisture, physical, and chemical characteristics on abiotic nitric 2 oxide production

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11 Abstract

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

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33 Introduction

34 The production of nitric oxide (NO) gas within
35 agricultural soil can lead to significant losses of
36 fertilizer nitrogen (N) and may also have several
37 different environmental impacts. Once emitted to

the atmosphere, NO is rapidly oxidized to nitrogen 38
dioxide (NO_2). The NO_x gases (NO and NO_2) 39
together with organic radical species regulate the 40
photochemical production of tropospheric ozone 41
(O_3) (Crutzen 1979). Because O_3 production in 42
rural areas tends to be limited by NO_x 43

44 concentrations, soil NO emissions may exert sig-
 45 nificant control over local O₃ levels (NRC 1992;
 46 Stohl et al. 1996). Plant damage from O₃ is
 47 responsible for more than \$2 billion y⁻¹ in crop
 48 losses in the U.S. (Delucchi et al. 1996), and there
 49 is increasing concern regarding violations of O₃ air
 50 quality standards in rural areas (Saylor et al.
 51 1998). Tropospheric O₃ is also recognized as a
 52 greenhouse gas, although its contribution to global
 53 warming is difficult to estimate due to its large
 54 regional and temporal variation (Prather et al.
 55 1995; Mickley et al. 2001). The eventual oxidation
 56 of NO_x gases to nitric acid (HNO₃) in the atmo-
 57 sphere contributes to downwind deposition of N
 58 and acidity (Crutzen 1979). Within the soil profile,
 59 the oxidation of NO may contribute to the pro-
 60 duction and subsequent leaching of nitrate (NO₃⁻)
 61 (Venterea and Rolston 2002; Venterea et al. 2004).
 62 The potent greenhouse gas nitrous oxide (N₂O)
 63 may be produced within the soil via NO reduction
 64 or via the reduction of NO₃⁻ arising from NO
 65 oxidation (Conrad 1995).

66 Measurements of NO emissions from agricul-
 67 tural soils have been reported across a range of
 68 edaphic, climatic, and agronomic conditions. One
 69 consistent finding has been the high variability of
 70 NO emissions, both spatially and temporally. For
 71 example, Veldkamp and Keller's (1997) review of
 72 23 field studies indicated that total growing-season
 73 NO emissions ranged widely, representing from
 74 <0.01 to >10% of fertilizer N inputs. This high
 75 variability, both within and across sites, combined
 76 with the large number of variables that may
 77 potentially influence NO emissions, has made the
 78 prediction of NO losses from agricultural systems
 79 a very uncertain endeavor. Another consistent
 80 finding has been that NO emissions tend to
 81 decrease with increasing soil water content. This
 82 trend has generally been attributed to (i) various
 83 microbiological responses to decreased oxygen
 84 (O₂) availability, and/or (ii) decreased gas diffu-
 85 sivity resulting from increased soil water content
 86 (e.g., Davidson 1993; Hutchinson and Davidson
 87 1993; McTaggart et al. 2002).

88 The aim of the current study was to examine the
 89 influence of soil moisture, and other physical and
 90 chemical factors, on the production of NO via
 91 abiotic reactions involving HNO₂. This source of
 92 NO (Figure 1), which has been recognized for
 93 several decades (Allison 1963; Stevenson et al.
 94 1970; Van Cleemput and Baert 1976; Venterea and

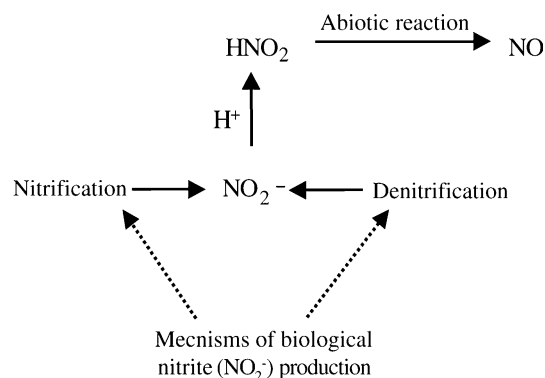


Figure 1. Illustration of the biotic/abiotic sequence of reactions leading to nitrous acid (HNO₂)-mediated nitric oxide (NO) production. The current study examines only the abiotic component.

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 NO₂⁻ via nitrification and/or denitrification.
 Nitrite is then protonated to form HNO₂, to an
 extent that depends on the pH, followed by the
 aqueous disproportionation of HNO₂ and other
 possible chemical reactions of HNO₂ with soil
 organic and/or mineral constituents leading to NO
 production. In the current study, we examined NO
 production in sterilized soils from eight agricul-
 tural fields in Minnesota, California, and Con-
 necticut in laboratory experiments following the
 addition of NO₂⁻ 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 pro-
 duction within and among soils.

Materials and methods

Soils and site information

Basic taxonomic, textural, and agronomic infor-
 mation 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 Sacra-
 mento valley. Soils from Minnesota (MN) and
 Connecticut (CT) were collected from tilled and
 non-tilled fields in long-term tillage management

Table 1. Properties of soils used in laboratory experiments.

| Series | California soils | | | | Minnesota soils | | Connecticut soils | |
|--|------------------|--------------|--------------|--------------|-----------------|--------------|-------------------|-----------|
| | 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.

142 experiments. The MN tillage experiment has been
 143 maintained since 1991 at the University of Min-
 144 nesota Agriculture Experiment Station in Rose-
 145 mount, MN (Hansmeyer et al. 1997). Samples for
 146 the current study were obtained from moldboard
 147 plowing and no till treatments within a continuous
 148 corn cropping system. The CT tillage experiment is
 149 located at the University of Connecticut Research
 150 Farm in Storrs, CT (Hooker et al. 2004). This
 151 study was initiated in 1972 and compares mold-
 152 board plowing with no tillage under continuous
 153 corn, with and without above-ground corn stover
 154 removal. Samples for the current study were
 155 obtained from the moldboard plowing and no till
 156 treatments, each with stover-return. For each CA
 157 soil, a single composite was generated by com-
 158 bining 10 individual samples taken at random
 159 locations from the upper 10 cm across fields
 160 measuring 1–3 ha. For each MN soil, a single
 161 composite was generated by combining six indi-
 162 vidual samples taken at random locations from the
 163 upper 10 cm within three replicate plots (each
 164 plot = 0.20 ha). For each CT soil, a single com-
 165 posite was generated by combining nine individual
 166 samples taken at random locations from the upper
 167 15 cm within three replicate plots (each plo-
 168 t = 0.026 ha). Soils were air dried, sieved to 2 mm,
 169 and stored in sealed plastic bags.

170 Portions of each composite were treated with
 171 3 Mrad of gamma radiation at Phoenix Memorial
 172 Laboratories, Ann Arbor, MI. Separate portions
 173 were preincubated and then autoclaved at 120 °C

for 30 min followed by an additional 48 h of
 174 incubation and a second autoclaving for 1 h. The
 175 gamma-irradiated soils were used for the majority
 176 of the experiments and for the data analysis,
 177 because this method of sterilization causes less
 178 severe alteration of chemical and physical prop-
 179 erties compared to autoclaving (Wolf and Skipper
 180 1994). Because there is some evidence that gamma
 181 radiation of soils may not completely inactivate
 182 extracellular enzymes (Cawse and Cornfield 1971),
 183 the autoclaved soils were tested in order to confirm
 184 that the general pattern of abiotic NO production
 185 observed in the irradiated soils occurred in the
 186 absence of extra-cellular enzyme activity. 187

Abiotic NO production

188
 189 Subsamples of each sterilized soil composite were
 190 amended with varying volumes of deionized water
 191 containing varying concentrations of potassium
 192 nitrite. For each soil, 4 or 5 levels of gravimetric
 193 water content (θ) were tested. At each θ level, 3
 194 levels of NO₂⁻ were added equivalent to approx-
 195 imately 0, 1, and 2 $\mu\text{g N g}^{-1}$ soil above the
 196 background (post-sterilization) soil NO₂⁻ con-
 197 centration, which varied from 0.03 to
 198 0.35 $\mu\text{g N g}^{-1}$. Solutions were mixed manually
 199 with soil for 1–3 min using a stainless steel spatula,
 200 and then immediately transferred to a glass
 201 (250 ml) or acrylic (450 ml) NO production mea-
 202 surement chamber (Venterea and Rolston 2000a).

203 Soil inside the reaction chamber was then contin-
 204 uously flushed with humidified air, which flowed
 205 to a chemiluminescent NO_x analyzer (Model 270B,
 206 Sievers Instruments, Boulder, CO, or Model
 207 LMA-3D, Unisearch Associates, Ontario, Canada¹)
 208 The net NO production rate (P_{net} , $\mu\text{g N g}^{-1} \text{h}^{-1}$)
 209 was calculated from:

$$P_{\text{net}} = \frac{q}{m} (\text{NO}_e - \text{NO}_i), \quad (1)$$

211 where q is the air flow rate ($0.03\text{--}0.06 \text{ m}^3 \text{ h}^{-1}$), m is
 212 the dry soil mass ($2\text{--}20 \text{ g}$), and NO_i and NO_e are the
 213 chamber influent and effluent concentrations
 214 ($\mu\text{g N m}^{-3}$), respectively. Valves installed on the
 215 flow lines allowed for rapid switching between
 216 measurement of NO_i and NO_e . The NO_e concen-
 217 tration vs. time data were output to a data acquisi-
 218 tion system for real-time viewing. Once each effluent
 219 signal stabilized (after $5\text{--}20 \text{ min}$), the NO_e value was
 220 recorded. Values of P_{net} were obtained at multiple
 221 inlet NO concentrations for each sample by blend-
 222 ing the chamber influent air with varying amounts of
 223 NO standard gas (balance N₂) using mass flowme-
 224 ters. The gross NO production rate (P_g) was then
 225 obtained from the y -intercept resulting from linear
 226 regression of P_{net} vs. NO_e by assuming first-order
 227 NO consumption kinetics as described by:

$$P_{\text{net}} = P_g - k_c \text{NO}_e, \quad (2)$$

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

238 Immediately following each P_{net} measurement,
 239 the soil was mixed with 2 N KCl solution adjusted
 240 to pH 8.0, extracted for 15 min on a reciprocating
 241 shaker, and centrifuged at 6000 rpm for 15 min
 242 (Stevens and Laughlin 1995). Soil:solution ratios
 243 of approximately 1:10 were used for the majority
 244 of extractions, except when low-level (ambient)
 245 NO₂⁻ concentrations were expected, in which
 246 cases higher ratios ($\sim 1:1$) were used. Resulting

247 supernatant was stored at 4 °C for 1–24 h, at
 248 which time the extract was analyzed for total
 249 NO₂⁻ + HNO₂ using the modified Griess–Ilosvay
 250 method (Keeney and Nelson 1982; Venterea and
 251 Rolston 2000a). Separate subsamples of each
 252 composite were mixed with an equal mass of 1 N
 253 KCl solution, stirred manually, and allowed to
 254 settle for 1 h before removal of supernatant for
 255 soil pH (pH_s) measurement. This method of pH_s
 256 measurement was found to be less variable than
 257 using 0.01 M CaCl₂ as the extracting solution
 258 (Venterea and Rolston 2000a). The above proce-
 259 dures were conducted at laboratory temperatures
 260 ($23\text{--}25 \text{ }^\circ\text{C}$). In addition, the procedures were re-
 261 peated using the Columbia loam from California
 262 in a temperature-controlled room at 20, 30, and
 263 $35 \text{ }^\circ\text{C}$ in order to examine the effect of temperature
 264 on NO production.

265 The HNO₂ concentration was calculated from
 266 the measured pH_s , total NO₂⁻ + HNO₂ concen-
 267 trations, and the acid dissociation constant for
 268 HNO₂ ($\text{p}K_a = 3.3$) (Van Cleemput and Samater
 269 1996) according to

$$[\text{HNO}_2] = \frac{[\text{H}^+][\text{NO}_2^- + \text{HNO}_2]_{\text{total}}}{[\text{H}^+] + 10^{-\text{p}K_a}}, \quad (3)$$

271 where the hydrogen ion activity [H^+] is estimated
 272 from 10^{-pH_s} , as previously described (Venterea
 273 and Rolston 2000a). As noted by Venterea and
 274 Rolston (2000a), the above expression for HNO₂
 275 concentration is operationally defined, since pH_s
 276 is itself operationally defined and can vary consid-
 277 erably depending on the type of solution and the
 278 solution–soil ratio used (Sumner 1994; Nilsson
 279 et al. 1995). For each soil at each θ , the rate
 280 coefficient (k_p) describing HNO₂-mediated NO
 281 production was obtained by linear regression of P_g
 282 vs. HNO₂ concentration, i.e.,

$$P_g = k_p [\text{HNO}_2] \quad (4)$$

284 according to (Venterea and Rolston 2000a, b,
 285 2002; Venterea et al. 2003). Strictly, k_p has units of
 286 ($\mu\text{g NO-N}$) ($\mu\text{g HNO}_2\text{-N}$)⁻¹ (h^{-1}), but here for
 287 the sake of simplicity we cancel the mass terms and
 288 express the units as h^{-1} . Since k_p is a derivative of
 289 HNO₂ and pH_s , it is also operationally defined.
 290 Values of k_p were calculated in the current study in
 291 order to examine how NO production per unit
 292 HNO₂ changed with respect to (i) soil water con-
 293 tent within each soil, (ii) temperature and soil

¹Mention 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.)

294 water content in the Columbia soil, and (iii) other
295 physical and chemical soil properties across soils.

296 If $\ln k_p$ is linearly related to the absolute tem-
297 perature, the apparent activation energy (E_a) for
298 the NO producing reaction at each θ level can be
299 calculated using the Arrhenius relation

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

301 where A_o represents the collision number, R is the
302 universal gas constant ($8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$), and
303 T is the absolute temperature (K^{-1}) (Pauling
304 1970). The term in parentheses represents the slope
305 of the regression line of $\ln k_p$ vs. K^{-1} , so that E_a
306 can be calculated from $E_a = -\text{slope} \cdot R$.

307 Other soil analysis

308 Particle size (texture), total carbon (C) total N,
309 cation exchange capacity (CEC), and extractable
310 manganese (Mn), iron (Fe), and copper (Cu) were
311 determined on irradiated composite samples. Total
312 C and N analyses were performed using combust-
313 tion with thermal conductivity detection (Carlo
314 Erba NA 1500) of finely milled samples. CEC was
315 determined using the ammonium acetate method
316 (Sumner and Miller 1996). Extractable Mn, Fe,
317 and Cu levels were selected for measurement based
318 on previous studies that have suggested these
319 metals may have a possible role in mediating abi-
320 otic NO production (Nelson 1982). Since the pri-
321 mary objective of the current study was to develop
322 potentially useful empirical relationships, the
323 diethylene-triamine-pentaacetic acid (DTPA)
324 extraction method, which is commonly used as an
325 index of plant-available trace metal concentra-
326 tions, was used for Mn, Fe, and Cu (Loeppert and
327 Inskeep 1996).

328 Modeling

329 Results of the current study were used in a previ-
330 ously developed model describing N oxide gas
331 transport and transformation following ammo-
332 nium (NH_4^+) fertilizer application (Venterea and
333 Rolston 2000c, 2002). The model was used to
334 simulate soil-to-air NO emissions resulting
335 from abiotic production of NO as a function of

336 water-filled pore space (WFPS), in a Yolo silt
337 loam. The model describes (i) both steps of nitrifi-
338 cation using Monod kinetics, (ii) pH dynamics in
339 response to nitrification, (iii) HNO_2 -mediated NO
340 production, (iv) NO consumption, and (v) diffu-
341 sive transport of dissolved and gaseous inorganic
342 N species. All parameters used in the current
343 simulations were identical to those used for the
344 Case 1 simulations in Venterea and Rolston
345 (2000c), except those listed in Table 2. Initial
346 conditions consisted of a fertilizer rate of 100 kg
347 $\text{NH}_4^+ \text{-N ha}^{-1}$ applied in a 5-cm thick band at
348 varying depths. The finite difference model used a
349 soil depth (z) grid of 1 mm over a total depth of
350 20 cm, and a time step of approximately 1.1 s. Soil
351 water content, temperature ($25 \text{ }^\circ\text{C}$), and dry bulk
352 density (1.2 g cm^{-3}) were assumed constant over
353 time and depth during each 20-day simulation.
354 While the assumption of fixed soil water content
355 and temperature for 20 days is certainly not real-
356 istic, these parameters were kept constant in each
357 simulation so that the effect of varying soil water
358 content could be examined more easily. Surface
359 NO flux was calculated at each time step using
360 Fick's equation and the gradient calculated from
361 the simulated NO concentration at the 1 mm
362 depth and the assumed atmospheric NO concen-
363 tration of 1 ppb. Total emissions over 20 days
364 were integrated by summing the fluxes calculated
365 at each time step. Further model details are given
366 in Venterea and Rolston (2000c).

Table 2. Key parameters used in model simulations.

| Parameter (units) | Value |
|--|---------------------|
| NO production rate coefficient (k_p) (h^{-1}) | $\exp(3.97-16.6)^a$ |
| NO consumption rate coefficient (k_c) ($\text{cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) | 16.2^b |
| NH_4^+ liquid-solid partitioning coefficient ($\text{cm}^3 \text{ g}^{-1}$) | 3.59^c |
| Initial soil pH (-) | 6.3 |
| pH buffering capacity ($\mu\text{g H}^+ \text{ g}^{-1} \text{ pH}^{-1}$) | 23.5^d |
| Inhibition factor, NO_2^- oxidation (-) | 6.5^e |

^aRelationship derived from current data.

^bMeasured 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.

^cMeasured data for Yolo silt loam (Venterea, unpublished data).

^dCalculated from total C, clay, and silt content using relationships in Curtin et al. (1996).

^eAssumed based on model-data comparisons in Venterea and Rolston (2000c).

367 **Results**368 *Water content effects*

369 In all soils tested, the gross NO production rate
 370 decreased with increasing θ following amendment
 371 with NO_2^- (Figure 2). At each θ level, NO pro-
 372 duction increased with increasing NO_2^- concen-
 373 tration over the range of approximately
 374 $0\text{--}2\ \mu\text{g N g}^{-1}$. The rate coefficient describing
 375 HNO_2 -mediated NO production (k_p) also de-
 376 creased with increasing θ in both gamma-irradiated
 377 and autoclaved soils (Figure 3). Natural logarithm
 378 (\ln)-transformed k_p values were negatively corre-
 379 lated with θ for each soil (Table 3). Autoclaved soils
 380 displayed higher rates of NO production at a given
 381 θ and HNO_2 level than the respective irradiated
 382 soils as reflected in the higher k_p values (Figure 3b).

383 *Differences among soils*

384 Within each group of soils, the highest NO pro-
 385 duction 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 $0.25\ \text{g H}_2\text{O g}^{-1}$.
 Because k_p values were log-normally distributed,
 single-factor regression analyses were performed
 using $\ln k_p$ vs. soil physical and chemical prop-
 erties. 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

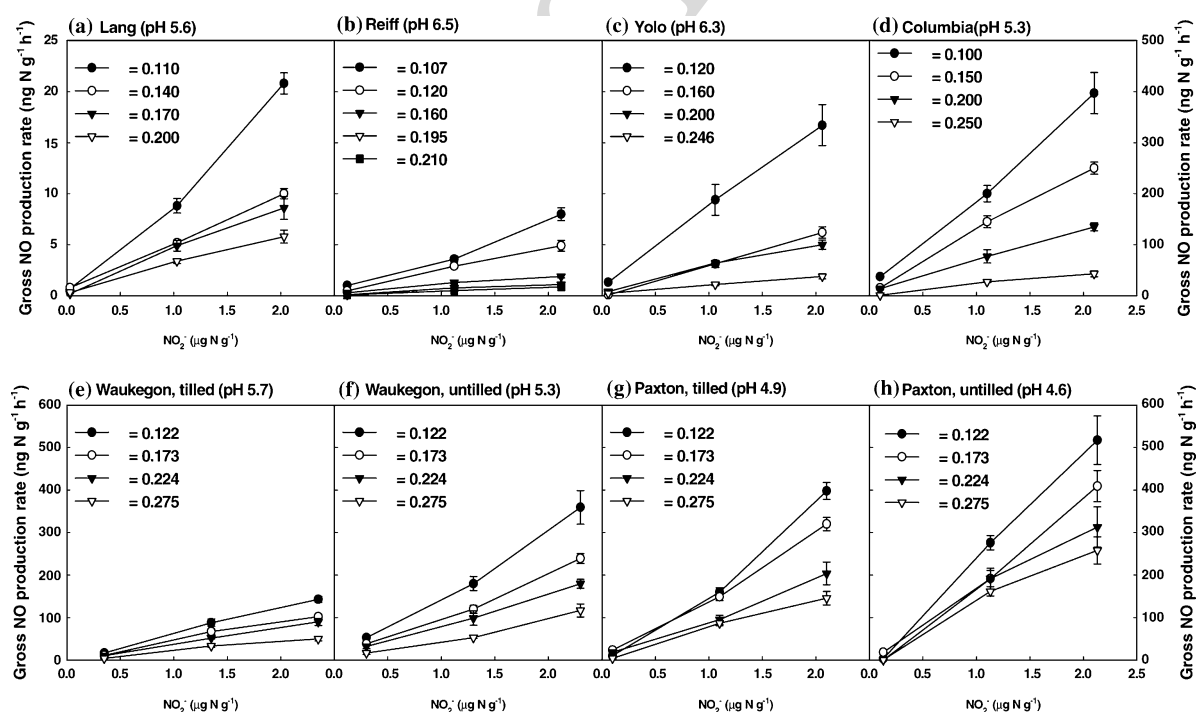


Figure 2. Gross NO production rate (P_g) at varying soil water content (θ) and soil nitrite (NO_2^-) concentration in gamma-irradiated soils sampled from agricultural fields in California (a–d), Minnesota (e, f), and Connecticut (g, h) (mean \pm standard error, $n = 2$). Note: In upper plates, left-hand vertical axis scale applies to (a–c), and right-hand vertical axis scale applies to (d).

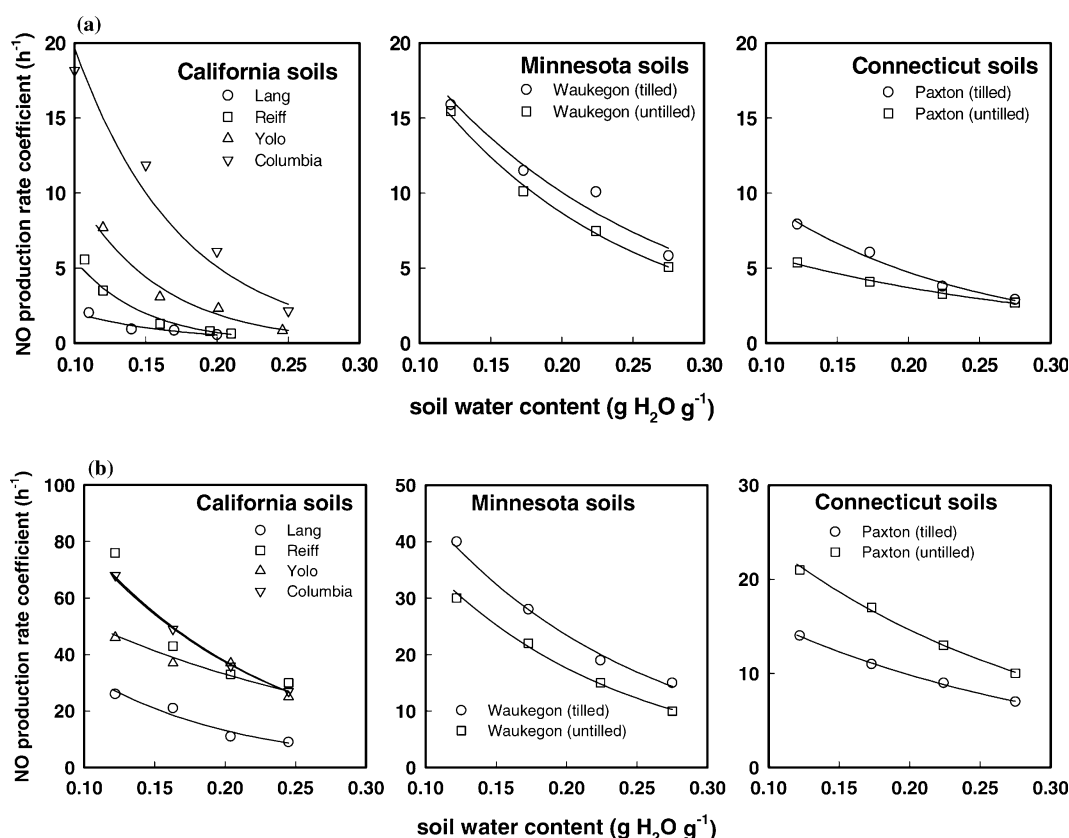


Figure 3. NO production rate coefficient (k_p) at varying soil water content (θ) in (a) gamma-irradiated soils and (b) autoclaved soils sampled from agricultural fields in California, Minnesota, and Connecticut. Regression lines for $\ln k_p$ vs. θ are shown. Further information regarding regression 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 |

^aCoefficient 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 2.

*Significant at the 0.05 probability level; **Significant at the 0.01 probability level; ***Significant at the 0.001 probability level.

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, clay, total C content, and the product $\theta \cdot \text{CEC}_{\text{cf}}$ 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

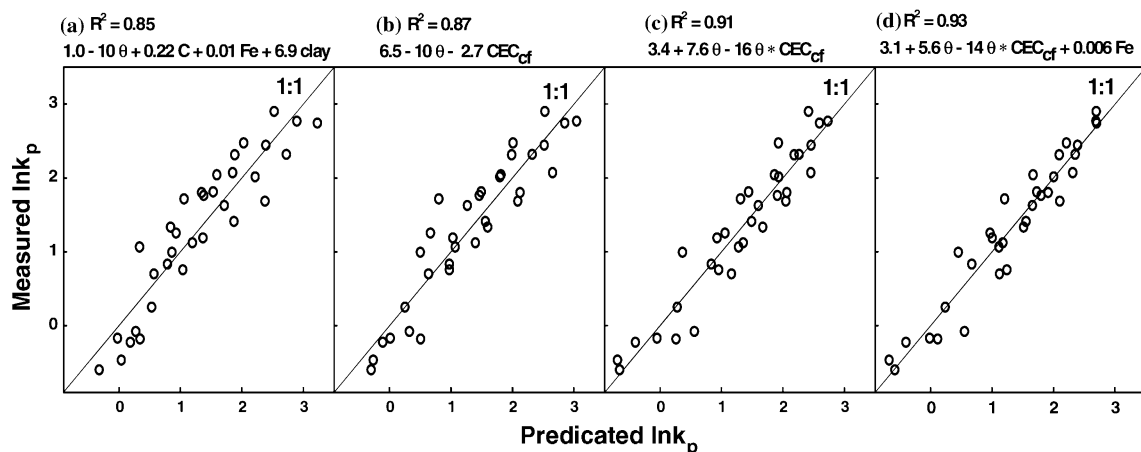


Figure 4. Results of multiple regression analysis describing \ln -transformed NO production rate coefficient (k_p) as function of different combinations of soil physical and chemical properties: gravimetric soil water content (θ , $\text{g H}_2\text{O g}^{-1}$), total C (%), DPTA-extractable iron concentration (Fe, $\mu\text{g g}^{-1}$), 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. $P < 0.001$, $n = 33$.

428 the E_a values at each level did not vary signifi-
 429 cantly ($P > 0.25$). Assuming that the Arrhenius
 430 relations in Figure 5 hold for the Columbia loam,
 431 calculations using Eqs. (4 and 5) indicate that at a
 432 soil NO_2^- concentration of $1 \mu\text{g N g}^{-1}$ with T
 433 varying over $20\text{--}35 \text{ }^\circ\text{C}$ and θ varying over 0.05--
 434 $0.20 \text{ g H}_2\text{O g}^{-1}$, abiotic NO production would be
 435 expected to vary by a factor of approximately 25,
 436 ranging from a lower limit of $33 \text{ ng N g}^{-1} \text{ h}^{-1}$ (at
 437 $T = 20 \text{ }^\circ\text{C}$, $\theta = 0.20$) to $810 \text{ ng N g}^{-1} \text{ h}^{-1}$ (at
 438 $T = 35 \text{ }^\circ\text{C}$, $\theta = 0.05$).

Table 4. Single-factor correlation results of $\ln k_p$ vs. soil physical and chemical factors at varying soil water content (θ , $\text{g H}_2\text{O g}^{-1}$).

| 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 |

^aPearson 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.

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 $1.4 \mu\text{g N g}^{-1}$ 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 (Figure 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

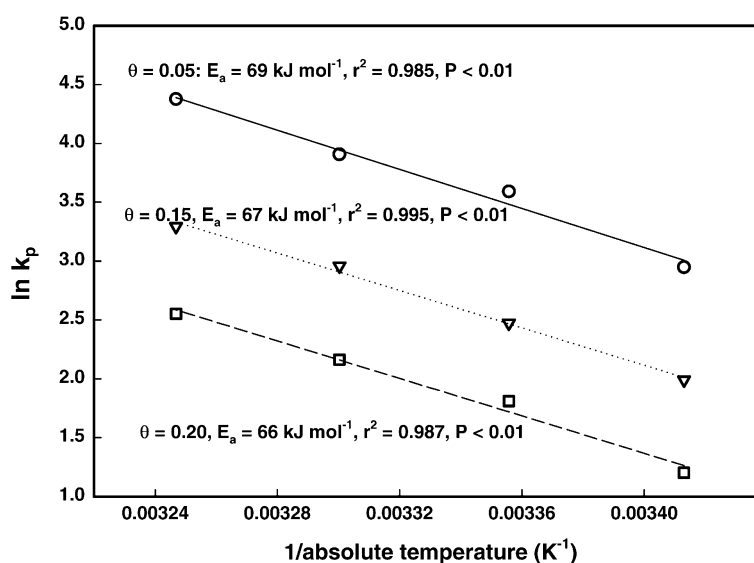


Figure 5. Arrhenius plots of ln-transformed NO production rate coefficient (k_p) vs. reciprocal of absolute temperature at gravimetric soil water content (θ) values of 0.05, 0.15, and 0.20 g H₂O g⁻¹ using Columbia loam. Activation energies (E_a) calculated using Eq. (5) are shown for each water content.

465 production is also highly sensitive to water con-
 466 tent. This particular effect, while generally consist-
 467 ent with the well-known ‘hole-in-the-pipe’ model
 468 of N trace gas emissions (Davidson and Verchot
 469 2000), has not previously been shown or consid-
 470 ered in interpreting data from field and laboratory
 471 studies. Most microbiological effects that have
 472 been examined are also expected to produce higher
 473 NO emissions with decreasing water content, at
 474 least to the point where low water content begins
 475 to limit nitrification rates (Davidson 1993). At
 476 higher water content, nitrification rates tend to be
 477 inhibited due to oxygen limitation, and presuma-
 478 bly nitrification-derived NO production is also
 479 diminished (Hutchinson et al. 1993; Bollmann and
 480 Conrad 1998). While denitrifying sources of NO
 481 may increase with water content, reductive
 482 microbial consumption of NO also increases, and
 483 gaseous diffusion of NO decreases resulting in
 484 greater residence times in the soil with increasing
 485 water content (Hutchinson and Davidson 1993).
 486 The net result of these biological and physical
 487 processes has generally been greatly reduced rates
 488 of NO emissions to the atmosphere as water-filled
 489 pore space increases above 50–60%.

490 While it is not possible to determine the relative
 491 importance of these various effects of water con-
 492 tent on NO emissions in a general sense, the cur-
 493 rent 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 H₂O g⁻¹.
 The kinetic data also indicate that the simulta-
 neous 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 NO₂⁻ accumu-
 lation (< 2 μ g N g⁻¹), can result in variations in
 NO emissions ranging from 0.05 to 11% of fertil-
 izer 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 pro-
 duction 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 NO₂⁻,
 such as anhydrous ammonia (Chalk et al. 1975;

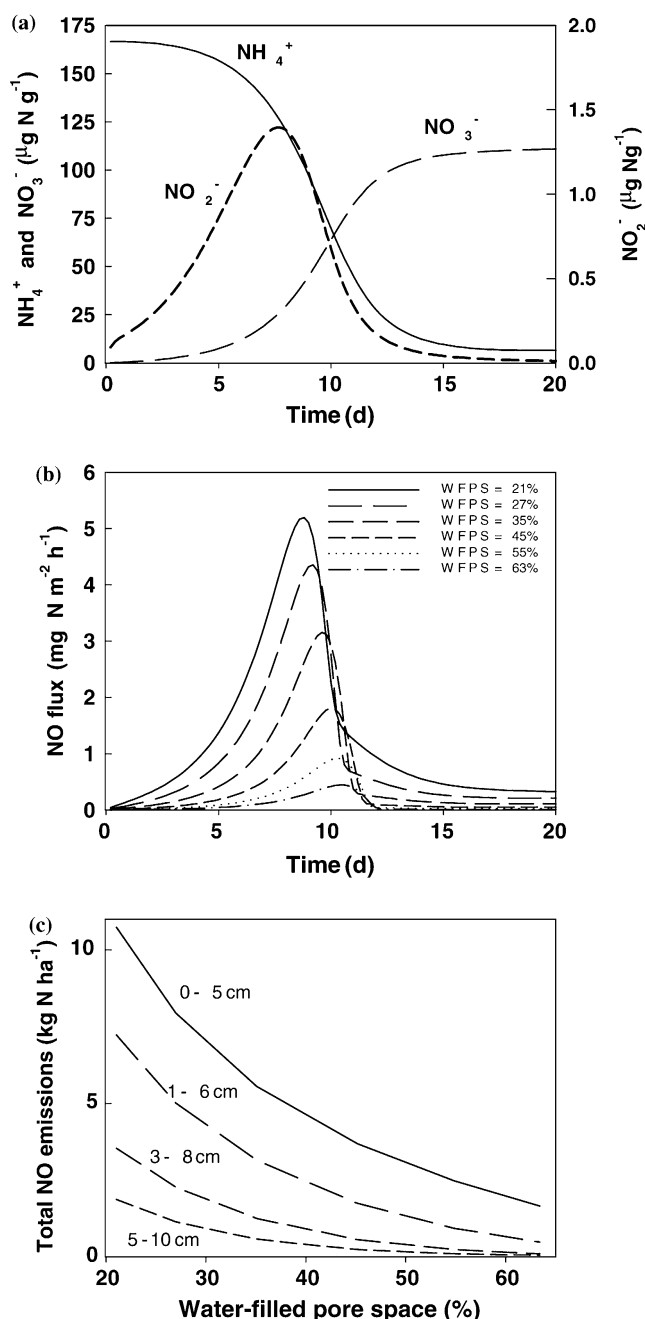


Figure 6. Simulated (a) inorganic N dynamics at center of 5-cm thick fertilizer band, (b) NO flux dynamics at varying water-filled pore space (WFPS) assuming 1–6 cm fertilizer application depth, and (c) total integrated NO emissions over 20 days as function of WFPS and varying application depths, following 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.

520 Venterea and Rolston 2000b) and urea
 521 (Christianson et al. 1979; Riley et al. 2001), the
 522 maintenance of moderate-to-high water contents
 523 during the first 6–12 days following fertilizer

application may greatly reduce NO emissions. In
 addition, management of soil pH, which is not
 frequently considered in this context, may also be
 effective in minimizing HNO_2 -mediated NO

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528 production. The overall cost-effectiveness of these
 529 practices is currently impossible to assess, since the
 530 impact of fertilizer-induced NO emissions on local
 531 O₃ formation, and its subsequent impacts on crop
 532 losses and air quality, has not been quantitatively
 533 assessed. Another implication of these data is that
 534 reduced tillage practices may have the unintended
 535 consequence of promoting NO losses due to
 536 reduced soil pH in the upper 10 cm of soil, which
 537 presumably results from reduced mixing of plant
 538 residues and NH₄⁺ fertilizers with underlying soil.
 539 It is not known if other factors such as differential
 540 NO consumption or NO₂⁻ dynamics in tilled vs.
 541 non-tilled soils may counteract this pH effect.

542 *Mechanisms*

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

559 For a given NO₂⁻ concentration on a per mass
 560 soil basis, as θ decreases, the bulk solution-phase
 561 NO₂⁻ concentration will increase in proportion to
 562 the decrease in θ . Thus, assuming well-mixed
 563 conditions, the mass of NO₂⁻ per mass soil that is
 564 in proximity to acidic surfaces will increase with
 565 decreasing θ . This would be expected to promote
 566 greater formation of HNO₂ via



568 and subsequently greater NO production per mass
 569 soil due to the aqueous-phase disproportionation
 570 of HNO₂ (Van Cleemput and Baert 1976) given
 571 by



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 solu-
 tion 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 vol-
 ume 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 deter-
 mining bulk soil CEC tends to overestimate the
 actual CEC for soils with pH < 7 (Sumner and
 Miller 1996). Thus, the strong and highly signifi-
 cant 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 sur-
 face 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 con-
 centration of NO₂⁻ in bulk solution, a higher
 CEC_{cf} would seem to promote less interaction of
 NO₂⁻ with surficial sources of acidity resulting in

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623 less HNO₂ formation and less NO production at a
624 given level of θ , NO₂⁻, and pH.

625 The occurrence of the product $\theta \cdot \text{CEC}_{\text{cf}}$ as a
626 highly significant ($P < 0.0001$) factor in multiple
627 regression models (Figure 4c, d) suggests an
628 interaction between θ and CEC_{cf} in regulating
629 $\ln k_p$. Consistent with this finding, single-factor
630 regression analyses (Table 4) indicate that the
631 slope of $\ln k_p$ vs. CEC_{cf} is increasingly negative
632 with increasing θ . While a mechanistic explanation
633 of this effect is not immediately clear, it appears
634 that the inhibition of HNO₂ formation by
635 increasing surface charge density is stronger at
636 higher water content.

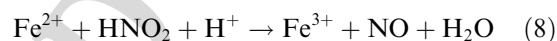
637 The current findings suggest that our previ-
638 ously derived method (Venterea and Rolston
639 2000a) of calculating soil HNO₂ concentration
640 [Eq. (3)] is overly simplistic from a mechanistic
641 standpoint. This formulation is based on acid
642 dissociation as would occur in a well-mixed
643 aqueous solution, and therefore does not account
644 for the pore-scale spatial distribution of H⁺
645 sources that is expected in soil. This is particu-
646 larly true because of our use of 1 M KCl for
647 determining soil pH, which is more efficient than
648 other extractants in accounting for both
649 exchangeable (surfacial) and active (solution-
650 phase) acidity (McBride 1994). However, while
651 this index of HNO₂ may not accurately represent
652 bulk solution concentration, it may be a decent
653 measure of the potential maximum HNO₂ con-
654 centration deriving from all sources of acidity
655 that is available for participating in the reaction
656 shown in Eq. (7). Thus, while Eqs. (3 and 4) may
657 imply that solution-phase HNO₂ concentration is
658 the single factor controlling the NO production
659 rate, and that k_p is simply a constant of pro-
660 portionality, the current findings suggest that
661 other factors including at least water content, clay
662 content, and surface charge density, are embed-
663 ded within k_p and serve to regulate the active
664 amount of HNO₂ that is available for producing
665 NO.

666 The magnitude of the activation energy
667 obtained here ($\sim 67 \text{ kJ mol}^{-1}$, Figure 5) provides
668 further support for a surface-mediated mechanism,
669 since this value is within the range expected for
670 surface-mediated processes (Sparks 2003). The
671 apparent independence of the activation energy
672 from soil water content further implies that the

673 fundamental nature of the reaction is not altered
674 with water content.

675 The positive correlations between $\ln k_p$ and
676 total C and DTPA-Fe in both simple (Table 4)
677 and multiple regression models (Figure 4a, d)
678 imply that there may be additional sources of NO
679 other than that indicated by Eq. (7), and therefore
680 that additional factors may be embedded within
681 the k_p term in Eq. (4). According to Stevenson
682 (1994), NO can be formed directly by the reaction
683 of HNO₂ with enolic functional groups of soil
684 organic matter, although evidence for this mech-
685 anism is not cited by Stevenson (1994). Soil
686 organic matter also contributes to surficial acidity,
687 and therefore total C may in part be correlated
688 with k_p for reasons discussed above.

689 The production of NO via the reduction of
690 HNO₂ by ferrous iron in soils according to



692 was proposed by Wullstein and Gilmour (1966).
693 Nelson and Bremner (1970) subsequently raised
694 doubts about the feasibility of this reaction
695 occurring in well-drained soils. Whether sufficient
696 quantities of Fe²⁺ to promote Eq. (8) could exist
697 in previously air-dried, sterile soils under aerobic
698 conditions is not known. The measure of Fe
699 availability used here (DPTA-extractable) is
700 known to correlate mainly with non-crystalline
701 'active' iron oxide minerals with high surface area,
702 but also, at lower pH, with organically bound Fe
703 (including possibly Fe²⁺) (Loeppert and Inskeep
704 1996). Thus, whether the correlations between k_p
705 and DTPA-extractable Fe found here indicate the
706 role of Eq. (8), or instead the role of amorphous
707 Fe as an additional source of surficial acidity
708 (McBride 1994), or perhaps indicate a correlation
709 with certain types of surface-active organic C, are
710 questions for further study. In the current study,
711 we found no significant correlation between
712 DTPA-extractable Fe and total organic C
713 ($P = 0.32$, $r^2 = 0.16$).

714 The main effect of soil water content shown
715 here, since it relies upon a source of NO₂⁻, will
716 also be subject to the constraints imposed by water
717 content on nitrification rates and possibly other
718 microbiological processes. More specifically, it is
719 the relative activity of the NH₄⁺ - and NO₂⁻-
720 oxidizing nitrifiers which controls the accumula-
721 tion NO₂⁻ (Morrill and Dawson 1967; Venterea

722 and Rolston 2000c). Therefore, the differential
723 effect of water content on this pair of biological
724 processes will greatly influence how the water
725 content effect on the abiotic component is actually
726 expressed in a live soil. There is no information
727 currently available to our knowledge regarding
728 water content effects on NO_2^- accumulation in
729 fertilized soils.

730 Conclusions

731 Our findings provide support for a mechanism by
732 which soil water content can affect the production
733 of NO that involves a strictly chemical process,
734 apart from previously demonstrated effects on
735 microbiological and physical processes. The vari-
736 ation in NO emissions as a consequence of this
737 effect appears to be significant and comparable to
738 that observed in many studies. The data also seem
739 to be consistent in supporting a mechanism of
740 abiotic production that is primarily surface medi-
741 ated, and therefore controlled not only by water
742 content but also by other properties including the
743 content of clay, organic matter, Fe, and the sur-
744 face charge density. Thus, another implication of
745 these findings is that Eqs. (3 and 4) are an over-
746 simplification of the abiotic processes regulating
747 gross NO production on a mechanistic level.
748 Nonetheless, for modeling purposes, the use of
749 Eq. (4) – with k_p modified using the relationships
750 obtained here (Table 3, Figure 4, Eq. (5)) – may in
751 fact be very efficient. Future comparisons of this
752 modeling approach to actual data, including field
753 emissions data, will provide one test of the use-
754 fulness of the relationships developed. An addi-
755 tional challenge of improving mechanistic models
756 of NO dynamics in soils will be to incorporate the
757 kinetics of abiotic production with those of
758 microbial sources (Conrad 1995; Beaumont et al.
759 2002).

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