

# Temperature Sensitivity of Nitrogen Dynamics of Agricultural Soils of the United States

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## Abstract

Soil temperature controls gaseous nitrogen losses through nitrous oxide (N<sub>2</sub>O) and ammonia (NH<sub>3</sub>) fluxes. Eight surface soils from agricultural fields across the United States were incubated at 10°C, 20°C, and 30°C, and N<sub>2</sub>O and NH<sub>3</sub> flux were measured twice a week for 91 and 47 d, respectively. Changes in cumulative N<sub>2</sub>O and NH<sub>3</sub> flux and net N mineralization at three temperatures were fitted to calculate Q<sub>10</sub> using the Arrhenius equation. For the majority of soils, Q<sub>10</sub> values for the N<sub>2</sub>O loss ranged between 0.23 and 2.14, except for Blackville, North Carolina (11.4) and Jackson, Tennessee (10.1). For NH<sub>3</sub> flux, Q<sub>10</sub> values ranged from 0.63 (Frenchville, Maine) to 1.24 (North Bend, Nebraska). Net soil N mineralization-Q<sub>10</sub> ranged from 0.96 to 1.00. Distribution of soil organic carbon and total soil N can explain the variability of Q<sub>10</sub> for N<sub>2</sub>O loss. Understanding the Q<sub>10</sub> variability of soil N dynamics will help us to predict the N loss.

## Keywords

Arrhenius Equation, Soil Organic Carbon, Inorganic Nitrogen, Gaseous Losses of Nitrogen

## 1. Introduction

Gaseous losses of nitrogen (N), nitrous oxide (N<sub>2</sub>O) denitrification and ammonia (NH<sub>3</sub>) volatilization, reduce fertilizer-N use efficiency and may cause environmental degradation [1]. Global estimates suggest approximate N losses of

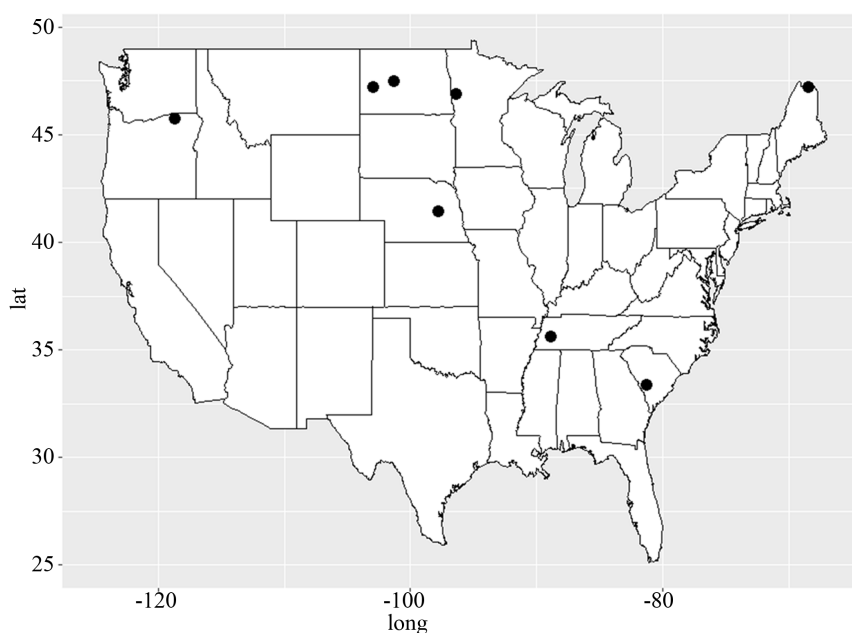
0.5% - 2% and 10% - 18% of initial N content through denitrification and volatilization respectively [2] [3]. Lack of studies regarding the temperature sensitivity of gaseous losses of N makes it difficult to model how changing spatial variability of crop, soil, and water management practices will impact the environment [4].

Soil temperature has significant control over N mineralization [5], denitrification [6], and volatilization [7]. Temperature sensitivity of the biological processes is generally expressed as the function of the increase in metabolic rate with 10°C rise in temperature or  $Q_{10}$ . For most modeling approaches,  $Q_{10}$  value was assumed to be close to 2, irrespective of soil type, climate and management practices [6] [8]. However, researchers reported a wide range of  $Q_{10}$  values ranging from 1 to 17.1 for denitrification [9], 1.4 to 5.0 for volatilization [10], and 1.67 to 2.43 for soil N mineralization [11].

A laboratory incubation study was conducted to determine the  $Q_{10}$  value of  $N_2O$  and  $NH_3$  flux, volatilization and N mineralization for eight soil samples collected across agricultural systems of the United States. If  $Q_{10}$  value is not affected by climate, soil type, or cropping system, measurements of  $Q_{10}$  will be equal to 2 regardless of soil evaluated. To test this hypothesis, we measured cumulative  $N_2O$  and  $NH_3$  flux and net N mineralization with incubation temperature, and temperature sensitivity or  $Q_{10}$  of  $N_2O$  and  $NH_3$  flux and net N mineralization at 10°C, 20°C, and 30°C. We then calculated the temperature sensitivity, or  $Q_{10}$  of  $N_2O$  and  $NH_3$  flux and net N mineralization for these agricultural soils.

## 2. Materials and Methods

Surface soil samples of 0 - 15 cm depth were collected from eight agricultural fields across the United States (Figure 1, Table 1). Soil samples were air-dried



**Figure 1.** Site locations for surface soil samples used to measure the temperature sensitivity of nitrogen loss.

**Table 1.** Site description, crop rotation, tillage management, basic soil properties, and annual average weather data of collected soils used for the incubation study.

State	Site	Location	Crop rotation	Tillage	Soil Series/texture	pH	EC (ds·m <sup>-1</sup> )	Soil organic carbon (g·kg <sup>-1</sup> )	Total Nitrogen (g·kg <sup>-1</sup> )	Inorganic Nitrogen* (mg·kg <sup>-1</sup> )	Field Capacity (g·g <sup>-1</sup> )	High Temp. † (°C)	Low Temp. † (°C)	Precipitation† (mm)
Maine	Frenchville	N 47.2161028, W -68.412227	Potato-grain-clover	Conventional	Plaisted gravelly loam	5.8	0.48	20	2.10	31.9	0.260	8.3	-1.1	850
Tennessee	Jackson	N 35.6230, W -88.8465	Continuous Cotton	No-tillage	Lexington silt loam	5.4	0.32	10	1.40	47.8	0.261	21.6	9.4	1375
South Carolina	Blackville	N 33.346539, W -81.297283	Continuous Corn	Strip-tillage	Duplin sandy loam	5.6	0.09	5.0	0.60	14.8	0.053	25.6	11	1198
Minnesota	Downer	N 46.8655, W -96.396806	Sugarbeet- Corn	Conventional	Lamoure silt loam	8.1	0.16	15.5	1.60	14.1	0.118	11.6	0	573
North Dakota	Bismarck	N 47.4630, W -101.2772	Spring Wheat-Soybean	No-tillage	Wilton silt loam	7.3	0.17	21.7	2.30	32.6	0.265	12.8	-1	453
North Dakota	Dickinson	N 47.19314, W -102.89661	Continuous Wheat	No-tillage	Vebar-Parshall fine sandy loam	5.2	0.14	17.0	1.70	16.9	0.239	12.8	-1	400
Nebraska	North Bend	N41.429308, W -97.794056	Corn-soybean	No-tillage	Nora silty clay loam	6.7	0.10	15.4	1.80	23.3	0.120	16.1	3.9	763
Oregon	Pendleton	N 45.718439, W -118.626883	Fallow-Winter Wheat	No-tillage	Walla Walla silt loam	6.0	0.40	12.0	1.20	29.8	0.291	17.2	5.0	322

\*Inorganic nitrogen-ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) concentrations; †Annual average.

and grounded to pass through 2 mm sieve. Soil pH and electrical conductivity were measured of 1:2.5 soil slurry with Oakton PC700 pH and EC meter. Soil organic carbon and total N were determined by automated dry combustion method [12]. Soil inorganic N concentration was measured by extracting soils with 2 M KCl and determining NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations using Timberline Ammonia (TL-2800) analyzer (Boulder, CO). Field capacity (at 0.33 bar) was determined using the pressure plate apparatus as described by [13].

Soil samples were incubated at 10°C, 20°C and 30°C using an incubation chamber. For incubation, 30 g soils moistened at field capacity level were placed in a 1-L clear jar (Table 1). One granule of urea (~40 mg) was weighed and added on the soil surface. Water loss was compensated by adding water based on the difference in jar weight. The cap of jar was fitted with the gas sampling port (butyl rubber septum) to sample headspace air and a metal wire attached to the cap to hold a 50 mL clear plastic beaker filled with 15 mL of 0.5 M phosphoric acid to trap NH<sub>3</sub> emission from soils. A total of 36 jars (8 sites × 4 replication + 4 blanks) were incubated for 91 days at each temperature. Headspace air was sampled approximately on days 1, 3, 6, 9, 12, 16, 19, 23, 26, 30, 34, 37, 40, 44, 47, 50,

56, 63, 70, 77, 84, and 91 for N<sub>2</sub>O flux and until day 47 for NH<sub>3</sub> flux. On each observation day, first headspace air sample was collected using a 10 mL syringe, followed by the removal of the acid trap, then the jar was aerated for half an hour, and soil moisture was readjusted to field capacity and then jars were capped and returned to the incubator.

The N<sub>2</sub>O concentration of headspace air samples was determined using a Shimadzu GC-2014 (Shimadzu Scientific Instruments Inc., Houston, TX) fitted with <sup>63</sup>Ni-electron capture detector. The GC oven was operated at 80°C and ECD was operated at 325°C, and N<sub>2</sub> carrier gas was supplied at 20 PSI. Instrument was calibrated using analytical N<sub>2</sub>O standards of: 0, 1, 5, 50, 100, 500, and 1000 μmole·ml<sup>-1</sup>. Compound peak was recorded and analyzed with Lab Solutions software (LabSolutions, Atlanta, Georgia). The N<sub>2</sub>O concentration was converted to mass unit using ideal gas equations and expresses as micrograms of N<sub>2</sub>O produced between sampling days per kg of soil [14] [15]. Soil-emitted NH<sub>3</sub> was trapped and replaced with fresh phosphoric acid solution at the same intervals as N<sub>2</sub>O flux measured. The collected acid solution was extracted with 25 mL of 2 M KCl with half an hour shaking the mixture in reciprocal shaker [14]. The extracts were then analyzed for NH<sub>4</sub><sup>+</sup> concentrations using an automated ammonia analyzer (TL 2800, Timberline Instruments, Boulder, CO). The amount of volatilization during each incubation interval was expressed in the form of microgram NH<sub>3</sub> per gram soil. Cumulative NH<sub>3</sub>-N loss (mg NH<sub>3</sub>-N kg soil) during the entire incubation was computed from the summation of NH<sub>3</sub> emission during all sampling periods.

After 91 days of incubation, soil samples from each jar were analyzed for inorganic N concentration (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) for each incubation temperature. Percent of net N mineralized during incubation was calculated using the following equation.

$$\text{Net N mineralization\%} = \frac{(\text{Initial soil-N} + \text{Urea-N}) - \text{Final soil-N}}{\text{Initial soil-N} + \text{urea-N}} \times 100$$

Urea-N was calculated by multiplying 0.46 with the weight of urea granule. The effect of temperature on of N<sub>2</sub>O and NH<sub>3</sub> flux, and net N mineralization% was evaluated by determination of the parameter  $E_a$  in the logarithmic form of the Arrhenius equation:

$$\ln(k) = \ln(A) - E_a/RT$$

where  $k$  is the rate of N<sub>2</sub>O and NH<sub>3</sub> flux,  $A$  is the preexponential constant,  $E_a$  is the activation energy (kJ·mol<sup>-1</sup>),  $R$  is the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>) and  $T$  is the absolute temperature in Kelvin (K). The activation energy was calculated from the slope ( $-E_a/R$ ) of the linear regression in the plot of log of N<sub>2</sub>O and NH<sub>3</sub> flux rate vs. the inverse incubation temperature, Q<sub>10</sub> value was calculated as

$$Q_{10} = \exp\left[\left(E_a/R\right)\left(1/(T_1 + 10) - 1/T_1\right)\right]$$

$$T_1 = 293^\circ\text{C equivalent to } 20^\circ\text{C}$$

Cumulative N<sub>2</sub>O and NH<sub>3</sub> flux at each incubation temperature, net N miner-

alization percentage and  $Q_{10}$  values were compared for different sites using the completely randomized design (CRD) with a mean separation at 95% significance level using SAS 9.4. For each site, incubation temperature effect on cumulative  $N_2O$  and  $NH_3$  flux were also determined using CRD with a mean separation at 95% significance level. Correlation coefficient and regression analyses were conducted to determine the relationship between soil properties and  $Q_{10}$  values using SAS 9.4.

### 3. Results and Discussion

Cumulative  $N_2O$  flux increased with temperature for most soils except those collected from Frenchville, Bismarck, and Pendleton (**Table 2**). At 10°C, soils from Pendleton had the highest cumulative flux, but statistically similar to Frenchville and Bismarck; whereas, the lowest value was observed for soils from Blackville. At 20°C, Pendleton soils had the highest cumulative  $N_2O$  flux, similar to Frenchville, and the lowest value was observed for soils from North Bend. At 30°C, Frenchville had the highest cumulative flux, significantly higher than rest, and the lowest value was found for soils from Dickinson. Temperature sensitivity,  $Q_{10}$  values of cumulative  $N_2O$  flux ranged between 0.23 at Bismarck, and 11.4 at Blackville. Soils from Jackson, TN had  $Q_{10}$  value of 10.1, statistically similar to Blackville. The rest of the six sites had similar  $Q_{10}$  values ranging between 0.23 - 2.14. Blackville and Jackson had lower soil organic C than other sites; low soil organic C or high recalcitrance of substrates should generally be more sensitive to temperature changes than that of more labile substrates, which could, in turn, increase the  $Q_{10}$  value. Researchers have also found that additions of C and N substrates reduced  $Q_{10}$  of  $N_2O$  due to increased soil microbial C and N use efficiency [15].

Increasing temperature reduced cumulative  $NH_3$  flux except for Downer, and North Bend, sites (**Table 2**). Soils from Blackville had the highest and Frenchville, had the lowest cumulative  $NH_3$  flux at all three temperatures. Soils from North Bend had the highest  $Q_{10}$  value for  $NH_3$ , but similar to Downer, and Pendleton. For the rest of the sites,  $Q_{10}$  value for  $NH_3$  ranged from 0.63 to 0.70. Most researchers observed an increase in volatilization loss with temperature [7] [16]. Researchers [7] reported a two-fold increase when temperature increased from 5°C to 25°C but a threefold when temperature increased from 25°C to 45°C. They concluded that greatly enhanced  $NH_3$  volatilization at 45°C compared with 25°C was related to the inhibition of nitrification at high temperature, which increased the supply of ammoniacal N for  $NH_3$  volatilization for a prolonged time. Our maximum incubation temperature of (30°C) was comparatively lower than the threshold for the inhibition of nitrification. Further, researcher [17] found that high temperatures (32°C) increased the initial rates of  $NH_3$ -N loss and they were proportionally reduced at later stages; on the contrary, the lowest temperature (12°C) resulted in the lowest initial  $NH_3$ -N loss rate but became highest for the last 76 hours.

**Table 2.** Control of incubation temperature on mean (standard deviation) of cumulative denitrification, volatilization and nitrogen mineralized from soils collected across agroecosystems of the United States.

State	Site	Incubation temperature			Q <sub>10</sub>
		10°C	20°C	30°C	
<b>Cumulative N<sub>2</sub>O-N flux (mg·kg<sup>-1</sup> soil)</b>					
Maine	Frenchville	12.9 <sup>Aa*</sup> (10.6)	13.2 <sup>Aa</sup> (2.94)	19.1 <sup>Aa</sup> (2.38)	1.40 <sup>C</sup> (0.39)
Tennessee	Jackson	0.16 <sup>Bc</sup> (0.14)	0.89 <sup>Cb</sup> (0.10)	1.39 <sup>Ca</sup> (0.49)	10.1 <sup>AB</sup> (14.9)
South Carolina	Blackville	0.07 <sup>Bb</sup> (0.05)	4.87 <sup>Bc</sup> (2.45)	5.39 <sup>Ba</sup> (1.88)	11.4 <sup>A</sup> (5.66)
Minnesota	Downer	2.39 <sup>Ba</sup> (2.22)	5.55 <sup>Ba</sup> (2.75)	4.63 <sup>Ba</sup> (2.70)	2.14 <sup>BC</sup> (1.65)
North Dakota	Bismarck	20.9 <sup>Aa</sup> (2.60)	1.11 <sup>Bc</sup> (0.37)	1.25 <sup>Cb</sup> (0.34)	0.23 <sup>C</sup> (0.05)
North Dakota	Dickinson	0.36 <sup>Bb</sup> (0.08)	0.77 <sup>Cab</sup> (0.30)	0.99 <sup>Ca</sup> (0.37)	1.65 <sup>C</sup> (0.23)
Nebraska	North Bend	0.58 <sup>Bb</sup> (0.10)	0.62 <sup>Cb</sup> (0.28)	1.50 <sup>Ca</sup> (0.39)	1.63 <sup>C</sup> (0.19)
Oregon	Pendleton	27.8 <sup>Aa</sup> (29.7)	15.7 <sup>Aa</sup> (7.65)	3.04 <sup>Bc</sup> (1.95)	0.53 <sup>C</sup> (0.42)
LSD (0.05)		16.3	4.64	2.35	8.25
<b>Cumulative NH<sub>3</sub>-N flux (µg·g<sup>-1</sup> soil)</b>					
Maine	Frenchville	14.7 <sup>Da</sup> (2.39)	9.40 <sup>Eab</sup> (5.63)	6.62 <sup>Cb</sup> (5.21)	0.63 <sup>B</sup> (0.25)
Tennessee	Jackson	51.1 <sup>Bab</sup> (24.7)	66.8 <sup>ABa</sup> (36.7)	19.6 <sup>Cb</sup> (6.12)	0.66 <sup>B</sup> (0.23)
South Carolina	Blackville	242 <sup>Aa</sup> (54.2)	85.2 <sup>Ab</sup> (17.8)	119 <sup>Ab</sup> (11.5)	0.70 <sup>B</sup> (0.09)
Minnesota	Downer	48.1 <sup>Bc</sup> (11.3)	46.7 <sup>Bc</sup> (4.25)	41.7 <sup>Ba</sup> (20.5)	0.91 <sup>AB</sup> (0.20)
North Dakota	Bismarck	29.3 <sup>BCDa</sup> (7.39)	27.4 <sup>CDEa</sup> (5.82)	12.9 <sup>Cb</sup> (4.75)	0.66 <sup>B</sup> (0.14)
North Dakota	Dickinson	16.1 <sup>CDa</sup> (3.17)	12.7 <sup>DEab</sup> (6.53)	7.39 <sup>Cb</sup> (2.72)	0.66 <sup>B</sup> (0.07)
Nebraska	North Bend	28.6 <sup>BCDa</sup> (5.51)	33.1 <sup>CDa</sup> (13.4)	43.1 <sup>Ba</sup> (12.1)	1.24 <sup>A</sup> (0.22)
Oregon	Pendleton	25.0 <sup>BCDab</sup> (8.02)	44.0 <sup>Bc</sup> (10.7)	19.8 <sup>Cb</sup> (16.3)	0.90 <sup>AB</sup> (0.53)
LSD (0.05)		32.0	23.5	16.8	0.37
<b>% Nitrogen mineralized</b>					
Maine	Frenchville	78.7 <sup>BCDa</sup> (2.65)	45.4 <sup>Bc</sup> (8.35)	79.6 <sup>Ba</sup> (1.13)	1.00 <sup>A</sup> (0.01)
Tennessee	Jackson	77.1 <sup>DEa</sup> (2.24)	28.2 <sup>EFc</sup> (8.12)	67.7 <sup>Db</sup> (2.02)	0.97 <sup>CDE</sup> (0.01)
South Carolina	Blackville	95.8 <sup>Aa</sup> (0.54)	86.9 <sup>Ab</sup> (8.91)	91.8 <sup>Aab</sup> (1.23)	0.99 <sup>AB</sup> (0.01)
Minnesota	Downer	78.7 <sup>BCDa</sup> (1.94)	44.9 <sup>CDc</sup> (4.77)	72.8 <sup>Cb</sup> (2.47)	0.98 <sup>BC</sup> (0.01)
North Dakota	Bismarck	80.7 <sup>Bc</sup> (1.18)	34.4 <sup>DEc</sup> (8.53)	67.7 <sup>Db</sup> (2.11)	0.96 <sup>E</sup> (0.01)
North Dakota	Dickinson	75.2 <sup>Ea</sup> (1.02)	23.3 <sup>Fc</sup> (6.14)	62.7 <sup>Eb</sup> (2.14)	0.96 <sup>E</sup> (0.01)
Nebraska	North Bend	78.2 <sup>CDa</sup> (1.77)	34.1 <sup>DEc</sup> (3.40)	68.2 <sup>Db</sup> (1.60)	0.97 <sup>DE</sup> (0.01)
Oregon	Pendleton	81.0 <sup>Ba</sup> (2.42)	56.1 <sup>Bc</sup> (8.46)	72.2 <sup>Cb</sup> (2.53)	0.97 <sup>CD</sup> (0.01)
LSD (0.05)		2.70	10.7	2.87	0.01

\*Different capital letters indicate significant differences among sites of the same incubation temperature and different small letters indicate significant differences among temperatures for the same site.

For all sites, net N mineralization was significantly lower at 20°C than 10°C, and 30°C, this might be caused due to greater N immobilization at 20°C. At all three temperatures, soils from Blackville had the highest, and Dickinson had the

lowest N mineralization. Temperature sensitivity or  $Q_{10}$  of net N mineralization varied from 0.96 to 1.00. Soils from Frenchville had the highest  $Q_{10}$  and soils from Bismarck and Dickinson had the lowest  $Q_{10}$ . Other researchers found that  $Q_{10}$  values of N mineralization varied from 1.03 to 11.89 with an average of 2.21 [11].

The Pearson relationship between soil organic C and total N showed a significant negative relationship with  $Q_{10}$  value of  $N_2O$  ( $-0.82$  and  $-0.72$ , respectively), but did not show any relationship with volatilization or N mineralization. Linear regression relationships showed that SOC and TN explained the 68 and 52 percent of the variation in  $Q_{10}$  of  $N_2O$ . With the rise in each unit ( $g \cdot kg^{-1}$ ) of SOC and total N,  $Q_{10}$  value of  $N_2O$  declines by 0.67 and 6.0, respectively. Similarly, other researchers [15] also observed a significant inhibition of pulse  $N_2O$  emissions following C addition, they hypothesized that C addition facilitates the microbial growth and in turn accelerates N immobilization rate.

#### 4. Conclusion

This study clearly indicates a wide variation in  $Q_{10}$  for  $N_2O$  (0.23 to 11.4), and small variations in  $Q_{10}$  for  $NH_3$  (0.63 to 1.24) and for the net N mineralization (0.96 to 1.00). Distribution of soil organic C can explain the spatial variation of  $Q_{10}$  for  $N_2O$  flux. Future research should explore the spatial variation in  $Q_{10}$  for soils within sensitive regions.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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