

Modification of the biophysical water function to predict the change in soil mineral nitrogen concentration resulting from concurrent mineralization and denitrification

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Georgallas, A., Dessureault-Rompré, J., Zebarth, B. J., Burton, D. L., Drury, C. F. and Grant, C. A. 2012. **Modification of the biophysical water function to predict the change in soil mineral nitrogen concentration resulting from concurrent mineralization and denitrification.** *Can. J. Soil Sci.* **92**: 695–710. Uncertainty in soil N supply is an important limitation in making crop fertilizer N recommendations. This study modified a biophysical water function developed to predict net soil N mineralization, making it possible to consider how both N mineralization and denitrification processes affect the rate of soil mineral N accumulation. Data were from a published experiment measuring changes in soil mineral N concentration in five soils of varying texture (loamy sand to clay loam) incubated for 3 mo with or without addition of red clover residue and at two levels of compaction. The biophysical water function was effective in fitting the relationship between scaled change in the rate of soil mineral N accumulation (ΔSMN) and scaled water-filled pore space (WFPS_s) across soils and treatments provided that $\text{WFPS}_s=1$ was set to the water content at which the transition from mineralization to denitrification occurs. The water content at $\text{WFPS}_s=1$ varied with soil type, but not residue addition or compaction treatments, and was closely related to clay content. The k_D parameter, which controls the denitrification term of the function, was influenced by soil type, whereas legume residue application had no significant effect on the k_D parameter despite a twofold increase in net N mineralization. The modified biophysical water function holds promise for improving estimates of soil N supply because it can predict changes in ΔSMN in response to N mineralization and denitrification processes across a wide range of soil water contents.

Key words: Organic amendments, relative compaction, soil type, water-filled pore space

Georgallas, A., Dessureault-Rompré, J., Zebarth, B. J., Burton, D. L., Drury, C. F. et Grant, C. A. 2012. **Modification de la fonction biophysique de l'eau pour prévoir l'évolution de la teneur en azote minéral du sol découlant à la fois de la minéralisation et de la dénitrification.** *Can. J. Soil Sci.* **92**: 695–710. Le fait qu'on ne sache pas exactement combien de N est présent dans le sol constitue un important facteur limitatif quand vient le temps de formuler des recommandations sur l'usage d'engrais azotés en agriculture. Les auteurs ont modifié une fonction biophysique de l'eau mise au point pour prédire la minéralisation nette du N dans le sol afin qu'elle tienne compte de la manière dont la minéralisation et la dénitrification affectent la vitesse à laquelle le N minéral s'accumule dans le sol. Les données émanaient d'une expérience publiée mesurant l'évolution de la teneur en N minéral dans cinq sols de texture différente (du sable loameux au loam argileux) qu'on avait incubé pendant trois mois avec ou sans résidus de trèfle rouge et à deux degrés de compactage. La fonction biophysique de l'eau permet d'ajuster efficacement les liens entre le changement progressif du taux d'accumulation du N minéral dans le sol (ΔSMN) et la variation des pores remplis d'eau (WFPS_s) selon le sol et le traitement, pourvu que $\text{WFPS}_s=1$ corresponde à la concentration d'eau à laquelle on passe de la minéralisation à la dénitrification. À $\text{WFPS}_s=1$, la teneur en eau varie avec la nature du sol, mais pas avec l'addition de résidus ni le compactage, et présente des liens étroits avec la concentration d'argile. Le paramètre k_D , qui régule le côté dénitrification de la fonction, subit l'influence du type de sol, alors que l'application de résidus de légumineuses n'a aucune incidence sur ce paramètre, bien que la minéralisation nette du N soit doublée. La fonction biophysique modifiée de l'eau promet d'obtenir une meilleure estimation de la concentration du N dans le sol, car elle prédit l'évolution de ΔSMN en réaction à la minéralisation et à la dénitrification du N pour une vaste gamme de concentrations d'eau.

Mots clés: Amendements organiques, compactage relatif, type de sol, pores remplis d'eau

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Abbreviations: RC, relative compaction; ΔSMN , rate of soil mineral N accumulation; SOC, soil organic carbon; WFPS, water-filled pore space

Nitrogen (N) limits non-leguminous plant growth in most terrestrial ecosystems. Understanding N transformations and its controlling factors is thus essential for understanding and managing ecosystem health and productivity (Robertson and Groffman 2007). Soil N processes are mostly mediated by soil microbes, and the rate at which soil microbes transform N depends largely on soil temperature, soil water content, O₂ availability and substrate availability and quality [i.e., nitrate (NO₃), ammonium (NH₄) and soil organic carbon (SOC)] (Davidson 1991; Bosatta and Agren 1999; Farquharson and Baldock 2008). In addition, the above regulators are strongly influenced by climate, vegetation, soil properties and land management (Firestone and Davidson 1989; Dobbie and Smith 2003; Seungdo and Bruce 2008). The complex controls on N transformations make uncertainty in soil N supply an important source of uncertainty in making agricultural crop fertilizer N recommendations (Scharf et al. 2006; Lobell 2007). Therefore, an improved understanding of the controls on soil N transformations can lead to greater efficiency of N utilization within agricultural cropping systems (Zebarth et al. 2009). In particular, the response of N processes to changes in soil water content needs to be better characterized in order to improve our ability to predict soil N supply.

While many studies have examined the effect of soil water content on soil N mineralization rate, relatively few studies have examined the prediction of mineralization rate across diverse soils (Paul et al. 2003; Dessureault-Rompré et al. 2011). Recently, the biophysical water function was introduced by Dessureault-Rompré et al. (2011) to predict the effect of soil water content on net soil N mineralization rate. This function includes consideration of two physical processes: the wetting of surfaces presented by soil particulate matter (i.e., clays, organic matter), and the filling of free volume between the particles (i.e., pores). Using 42 soils from published studies, the biophysical water function was effective in predicting the response of net soil N mineralization rate to soil water content, and has the advantage that the three fitted parameters all have a biophysical interpretation. However, this function only predicts the change in soil mineral N, the product of net soil N mineralization, at water contents for which denitrification is expected to be limited.

Water controls microbial activity in soil and thus rates of N transformation. Mineralization and denitrification respond differently to soil water status, largely due to the effect of water on oxygen diffusion, but also due to the gaseous or aqueous diffusion of substrates and products associated with these biological processes (Farquharson and Baldock 2008). At low soil water content, soil N mineralization is affected by the decline in microbial activity attributed to the decreased diffusion of soluble substrates to microbial cells, the reduced microbial mobility that limits access to substrates, the lowering of intracellular water potential which alters

enzyme conformation and inhibits activity (Zak et al. 1999), and the physical protection of bacteria from predation by protozoan grazers (Killiam et al. 1993). Although water stress can limit biological processes below a critical level, the ranges of water contents within which microorganisms multiply and metabolize substrates are wide (Pal and Broadbent 1975; El-Harris et al. 1983). Maximum rates of microbial respiration, nitrification and mineralization occur at the highest water content at which soil aeration remains non-limiting (Linn and Doran 1984). This is commonly assumed to occur near field capacity when there are sufficient air-filled macropore spaces to facilitate O₂ diffusion and sufficient water-filled micropore spaces to facilitate diffusion of soluble substrates (Davidson et al. 2000). Higher soil water contents allow substrates to diffuse within a greater proportion of the soil pore volume making the substrates more available to microorganisms (Drury et al. 1992; Amador et al. 2005). Decreases in activity of aerobic microbes in very wet soils are usually attributed to oxygen deprivation caused by slow diffusion. Oxygen is needed for aerobic respiration and soluble organic substrates are used as energy sources by heterotrophic microorganisms. Anaerobic conditions favourable for denitrification often exist in microsites where a high O₂ demand from intense respiratory activity exceeds the supply (Parkin 1987). Nitrate serves as an alternative electron acceptor when O₂ becomes limiting resulting in the conversion of NO₃⁻ to N₂O and ultimately to N₂ via denitrification (Franzluebbers 1999).

Considerable effort has been put into developing models that can predict denitrification rates. In simulation models, it is the water content correction factor that activates denitrification when a given water content threshold is reached, and consequently the response of denitrification to soil water content is important to understand (Cannavo et al. 2008). Although denitrification is truly driven by the non-availability of oxygen, most authors argue that oxygen dynamics in soil are difficult to measure, and consequently water content is used as a surrogate for oxygen availability (Heinen 2006). In the literature, soil water effects on N emissions have commonly been expressed in terms of water-filled pore space (WFPS) because this provides information on aeration (Petersen et al. 2008). As the water content increases, the air-filled porosity decreases, thus decreasing oxygen content and supply rate. Since oxygen diffusion coefficients are non-linearly related to air-filled pore space (e.g., Bakker et al. 1987), it is appropriate to use a steep, non-linear relationship for the water content correction factor (Heinen 2006). Different mathematical functions exist describing the effect of water content on N processes including denitrification, most of them having been integrated into detailed, process-oriented simulation models (Heinen 2006; Klier et al. 2011). For example, power functions (Grundmann and Rolston 1987; Van Dam

et al. 1997), linear-plateau functions (Molina et al. 1983; Hansen et al. 1991; Birkinshaw and Ewen 2000), exponential functions (Kersebaum 1995; Kersebaum and Beblík 2001) and Michaelis–Menten type functions (Priesack et al. 2001) have been used. However, the commonly used water functions in these models generally lack biological and physical meaning and therefore the interpretation of the fitted parameters is difficult if not impossible. In addition, it is preferable for the water functions to be suitable for use with models that aim to have a water modifier that can be applied to a range of soil types and climatic conditions without the need for modification for individual sites.

The objective of this study was to modify the biophysical water function of Dessureault-Rompré et al. (2011) to predict the effect of soil water content on the rate of soil mineral N accumulation as influenced by both N mineralization and denitrification processes, such that the modified biophysical water function can be applied over the full range of soil water contents. This study utilized data from a laboratory incubation experiment reported by Drury et al. (2003). In addition, the effects of soil type, residue addition and compaction on the denitrification term of the biophysical water function were investigated.

THEORY

The Biophysical Water Function

The biophysical water function as presented by Dessureault-Rompré et al. (2011) predicts the effect of scaled soil water content ($x = WFPS_s$) on net soil N mineralization rate over the range of water contents for which denitrification is expected to be limited, and has the form:

$$f(x) = \lambda \frac{(1 - e^{-bx})}{(1 - e^{-b})} + 2(1 - \lambda) \times \frac{(e^g - e^{-g(x-1)})}{(e^g - 1)(1 + e^{-g(x-1)})} \tag{1}$$

where $f(x)$ represents the scaled net N mineralization rate,

$$\left[\frac{\frac{d}{dt} N_{min}}{\left(\frac{d}{dt} N_{min}\right)_{max}} \right] = \frac{k}{k_{ref}} \tag{2}$$

where N_{min} is net soil N mineralization, k is the mineralization rate constant and k_{ref} is the “reference” mineralization rate constant at $x=1$. It can be shown for small values of the N mineralization rate constants or for short incubations that

$$\left[\frac{\frac{d}{dt} N_{min}}{\left(\frac{d}{dt} N_{min}\right)_{max}} \right], \left[\frac{N_{min}}{N_{max}} \right] \text{ and } \left[\frac{k}{k_{ref}} \right]$$

are all interchangeable candidates for the y -axis (see Appendix) and are all expression of $f(x)$, the biophysical water function; therefore,

$$\left[\frac{\frac{d}{dt} N_{min}}{\left(\frac{d}{dt} N_{min}\right)_{max}} \right] = \frac{\Delta SMN}{\Delta SMN_{max}} \approx \frac{N_{min}}{N_{max}} \approx \frac{k}{k_{ref}} = f(x) \tag{3}$$

where ΔSMN is the change in soil mineral N accumulation and ΔSMN_{max} is the maximum change in soil mineral N accumulation.

The biophysical water function (Eq. 1) is comprised of two terms. The first term describes the contribution of surface wetting processes to net N mineralization and the second term describes the contribution of pore filling to net N mineralization. The biophysical water function (Eq. 1) is characterized by three different fitting parameters: λ , b and g . The λ represents the fraction of the scaled N mineralization rate that can be attributed to surface activity, the b is the surface term and represents the increase in scaled N mineralization rate associated with wetting surfaces presented by soil particulate matter (i.e., clays, organic matter), and the g is the volume term and represents the increase in scaled N mineralization rate associated with the filling of free volume between the particles (i.e., pores).

The Denitrification Term

In order to modify the biophysical water function to include the denitrification process, we make four assumptions. The first assumption specifies that by denitrification we mean the removal of mineral N by the denitrification process, which may be expressed as:

$$\Delta SMN = N_{min} - N_D \tag{4}$$

where the change in soil mineral N accumulation, ΔSMN , is equal to the net N mineralization (N_{min}) less the rate of N removed by denitrification (N_D), which gives

$$\frac{\Delta SMN}{\Delta SMN_{max}} = \frac{N_{min} - N_D}{C \cdot N_{max}} = \frac{N_{min}}{C \cdot N} - \frac{N_D}{C \cdot N_{max}} \tag{5}$$

and where C is a normalization constant which ensures that

$$\frac{\Delta\text{SMN}}{\Delta\text{SMN}_{\max}} = \frac{N_{\min} - N_{\text{D}}}{C \cdot N_{\max}}$$

has a value of 1 at its maximum.

The second assumption specifies that the rate at which denitrification occurs is not limited by NO_3^- supply. Also, we assume no new kinetics, whether physical processes (e.g., diffusion) or biological processes (e.g., bacterial growth or response), are associated with N_{D} . The only source of new NO_3^- (i.e., in addition to what NO_3^- is present in the soil at time zero) is mineralization. The process of nitrification is also ignored (i.e., we do not consider the need for the ammonium produced by mineralization to be converted to nitrate prior to denitrification). This being the case, N_{D}/N_{\max} is only a function of the water content, thus:

$$\frac{N_{\text{D}}}{N_{\max}} = f_{\text{D}}(x) \quad (6)$$

The third assumption specifies that the denitrification process does not begin abruptly at some value of x . The denitrification process is continuous from $x \geq 0$, though possibly negligible for small x , and becoming greater as x increases. Thus, $f_{\text{D}}(x)$ is a positive, continuous, increasing function of x in the range $x \geq 0$.

The fourth assumption specifies that the function that describes denitrification must have the following characteristics: $f_{\text{D}}(x) = 0$ for $x = 0$, and the function must be shallow concave up for $x < 1$ and subsequently rise steeply (Nommik 1956; Linn and Doran 1984; De Klein and Van Logtestijn 1996). One function with these characteristics has the form:

$$f_{\text{D}}(x) = A(e^{k_{\text{D}}(x-1)} - e^{-k_{\text{D}}}) \quad (7)$$

This function has one free parameter, k_{D} , a rate constant which represents the response to water content of the denitrification process. The value of the constant A will be determined from the condition that the total function, i.e., the modified biophysical water function including the additional term for denitrification, must have a maximum at $x = 1$.

Combining Eqs. 3, 5, 6 and 7 we obtain:

$$\begin{aligned} \frac{\Delta\text{SMN}}{\Delta\text{SMN}_{\max}} &= \frac{N_{\min}}{C \cdot N_{\max}} - \frac{N_{\text{D}}}{C \cdot N_{\max}} = \frac{f(x) - f_{\text{D}}(x)}{C} \\ &= \frac{f(x) - f_{\text{D}}(x)}{1 - A(1 - e^{-k_{\text{D}}})} \end{aligned} \quad (8)$$

where the expression for C is obtained from the condition that $\frac{f(x) - f_{\text{D}}(x)}{C} = 1$ at $x = 1$, i.e.,

$$C = f(1) - f_{\text{D}}(1) = 1 - A(1 - e^{-k_{\text{D}}}) \quad (9)$$

It remains to determine the value of A , which may be evaluated from the condition for a maximum at $x = 1$, i.e.,

$$\frac{d}{dx} [f(x) - f_{\text{D}}(x)] = 0 \text{ at } x = 1 \quad (10)$$

After differentiation, we obtain

$$A = \frac{\lambda b e^{-b}}{1 - e^{-b}} + \frac{(1 - \lambda)}{2} g \left(\frac{e^g + 1}{e^g - 1} \right) \quad (11)$$

The Modified Biophysical Water Function

The complete modified biophysical water function can therefore be represented as:

$$\frac{\Delta\text{SMN}}{\Delta\text{SMN}_{\max}} = \frac{f(x) - f_{\text{D}}(x)}{1 - A(1 - e^{-k_{\text{D}}})} \quad (12)$$

where $f(x)$ is the biophysical water function (Eq. 1)

$$f(x) = \lambda \frac{(1 - e^{-bx})}{(1 - e^{-b})} + 2(1 - \lambda) \frac{(e^g - e^{g(x-1)})}{(e^g - 1)(1 + e^{-g(x-1)})}$$

where $f_{\text{D}}(x)$ is the denitrification term (Eq. 7) and

$$f_{\text{D}}(x) = A(e^{k_{\text{D}}(x-1)} - e^{-k_{\text{D}}})$$

$$\text{with } A = \frac{\lambda b e^{-b}}{1 - e^{-b}} + \frac{(1 - \lambda)}{2} g \left(\frac{e^g + 1}{e^g - 1} \right)$$

This model has the same three parameters λ , b and g of the original biophysical water function, and with the corresponding same biophysical meanings for each parameter, with one additional parameter, k_{D} , a rate constant which represents the response to scaled water content of the denitrification process.

MATERIALS AND METHODS

Data Set

This study used data from a published incubation experiment (Drury et al. 2003). Treatments included five soils incubated at eight water contents (20, 35, 50, 65, 80, 85, 90 and 95% WFPS), two rates of legume residue addition [0 (L = 0) and 100 (L = 100) mg legume N kg⁻¹ soil] and two levels of relative soil compaction. The soils included Brady sandy loam (Brady-SL), Fox loamy sand (Fox-LS), Conestogo loam (Conestogo-L), Perth silty loam (Perth-SiL) and Brookston clay loam (Brookston-CL). The soils were selected to cover a range of soil properties and had clay contents ranging from 46 to 378 g kg⁻¹ and SOC contents ranging from 13 to 28 g kg⁻¹ (Table 1). The legume residue was above-ground biomass of red clover (*Trifolium pratense* L.), which was dried at 68°C and ground to pass a 1-mm screen. The red clover residue contained 29.5 g N kg⁻¹ and 445 g C kg⁻¹ with a C/N ratio of 15. Soils were packed to a relative compaction (RC) of 0.83 or 0.91 where:

$$\text{RC} = \text{actual soil bulk density}/\text{reference bulk density} \quad (13)$$

Table 1. Selected properties of the five soils used in the present study [adapted from Drury et al. (2003)]

	Brady-SL	Fox-LS	Conestogo-L	Perth-SiL	Brookston-CL
Clay (g kg ⁻¹)	46	69	148	267	378
Silt (g kg ⁻¹)	307	167	461	493	351
Sand (g kg ⁻¹)	647	764	391	240	271
SOC (g kg ⁻¹) ^z	26.2	13.0	28.1	15.0	18.0
Total N (g kg ⁻¹)	1.99	0.64	1.61	0.99	1.54
C/N	13.2	20.3	17.5	15.2	11.7
pH	7.7	6.9	6.5	7.7	7.5
Initial NH ₄ -N+NO ₃ -N (mg kg ⁻¹)	10.6	17.2	42.3	8.3	10.3
Bulk density (Mg m ⁻³)					
at RC=0.83 ^y	1.19	1.41	1.21	1.28	1.26
at RC=0.91	1.30	1.55	1.33	1.40	1.38
Water content (m ³ m ⁻³)					
at -0.01 MPa and RC=0.83	0.36	0.25	0.44	0.40	0.45
at -1.5 MPa and RC=0.83	0.13	0.08	0.17	0.20	0.24
at -10 MPa and RC=0.83 ^x	0.09	0.05	0.12	0.15	0.19
at -0.01 MPa and RC=0.91	0.41	0.27	0.49	0.43	0.49
at -1.5 MPa and RC=0.91	0.15	0.09	0.19	0.21	0.26
at -10 MPa and RC=0.91	0.10	0.06	0.13	0.16	0.20

^zSOC, soil organic carbon.

^yRC, relative compaction.

^xThe value of water content at -10 MPa for each soil was calculated using the Campbell equation (Campbell 1974).

and where the reference bulk density was determined by using a modification of the method of Häkansson (1990) in which about 100 g oven dry equivalent weight of soil was puddled, vacuum saturated, poured into a Rowe cell (7-cm i.d.), a load of 200 kPa applied until drainage had ceased, the pressure released, and bulk density determined after 15 min. These values of relative compaction represent values commonly found under conventional till (0.83) and no-till (0.91) across a range of soil textures, SOC contents, and climates (Kay et al. 1997). Values of relative compaction have little or no dependence on texture and SOC contents and are, therefore, preferred to bulk density as a treatment variable in experiments with soils of different texture and SOC contents. For each soil, the actual soil bulk density values and water contents at -1.5 MPa and -0.01 MPa are presented in Table 1. Samples were incubated for 3 mo in a controlled environmental room at 20±2°C. A more detailed description of the incubation method and soil analyses are presented in Drury et al. (2003).

Normalization of the Data Set

The data were normalized with respect to both the soil water content and the net soil N mineralization rate. The normalization of the water content was done similar to the approach described by Dessureault-Rompré (2011). The soil water content, expressed as WFPS, was scaled to represent the proportion of available water range (WFPS_s) and was defined as:

$$WFPS_s = (WFPS - WFPS_0) / (WFPS_{max} - WFPS_0) \quad (14)$$

where WFPS is the actual water content expressed in units of % WFPS; WFPS₀ is water content at which the net N mineralization rate is minimal; and WFPS_{max} is

the water content at the maximum rate of ΔSMN (ΔSMN_{max}). Previously, Dessureault-Rompré et al. (2011) used a value of 5% WFPS for WFPS₀ since actual data for moisture retention of individual soils were not available. The use of 5% WFPS for WFPS₀ generally allowed representation of the range of water contents in the data sets and avoided having negative values for WFPS_s. In the present study, setting WFPS₀ to 5% WFPS was considered inadequate because mineralization rate approached zero at values of WFPS greater than 5%. Information on water retention was available in the present study and therefore the identification of a matric potential which would be suitable for selecting WFPS₀ was evaluated. The use of permanent wilting point (-1.5 MPa) as well as the -4 MPa used by Myers et al. (1982) resulted in negative values of scaled WFPS when net mineralization was greater than zero. Orchard and Cook (1983) reported that minimal soil respiration occurred at a soil matric potential of -10 MPa, and consequently WFPS₀ was chosen to represent the WFPS at this matric potential. The value of WFPS at -10 MPa for each soil (Table 1) was calculated using the Campbell equation (Campbell 1974):

$$\theta = \theta_s(\psi/\psi_e)^{-1/b} \quad (15)$$

where θ is the water content at matric potential ψ, θ_s is the water content at saturation, ψ_e is the air entry potential and b is a fitting parameter. When two values of θ and ψ are known, in this study the value of θ at -0.01 MPa and at -1.5 MPa, the values of ψ_e and b can be estimated directly using the Campbell function fit of the SoilPar 2.0 software (Acutis and Donatelli 2003). Setting WFPS₀ to WFPS at -10 MPa still produced

negative WFPS_s values for some soils at 20% WFPS and 35% WFPS; however, in all but two cases the net mineralization was low (<4.7 mg N kg⁻¹), and these values were removed from the data set. In addition, in some cases a depletion of nitrate was observed at high %WFPS and consequently the loss of nitrate by denitrification may have been limited by nitrate supply. Ryden (1983) suggested that denitrification is NO₃ limited when NO₃ concentrations are lower than 5–10 mg N kg⁻¹ whereas other studies suggest denitrification may be limited at NO₃ concentrations up to 40 mg N kg⁻¹ (Bowman and Focht 1974; Knowles 1982). In this study, eight cases where soil had a NO₃ concentration below 5 mg N kg⁻¹ at the end of the incubation were removed from the data set.

Soil N mineralization rate was scaled by Dessureault-Rompré et al. (2011) as $(N_{\min} - N_{\text{minimum}})/(N_{\max} - N_{\text{minimum}})$, where N_{\min} is the net soil N mineralization at each water content and N_{minimum} was assumed to be ≈ 0 , and consequently this reduced to N_{\min}/N_{\max} , where N_{\max} is the maximum numeric value of N mineralization rate. This scaling approach (i.e., ΔSMN_{\max} was chosen to be the highest numeric value of ΔSMN) was not satisfactory in the current study in the case where several data points had values of ΔSMN close to the maximum numeric value. Instead, scaling was done with reference to the ΔSMN at the highest water content before a substantial decrease in ΔSMN occurred, where the decrease in ΔSMN was attributed to nitrate loss through denitrification. This value of ΔSMN is assumed to represent the transition from ΔSMN controlled primarily by net mineralization to ΔSMN controlled primarily by denitrification, and is hereafter referred to $\Delta\text{SMN}_{\text{tr}}$. Thus, scaling was based on $\Delta\text{SMN}_{\text{tr}}$ at WFPS_s = 1.

Parameterization of the Biophysical Water Function

The biophysical water function, modified as described in the theory section to consider denitrification, is characterized by four parameters (Eq. 12). Dessureault-Rompré et al. (2011) fit the biophysical water function without the denitrification term (Eq. 1) using 42 soils of varying geographic origins, land uses and soil properties. Fitted values of the surface activity parameter (λ), and the b parameter, which reflects the increase in net N mineralization rate associated with surface wetting, were 0.816 and 3.8, respectively. Dessureault-Rompré et al. (2011) found that the shape of the biophysical water function was relatively insensitive to the value of g , the pore-filling parameter, for example changing the value of g from 5 to 15 had a limited effect on the shape of the function, and therefore the value of g was fixed to 15. In the present study where the denitrification term was included in the biophysical water function, values for λ and b were fixed to 0.816 and 3.8 as those values were found to represent a large variety of soils from around the world (Dessureault-Rompré 2011). How-

ever, with the present data, setting the value of g to 15 often resulted in convergence problems or resulted in a fitted curve having two maximum values, including one maximum value at a water content below the expected maximum value at WFPS_s = 1. In this study, these issues were resolved by fixing the value of g to 8. Fixing the values of λ , b and g to 0.816, 3.8 and 8, respectively, resulted in an adequate fit to the experimental results across soils, amendment treatments and compaction treatments. Therefore, for the purpose of the current study, the biophysical water function is characterized by only one free parameter, the k_D parameter of the denitrification term.

Fitting the Modified Biophysical Water Function and Comparison of k_D among Soil Types and Treatments

The need for normalization of soil water content and N mineralization was firstly evaluated. The modified biophysical water content function was fitted using a single soil and treatment (Brady-SL soil with no legume residue application and a relative compaction of 0.83), and the complete data set, to illustrate the improvements associated with the changes in normalization. Second, the modified biophysical water function was decomposed into its three components, the surface term, the volume term and the denitrification term, using the complete data set. In addition, a range of k_D values (1 to 5) was used to illustrate how changes in the value of k_D change the denitrification term of the function. Third, the data set of the current study was used to examine if the relationship between water content and the denitrification term k_D was influenced by the soil type, residue application or compaction level. Finally, differences among soil type and treatments were evaluated with respect to the water content (%WFPS) at WFPS_s = 1. Relationships were determined between the clay content of the soils and the water content expressed as one of: (1) WFPS (%) at WFPS_s = 1 (i.e., at $\Delta\text{SMN}_{\text{tr}}$, the value of ΔSMN at the highest water content before a substantial decrease in ΔSMN occurred); (2) WFPS (%) at -0.01 MPa; and (3) WFPS (%) at -0.33 MPa.

Statistics

The adjusted coefficient of determination (R^2) and the normalized root mean square error (NRMSE) (Anderson and Woessner 1992) were used to assess the goodness-of-fit. In addition the Bootstrap 95% Confidence Interval (SYSTAT Software Inc., Richmond, CA), which tests the true value of the parameter based on the sample estimate, was obtained for each parameter value to distinguish the statistical significance of differences among soil types and treatments. Differences among soil type and treatments for water content and unscaled values of ΔSMN at WFPS_s = 1 were evaluated using analysis of variance followed by the post-hoc Tukey's Honestly-Significant-Difference Test

[SYSTAT 11.0 (SYSTAT Software Inc., Richmond, CA)].

RESULTS

Normalization and Fitting of the Data Set

Options for improving the scaling of ΔSMN and water content were explored using the Brady-SL soil with no legume residue addition and relative compaction of 0.83 (Fig. 1), although similar responses were observed with most soils and treatments. Scaling of ΔSMN based on $\Delta\text{SMN}_{\text{tr}}$, the ΔSMN at the highest water content before a substantial decrease in ΔSMN occurred (Fig. 1b, d), resulted in a better fit (i.e., higher R^2 , and within 1 SE of measured data for most data points) to the experimental data compared with scaling of ΔSMN based on $\Delta\text{SMN}_{\text{max}}$, the maximum numeric value of ΔSMN (Fig. 1a, c). The proximity of several data points surrounding the maximum numeric value of ΔSMN which are not statistically different resulted in a fitted curve where predicted zero ΔSMN for $\text{WFPS}_s > 1$ occurred at a lower water content than was observed with the measured data. In addition, scaling

based on $\Delta\text{SMN}_{\text{max}}$ often resulted in a fitted curve with two maximum values, whereas the fitted curve should only have one maximum value of ΔSMN at $\text{WFPS}_s = 1$. Scaling of water content by setting WFPS_0 to the WFPS at -10 MPa (Fig. 1c, d) instead of 5% WFPS (Fig. 1a, b) as was done previously by Dessureault-Rompré et al. (2011) generally improved the fit to the experimental data at low water contents, although it is less clear in the case of this specific soil than for other soils in the data set. In addition, setting $g = 8$ resulted in a better fit to the experimental data, avoided two maximum values in the fitted curve, and was more consistent in converging to a solution in curve-fitting, compared with setting $g = 15$ as was done previously by Dessureault-Rompré et al. (2011).

The options for scaling of ΔSMN and water content chosen for use in the current study are shown for the Brady-SL soil (Fig. 1d using $g = 8$) and for the entire data set (Fig. 2 using $g = 8$). These options result in only one maximum value of ΔSMN at $\text{WFPS}_s = 1$ for individual cases and for the data set as a whole. The values of λ and b used for curve-fitting are the same as

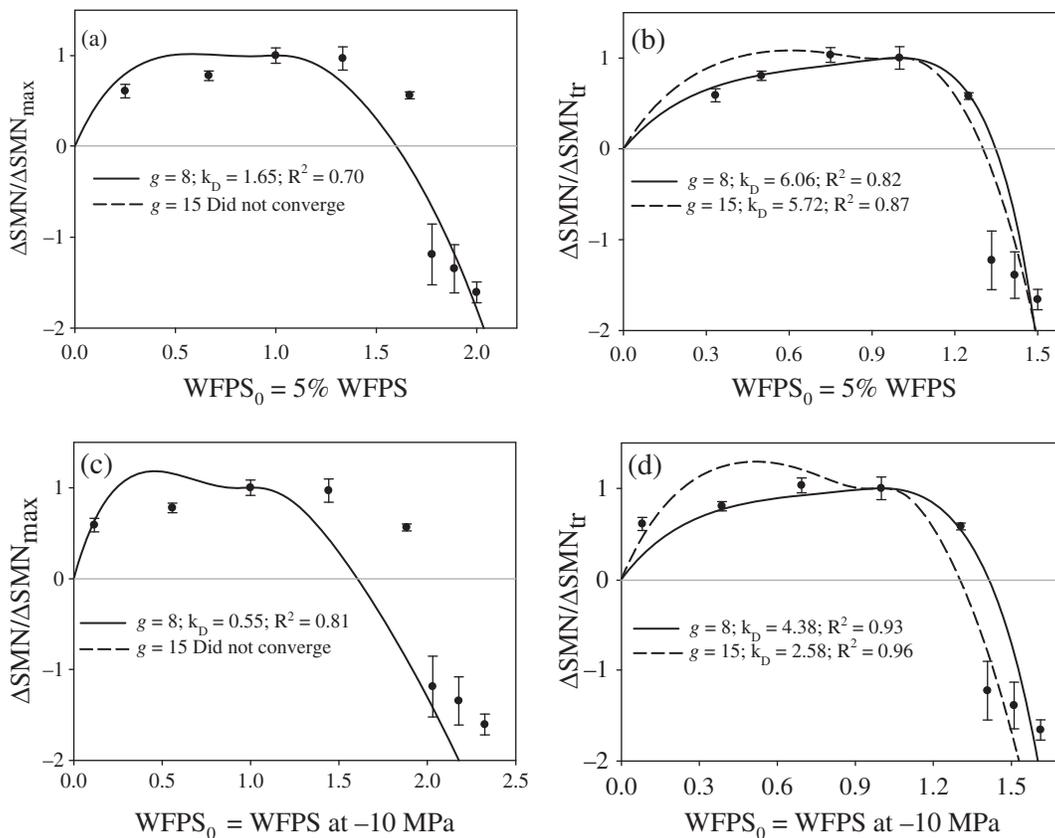


Fig. 1. Options for normalization and fitting of the biophysical water function ($\lambda = 0.816, b = 3.8$) using the Brady-SL soil with no legume residue addition and a relative compaction of 0.83 as an example: (a) Normalization using $\text{WFPS}_0 = 5\% \text{ WFPS}$ and $\Delta\text{SMN}_{\text{max}}$ (i.e., highest numeric value of ΔSMN); (b) Normalization using $\text{WFPS}_0 = 5\% \text{ WFPS}$ and $\Delta\text{SMN}_{\text{tr}}$ (i.e., ΔSMN before a substantial decrease in ΔSMN occurred); (c) Normalization using $\text{WFPS}_0 = \text{WFPS at } -10 \text{ MPa}$ and $\Delta\text{SMN}_{\text{max}}$; and (d) Normalization using $\text{WFPS}_0 = \text{WFPS at } -10 \text{ MPa}$ and $\Delta\text{SMN}_{\text{tr}}$. Error bars represent the standard deviation ($n = 3$).

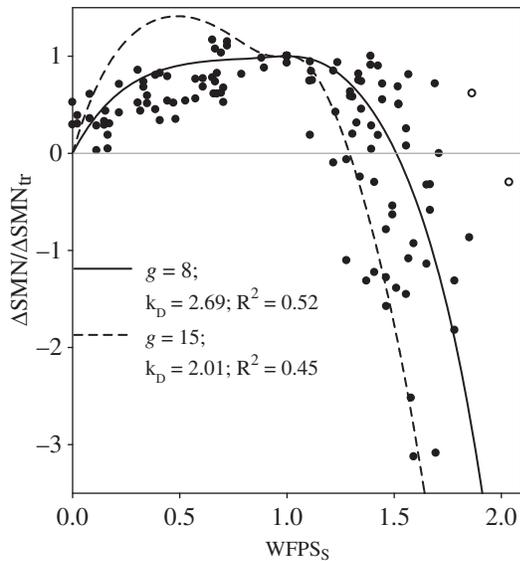


Fig. 2. Fitting of the modified biophysical water function using the complete data set ($\lambda=0.816$, $b=3.8$, $WFPS_0$ set to the $WFPS$ at -10 MPa). Open symbols identify two outliers that were not included for the curve fitting procedure.

determined previously from an entirely different set of data (Dessureault-Rompré et al. 2011). The choice of $g=8$ is not inconsistent with the previous choice of $g=15$ made by Dessureault-Rompré et al. (2011) because in that study the curve fitting was not sensitive to g for values of g from 5 to 15. Given these options for scaling and selection of parameters, this function can be fit to the data using one free parameter, the k_D parameter of the denitrification term of the biophysical water function.

Breakdown of the Complete Function into its Terms

It is useful to consider the overall shape of the biophysical water function, and the contribution of the individual terms of the function, in estimating ΔSMN of the complete data set (Fig. 3). The overall function rises steeply with increasing water content for values of $WFPS_s$ of 0 to about 0.3, then increases slowly with increasing water content to a maximum at $WFPS_s=1$, then subsequently decreases rapidly as $WFPS_s$ increases above 1. The breakdown of the complete function into its terms indicates that most N mineralization is associated with the surface wetting term. The surface term rises rapidly from 0 to about 0.3 $WFPS_s$ reflecting the increase in N mineralization described by the complete function. The increase in the volume (i.e., pore filling) term and the decrease in the denitrification term are very similar from $WFPS_s$ of about 0.5 to 1.2. The slow increase in ΔSMN in the overall function $WFPS_s$ of 0.5 to 1.0 primarily reflects the difference between the pore filling and denitrification terms over this range of water contents. The denitrification term

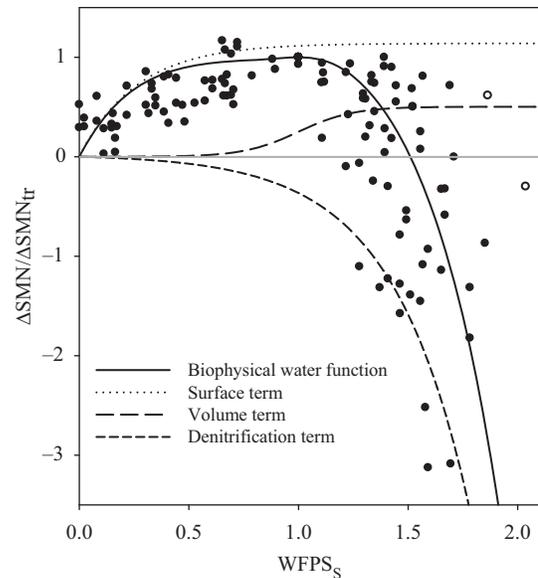


Fig. 3. Biophysical water function fitted to the complete data set in comparison with the surface term, the volume term and the denitrification term of the function ($\lambda=0.816$, $b=3.8$, $g=8$, $k_D=2.84$). Open symbols identify two outliers that were not included for the curve fitting procedure.

decreases very rapidly above $WFPS_s=1$ and the overall function is controlled primarily by the denitrification term for $WFPS_s$ greater than 1.

In order to better understand the influence of the value of the k_D on the denitrification term, the denitrification term was plotted as a function of $WFPS_s$ for a series of values for k_D (Fig. 4). In general, the higher the value of k_D , the higher the scaled water content before measurable denitrification occurs, the lower the absolute value of the denitrification term (i.e., closer to zero) at $WFPS_s=1$, and the more steeply the denitrification term decreases with increasing water

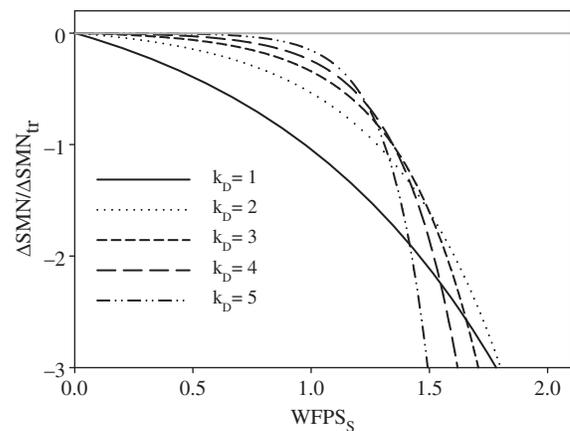


Fig. 4. Influence of the value of k_D on the denitrification term of the biophysical water function ($\lambda=0.816$, $b=3.8$, $g=8$).

content above $WFPS_S = 1$. It is important to note, however, that this refers not to the absolute denitrification rate, but rather the loss of nitrate relative to the scaled ΔSMN .

Influence of Soil Type, Residue Addition and Soil Compaction

The fitted values of the denitrification term k_D were compared among soil types and among residue application and compaction treatments. Among soil types, the k_D term increased numerically in the following order: Perth-SiL < Conestogo-L < Brady-SL < Fox-LS < Brookston-CL (Table 2). However, not all soils were statistically different; the Perth-SiL was not significantly different from the Brady-SL, and the Brady-SL was not significantly different from the Conestogo-L. The two soils characterized by the highest k_D values (Fox-SL and Brookston-CL) were significantly different from each other and from the other soils examined. With respect to legume residue and compaction treatments, the treatment with legume residue addition and RC = 0.83 had a significantly higher value of k_D than the other three treatment combinations for which the value of k_D did not differ significantly (Table 2).

The water content at ΔSMN_{tr} (i.e., WFPS at $WFPS_S = 1$) varied with soil type (Table 3). The Brookston-CL had the highest water contents (80% WFPS) at $WFPS_S = 1$, and was significantly different from the two soils characterized by the lowest water content, the Brady-SL and the Fox-LS with 65% WFPS at $WFPS_S = 1$ (Table 3). For the five soils examined, the value of WFPS at $WFPS_S = 1$ increased linearly ($R^2 = 0.97$) with increasing clay content (Fig. 5). There was also a linear increase of WFPS at -0.01 and -0.33 MPa with clay content (R^2 of 0.47 and 0.83, respectively); however, the fit with clay content was not as

good as with the WFPS at $WFPS_S = 1$. In each soil, the WFPS at $WFPS_S = 1$ was greater than the WFPS at field capacity, where field capacity was taken to be represented by matric potentials of -0.01 MPa for the Fox-LS and -0.33 MPa for all other soils.

The soils examined also differed in the actual ΔSMN_{tr} at $WFPS_S = 1$ (i.e., unscaled value of ΔSMN_{tr} at $WFPS_S = 1$) (Table 3). The lowest values for ΔSMN_{tr} were observed for the Fox-LS soil followed by the Perth-SiL soil. The Fox-LS and the Perth-SiL soils are characterized by the lowest SOC and total N content (Table 1). The highest value of ΔSMN_{tr} was observed for the Brady-SL soil, which was significantly different from the Fox-LS soil. The Brady-SL is characterized by the highest SOC and total N contents of the soils examined (Table 1). A significant relationship was found between the unscaled value of ΔSMN_{tr} and the total N content of the soils ($R^2 = 0.79$, $P < 0.05$), but not with the SOC content ($R^2 = 0.39$, $P = 0.15$) (data not presented).

The soil residue application and the compaction treatments also influenced the ΔSMN_{tr} at $WFPS_S = 1$, but not the WFPS at $WFPS_S = 1$ (Table 3). The values of ΔSMN_{tr} were significantly increased with the addition of red clover residues regardless of relative compaction.

DISCUSSION

The Modified Biophysical Water Function

Several studies have examined the relationship between water content and net soil N mineralization rate. For Paul et al. (2003) and Dessureault-Rompré et al. (2011), this relationship was examined across a range of diverse soils. However, this relationship is commonly examined only for a portion of the range of soil water content, and excludes high soil water contents where denitrification may occur. Other studies have examined the relationship

Table 2. The estimated value of k_D as influenced by soil type and by legume residue addition and compaction treatments. The value of k_D was obtained by fitting the biophysical water function where $\lambda = 0.816$, $b = 3.8$, and $g = 8$

	k_D	Bootstrap 95% confidence intervals ^z		R^2	NRMSE ^y (%)
<i>Influence of soil type^x</i>					
Brady-SL	2.8	2.1	3.5	0.37	24
Fox-LS	4.8	4.4	5.1	0.68	15
Conestogo-L	2.7	2.3	3.1	0.68	9.1
Perth-SiL	1.5	0.8	2.2	0.54	22
Brookston-CL	7.8	6.9	8.7	0.87	15
<i>Influence of legume residue addition and compaction treatments^w</i>					
L = 0; RC = 0.83	2.2	1.5	3.0	0.36	22
L = 0; RC = 0.91	2.2	1.9	2.5	0.83	5.9
L = 100; RC = 0.83	5.6	5.2	6.0	0.75	17
L = 100; RC = 0.91	2.7	2.5	3.0	0.83	10

^zThe Bootstrap 95% Confidence Interval tests the true value of the parameter based on the sample estimate, and are used distinguish the statistical significance of differences among soil types and treatments.

^yNormalized root mean square error.

^xThe influence of soil type was evaluated across treatments.

^wThe influence of treatments was evaluated across soil types.

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Table 3. Influence of soil type, legume addition and compaction treatments on the WFPS at $WFPS_S=1$, and the ΔSMN at $WFPS_S=1$

	WFPS at $WFPS_S=1$ (%WFPS) ^z	Unscaled value of ΔSMN_{tr} at $WFPS_S=1$ (mg N kg ⁻¹) ^z
<i>Influence of soil type (n=4)^y</i>		
Brady-SL	65 (± 0)a	46 (± 18)b
Fox-LS	65 (± 0)a	19 (± 16)a
Conestogo-L	69 (± 7.5)ab	28 (± 10)ab
Perth-SiL	72 (± 8.7)ab	23 (± 8.4)ab
Brookston-CL	80 (± 11)b	28 (± 12)ab
<i>Influence of soil residue application and compaction level (n=5)^x</i>		
L=0; RC=0.83	65 (± 0)a	18 (± 10)a
L=0; RC=0.91	72 (± 9.7)a	18 (± 10)a
L=100; RC=0.83	68 (± 6.7)a	42 (± 16)b
L=100; RC=0.91	76 (± 11)a	36 (± 8)b

^zValues are means (± 1 SD).

^yThe influence of soil type was across evaluated residue application and compaction treatments.

^xThe influence of treatments was evaluated across soil types.

a, b Means in a column followed by the same letter are not significantly different at $P < 0.05$ from the Tukey's Honestly Significant-Difference Test.

between denitrification and water content (Weier et al. 1993; Dobbie and Smith 2001; Guo et al. 2010), or attempted more particularly to predict the denitrification rate as a function of water content (Grundmann and Rolston 1987; Hénault and Germon 2000; Kersebaum and Beblík 2001). In this study, we examine the feasibility of predicting the response of net soil mineral N accumulation across a wide range of soil water contents, by taking into account the potential for denitrification to occur. Using five soils covering a range of soil textures, in addition to legume residue addition and compaction treatments, we demonstrated the potential to characterize the response of net soil mineral N accumulation to a wide range of water content (20 to 95% WFPS) across soil types and treatments using a single function. Only the k_D parameter, and the WFPS

at $WFPS_S=1$ and at -10 MPa, were needed to characterize the individual soils and treatments.

Generally, the modified biophysical water function showed a better fit to the experimental data for $WFPS_S$ from 0 to 1 than for $WFPS_S > 1$. This likely reflects that for $WFPS_S > 1$, the ΔSMN is controlled primarily by the denitrification term whereas the scaling was based primarily on a net mineralization rate basis rather than on a denitrification rate basis. Given that the controls on the mineralization and denitrification processes are different, scaling based primarily on the basis of mineralization may introduce errors over the range of the function where denitrification predominates. However, this may also reflect the high inherent variability associated with the denitrification process.

The scaling of water content was critical to the successful application of the modified biophysical water function. Setting $WFPS_S=1$ to the highest water content before there was a substantial reduction in net soil mineral N accumulation (i.e., at ΔSMN_{tr}), attributed to denitrification, was important. This point corresponds approximately to the inflection point of the pore-filling sigmoidal term of the complete biophysical water function. This water content represents a transition from increasing water content primarily contributing to increased aerobic microbial activity and increased net N mineralization to increased water content inducing greater anaerobic activity and denitrification. The increase in net N mineralization is attributed to enhanced substrate diffusion and availability for microorganisms (Davidson et al. 2000; Amador et al. 2005). The induced denitrification is attributed to oxygen deprivation (Franzluebbers 1999).

The water content at the transition from mineralization to denitrification, i.e., at $WFPS_S=1$, varied with soil type. It is interesting to note that for each soil examined in this study, $WFPS_S=1$ occurred at a WFPS greater than field capacity. In particular, there was a very strong relationship between the water content,

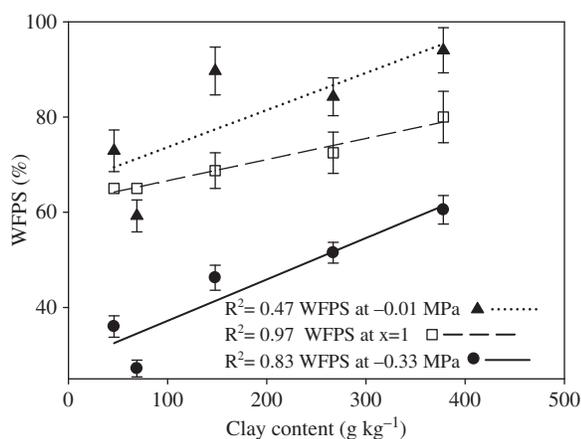


Fig. 5. Relationship between water content and clay content where water content is: (1) %WFPS at $WFPS_S=1$ (i.e., at ΔSMN_{tr} , the ΔSMN at the highest water content before a substantial decrease in ΔSMN occurred); (2) %WFPS at -0.01 MPa; and (3) %WFPS at -0.33 MPa.

expressed as %WFPS at $WFPS_S=1$, and the clay content of the soils. A range of studies have identified soil WFPS as a predictor of microbial processes in soil, and have proposed 60% WFPS as a threshold for denitrification and N_2O emissions as a result of O_2 limitation (Linn and Doran 1984; Nommik and Larsson 1989; Bateman and Baggs 2005). In a recently revised version of the classic Linn and Doran (1984) work showing the relationship between WFPS and soil nitrification, denitrification, and respiration, Robertson and Groffman (2007) identify a direct link between mineralization and respiration, and emphasize the concept of a water content at which there is a transition from aerobic to anaerobic processes. Presumably $WFPS_S=1$ reflects this transition point or threshold which acts as a trigger for the denitrification process. Others have stressed that the threshold will depend on soil properties (Weier et al. 1993; De Klein and Van Logtestijn 1996; Robertson and Groffman 2007). De Klein and Logtestijn (1996) found from a laboratory experiment that denitrification rates were very low when the soil WFPS had decreased below a threshold value, which varied with soil texture. When the WFPS of a sand, loam and peat soil had dropped below 82, 83 and 71%, respectively, denitrification activity was small, whereas above this critical threshold value, denitrification rates sharply increased (De Klein and Logtestijn 1996). Weier et al. (1993) showed that in a silty clay loam and a silty loam, denitrification rates increased sharply when WFPS increased from 75 to 90%, whereas in a sandy soil the increase in denitrification was more gradual. Although there was a large range of threshold values reported in their study, in general, water thresholds decreased when soil texture became finer. In the present study the WFPS at $WFPS_S=1$ increased with increasing clay content.

The water threshold for the transition from mineralization to denitrification would also be expected to vary with the amendment application and compaction treatments. With addition of a plant residue, it is expected that the oxygen demand would be greater, and therefore one would expect denitrification to be induced at a lower water content compared with a treatment without plant residue addition. In addition, soil compaction reduces total porosity, and as a result a more compact soil will have less total porosity, and less continuous air-filled porosity, than a less compact soil even at the same value of %WFPS. In the present study, despite a large effect of plant residue application on net mineral N accumulation, neither the plant residue addition or the soil compaction had a significant effect on water content at $WFPS_S=1$. This suggests that the water threshold is primarily a function of soil type, particularly clay content, and that the same modified biophysical water function can be applied effectively across soil types and across these treatments, through changes in the water content at $WFPS_S=1$ and through estimation of the appropriate value of k_D .

Practical application of this function would require knowledge of this transition point (i.e., at what WFPS does $WFPS_S=1$) and the net mineral N accumulation rate occurring at this water content. There is evidence that the WFPS at $WFPS_S=1$ can be predicted based on soil clay content, and would therefore not need to be determined experimentally for all soils. If this is possible, the function can be applied much more readily in practice

Influence of Soil Type, Residue Addition and Soil Compaction on the k_D Parameter

Higher rates of denitrification have been reported in finer-textured soils (Groffman and Tiedje 1989; Weier et al. 1993; D'Haene et al. 2003). In the present study, the soil texture significantly influenced the k_D parameter of the denitrification term of the modified biophysical water function. The k_D parameter was generally lower (i.e., denitrification becomes greater relative to mineralization at lower WFPSs) for fine-textured (i.e., Perth-SIL) than coarse-textured (i.e., Fox-LS) soils. There was a high Pearson correlation coefficient between the value of k_D and the soil clay content ($r=0.80$, data not presented); however, this correlation was not statistically significant, perhaps due to the limited number of soils included in the study. Increasing clay contents are often accompanied by increasing nutrient contents, increasing microbial biomass, and increasing limitation of gas diffusion therefore leading to higher production of NO and N_2O (Kaiser et al. 1992; Garrido et al. 2002).

Denitrification has been found to respond differently to crop residues depending on their C/N ratio. The C/N ratio of the red clover residue added to the soils of the present study was 15:1 (Drury et al. 2003). Plant residues with low C/N ratios and composed of labile C compounds, such as red clover, promote net N mineralization and creation of anaerobic microsites, which stimulate denitrification, whereas incorporation of residues with high C/N ratios, such as barley straw, may cause net immobilization of soil N (Baggs et al. 2000). Most denitrifying bacteria are heterotrophs and, therefore, C availability is an important factor controlling denitrification directly by increasing the energy and electron supply to denitrifiers, and indirectly through enhanced microbial growth and metabolism thereby stimulating high O_2 consumption (Knowles 1982; Beauchamp et al. 1989; Garcia-Montiel et al. 2003). In the present study, the effect of residue addition was less pronounced than the effect of soil type. The residue addition increased the k_D value only at the lowest relative compaction level. It should be noted that the residue addition increased significantly the unscaled value of ΔSMN_{tr} . Consequently, although the addition of red clover residue resulted in an increased N mineralization, the expected shift of the balance between supply and demand of O_2 locally (Sexstone et al. 1985; Parkin 1987), which might be expected to occur due to the addition of readily biodegradable organic materials

(Neeteson and VanVeen 1987; Gok and Ottow 1988), was not predominant in the present study.

In the present study, the effect of relative compaction on the k_D parameter was significant only when red clover residue was added. The compaction reduced the k_D term and therefore increased the denitrification rate relative to the $WFPS_S = 1$ compared with the lowest compaction treatment. This is in agreement with the general knowledge on soil compaction that stipulates that the compaction of soil affects nearly all properties and functions of the soil, physical, chemical and biological (Håkansson et al. 1988; Whalley et al. 1995). Compaction alters soil structure by crushing aggregates or combining them into larger units, increasing bulk density and decreasing the number of macropores (Wolkowski 1990; Needham 2004; Delgado et al. 2007). Soil compaction compresses and displaces gases from the soil matrix increasing the proportion of WFPS and the formation of anoxic microsites (Granli and Bøckman 1994; Stalham et al. 2005) and therefore increases the anaerobic fraction of the soil (Uchida et al. 2008). The reduced porosity and the shifts in the pore size distribution toward smaller pores of compacted zones (Beare et al. 2009) increases WFPS and limits the oxygen diffusion rate, resulting in an increased volume of soil in an anaerobic state (Dexter 1997; Gregorich et al. 2006; Ball et al. 2008). These changes in structure resulting from compaction, along with any reductions in macropore diameter and continuity, may increase denitrification (Barken et al. 1981; Batey and Killham 1986; Bhandral et al. 2007).

CONCLUSIONS

This study modified the published biophysical water function in order to predict the effect of soil water content on the rate of soil mineral N accumulation as influenced by both N mineralization and denitrification processes, such that the modified biophysical water function can be applied over the full range of soil water contents. The three parameters of the published biophysical water function that characterized the scaled N mineralization rate increases in response to increasing water content were fixed to values identified to reflect a large variety of soils from around the world (Dessureault-Rompré 2011). Therefore, the modified biophysical function has only one free parameter, k_D , that characterizes the loss of nitrate due to denitrification. Other factors that improved the application of the modified biophysical water content included setting $WFPS_0$ to the WFPS at -10 MPa, and setting $WFPS_S = 1$ to be the WFPS at ΔSMN_{tr} . Generally the modified biophysical water function showed a better fit to the experimental data for $WFPS_S$ from 0 to 1 than for $WFPS_S > 1$. This was attributed to the ΔSMN being controlled primarily by the denitrification term for $WFPS_S > 1$, whereas the scaling was primarily on a net mineralization rate basis. The $WFPS_S = 1$ was found to correspond approximately to the inflection point of the

pore-filling sigmoidal term of the complete biophysical water function, and represents a transition from increasing water content primarily contributing to increased aerobic microbial activity and net N mineralization to increased water content inducing anaerobic activity and denitrification. This transition point was found to vary with soil type and to be closely related to the clay content of the soils. The denitrification parameter, k_D , was also found to vary with the soil type and was generally lower for fine-textured than coarse-textured soils. Despite a large effect of plant residue application on net soil mineral N accumulation, neither the plant residue addition nor the soil compaction had a significant effect on water content at $WFPS_S = 1$ and on the k_D parameter. This suggests that the same modified biophysical water function can be applied effectively across soil types and across these treatments. Application of the modified biophysical water function requires only the value of the k_D parameter, and the WFPS at $WFPS_S = 1$ and at -10 MPa, to characterize the individual soils and treatments. In addition, there is evidence that the WFPS at $WFPS_S = 1$ can be predicted based on soil clay content; if this is possible, the function can be applied much more readily in practice.

It is also important, however, to recognize some limitations of the results reported here. The experimental system used in this study was highly disturbed and is somewhat artificial compared with the field situation. It would therefore be useful to test the ability of modified biophysical water function to predict changes in ΔSMN under field conditions. In addition, future research should include independent measurement of the rates of net N mineralization and denitrification across a wide range of water contents such that the individual terms of the modified biophysical water function can be evaluated. For example, the decrease in ΔSMN at high soil water contents may reflect both a decrease in net N mineralization rate due to oxygen limitation and loss of nitrate to denitrification, however the former is not considered in the current function.

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APPENDIX

Here we consider which parameters can be represented on the “y axis” when plotting the modified biophysical water function against soil water content. For this comparison, we use the following definitions:

- N_{min} , the net N mineralized which has units of mass of N per mass of soil.
- N_{max} , the value of N_{min} which is a maximum.
- $\frac{d}{dt}N_{min}$, the rate of net N mineralization, which has units of mass of N per mass of soil per unit time.
- k , the mineralization rate constant which governs $\frac{d}{dt}N_{min}$. In a first order kinetic approximation $\frac{d}{dt}N_{min} = k(N_0 - N_{min})$ which leads to $N_{min} = N_0(1 - e^{-kt})$, where N_0 is the initial quantity of mineralizable N. It has units of $(\text{time})^{-1}$.
- k_{ref} , the “reference” mineralization rate constant associated with N_{max} . It is related to k through the “biophysical water function” $f(x)$, through $k = k_{ref}f(x)$.

Firstly, we will establish the relationship between the mass of N mineralized $\frac{N_{min}}{N_{max}}$ and the “biophysical water function” $\frac{k}{k_{ref}} = f(x)$ by first-order kinetics:

$$\frac{N_{min}}{N_{max}} = \frac{N_0(1 - e^{-kt})}{N_0(1 - e^{-k_{ref}t})} = \frac{(1 - e^{-kt})}{(1 - e^{-k_{ref}t})}$$

For small values of the exponential argument, i.e., for $k_{ref}t < 1$, we can expand the exponential using a Taylor series:

$$\frac{N_{min}}{N_{max}} = \frac{\left[1 - \left(1 - kt + \frac{k^2t^2}{2} - o(kt)^3\right)\right]}{\left[1 - \left(1 - k_{ref}t + \frac{k_{ref}^2t^2}{2} - o(k_{ref}t)^3\right)\right]} = \frac{\left(k + \frac{k^2t^2}{2} - o(k^3t^2)\right)}{\left(k_{ref} + \frac{k_{ref}^2t^2}{2} - o(k_{ref}^3t^2)\right)}$$

So that

$$\frac{N_{min}}{N_{max}} \approx \frac{\left(k + \frac{k^2t}{2}\right)}{\left(k_{ref} + \frac{k_{ref}^2t}{2}\right)} = \frac{k\left(1 + \frac{kt}{2}\right)}{k_{ref}\left(1 + \frac{k_{ref}t}{2}\right)}$$

Now since $k < k_{ref}$, the critical term is $k_{ref}t$. If $k_{ref}t/2 \ll 1$ we are justified in writing

$$\frac{N_{min}}{N_{max}} \approx \frac{k}{k_{ref}} = f(x) \tag{A1}$$

which are the last three terms of Eq. 3 in the text.

In terms of ΔSNM , the change in soil mineral N accumulation,

$$\frac{\frac{d}{dt} N_{\min}}{\left(\frac{d}{dt} N_{\min}\right)_{\max}} = \frac{\frac{\Delta\text{SNM}}{\Delta t}}{\frac{\Delta\text{SNM}_{\max}}{\Delta t}} = \frac{\Delta\text{SNM}}{\Delta\text{SNM}_{\max}} \quad (\text{A2})$$

Again the first order rate equation gives:

$$\begin{aligned} \frac{\frac{d}{dt} N_{\min}}{\left(\frac{d}{dt} N_{\min}\right)_{\max}} &= \frac{k(N_0 - N_{\min})}{k_{\text{ref}}(N_0 - N_{\max})} = \frac{k\left(1 - \frac{N_{\min}}{N_0}\right)}{k_{\text{ref}}\left(1 - \frac{N_{\max}}{N_0}\right)} = \frac{k[1 - (1 - e^{-kt})]}{k_{\text{ref}}[1 - (1 - e^{-k_{\text{ref}}t})]} = \frac{ke^{-kt}}{k_{\text{ref}}e^{-k_{\text{ref}}t}} \\ &= \frac{k}{k_{\text{ref}}} \left(\frac{1 - kt + O(kt)^2}{1 - k_{\text{ref}}t + O(k_{\text{ref}}t)^2} \right) \end{aligned}$$

and again if $k_{\text{ref}}t \ll 1$ (and hence $kt \ll 1$) we are justified in writing

$$\frac{\Delta\text{SNM}}{\Delta\text{SNM}_{\max}} = \frac{\frac{d}{dt} N_{\min}}{\left(\frac{d}{dt} N_{\min}\right)_{\max}} \approx \frac{k}{k_{\text{ref}}} \quad (\text{A3})$$

Equations A1–A3 complete our demonstration of Eq. 3 in the Theory section, which allows us to put forward Eq. 4 as a basis for a mathematical description of denitrification.