

A simple denitrification model?
Literature review, sensitivity analysis, and application

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ABSTRACT

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Denitrification is a complex process. In literature, this process is mostly described by a simplified process model. From a literature review, the consensus model describes actual denitrification rate as being equal to some potential denitrification rate subsequently reduced by soil environmental conditions; typically, potential denitrification is reduced by nitrate content, degree of saturation (water content) as a measure for anaerobic conditions, soil temperature, and possibly soil pH. There is, however, much less consensus about the actual shape of the reduction functions. This indicates that these reduction functions are site (soil) specific. From a sensitivity analysis it follows that this model is most sensitive to the water content reduction function. Available data sets were used to determine if these can be used to parameterise the reduction functions. It appears that this is rather difficult, since mostly the measured actual denitrification rate is much less than the potential denitrification rate. Therefore, the reduction functions need to be determined independently.

Keywords: actual denitrification, potential denitrification, nitrate content, water content, degree of saturation, temperature, simple model, reduction function, sensitivity analysis, parameter optimisation

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Preface

This study was carried within the framework of the Dutch research programme “*Onderzoek naar emissieroutes en effecten van maatregelen bij bepaalde bedrijfssystemen (Mest- en Mineralenprogramma 398-II)*”, project III-B “*Denitrificatie in de boven- en ondergrond en relatie met nitraatuitspoeling: modelverkenningen*”, financed by the Dutch ministry of Agriculture, Nature conservation and Fisheries. Special thanks to Christy van Beek (Alterra), Gerard Velthof (Alterra) and Wim Corré (Plant Research International) for making available their data. Peter de Willigen and Gerard Velthof (both Alterra) gave critical comments to the earlier draft of this report.

Samenvatting

Aanleiding

Denitrificatie is het microbiële bodemproces waarbij nitraat wordt omgezet in gasvormige stikstofverbindingen. Denitrificatie treedt alleen op onder zuurstofloze omstandigheden, waardoor neerslagoverschot en grondwaterstand een groot effect (kunnen) hebben op denitrificatie. Naast het gehalte aan nitraat en zuurstof is het gehalte aan gemakkelijk afbreekbare organische stof in de bodem een belangrijke sturende factor; denitrificatie neemt toe naarmate er meer gemakkelijk afbreekbare organische stof aanwezig is in de bodem.

Het Nederlandse mestbeleid is er op gericht om de stikstof- en fosfaatemissies uit de landbouw te beperken, zodat wordt voldaan aan de milieukwaliteitsdoelstellingen voor grond- en oppervlaktewater. Hierbij wordt gebruik gemaakt van het mineralen aangiftesysteem MINAS, een systeem gebaseerd op stikstofbalansen, waarbij boeren heffingen moeten betalen indien het stikstofoverschot een bepaalde waarde (de verliesnorm) overschrijdt. De hoogte van stikstofverliesnormen in MINAS zijn er op gericht om de belasting van het grondwater met nitraat te beperken tot maximaal 50 mg per liter en de belasting van het oppervlaktewater te verminderen. In MINAS wordt een grove schatting toegepast voor denitrificatie, ca. 50% van het totale stikstofverlies wordt toegeschreven aan denitrificatie.. Voor de onderbouwing van het mestbeleid is een betere kwantificering van de denitrificatieverliezen en de verhouding tussen denitrificatie en nitraatuitspoeling bij verschillende combinaties van grondsoort – grondwaterstand – grondgebruik noodzakelijk.

Eén van de beoogde onderzoeksprodukten uit het LNV onderzoeksprogramma “*Onderzoek naar emissieroutes en effecten van maatregelen bij bepaalde bedrijfssystemen*” (Mest en Mineralenprogramma 398-II) luidt: kwantitatieve inzicht verkrijgen door experimentele metingen naar verliezen via denitrificatie en nitraatuitspoeling bij een groot aantal combinaties grondsoort – grondwaterstand – grondgebruik (hoofdthema III). In programma 398-II wordt deze onderzoeksvraag ondersteunt in het project “*Denitrificatie in de boven- en ondergrond en relatie met nitraatuitspoeling: modelverkenningen*” (project III-B). In zusterproject III-A vindt experimenteel onderzoek plaats naar denitrificatie.

Omdat kwantitatief inzicht in denitrificatie niet overal en niet continu kan plaatsvinden, wordt in project III-B een eenvoudige rekenregel opgesteld om denitrificatie te kunnen schatten. Deze rekenregel zal worden getoetst aan o.a. de binnen 398-II verzamelde meetgegevens. Omdat bekend is dat denitrificatie een zeer complex proces is dat onderhevig is aan ruimtelijke en temporele variabiliteit, wordt hier gekozen voor een eenvoudige rekenregel. De eenvoud wordt geïnterpreteerd als zijnde een rekenregel gebaseerd op eenvoudige meetbare, c.q. te simuleren met procesmodellen, grootheden en bodemeigenschappen. Meer specifiek kan hierbij gedacht worden aan de grootheden watergehalte, nitraatgehalte, bodemtemperatuur, en aan de bodemeigenschap potentiële denitrificatie. Onder potentiële denitrificatie wordt in dat geval verstaan de denitrificatiesnelheid gemeten bij overmaat nitraat onder zuurstofloze (anaërobe) omstandigheden bij een gegeven referentietemperatuur.

Dit rapport

Er is nagegaan wat voor type denitrificatie rekenregels er in de literatuur worden toegepast, met name gericht op eenvoudige beschrijvingen. Er zijn beschrijvingen van ruim vijftig simulatiemodellen, c.q. denitrificatiemodellen, verzameld. Dit betekent niet dat er meer dan vijftig

compleet verschillende beschrijvingen van denitrificatie zijn aangetroffen, omdat vaak van elkaars (sub)procesbeschrijvingen gebruik wordt gemaakt.

In hoofdstuk 1 wordt een algemene inleiding gegeven. Grofweg kan men drie typen denitrificatie beschrijvingen onderscheiden: 1) microbiële groeimodellen, 2) bodemstructuurmodellen, en 3) vereenvoudigde denitrificatiemodellen. Hier richten wij ons op het derde type. In dergelijke vereenvoudigde denitrificatiemodellen wordt veelal gebruik gemaakt van empirische responsiefuncties. Een dergelijke responsiefunctie geeft aan in welke mate de potentiële denitrificatie wordt gereduceerd; bijvoorbeeld, door gebrek aan nitraat, of door droogte (lees hoger zuurstofgehalte), of door een lagere temperatuur. Uit de grote variatie in die responsiefuncties blijkt eens te meer dat denitrificatie een moeilijk te modelleren proces is. In één van de vergelijkingsstudies in de literatuur werd geconcludeerd dat in de periode 1980-1990 er weinig progressie is geweest in de mathematische beschrijving van het denitrificatieproces, hetgeen uit onderhavige studie kan worden uitgebreid tot de periode 2002.

In hoofdstuk 2 wordt een algemene eenvoudige rekenregel voor denitrificatie gegeven welke in meeste van de ruim vijftig modellen wordt toegepast (in bijlage A zijn korte beschrijvingen van de afzonderlijke ruim vijftig modellen gegeven). Deze rekenregel kent de volgende twee vormen.

- 1) Denitrificatie wordt als een eerste orde afbraakproces verondersteld gereduceerd door bodemomstandigheden. De maximale denitrificatiesnelheid is gelijk aan een afbraakconstante maal het actuele nitraatgehalte. Deze maximale snelheid wordt vervolgens verlaagd via reductiefuncties voor watergehalte, temperatuur, en eventueel zuurgraad.
- 2) Actuele denitrificatiesnelheid wordt berekend als de potentiële denitrificatiesnelheid gereduceerd door bodemomstandigheden. De potentiële denitrificatie is gedefinieerd als denitrificatie bij overmaat nitraat onder anaërobe omstandigheden bij een gegeven referentietemperatuur. De reductiefuncties hebben betrekking op nitraatgehalte, watergehalte, bodemtemperatuur, en eventueel zuurgraad. In een vergelijking uitgedrukt ziet deze rekenregel er als volgt uit:

$$D_a = D_p f_N f_W f_T f_{pH}$$

hierin is D_a de actuele denitrificatiesnelheid, D_p de potentiële denitrificatiesnelheid, f_N de reductiefunctie voor nitraatgehalte in de bodem, f_W reductiefunctie voor watergehalte in de bodem, f_T de reductiefunctie voor bodemtemperatuur, en f_{pH} de reductiefunctie voor de zuurgraad (pH) in de bodem.

In sommige gevallen zijn de afbraakconstante en potentiële denitrificatiesnelheid gerelateerd aan de koolstofafbraak (respiratie) of koolstofgehalte. De reductie door bodemomstandigheden wordt empirisch beschreven als een product van dimensieloze factoren voor watergehalte, nitraatgehalte, bodemtemperatuur en bodem pH . Hoewel er dus redelijke consensus bestaat in de literatuur over een eenvoudige rekenregel, de invulling van de exacte vorm van de reductiefuncties laat zien dat er grote verschillen bestaan. Dit zou er op kunnen duiden dat dergelijke reductiefuncties afhankelijk zijn van grondsoort en bodemgebruik. Voor relatief nauwkeurige schattingen van denitrificatie dienen deze reductiefuncties mogelijk per locatie te worden vastgesteld. Hierbij moet wel worden gemeld dat onderlinge vergelijking van de afzonderlijke reductiefuncties uit verschillende studies niet zuiver is omdat diverse combinaties van reductiefuncties kunnen leiden tot dezelfde overall reductie. Echter, om inzicht te krijgen in wat er zoal aan reductiefuncties worden gebruikt is een dergelijke vergelijking wel uitgevoerd. De nitraat reductiefunctie wordt meestal door een Michaelis-Menten functie beschreven. De temperatuur reductiefunctie wordt meestal door een Q_{10} of Arrhenius functie beschreven. Reductie voor bodem pH wordt niet altijd toegepast, waarschijnlijk omdat de pH in veel omstandigheden niet veel fluctueert. De grootste verschillen worden waargenomen in de

watergehalte reductiefuncties. Deze functies hebben als overeenkomst dat ze steile trajecten hebben, hetgeen de grote gevoeligheid (zie hoofdstuk 3) verklaard.

In hoofdstuk 3 is een gevoeligheidsanalyse uitgevoerd op de rekenregel op basis van de potentiële denitrificatiesnelheid met reductiefuncties (zie hoofdstuk 2; rekenregel van vorm 2 zoals hierboven gegeven). Op deze manier kan worden vastgesteld wat het effect is van een verandering van een parameter voorkomend in een reductiefunctie op de berekende actuele denitrificatie. Tevens is dit gedaan voor veranderingen in de grootheden nitraatgehalte, watergehalte en bodemtemperatuur. Hoe groter het effect, des te gevoeliger is de schatting van de actuele denitrificatie met behulp van de rekenregel voor die parameter c.q. grootheid. Parameters die een groot effect hebben op de schatting van de actuele denitrificatie moeten nauwkeurig worden vastgesteld. Voor de in dit rapport toegepaste reductiefuncties konden deze effecten analytisch worden vastgesteld. De grootste gevoeligheid ligt in de reductiefunctie voor watergehalte. Omdat in feite niet het absolute watergehalte wordt gebruikt maar de mate van verzadiging, d.w.z. watergehalte gedeeld door het poriënvolume, moet ook het poriënvolume nauwkeurig bekend zijn. Vervolgens is de rekenregel op basis van potentiële denitrificatiesnelheid toegepast op een aselechte dataset van bodemgrootheden, waarbij standaard parameterwaarden uit de literatuur zijn gebruikt. Actuele denitrificatie zal alleen dan gelijk zijn aan de potentiële denitrificatie indien de omstandigheden voor denitrificatie optimaal zijn: overmaat nitraat, anaëroob (verzadigd) en bij de referentietemperatuur. In werkelijkheid zijn de grootheden limiterend, wat leidt tot lagere denitrificatiesnelheden. Uit deze test blijkt dat de actuele denitrificatie meestal veel lager is dan de potentiële denitrificatie. In 70% van de combinaties nitraat-watergehalte-temperatuur was de actuele denitrificatie minder dan 15% van de potentiële denitrificatie. Tenslotte is via een soort Monte-Carlo analyse gekeken naar het effect van spreiding in de parameterwaarden op de berekende denitrificatie, gebaseerd op één set aselechte combinaties nitraat-watergehalte-temperatuur. Ook hieruit volgt dat de parameters van de water reductiefunctie het meest bepalend zijn.

In hoofdstuk 4 wordt met behulp van optimalisatietechnieken nagegaan of de parameters van de eenvoudige rekenregel uit hoofdstuk 2 op een gemakkelijke en unieke wijze kunnen worden vastgesteld op enkele beschikbare datasets. Er waren verschillende datasets beschikbaar voor zand (droog, nat), zavel, zware zavel, veen en (anaëroob) zanderig veen. Er waren grote verschillen tussen de in de studies gemeten actuele denitrificatie en de met de rekenregel (op basis van potentiële denitrificatie) berekende actuele denitrificatie. Vaak kan met behulp van de optimalisatietechnieken geen goede schatting voor de parameters worden verkregen. Een redelijke overeenkomst kon worden verkregen voor een zavelgrond. Voor een droge zandgrond was de overeenkomst slecht. De verklaring voor de verschillen tussen gemeten en berekende denitrificatie moet gezocht worden in het feit dat de gemeten actuele denitrificatie zeer veel lager is dan de potentiële denitrificatie. Hierbij moet worden opgemerkt dat er ook allerlei onzekerheden zijn bij de metingen van de actuele denitrificatie, en dat niet altijd alle grootheden waren gemeten en dus moesten worden geschat. Het verdient de voorkeur om zoveel mogelijk parameters op een onafhankelijke wijze vast te stellen.

In 2003 worden rekenregels afgeleid op basis van experimenteel onderzoek naar potentiële denitrificatie en effecten van nitraatgehalte, watergehalte en temperatuur op de potentiële denitrificatie. De rekenregel zal worden getoetst op locaties waar metingen van actuele denitrificatie worden uitgevoerd. Uiteindelijk worden met de rekenregel en een simulatiemodel de verliezen via denitrificatie en nitraatuitspoeling bij een groot aantal combinaties grondsoort – grondwaterstand – grondgebruik doorgerekend. De uitkomsten worden in overzichtelijke tabellen weergegeven die gebruikt kunnen worden bij onderbouwing en verfijning van het mestbeleid.

Summary

Brief background

Denitrification is a microbial process in the soil that transforms nitrate into gaseous nitrogen. Denitrification occurs when oxygen is lacking. Surplus of rain and groundwater level thus have a large effect on denitrification. Besides nitrate content and oxygen content, the content of easily decomposable organic matter in the soil is a steering factor. Denitrification increases when more easily decomposable organic matter is present.

The Dutch fertiliser policy aims at a reduction of agricultural emissions of nitrogen and phosphorus, so that environmental quality measures for groundwater and open water are fulfilled. In this policy, use is made of the Dutch mineral registration system (MINAS), a system based on nitrogen balances, where farmers must pay levies when the nitrogen surplus exceeds a certain threshold. These thresholds are chosen such that the load of nitrate towards the groundwater is restricted to 50 mg per litre, and that the load of nitrate towards open water systems is decreased. In MINAS a rough guess for denitrification is used, about 50% of the total nitrogen loss is attributed to denitrification. For a better foundation of the policy, a better quantification of denitrification losses is required, as well as quantification of the ratio between denitrification and leaching at different combinations of soil type – groundwater level – land use.

This study was carried within the framework of the Dutch research programme “*Onderzoek naar emissieroutes en effecten van maatregelen bij bepaalde bedrijfssystemen (Mest- en Mineralenprogramma 398-II)*”, project III-B “*Denitrificatie in de boven- en ondergrond en relatie met nitraatuitspoeling: modelverkenningen*”, financed by the Dutch ministry of Agriculture, Nature conservation and Fisheries. Because denitrification cannot be continuously quantified, in project III-B a simple denitrification model will be chosen and tested. By a simple model we mean a model that is based on easily measurable, or simulated with process models, quantities and soil properties. More specifically, one can think of the quantities nitrate content, water content, soil temperature, and of the soil property potential denitrification. Potential denitrification then is defined as denitrification measured with ample nitrate under anaerobic conditions at a given reference temperature.

This report

This report gives a review of simple denitrification models that have been used in literature. Descriptions of more than fifty simulation models, or denitrification models, were collected. This does not mean that more than fifty different denitrification descriptions were obtained, as several models use each others descriptions.

Chapter 1 gives a general introduction. Roughly, three types of denitrification descriptions can be distinguished: 1) microbial growth models, 2) soil structural models, and 3) simplified process models. This report considers the third type. One argument to choose for simplified models may be: the ideal behaviour of any particular reaction system is obscured by the averaging implicit in measuring denitrification in a volume of a real soil, so precise kinetic formulations are unhelpful. Literature reviews on (denitrification) simulation models have been carried out previously. In simplified models use is made of empirical response functions. These response functions differ between the studies, which indicates that denitrification is hard to model. In one of the review studies it was concluded that during the period 1980-1990 little progress (if at all) was achieved in the mathematical description of denitrification. This period can be extended to the present date 2002.

In chapter 2 a simple, universal denitrification model is given that is used by most of the fifty models considered (in appendix A short descriptions of the more than fifty models are given). This model includes two major descriptions:

- 1) Denitrification is considered to be a first order decay process that can be reduced by the governing soil conditions. The maximum denitrification rate is equal to a decay constant times the actual nitrate content. This maximum rate is subsequently reduced by reduction functions for water content, temperature and possibly soil pH.
- 2) Actual denitrification rate is the potential denitrification rate reduced by the governing soil conditions. Potential denitrification is defined as denitrification at excess amount of nitrate under anaerobic conditions at a given reference temperature. The reduction functions pertain to nitrate content, water content, soil temperature and possibly soil pH. Written as an equation, this model is given as

$$D_a = D_p f_N f_W f_T f_{pH}$$

where D_a is the actual denitrification rate, D_p is the potential denitrification rate, f_N is the reduction function for nitrate content in the soil, f_W is the reduction function for water content in the soil, f_T is the reduction function for soil temperature, and f_{pH} is the reduction function for soil pH.

In some cases the first order decay constant and potential denitrification rate are related to organic carbon decay (respiration) or organic carbon content. The reduction by soil conditions is empirically given as the product of dimensionless reduction functions for water content, nitrate content, soil temperature, and soil pH . Despite the consensus about the shape of the simple denitrification model, the expressions of the reduction functions sometimes differ markedly between the several studies. This indicates that these reduction functions are likely to be dependent on soil type and soil usage. For accurate estimates of denitrification these reduction functions thus must be determined for each location. Because several combinations of values of the reduction functions lead to the same overall reduction, it is not pure to compare the reduction functions between the several models. However, to get an impression of the different shapes of the reductions function used in the literature, such a comparison was done here. The nitrate content reduction function is mostly described by a Michaelis-Menten function. The soil temperature reduction function is generally described by a Q_{10} or Arrhenius function. Reduction for soil pH is not always considered, presumably because soil pH does not fluctuate much. The greatest differences are encountered in the water content reduction function. These descriptions have in common that they have steep parts that results in the great sensitivity as shown in chapter 3.

In Chapter 3 a sensitivity analysis is carried out for the simple denitrification model based on potential denitrification. In this way it can be determined what the effect is of a change in a parameter, appearing in a reduction function, on the computed actual denitrification. This was also done for the soil conditions nitrate content, water content and soil temperature. The larger the effect, the more sensitive the denitrification model is for the specific parameter or soil condition. In that case, the specific parameter or soil condition needs to be determined with great accuracy. For the reduction functions in the current model, these effects could be given analytically. The greatest sensitivity was found in the water content reduction function. Since not the actual water content is used but the degree of saturation (water-filled pore space), i.e. water content divided by porosity, means that porosity needs to be determined with great accuracy too. Next, the denitrification model was applied to a random set of soil conditions using a standard set of parameters from the literature. Actual denitrification is only equal to potential denitrification when the conditions are optimal: excess amount of nitrate, anaerobic, saturated conditions, and at the reference temperature. In reality, these soil conditions will mostly be limiting, resulting in lower actual denitrification rates. From this test it appears that actual

denitrification is mostly much lower than potential denitrification. In 70% of the random soil conditions the actual denitrification was less than 15% of potential denitrification. Finally, via a Monte-Carlo analysis the effect of uncertainty in the parameter values on the computed denitrification was determined, for a given set of random soil conditions. Of course, the parameters of the water content reduction function are the most dominant. The coefficient of variation of the computed relative denitrification rate (actual divided by potential) was about the same as the maximum deviation of the tested parameters. When the parameters are determined with a certain uncertainty, say 10%, then the relative denitrification rate has a coefficient of variation of, in this case, 10%.

In chapter 4 it is investigated if the parameters of the simple denitrification model can be easily and uniquely determined from some available data sets. The data sets used refer to sand (wet and dry), loam, heavy loam, peat, and (anaerobic) sandy peat soils. Parameter optimisation was not easy. That means that great differences exist between measured and computed denitrification. Often, no unique minimum in the optimisations could be obtained, so that no good estimates for the parameters could be obtained. A fairly good comparison was obtained for a loam soil. For a dry sand soil the comparison was bad. The explanation for the differences between measured and computed denitrification must be attributed to the fact that the measured actual denitrification is much lower than potential denitrification (in these data sets). Furthermore, it is generally known that measured actual denitrification rates have large measurement errors, and not all soil properties (conditions) were measured and needed to be guessed. Therefore, the conclusion is to independently determine as many as possible the parameters in the reduction functions.

1 Introduction

Denitrification is a complex process in the nitrogen cycle in soils (e.g. Smith and Arah, 1990). It is a microbial process under anaerobic conditions where microbes use nitrate as oxygen donor. This process is further driven by the availability of easily decomposable carbon, temperature and pH. In case excess amounts of nitrate are present in the rooting zone, denitrification will reduce the nitrate content, so that less nitrate remains that can leach downwards. In case only small amounts of nitrate are present in the rooting zone, denitrification can result in too low nitrate contents so that root uptake can be hindered. In all situations, however, denitrification is also a source of burden, as it is a source of N_2O emission. For example, Beauchamp (1997) gives some management practices for controlling N_2O (and thus denitrification) emissions from agroecosystems. To study the effects of denitrification on the nitrogen balance in agricultural systems, simulation models, and thus a denitrification submodel, can be a helpful tool.

A number of different approaches have been used to develop denitrification submodels in N cycling models (Parton *et al.*, 1996): (1) microbial growth models, (2) soil structural models, and (3) simplified process models. The microbial growth models consider the dynamics of microbial organisms responsible for the N cycling processes; examples can be found in Leffelaar (1988) and Leffelaar and Wessel (1988; model DENLEFWAT), in the DNDC model (Li *et al.*, 1992^{ab}; 2000), in the NLOSS model (Riley and Matson, 2000), in the ECOSYS model (Grant, 2001), and in the RZWQM model (Ma *et al.*, 2001). The soil structural models consider gaseous diffusion of gases into and out of aggregates. The distribution of aggregates is considered and denitrification occurs only in the anoxic parts of aggregates; examples can be found in e.g. Arah and Smith (1989), Grant (1991), and Vinten *et al.* (1996). For example, Vinten *et al.* (1996) consider two models: 1) a “simple-structure, randomly distributed, pore model, which is similar (although details differ) to the description used in ANIMO (Groenendijk and Kroes, 1999), and 2) an “aggregate assembly model” developed by Arah and Smith (1989). Simplified process models are easier to use and do not consider microbial processes or gaseous diffusion. Denitrification is assumed to be determined by easily measurable parameters such as degree of saturation, soil temperature and nitrate content of the soil. Such models are practical to use in studies where denitrification at field scale is to be determined. One argument why complex models sometimes are unhelpful may be (Colbourn, 1993): “... the ideal behaviour of any particular reaction system is obscured by the averaging implicit in measuring denitrification in a volume of a real soil, so precise kinetic formulations are unhelpful.”

In some nitrogen mass balance (nitrogen budget) studies denitrification is set equal to the difference between N available for leaching and the amount of N estimated to have been leached from the rooting zone (e.g. Barry *et al.*, 1993). Annual denitrification is sometimes estimated from measured actual denitrification rates by extrapolating mean daily rates, assuming 274 days of activity per year (Groffman *et al.*, 2001). Annual denitrification is sometimes modelled as a fraction (e.g. 0.5) of the yearly amount of nitrification plus nitrate deposition (Bakken and Bleken, 1998). In other (simulation) studies denitrification was disregarded; e.g. the model STICS (Brisson *et al.*, 1998) does not consider denitrification. De Willigen (1991) compared fourteen models, six of which did not consider denitrification in the nitrogen balance. Arguments why denitrification is excluded may be the fact that its contribution to the total budget is only small or is difficult to describe.

Model comparisons or model reviews can be found in the literature. For example, de Willigen (1991) compared fourteen models of which seven considered denitrification. These models were used on a standard data set. One of these models (ANIMO) predicted a much higher loss of

nitrogen due to denitrification (85 kg ha^{-1}) than the other models ($15\text{-}20 \text{ kg ha}^{-1}$) (LEACHM, SOILN, MATHILD, SWATNIT, DAISY, Grant's). Hansen *et al.* (1995) superficially described the description of denitrification of five models (ANIMO, SOILN, OMNI, NLEAP, DAISY). They stated: “*Different models have used a number of different empirical response functions in order to describe the influence of the physical environment on the denitrification process. Comparing the approaches at the 1980 and 1990 workshops, it is evident that only a limited progress, if any, has occurred in the mathematical modeling of denitrification.*”. Marchetti *et al.* (1997) compared denitrification descriptions of six models (EPIC, CropSyst, CREAMS, GLEAMS, CERES-N, NLEAP). These authors concluded “... *the quality of the examined submodels could be improved by a better evaluation of the influence of the soil water content, in interaction with soil hydrological properties, on the denitrification process.... The estimate of denitrification losses by EPIC and CREAMS algorithms was more inaccurate than that of the other models. On the other hand, they were not specifically developed for the simulation of the soil N dynamics. Therefore, applying models with purposes that differ from those for which they were originally designed may be questionable*”. Rodrigo *et al.* (1997) compared the effects of temperature and water content on microbial processes of nine models (SOILN, MATHILD, SUNDIAL, TRITSIM, DAISY, NLEAP, NCSOIL, CANTIS, Kersebaum's) of which five models considered denitrification. These authors conclude (not specifically for denitrification but for all microbial processes) “*Except for NLEAP and NCSOIL models, little differences in effect of water content between models were observed in the climatic conditions tested, because the models are similar in the wet range of soil moisture.... In drier conditions, very large differences between all models were observed.*”. Frohling *et al.* (1998) compared the prediction of N_2O emissions by four models (CENTURY, DNDC, Expert-N, NASA-CASA). Ma and Shaffer (2001) reviewed carbon and nitrogen processes in nine US soil nitrogen dynamics models (NTRM, NLEAP, RZWQM, CENTURY, CERES, GLEAMS, LEACHM, NCSOIL, EPIC). They came up with a general conclusion “*The vast differences among the nine models reflect our understanding of the soil C and N processes. There are no right or wrong answers to the approaches used in the models. All of them are based on a general understanding of the heterogeneity of soil organic matter and residues, supported by limited experimental data. ...the denitrification process is ... simulated differently among the nine models. There is no mechanistic simulation of the denitrification processes as in the NTRM and CENTURY models. Thus far, only the CERES model has a special version for wetland soils when it is used in the CERES-rice model. Denitrification can be triggered by days with precipitation (e.g. NLAEP) or by soil water content (e.g. CERES, RZWQM, EPIC). The denitrification rate can be zero order (e.g. NCSOIL), first order (RZWQM, NLEAP), or Michaelis-Menten (LEACHM). In addition to soil water content, the denitrification rate is also affected by soil temperature and carbon substrate availability as an energy source for denitrifiers (e.g. CERES, NCSOIL, RZWQM, EPIC, NLEAP, DAYCENT).*” McGechan and Wu (2001; see also Wu and McGechan, 1998) reviewed carbon and nitrogen processes in eight European soil nitrogen dynamics models (ANIMO, SOILN, DAISY, SUNDIAL, CANDY, Verberne model (only C dynamics), and three adapted version of SOILN, i.e. SOILN_NO (Norwegian version), SWATNIT (Belgium version), SOILN_NL (Dutch version)). Another comparison study can be found in Renault (1999; models: NGAS, NLEAP, ECOSYS, DNDC). In the book *Modelling Carbon and Nitrogen Dynamics for Soil Management* by Shaffer *et al.* (2001) several models are presented (ECOSYS, RZWQM, DAYCENT, NLEAP, NLOS, SOIL+SOILN, EXPERTN, DAISY, HERMES+MINERVA, WAVE), and two chapters deal with model comparisons (i.e. Ma and Shaffer, 2001; McGechan and Wu, 2001). A large number of models is described in the (German) book of Engel *et al.* (1993). In most cases model comparisons consider only total model outcome. Specific comparisons about model components, e.g. denitrification, is done seldom.

It is the scope of this study to determine what types of simplified denitrification models exist in literature. For that purpose a literature review was carried out based on a literature search from 1990-2001. The idea was that if older models have proven to be good as well, that they are referred to in the current literature, which then have been included in this study too. We were

only interested in total denitrification in the top soil. Therefore, we did not explicitly look for models that determine the N_2O emission or at models that include chemo-denitrification. However, some of the models considered here do compute (are primarily used to compute) N_2O emission occurring from the denitrification process (e.g. NGAS): total denitrification is split in N_2O and N_2 emission with their ratio being dependent on environmental factors (e.g. degree of saturation).

In chapter 2 a summary is presented of existing simple denitrification models that were obtained in a literature review. All models are listed in Appendix A; Table 1-1 gives a list of the models. Many of the models in the literature use similar concepts, so that a suggestion is made for what type of model one could use in the future.

In chapter 3 the 'general' model given in chapter 2 is used in a sensitivity analysis to determine what parameters and soil conditions are the most determining in computing actual denitrification.

In chapter 4 a few denitrification data sets were used in a parameter optimisation procedure to see if the model of chapter 2 can be used to fit measured data.

Table 1-1. Models that are listed in Appendix A, alphabetically ordered.

Model	Reference
ANIMO	Groenendijk and Kroes (1999)
Boundary line model, 1	Elliott and de Jong (1993)
Boundary line model, 2	Bergstrom and Beauchamp (1993)
CANDY	Franko <i>et al.</i> (1995)
CERES	Godwin and Jones (1991)
Colbourn	Colbourn (1993)
COUPMODEL	Jansson and Karlberg (2001)
CREAMS	Knisel (1980) as presented by Marchetti <i>et al</i> (1997)
CREAMS-NT	Deizman and Mostaghimi (1991)
CRISP	Nielsen <i>et al.</i> (1999)
CROPSYST	Stöckle and Nelson (1995) as presented by Marchetti <i>et al</i> (1997)
DAISY	Hansen <i>et al.</i> (1990; 1991)
DAYCENT	Parton <i>et al.</i> (2001), Del Grosso <i>et al.</i> (2001)
DRAINMOD-N	Brevé <i>et al.</i> (1997)
EPIC	Sharply and Williams (1990) as presented by Marchetti <i>et al</i> (1997)
EXPERT-N	Priesack <i>et al.</i> (2001)
GLEAMS	Leonard <i>et al.</i> (1987) as presented by Marchetti <i>et al</i> (1997)
ADAPT	Desmond <i>et al.</i> (1995)
Grundmann & Rolston	Grundmann and Rolston (1987)
HERMES	Kersebaum (1995)
MINERVA	Kersebaum and Beblik (2001)
IMPACT	Andrews <i>et al.</i> (1997)
LASCAM-NP	Viney <i>et al</i> (2000)
LEACHM	Wagenet and Hutson (1989) as presented by Ramos and Carbonell (1991)
LEACHMN	Sogbedi <i>et al.</i> (2001)
Lippold and Matzel	Lippold and Matzel (1992)
MATHILD	Lafolie (1991)
MELEF	Morell <i>et al.</i> (1996)
NCSOIL (NCSWAP)	Molina <i>et al.</i> (1983)

Model	Reference
NEMIS	Hénault and Germon (2000)
NGAS	Parton <i>et al.</i> (1996)
NICCCE	van Dam and van Breemen (1995)
NITDEN	Conijn and Heinen (2001); Conijn (2002)
NITS	Birkinshaw and Ewen (2000)
NITWAT	McIssac <i>et al.</i> (1993)
NLEAP	Shaffer <i>et al.</i> (1991; 2001); Xu <i>et al.</i> (1998)
NLOS	Bittman <i>et al.</i> (2001)
NUCM	Sogn and Abrahamsen (1997)
NUCSAM	Kros (2002)
REMM	Inamdar <i>et al.</i> (1999)
RENLEM	Kragt and de Vries (1989)
RESAM	de Vries <i>et al.</i> (1988; 1994; 1995); Kros (2002)
SMART2	Kros (2002)
SOILN	Johnsson <i>et al.</i> (1987; 1991)
SOILN-modified	Vold <i>et al.</i> (1999)
SONICG	Bril <i>et al.</i> (1994)
STOTRASIM	Feichtinger (1996)
SUNDIAL	Bradbury <i>et al.</i> (1993)
SWAP	van Dam <i>et al.</i> (1997)
SWATNIT	Vereecken <i>et al.</i> (1990; 1991)
SWMS_2D	Šimuněk <i>et al.</i> (1994)
WANISIM	Antonopoulos and Wyseure (1998)
WASMOD	Reiche (1994; 1996)
WAVE	Vanclooster <i>et al.</i> (1996)
WHNSIM	Huwe and Totsche (1995); Huwe (1993)

2 General formulation of a simple denitrification function?

Several comparison studies of models and processes described by these models have not yet led to a universal (simple) description of denitrification (see also 'Introduction'). In this study more than fifty models or denitrification process descriptions have been collected (Table 1-1; Appendix A). The majority of these (simple) models are based on potential denitrification (either measured as a soil's property or computed from organic C dynamics), or consider denitrification as a first-order decay process. As it is generally accepted that environmental soil conditions affect the denitrification process, reduction functions are used. Although denitrification is truly driven by the non-availability of oxygen, most authors argue that oxygen dynamics in soil is hard to simulate, e.g. while it is modified by soil aggregation. Therefore, water content is used as a complementary for oxygen. The higher the water content, the less oxygen will be present. However, water content *per se* does not account for the oxygen diffusion process and thus oxygen availability. Other factors that influence denitrification are soil temperature and soil acidity (*pH*). From this, one can conclude that the following general mathematical function can be used to describe actual denitrification either at the local point scale or from a certain soil layer

$$D_a = \mathbf{a} f_N f_W f_T f_{pH} \quad (2-1)$$

where

D_a	actual denitrification rate (see section 2.1)
\mathbf{a}	parameter depending on exact formulation as discussed in section 2.2
f_N	(dimensionless reduction) function for nitrate content in soil (see section 2.3)
f_W	dimensionless reduction function for water content in soil (see section 2.4)
f_T	dimensionless reduction function for temperature in soil (see section 2.5)
f_{pH}	dimensionless reduction function for soil <i>pH</i> (see section 2.6)

In some cases an additional reduction function for some measure of soil carbon (degradation) is used in Eq. (1). In most cases this will be considered in one of the possibilities of the parameter \mathbf{a} below. In two cases another additional reduction function was introduced to allow for soil depth dependency. We will not consider this, as we assume that \mathbf{a} is (or can be) a function of soil depth: $\mathbf{a} = \mathbf{a}(z)$ The components of Eq. (1) will be described in the forthcoming sections.

It is stressed here that comparison of individual reduction functions should be done with care. In principal they may be dependent on the total model for denitrification. Nevertheless, to give insight in the types used, we will present graphs for water content and temperature reduction functions (and for *pH*) in which a large number of reduction functions are plotted that occur in the models as listed in Appendix A. For the nitrate reduction function this is not done, as for nitrate different units of measure are used, so that comparison is not possible.

Finally, note that actual denitrification is based on some reference variable multiplied with a set of reduction functions. For a given value of the reference, an observation of actual denitrification could be achieved by a innumerable number of combinations of reduction functions. For example, if actual denitrification equals about half the reference, this could be achieved by one reduction function being equal to 0.5 while the others are equal to 1, or by a combination of three reduction function having values 0.7, 0.8, 0.9 ($0.7 \cdot 0.8 \cdot 0.9 \sim 0.5$) or by other possible combinations. Therefore, calibration and validation of Eq. (1) must be accompanied by the availability of environmental conditions as used in the expressions for the reduction functions.

2.1 Actual denitrification D_a

Actual denitrification can be computed at the point scale or at some spatial scale for a certain soil layer. The variable D_a can have the following units:

- $\text{g N kg}^{-1} \text{ d}^{-1}$ when denitrification refers to the local point scale; loss of N on dry soil weight basis;
- $\text{g N m}^{-3} \text{ d}^{-1}$ when denitrification refers to the local point scale; loss of N on soil volume basis;
- $\text{kg N ha}^{-1} \text{ d}^{-1}$ when denitrification refers to a certain layer; in that case the user must indicate to what soil layer thickness the number D_a refers;
- $\text{mg N L}^{-1} \text{ d}^{-1}$ when denitrification refers to the loss of nitrogen from the soil solution (L refers to volume of soil solution) (see section “Nitrate reduction function f_N ”).

2.2 The parameter a

The parameter a indicates the type of denitrification model. Three types can be considered:

- 1) a represents the potential denitrification rate D_p (same units as D_a), and
- 2) a represents a first-order denitrification coefficient (constant) k_d

For both cases, a can be a constant parameter or can be related to carbon dynamics.

ad 1)

When a represents potential denitrification rate we have

$$a = D_p \quad (2-2)$$

where

D_p potential denitrification rate (same units as D_a)

In this concept it is assumed that the particular point or layer in the soil can be characterised by the property potential denitrification rate. The thought behind this choice is, of course, that this is a measure for the decomposition of organic matter. It can be measured relatively simple under optimal conditions, i.e. *in-situ* or on soil samples with high nitrate contents (so that nitrate never will be limiting), under anaerobic conditions (saturated, flushed with N_2 , so that oxygen is lacking) and at the default or reference temperature. With respect to Eq. (1) this would mean that during these measurements all reduction functions remain one (see forthcoming sections). If the organic matter conditions in the soil remain constant in time so will D_p . However, as this is most likely not the case, D_p should be measured as a function of time (e.g. Hénault and Germon, 2000). About 20% of all models listed in Appendix A used the model with $a = D_p$, all in combination with a Michaelis-Menten type function for f_N .

The potential denitrification rate D_p should not be confused with the maximum measured D_a , which is sometimes used as reference.

Models that compute D_p from carbon dynamics are listed in Table 2-1 which also gives the expression for D_p .

Table 2-1. Expression for potential denitrification rate D_p as a function of carbon degradation as used in some of the models listed in Appendix A.

Expression for D_p	Carbon parameter	Model
$\frac{4}{5} \frac{dC}{dt}$	dC/dt : carbon degradation rate	SONICG
$0.1 \frac{dCO_2}{dt}$	dCO_2/dt : CO_2 evolution rate	DAISY
$D_p \frac{dCO_2/dt}{K_C + dCO_2/dt}$	D_p : potential denitrification rate dCO_2/dt : CO_2 evolution rate K_C : Michaelis-Menten half-saturation constant	SOILN-modified

ad 2)

Several models consider denitrification by a first-order decay process. In that case a represents the decay coefficient, i.e.

$$a = k_d \quad (2-3)$$

where

$$k_d \quad \text{first-order denitrification coefficient} \quad d^{-1}$$

Coefficient k_d refers to the situation of optimal conditions. Actual denitrification will be influenced by environmental conditions by the reduction functions for water content and temperature (see Eq. (1)).

When first-order decay is considered, the function f_N in Eq. (1) is no longer a dimensionless reduction function, but it represents the nitrate content of the soil, i.e.

$$f_N \rightarrow [NO_3 - N] \quad (2-4)$$

where

$$[NO_3 - N] \quad \text{nitrate-N content of the soil}$$

The dimension of $[NO_3 - N]$ depends on the units of D_a . Thus, possible units are: $mg\ N\ kg^{-1}$, $mg\ N\ m^{-3}$, $kg\ N\ ha^{-1}$, $(mg\ N\ L^{-1})$.

The majority, about 70%, of the models listed in Appendix A use first-order decay to describe denitrification. Models in Appendix A that differ from the general concept (Eq. (1)) are: NGAS, DAYCENT, NLEAP, EPIC, CROPSYST, CREAMS, GLEAMS, SMART2, EXPERT-N, REMM.

In case first-order decay denitrification is used, the parameter k_d represents the decay coefficient. It has the dimension per day. In most cases it is considered as a parameter with a value obtained from experimental data. Table 2-2 lists some values for k_d . The values are likely to be a function of soil type and may depend on whether nitrate content or nitrate concentration is considered.

Table 2-2. Examples of k_d values used in some of the models listed in Appendix A.

k_d	Units	Units of $[\text{NO}_3\text{-N}]$	Model
0.1	d^{-1}	kg N m^{-3}	DAISY
0.001-0.005	d^{-1}	g N m^{-2}	LEACHM
0.01	d^{-1}	mg N L^{-1}	SWATNIT
0.1	d^{-1}	kg N ha^{-1}	IMPACT
10	yr^{-1}	mol N ha^{-1}	NUCSAM
0.004 – 1.08	d^{-1}	g N m^{-3}	DRAINMOD-N

In some of these models the denitrification coefficient k_d is computed from some soil carbon C information, e.g. respiration rate, total carbon content, water soluble carbon content. Expressions for $k_d(C)$ are given in Table 2-3. In these expressions another decay coefficient appears, which has the dimension of (1 over dimension of C) per day, so that k_d gets its dimension per day.

Table 2-3. Expression for denitrification rate coefficient k_d as a function of carbon degradation as used in some of the models listed in Appendix A.

Expression for k_d	Carbon parameter	Model
kC	C : water soluble carbon content	Grundmann and Rolston
kC	C : carbon content of biologically active soil organic matter	CANDY
kC $C = 24.5 + 0.0031C_s$	C : total water extractable carbon C_s : 58% of the stable humic fraction	CERES
kC $C = 24.5 + 0.0031fH + 0.4CH$	C : total water extractable carbon f : conversion factor to allow for bulk density and layer thickness H : mass of humus (stable) organic matter in soil layer CH : carbohydrate fraction of organic matter in soil layer	CERES in DSSAT
kC $C = 0.58116OM / q$	C : concentration of soluble organic matter OM : easily mineralisable organic matter	WHNSIM(1)
$0.06 + 0.026C_t$	C_t : total carbon content	WHNSIM(2)
$k \frac{d\text{CO}_2/dt}{5}$	$d\text{CO}_2/dt$: the weekly CO_2 evolution rate	SUNDIAL
kC	C : carbon content of organic matter	STOTRASIM
$k \left(24.5 + 0.0031 \frac{C}{2} \right)$	C : organic C content	WASMOD
$0.41C - 0.35MGWL$	C : carbon content of the soil (%) $MGWL$: mean groundwater level (m)	WAVE (sandy soils)
$0.51-0.049L + 0.20C$	C : carbon content of the soil (%) L : clay content (%)	WAVE (clay soils)
kC $C = 0.0087TOC$	C : dissolved C concentration TOC : total C concentration	NITWAT

2.3 Nitrate content reduction function f_N

Based on detailed studies of the reaction of denitrifying bacteria on the presence of nitrate it appears that the bacterial activity is related to nitrate via a Michaelis-Menten type relation. At high nitrate concentrations nitrate is not limiting (*c.f.* zero-order process), while at low nitrate concentrations nitrate becomes limiting (*c.f.* first-order process). Therefore, in most models the nitrate reduction function f_N is considered to be of Michaelis-Menten form

$$f_N = \frac{[\text{NO}_3 - \text{N}]}{K_{MM} + [\text{NO}_3 - \text{N}]} \quad (2-5)$$

where

f_N	nitrate function in the range [0,1]	dimensionless
$[\text{NO}_3 - \text{N}]$	nitrate content of soil, or nitrate concentration in soil solution	(see below)
K_{MM}	Michaelis-Menten half-saturation constant, or the nitrate content or concentration at which $f_N = 0.5$ (same units as $[\text{NO}_3 - \text{N}]$)	(see below)

The variable $[\text{NO}_3 - \text{N}]$ can have units the following units:

- g N kg^{-1} nitrate-N content based on dry soil weight basis;
- g N m^{-3} nitrate-N content based on soil volume basis;
- $\text{kg N ha}^{-1} \text{ d}^{-1}$ nitrate-N content of a certain layer; in that case the user must indicate to what thickness the number $[\text{NO}_3 - \text{N}]$ refers;
- mg N L^{-1} nitrate-N concentration in the soil solution (L refers volume of soil solution).

When nitrate-N concentration is used, an intrinsic effect of water content is included in f_N ; due to changes in water content the nitrate-N concentration may change, while the nitrate-N content remains the same. Equation (1) more or less implicitly implies that the effects of environmental factor act independently, so that the usage of nitrate-N concentration should be dissuaded.

In Table 2-4 an overview is presented of the units and values of K_{MM} used by the models listed in the Appendix. About 20% of all models listed in Appendix A used the model with a Michaelis-Menten type function for f_N all in combination with $a = D_p$.

Table 2-4. Units and values for the Michaelis-Menten half-saturation constant K_{MM} for the models listed in Appendix A.

Units	K_{MM}	Model
mg N kg^{-1}	22	NEMIS
mg N kg^{-1}	117 – 138	SONICG
mg N L^{-1}	10	SOILN, COUPMODEL, LEACHMN
$\text{kg N ha}^{-1} 30 \text{ cm}^{-1}$	$70 (\text{kg N ha}^{-1} 30 \text{ cm}^{-1})^2$	HERMES, MINERVA

Special cases

- As mentioned in the previous section (section 2.2, ad 2), f_N has a special meaning in case first-order denitrification is considered (Eq. (4)): $f_N = [\text{NO}_3 - \text{N}]$.
- The model NITDEN included the N_2O concentration in the Michaelis-Menten function to account for the fact that both NO_3 and N_2O can supply electrons for the denitrification process.
- A regression equation for f_N is sometimes used, for example, as obtained by boundary line models.
- A sigmoidal shaped function was used in the NGAS model.

- In one case, the squared nitrate content in the soil was used in Eq. (5) (HERMES and MINERVA).

According to the Michaelis-Menten function, Eq. (2-5), at high nitrate contents nitrate is non-limiting and the process approaches a zero-order equation. At low nitrate contents nitrate becomes limiting and the process approaches a first-order equation. Under natural conditions the nitrate-N content is relatively low, which explains why in many studies a first-order decay denitrification function is used. For example, assume that the linearization of the Michaelis-Menten curve is valid for $[\text{NO}_3\text{-N}]$ of the same magnitude as K_{MM} and we assume that in the denominator $[\text{NO}_3\text{-N}]$ is constant and equal to K_{MM} , then it can be easily derived that $D_p/2K_{MM}$ represents the first-order decay coefficient (c.f. k_d). For $D_p = 1.5 \text{ g N m}^{-3} \text{ d}^{-1}$ (or $3 \text{ kg N ha}^{-1} \text{ d}^{-1}$ from a layer of 0.2 m) and $K_{MM} = 30 \text{ g N m}^{-3}$ (or 22 mg N kg^{-1} (Table 2-4) for a soil with bulk density of 1350 kg m^{-3}), the estimate for the first-order decay coefficient would be 0.025 d^{-1} , which falls in the range used by the DRAINMOD-N model as mentioned in Table 2-2.

2.4 Water content reduction function f_w

As the water content increases, the air-filled porosity decreases, thus affecting oxygen supply rate. Therefore, it seems reasonable to use a steep, non-linear relationship for the water content reduction function. Many models use a power reduction function of the form

$$f_{w,1} = \begin{cases} 0 & S < w_1 \\ \left(\frac{S - w_1}{w_0 - w_1} \right)^{w_2} & w_1 \leq S \leq w_0 \\ 1 & w_0 < S \end{cases} \quad (2-6)$$

where

$f_{w,1}$	power water reduction function in the range [0,1]	dimensionless
S	degree of saturation or water-filled pore space, defined as q/q_s ; S is always in the range [0,1]	dimensionless
q	volumetric water content	mL cm^{-3}
q_s	q at saturation	mL cm^{-3}
w_0	S above which $f_{w,1} = 1$	dimensionless
w_1	S below which $f_{w,1} = 0$	dimensionless
w_2	shape parameter determining the steepness of the curve	dimensionless

In most cases $w_0 = 1$, however in a few occasions $w_0 = 0.9$ has been used. That means that even for water-filled pores spaces of less than 100% denitrification can occur at optimal rate, provided non-limiting nitrate and temperature conditions. The parameter w_1 is determined experimentally, or is related to a soil property, mostly S at field capacity. The parameter w_2 is a measure for the steepness of the curve, usually $w_2 > 1$; it is $(1-w_1)$ times the slope of the curve at $S = w_0$. Special cases for w_2 are: $w_2 = 0$, what means that $f_{w,1}$ represents a step function with $f_{w,1} = 0$ below w_1 and $f_{w,1} = 1$ above w_1 ; and, $w_2 = 1$, which means that $f_{w,1}$ increases linearly from zero at w_1 to one at w_0 . Table 2-5 presents values for w_0 , w_1 and w_2 found in the models of Appendix A. About 50% of all models listed in Appendix A use Eq. (6) or a closely resembling function.

Table 2-5. Values for the power water reduction function, Eq. (2-6), parameters w_0 , w_1 and w_2 as used by models listed in Appendix A. Models that used same representation but did not explicitly give values for these parameters are (except $w_0 = 1$): LEACHMN, SWATNIT, WANISIM, MATHILD, GLEAMS, ADAPT.

w_0	w_1	w_2	Model
1.0	0.62	1.74 (1.735)	NEMIS, Grundmann and Rolston
1.0	0.577	2.0	SONICG
1.0	0.5	2.5	NITDEN
1.0	0.6	1.0	CERES
1.0	0.58 c	2.0	SOILN
0.9	0.55 c	2.134 c	NGAS, DAYCENT
1.0	0.9 or S_{FC}	1.0	WHNSIM
1.0	0.9	0.0	LASCAM-NP, EPIC
1.0	S_{FC}	0.0	CREAMS(-NT)
1.0	$0.9 - (T - 10)/100$	1.0	STOTRASIM
1.0	?	2.0	DRAINMOD-N
1.0	S_{FC}	1.0	WASMOD, Lippold and Matzel
1.0	0.8	2.0	WAVE
1.0	0.9	1.0	NITWAT
c: computed or calibrated from available data			

In some models the parameter w_1 is a calibrated parameter, while other models set w_1 equal to S at field capacity S_{FC} or have w_1 be a function of S_{FC} . In one case, w_1 is dependent on soil temperature.

Special cases

Other forms of water reduction functions used in the literature are:

- $f_w = 1$ no reduction based on water content: NUCM, IMPACT
- slightly modified version of Eq. (6) SOILN, COUPMODEL
- regression equation for example as obtained by boundary line models
- broken-line, linear DAISY, NITS, NCSOIL
- sigmoidal (see below) NGAS, DAYCENT
- exponential decrease in time if not raining or irrigating NLEAP
- exponential function of q CROPSYST, HERMES, MINERVA, REMM
- power function of q SWAP
- based on groundwater level mostly when denitrification on large spatial and time scale is computed: RESAM, NUCSAM, SMART
- a Michaelis-Menten type function EXPERT-N

Water reduction function and soil texture

The reduction function given above implies that differences between soils (texture) is reflected only in the values of the parameters. However, some studies have explicitly indicated that for different soil types different types of reduction functions apply (NGAS: Parton *et al.*, 1996; DAYCENT: Parton *et al.*, 2001, Del Grosso *et al.*, 2000, 2001). Except for clay soils, the NGAS model uses Eq. (2-6) as well, i.e. for loam and sandy loam soils. For Clay soils a sigmoidal power function for $f_{w,2}$ is used according to

$$f_{w,2} = ab^{-cb^{-ds}} \quad (2-7)$$

where

$f_{w,2}$ sigmoidal power water reduction function in the range [0,1] dimensionless

S	degree of saturation or water-filled pore space, defined as q/q_s ; S is always in the range [0,1]	dimensionless
a, b, c, d	empirical parameters	dimensionless

Based on data read from their graph, the parameters were calibrated as: $a = 3.149$, $b = 36.919$, $c = 23.695$, and $d = 1.326$; $f_{w,2} = 1$ at $S = 0.9$ In general, denitrification in clay soils is less reduced at some value for S than in loam and sandy loam soils.

Later, in the DAYCENT model, the water content reduction function is expressed as a sigmoidal arctangent function $f_{w,3}$ according to

$$f_{w,3} = 0.5 + \frac{\arctan[60p(0.1S - a)]}{p} \quad (2-8)$$

where

$f_{w,3}$	water reduction function in the range [0,1]	dimensionless
S	degree of saturation or water-filled pore space, defined as q/q_s ; S is always in the range [0,1]	dimensionless
a	measure for S at the point of inflection, i.e. $a = 0.1S_{inflection}$	dimensionless

The parameter a is a function of soil gas diffusivity at field capacity D_{FC} and soil respiration rate CO_2 according to

$$a = 0.90 - M(CO_2) \quad (2-9)$$

where M is a multiplier that is a function of soil gas diffusivity at field capacity D_{FC} and can be computed from

$$M = 0.36 - 3.05 * \min[0.113, D_{FC}] \quad (2-10)$$

Based on repacked soil data, Del Grosso *et al.* (2000) concluded that this inflection point occurs at lower values of S for coarser soils (see Table 2-6). For intact soils the authors concluded that for loam soils the point of inflection was not much influenced by the respiration rate, while for clay soils the point of inflection moved towards lower values of S with increasing respiration rates (see Table 2-6).

Table 2-6. Water-filled pore space at inflection points of the arctangent water reduction function (i.e. 10a), Eq. (2-8), undisturbed and disturbed soils with different textures and respiration rates (from Del Grosso et al., 2000).

Repacked soils			Intact soils			
Coarse	Medium	Fine	Loam, low CO_2	Loam, high CO_2	Clay, low CO_2	Clay, high CO_2
0.63	0.75	0.85	0.89	0.81	0.85	0.53

In Figure 2-1 the arctangent water reduction functions (Eq. (2-8)) are shown for $a = 0.01$ to 0.1 (from left to right) as well as the sigmoidal power function (Eq. (2-7)) and the power function of Eq. (2-6) for the NGAS and NEMIS data set. Note the great resemblance between the shapes for a large range of S , except for a model (e.g. NEMIS) that uses $w_0 = 1$. The largest differences occur at the beginnings and the ends of the curves. Finally, it should be noted that the type of reduction function may be dependent on the total denitrification model chosen, so that direct comparison of individual reduction functions should be done with care (see also the beginning of this chapter).

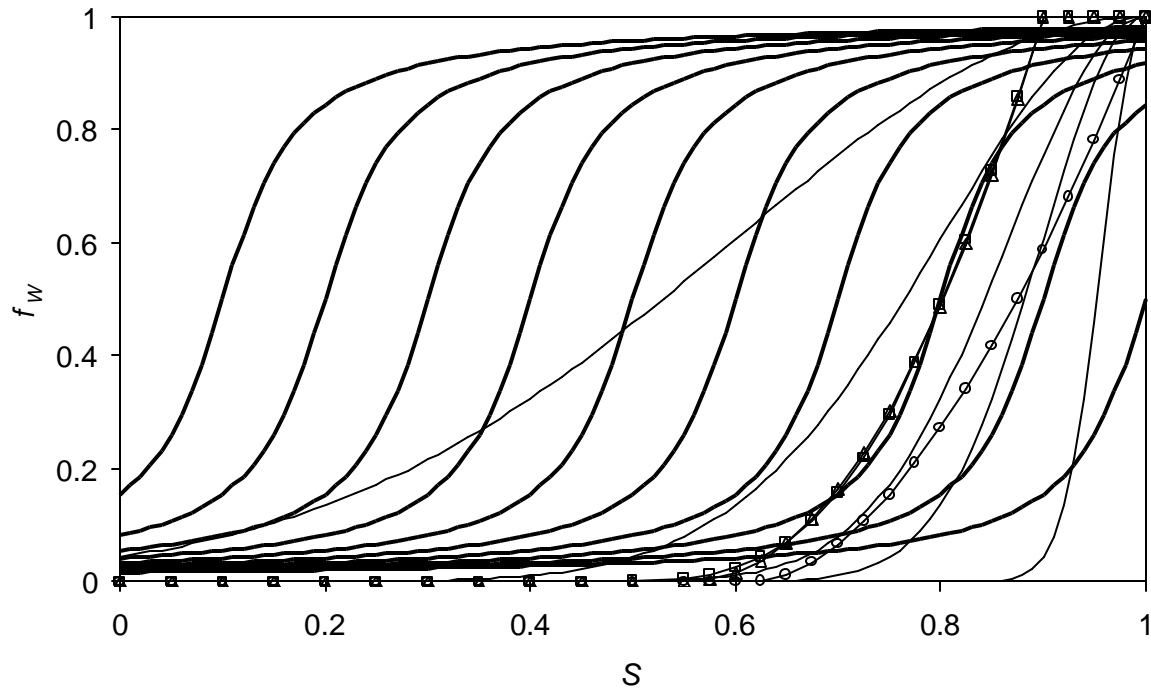


Figure 2-1. Examples of sigmoidal water reduction functions: arctangent, Eq. (2-8), for $a = 0.01$ to 0.1 (thick lines from left to right); sigmoidal power function, ? Eq. (2-7); power function, Eq. (2-6), for two cases, ?,?; exponential polynome, Eq. (2-12), for $k_p = 2.5, 5, 7.5, 10, 25$ (thin lines from left to right).

The disadvantage of the four-parameter sigmoidal water reduction function is that it has four parameters that need to be determined, all of which *a-priori* do not have a physical meaning. The arctangent sigmoidal curve only has one parameter that is related to some physical parameters. The arctangent functions never end at $f_w = 1$ at $S = 1$. If this requirement is, however, to be met, than one could choose to use a second-order exponential polynome:

$$f_{w,4} = \exp(a + bS + cS^2) \quad (2-11)$$

Such a polynome is a bell-shaped function. For our purposes $b > 0$ and $c < 0$ is the most interesting case. Setting the maximum to occur at $S = 1$, it can be shown that the exponential polynome can be restated by the following one-parameter model (*c.f.* Heinen, 1999)

$$f_{w,4} = \exp(-0.5k_p^2(1-S)^2) \quad (2-12)$$

This function has a point of inflection where $f_{w,4}^* = 1/\sqrt{e}$ and $S^* = 1 - 1/k_p$ (superscript $*$ refers to point of inflection); thus the single parameter k_p is related to S^* (similar to the arctangent function before) according to $k_p = 1/(1-S^*)$. In Figure 2-1 some exponential polynomes (thin lines) are presented as well. For small k_p the curves have less steep slopes than the arctangent curves. For larger values of k_p , say $k_p = 7.5$, the slopes are similar to the ones of the arctangent functions, the four-parameter sigmoidal functions and the power function.

Pressure head and hysteresis

In a few cases reduction was not based on water content but on pressure head (or total head) (MELEF, NICCCE, SUNDIAL). The argument is that bacterial activity is related to pressure head. Water content and pressure head are related through the water retention characteristic. However, the water retention characteristic is not a unique relationship as it exhibits hysteresis. Finally, hysteresis itself is an important process that should be considered in simulation models in order to simulate water content (and pressure head) which then is used to predict denitrification (Groffman and Tiedje, 1988).

Overview of water content reduction functions

Figure 2-2 gives an overview of water content reductions functions as used by the authors of the models as listed in Appendix A. There is an extreme wide range of functions, but most of them have $f_w = 0.5$ at $S > 0.7$ (Figure 2-2a). The most extreme function at the left of the graph (with $f_w = 0.5$ at $S = 0.1$) is from EXPERT-N; at the right of the graph are the COUPMODEL functions. Three models, i.e. RESAM, NUCSAM and SMART2, compute denitrification losses on a yearly basis, and have water content reduction based on average highest groundwater (AHG) level (RESAM) or mean spring water (MSW) level (NUCSAM, SMART2) and are shown separately in Figure 2-2b.

2.5 Soil temperature reduction function f_T

The rate of biological processes generally increases exponentially with increasing temperature. At higher temperatures this increase levels off followed by a decrease. The description of exponential increase are mostly based on the van 't Hoff or Arrhenius laws (e.g. Rodrigo *et al.*, 1997). The exponential increase according to van 't Hoff can be described by

$$f_T = \exp(k_H(T - T_{ref})) = Q_{10}^{(T - T_{ref})/10} \quad (2-13)$$

where

T	temperature	K
T_{ref}	reference temperature where $f_T = 1$	K
k_H	exponential increase coefficient	(K) ⁻¹
Q_{10}	increase factor in f_T at an increase in T of 10 K (or 10 °C); $Q_{10} = \exp(k_H/10)$	

One should be aware that, although mostly considered to be a constant, Q_{10} is dependent on the temperature range it was determined for. Typical values used for Q_{10} are 2 or 3.

The exponential increase according to Arrhenius, that has a thermodynamic basis, can be described by

$$f_T = \exp\left(k_A \frac{(T - T_{ref})}{T_{ref} T}\right) \quad (2-14)$$

where

T	temperature	K
T_{ref}	reference temperature where $f_T = 1$	K
k_A	exponential increase coefficient	K

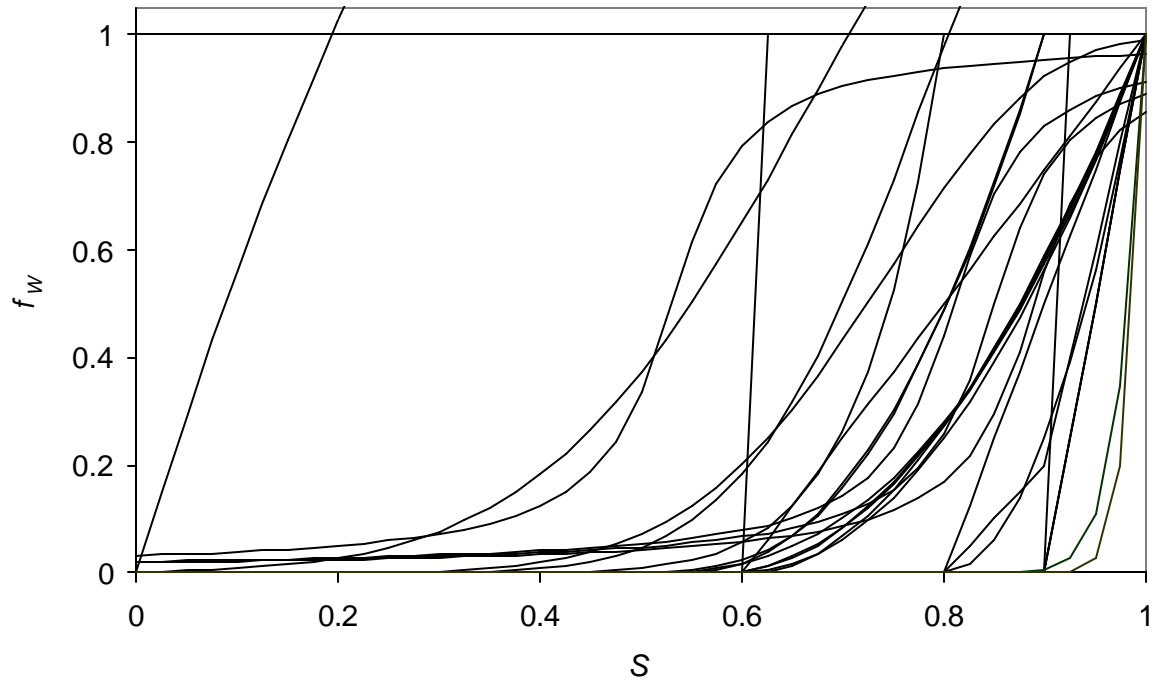
The coefficient k_A is equal to E_A/R , where E_A is the activation energy (J mol⁻¹) and R is the ideal gas constant (8.3144 J mol⁻¹ K⁻¹). A typical value is $k_A = 6352$ K (e.g. Rodrigo *et al.*, 1997).

It can be shown that Q_{10} and k_A are related through

$$Q_{10} = \exp\left(\frac{10k_A}{T_{ref} T}\right) \quad (2-15)$$

This shows that Q_{10} varies with temperature.

a



b

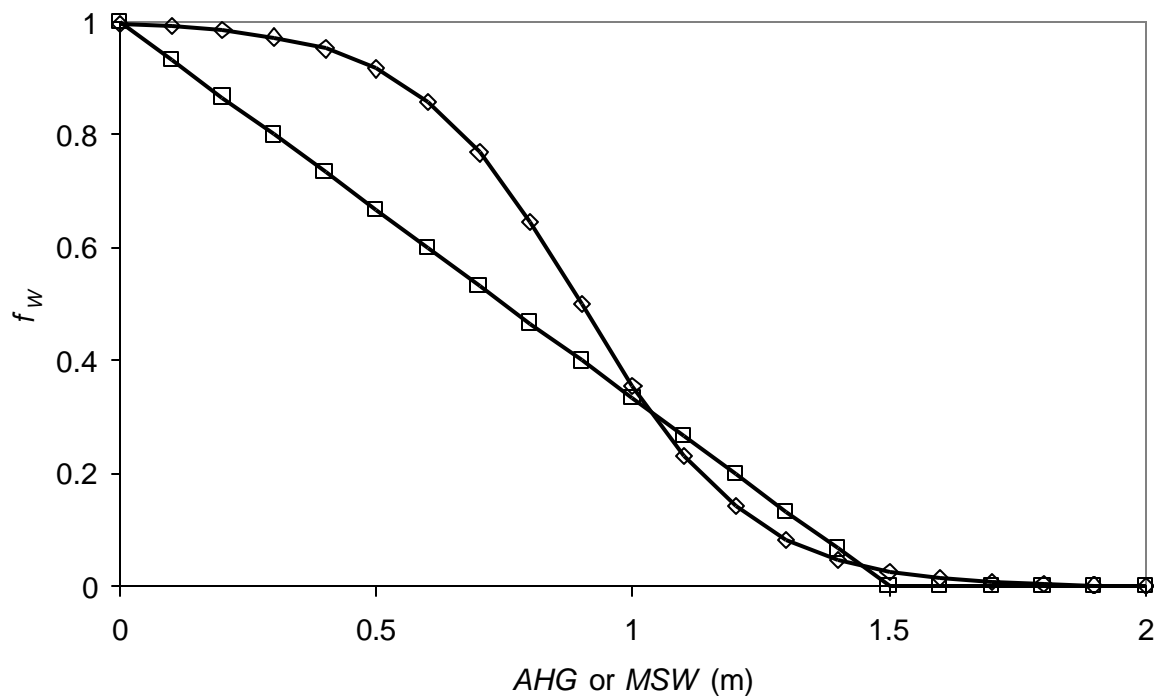


Figure 2-2. Overview of water reduction functions found in the models listed in Appendix A.

a) Based on water-filled pore space: NEMIS, Grundmann and Rolston; SONICG; NITDEN; CERES; SOILN; NGAS; DAYCENT; WHNSIM; LASCAM-NP, EPIC; CREAMS(-NT), $SFC=0.6$; STOTRASIM, $T=10$; STOTRASIM, $T=20$; DRAINMOD-N, $w1=0.5$; WAVE; NITWAT; signoidal power, NGAS; arctan, Loam, low CO_2 , NGAS; arctan, Loam, high CO_2 , NGAS; arctan, Clay, low CO_2 , NGAS; arctan, Clay, high CO_2 , NGAS; DAISY, NITS, NCSOIL; NUCM, IMPACT; CROPSYST, $WCS=0.4$; CROPSYST, $WCS=0.6$; HERMES, MINERVA; EXPERT-N; SWAP, 0.8, 10; COUPMODEL, $WCS=0.4$; COUPMODEL, $WCS=0.6$;

b) Based on average highest groundwater level AHG (RESAM; ?) or mean spring groundwater level MSW (NUCSAM, SMART2; ?).

The Arrhenius equation can be rewritten as

$$f_T = A^{(T-T_{ref})} \quad (2-16)$$

where

$$A = \exp\left(\frac{k_A}{T_{ref} T}\right) \quad (2-17)$$

The parameter A is not a constant as it depends on temperature. However, for the ranges of temperature considered in soils, say $273 \text{ K} < T < 313 \text{ K}$ and $T_{ref} = 293 \text{ K}$, and for a typical value for k_A of 6352 K , it follows from Eq. (2-17) that $1.072 < A < 1.083$, i.e. A can be considered as a constant.

Q_{10} and A are related by

$$Q_{10} = A^{10} \quad (2-18a)$$

or

$$A = Q_{10}^{0.1} \quad (2-18b)$$

For example, for $A = 1.08$, $Q_{10} = 2.16$.

About 40% of all models listed in Appendix A used a Q_{10} - (25%) or Arrhenius- (15%) type temperature reduction function. Examples of values for Q_{10} , A and T_{ref} as found in the models listed in Appendix A are given in Table 2-7.

Table 2-7. Values for the temperature reduction function parameters Q_{10} (Eq. (2-13)) or A (Eq. (2-16)) and reference temperature T_{ref} as used in models listed in Appendix A. Between square brackets the computed values according to Eq. (2-18) are given.

Q_{10}	A	T_{ref}	Model
2.1 / 89 ¹	[1.08] / [1.57]	20 °C	NEMIS
3.0	[1.12]	20 °C	SOILN
2.3	[1.09]		LEACHM
2.0	[1.07]		LEACHMN
1.6	[1.05]		SMART2
3.0	[1.12]	16 °C	WAVE
[2.2]	1.083	20 °C	WANISIM
[2.0]	1.07	15 °C	NUCM
[2.0]	1.07	21 °C	IMPACT
[2.0]	1.072		MATHILD
[2.2] / [1.3]	1.08 / 1.03 ²	15 °C / 10 °C	CROPSYST
[2.2]	1.08	35 °C	CREAMS-NT

¹ two functions were used which intersect at the rupture temperature $T = 11 \text{ °C}$; for $T < 11 \text{ °C}$ a $Q_{10} = 89$ and 2.1 was used, and above it a $Q_{10} = 2.1$ was used

² two functions were used which intersect at the rupture temperature $T = 10 \text{ °C}$; for $T < 10 \text{ °C}$ an $A = 1.03$ was used, and above it an $A = 1.08$ was used

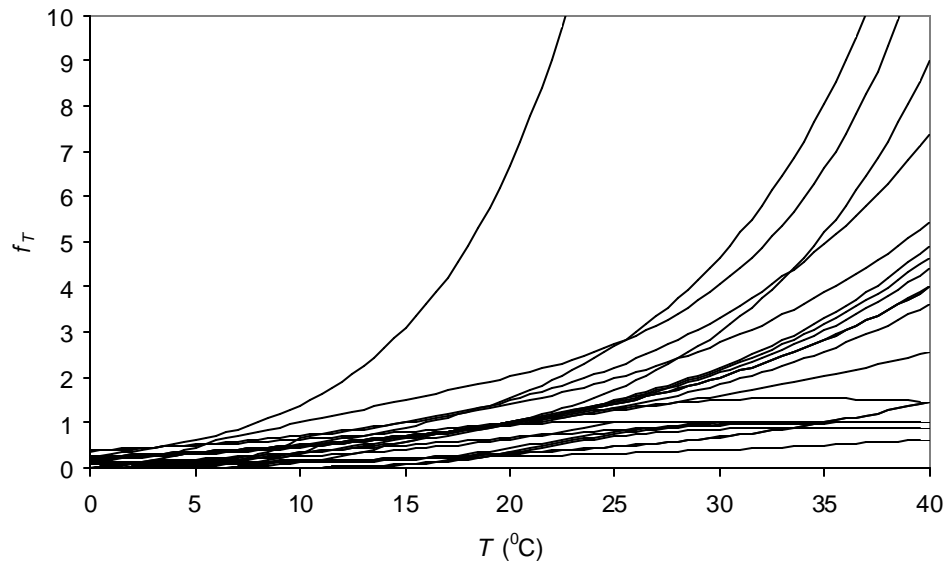
In some cases it is argued that at freezing temperatures ($T < 0 \text{ °C}$) microbial activity equals zero, and thus $f_T = 0$.

In a few models the temperature reduction functions is split in parts (e.g. NEMIS, DAISY, CROPSYST, COUPMODEL). One reason to do so is that different types of denitrifying bacteria operate at each temperature interval. Such an approach requires more parameters and information on the temperature effect.

Overview of temperature reduction functions

In Figure 2-3 an overview is given of temperature reductions as found in models listed in Appendix A. One should realise that in most models a reference temperature is incorporated where $f_T = 1$. As these differ among the models, so will the shape f_T . Therefore, in Figure 2-3b f_T of those models with T_{ref} included are shown as a function of the normalised temperature T/T_{ref} .

a



b

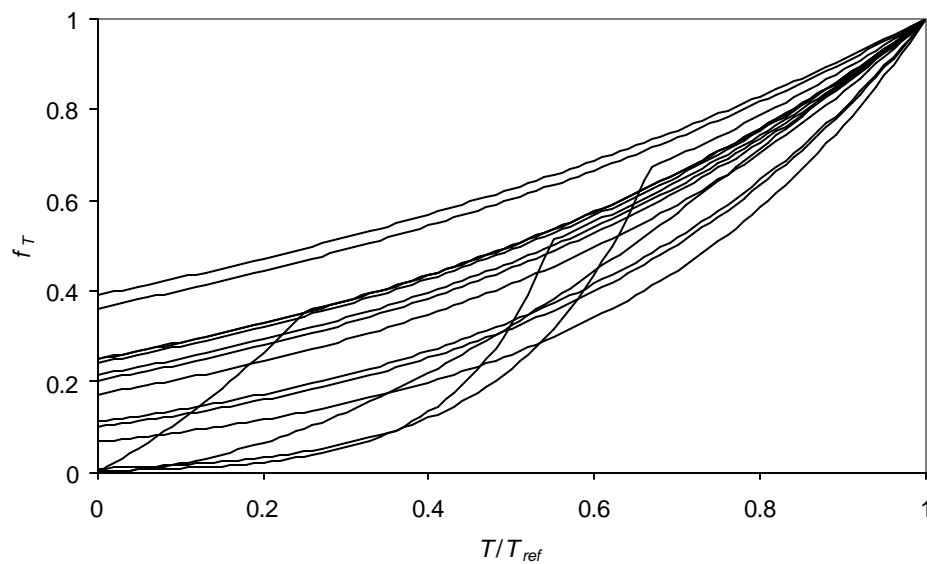


Figure 2-3. Overview of water reduction functions found in the models listed in Appendix A.

a) Based on soil temperature: NEMIS; NITDEN; CERES, WASMOD; DAISY; SOILN; LEACHM(N), 20; WANISIM; NUCM; IMPACT; WHNSIM; MATHILD, 20; NLEAP; EPIC, GLEAMS; CROPSYST; CREAMS-NT; SMART2, 20; STOTRASIM; HERMES, MINERVA; EXPERT-N; REMM, Q10=2.5; SWAP, A=1.08; WAVE; COUPMODEL; NITWAT;

b) Based on normalised soil temperature: NEMIS; NITDEN; SOILN; LEACHM(N), 20; WANISIM; NUCM; IMPACT; MATHILD, 20; CROPSYST; CREAMS-NT; SMART2, 20; REMM, Q10=2.5; SWAP, A=1.08; WAVE; COUPMODEL.

2.6 Soil pH reduction function f_{pH}

Laboratory experiments on the effect of pH on denitrifiers activity have clearly showed that pH has a remarkable effect on denitrification (e.g. Šimek and Hopkins, 1999; Peterjohn, 1991). A clear optimum in denitrification rate exists around $pH = 7$ to 7.5, and denitrification almost ceases for $pH < 4$ or $pH > 10$ to 11.5. The curves shown by these authors is bell-shaped. About 15% of all models listed in Appendix A have a reduction function for pH included. Recently, Šimek and Cooper (2002) reviewed the interactions between pH and denitrification.

Under normal agricultural conditions it is not likely that pH will fluctuate much. If potential denitrification or the decay coefficient are determined under the same pH conditions, it is then not necessary to include the effect of pH in Eq. (1). Errors will arise only during periods after liming. Of course, when effects of soil acidification is considered by the model (e.g. RESAM, NUCSAM, SMART2), including pH effects is required.

Overview of pH reduction functions

Figure 2-4 shows the average pH reduction functions derived from Šimek and Hopkins (1999) and Peterjohn (1991) and the reduction functions used by some of the models listed in Appendix A. Models WHNSIM(2) and CREAMS-NT are about similar to the those of Šimek and Hopkins (1999) and Peterjohn (1991). For $pH < 7$, this is also the case for the RESAM, NUCSAM and SMART models, but for $pH > 7$ it remains equal to one. The models EXPERT-N and NITDEN have extremely different f_{pH} functions (right y -axis), yielding values larger than one.

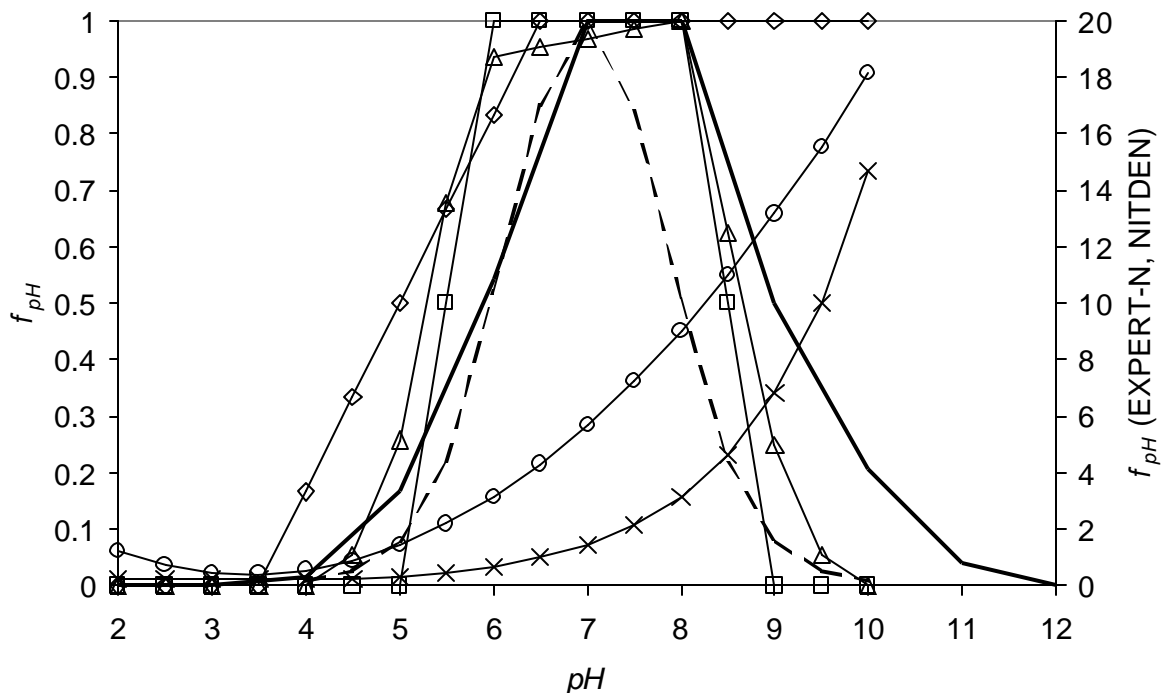


Figure 2-4. Reduction function for pH derived from Šimek and Hopkins (1999) (solid line) and Peterjohn (1991) (broken line), and the reduction functions used by some of the models listed in Appendix A: WHNSIM (?), RESAM, NUCSAM, SMART2 (?), CREAMS-NT (?), Expert-N(3) (?), NITDEN (x).

2.7 Conclusions

In literature many authors use a comparable simple denitrification model. However, no agreement exists about the reduction functions in this model, which accounts for reduction due to nitrate content, degree of saturation, soil temperature, and soil pH. The functions used so far are empirical, and have been calibrated for own studies. In that sense, it is impossible to conclude what function needs to be used in future studies. The transferability of the parameters to other situations (soils, environmental conditions) is questionable. This can, for example, be deducted from the wide range of reduction functions for water and temperature as shown above. Detailed process descriptions of denitrification requires much more input, that is not always easy to collect. Therefore, such models are not widely used.

If denitrification is to be included in models or decision rules, simple denitrification functions can be used, provided that they are calibrated for the circumstances to which it is to be used. Based on the models listed in Appendix A, two major simple models can be distinguished. First, models that describe denitrification as a first-order decay process:

$$D_a = k_d[\text{NO}_3 - \text{N}]f_Wf_T \quad (2-19)$$

Secondly, models that describe denitrification to be related to a potential denitrification rate that can be considered to be a measure for the decomposition of organic matter:

$$D_a = D_p f_N f_W f_T \quad (2-20)$$

When nitrate-N contents in the soil are relatively low, and the f_N function is given as a Michaelis-Menten function, the nitrate reduction is approximately linear to the nitrate-N content. In that case, the difference between the two models will vanish.

Next, per parameter it is indicated how they can be determined.

k_d

measure at nitrate-N contents commonly occurring in the soil

determine at $T = T_{ref}$, where $f_T = 1$

determine under anaerobic conditions where $f_W = 1$

$[\text{NO}_3\text{-N}]$

preferably expressed in units mg N kg^{-1} or kg m^{-3} (dry soil)

D_p

determine under non-limiting nitrate-N contents

determine under anaerobic conditions where $f_W = 1$

determine at $T = T_{ref}$, where $f_T = 1$

f_N

Michaelis-Menten function as a function of $[\text{NO}_3\text{-N}]$

$$f_N = \frac{[\text{NO}_3 - \text{N}]}{K_{MM} + [\text{NO}_3 - \text{N}]} \quad (2-21)$$

determine under anaerobic conditions where $f_W = 1$

determine at $T = T_{ref}$, where $f_T = 1$

f_W

power function following Grundmann and Rolston (1987)

$$f_{w,1} = \begin{cases} 0 & S < w_1 \\ \left(\frac{S - w_1}{w_0 - w_1} \right)^{w_2} & w_1 \leq S \leq w_0 \\ 1 & w_0 < S \end{cases} \quad (2-22)$$

or sigmoidal function following Parton *et al.* (2001)

$$f_{w,2} = ab^{-cb^{-ds}} \quad (2-23)$$

or (comparable shapes can be obtained)

$$f_{w,3} = 0.5 + \frac{\arctan[60p(0.1S - a)]}{p} \quad (2-24)$$

or

$$f_{w,4} = \exp(-0.5k_p^2(1 - S)^2) \quad (2-25)$$

determine under non-limiting nitrate-N contents

determine at $T = T_{ref}$, where $f_T = 1$

f_T

following commonly observed Arrhenius-type or Q_{10} -type (i.e. van 't Hoff-type) behaviour of denitrifiers, such a relationship can be used

$$\begin{aligned} f_T &= Q_{10}^{(T - T_{ref})/10} \\ f_T &= A^{(T - T_{ref})} \end{aligned} \quad (2-26)$$

these two formulations are equivalent: $Q_{10} = A^{10}$ or $A = Q_{10}^{0.1}$.

f_{pH}

As argued in section “Soil pH reduction function f_{pH} ” pH will only have effect when soil pH fluctuates. Except for liming occasions and for soil acidification studies, one can disregard f_{pH} , i.e. keep $f_{pH} = 1$.

The parameters appearing in the reduction functions can be determined from separate experiments as indicated above. The alternative could be to optimise these parameters in a data set containing information on D_a , D_p , $[\text{NO}_3\text{-N}]$, S and T . Examples of such parameter optimisation are presented in Chapter 4.

3 Sensitivity analysis

For Eqs (2-5), (2-6), (2-8), (2-12), and (2-13) it is possible to determine analytically the sensitivity of the reductions functions with changing parameters (Appendix B gives sensitivity of Eq. (2-7)). In what follows I will give the relative change in the reduction function with respect to the relative change in a parameter, which will be called “effect”. In that way, the effects can be compared. An effect equal to one indicates that the reduction function changes proportional and to the same extent to the change in the parameter. A negative effect means that the reduction function becomes less with increasing values of a parameter. The larger the absolute effect the larger is the influence of a change in parameter. Such parameters need to be determined with great care and accuracy.

3.1 Nitrate content reduction function f_N

The relative change of f_N at relative change in K_{MM} is given by

$$\frac{K_{MM}}{f_N} \frac{df_N}{dK_{MM}} = - \frac{K_{MM}}{K_{MM} + [\text{NO}_3 - \text{N}]} \quad (3-1)$$

This effect is not linearly dependent on K_{MM} and not linearly dependent on $[\text{NO}_3 - \text{N}]$.

The relative change of f_N at relative change in $[\text{NO}_3 - \text{N}]$ is given by

$$\frac{[\text{NO}_3 - \text{N}]}{f_N} \frac{df_N}{d[\text{NO}_3 - \text{N}]} = \frac{K_{MM}}{K_{MM} + [\text{NO}_3 - \text{N}]} \quad (3-2)$$

This effect is not linearly dependent on $[\text{NO}_3 - \text{N}]$.

Note that Eqs. (3-1) and (3-2) only differ in the sign.

3.2 Water content reduction function f_w

Equation (2-6): $f_{w,1}$

The relative change of $f_{w,1}$ at relative change in w_1 is given by (for $w_1 < S < w_0$)

$$\frac{w_1}{f_{w,1}} \frac{df_{w,1}}{dw_1} = -w_1 w_2 \frac{(w_0 - S)}{(w_0 - w_1)(S - w_1)} \quad (3-3)$$

This effect is not linearly dependent on w_1 and not linearly dependent on S .

The relative change of $f_{w,1}$ at relative change in w_2 is given by (for $w_1 < S < w_0$)

$$\frac{w_2}{f_{w,1}} \frac{df_{w,1}}{dw_2} = w_2 \ln \left(\frac{(S - w_1)}{(w_0 - w_1)} \right) \quad (3-4)$$

Since $S = w_0$, Eq. (3-4) always result in a negative effect. This effect is linearly dependent on w_2 and not linearly dependent on S .

The relative change of $f_{w,1}$ at relative change in S is given by (for $w_1 < S < w_0$)

$$\frac{S}{f_{w,1}} \frac{df_{w,1}}{dS} = w_2 \frac{S}{(S - w_1)} \quad (3-5)$$

This effect is not linearly dependent on S .

The relative change of $f_{w,1}$ at relative change in w_0 is given by (for $w_1 < S < w_0$)

$$\frac{w_0}{f_{w,1}} \frac{df_{w,1}}{dw_0} = -w_0 \frac{w_2}{(w_0 - w_1)} \quad (3-6)$$

This effect is not linearly dependent on w_0 and independent of S .

In what follows, $w_0 = 1$.

S is defined as volumetric water content q (mL cm³) divided by porosity f_p (cm³ cm⁻³). Thus $f_{w,1}$ can also be written as ($w_0 = 1$)

$$f_{w,1} = \begin{cases} 0 & \frac{q}{f_p} < w_1 \\ \left[\frac{\frac{q}{f_p} - w_1}{1 - w_1} \right]^{w_2} & \frac{q}{f_p} \geq w_1 \end{cases} \quad (3-7)$$

The relative change of $f_{w,1}$ at relative change in q is given by (for $q/f_p > w_1$)

$$\frac{q}{f_{w,1}} \frac{df_{w,1}}{dq} = \frac{qw_2}{(q - w_1 f_p)} \quad (3-8)$$

This effect is not linearly dependent on q . The magnitude of this effect is the same as the magnitude of the effect given by Eq. (3-5).

The relative change of $f_{w,1}$ at relative change in f_p is given by (for $q/f_p > w_1$)

$$\frac{f_p}{f_{w,1}} \frac{df_{w,1}}{df_p} = \frac{qw_2}{(w_1 f_p - q)} \quad (3-9)$$

This effect is not linearly dependent on f_p . The absolute magnitude of this effect is the same as the absolute magnitude of the effect given by Eq. (3-5) or Eq. (3-8); there is only a difference in sign.

In some cases porosity is computed from dry bulk density and the density of the solid phase. Then Eq. (2-6) is written as ($w_0 = 1$)

$$f_{w,1} = \begin{cases} 0 & \frac{q}{1 - \frac{r_d}{r_s}} < w_1 \\ \left[\frac{\frac{q}{1 - \frac{r_d}{r_s}} - w_1}{1 - w_1} \right]^{w_2} & \frac{q}{1 - \frac{r_d}{r_s}} \geq w_1 \end{cases} \quad (3-10)$$

The relative change of $f_{w,1}$ at relative change in q is given by (for $q/f_p > w_1$)

$$\frac{\mathbf{q}}{f_{w,1}} \frac{df_{w,1}}{d\mathbf{q}} = \frac{\mathbf{r}_s w_2 \mathbf{q}}{(\mathbf{r}_s (\mathbf{q} - w_1) + \mathbf{r}_d w_1)} \quad (3-11)$$

The relative change of $f_{w,1}$ at relative change in \mathbf{r}_d is given by (for $\mathbf{q}/\mathbf{f}_p > w_1$)

$$\frac{\mathbf{r}_d}{f_{w,1}} \frac{df_{w,1}}{d\mathbf{r}_d} = \frac{\mathbf{r}_d \mathbf{r}_s w_2 \mathbf{q}}{(\mathbf{r}_s - \mathbf{r}_d)(\mathbf{r}_s (\mathbf{q} - w_1) + \mathbf{r}_d w_1)} \quad (3-12)$$

The expressions Eq. (3-12) and Eq. (3-5) are not identical, their ratio is equal to $\mathbf{r}_d/(\mathbf{r}_s - \mathbf{r}_d) = 1/\mathbf{f}_p$. For consistent values of S , \mathbf{q} , \mathbf{r}_d and \mathbf{r}_s , however, the magnitude of the effect is the same as the magnitude of the effect given by Eq. (3-5).

The relative change of $f_{w,1}$ at relative change in \mathbf{r}_s is equal to minus the relative change of $f_{w,1}$ at relative change in \mathbf{r}_d , i.e. (for $\mathbf{q}/\mathbf{f}_p > w_1$)

$$\frac{\mathbf{r}_s}{f_{w,1}} \frac{df_{w,1}}{d\mathbf{r}_s} = - \frac{\mathbf{r}_d \mathbf{r}_s w_2 \mathbf{q}}{(\mathbf{r}_s - \mathbf{r}_d)(\mathbf{r}_s (\mathbf{q} - w_1) + \mathbf{r}_d w_1)} \quad (3-13)$$

The absolute magnitude of this effect is the same as the absolute magnitude of the effect given by Eq. (3-12); there is only a difference in sign.

Equation (2-8): $f_{w,3}$

The relative change of $f_{w,3}$ at relative change in a is given by

$$\frac{a}{f_{w,3}} \frac{df_{w,3}}{da} = - \frac{60a}{\left(1 + (60p(0.1S - a))^2\right) \left(0.5 + \frac{\arctan(60p(0.1S - a))}{p}\right)} \quad (3-14)$$

This effect is not linearly dependent on a , and not linearly dependent on S .

The relative change of $f_{w,3}$ at relative change in S is given by

$$\frac{S}{f_{w,3}} \frac{df_{w,3}}{dS} = \frac{6S}{\left(1 + (60p(0.1S - a))^2\right) \left(0.5 + \frac{\arctan(60p(0.1S - a))}{p}\right)} \quad (3-15)$$

This effect is not linearly dependent on S .

From Eqs (3-14) and (3-15) it can be shown that the ratio $df_{w,3}/da$ over $df_{w,3}/dS$ is equal to -10 , and that the ratio of the relative effects, Eq. (3-14) over Eq. (3-15), at the point of inflection is equal to -1 .

As for $f_{w,1}$ S in $f_{w,3}$ can be replaced by \mathbf{q}/\mathbf{f}_p or by $\mathbf{q}/(1 - \mathbf{r}_d/\mathbf{r}_s)$. Then the following effects can be given:

$$\frac{\mathbf{q}}{f_{w,3}} \frac{df_{w,3}}{d\mathbf{q}} = - \frac{6\mathbf{q}}{\mathbf{f}_p \left(1 + \left(60p \left(0.1 \frac{\mathbf{q}}{\mathbf{f}_p} - a\right)\right)^2\right)} f_{w,3} \quad (3-16)$$

$$\frac{\mathbf{f}_p}{f_{w,3}} \frac{df_{w,3}}{d\mathbf{f}_p} = - \frac{\mathbf{q}}{f_{w,3}} \frac{df_{w,3}}{d\mathbf{q}} \quad (3-17)$$

and

$$\frac{\mathbf{q}}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{q}} = - \frac{6\mathbf{r}_s \mathbf{q}}{(\mathbf{r}_s - \mathbf{r}_d) \left(1 + \left(60p \left(0.1 \frac{\mathbf{r}_s \mathbf{q}}{\mathbf{r}_s - \mathbf{r}_d} - a \right) \right)^2 \right) f_{W,3}} \quad (3-18)$$

$$\frac{\mathbf{r}_d}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{r}_d} = \frac{\mathbf{r}_d}{\mathbf{r}_s - \mathbf{r}_d} \frac{\mathbf{q}}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{q}} \quad (3-19)$$

$$\frac{\mathbf{r}_s}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{r}_s} = - \frac{\mathbf{r}_d}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{r}_d} = - \frac{\mathbf{r}_d}{\mathbf{r}_s - \mathbf{r}_d} \frac{\mathbf{q}}{f_{W,3}} \frac{df_{W,3}}{d\mathbf{q}} \quad (3-20)$$

The effects with respect to a are not given, as they follow simply from Eq. (3-14) by replacing S by \mathbf{q}/\mathbf{f}_p or by $\mathbf{q}/(1-\mathbf{r}_d/\mathbf{r}_s)$, respectively.

Equation (2-12): $f_{W,4}$

The relative change of $f_{W,4}$ at relative change in k_p is given by

$$\frac{k_p}{f_{W,4}} \frac{df_{W,4}}{dk_p} = -k_p^2(1-S)^2 \quad (3-21)$$

This effect is quadratic dependent on k_p , and quadratic dependent on S .

The relative change of $f_{W,4}$ at relative change in S is given by

$$\frac{S}{f_{W,4}} \frac{df_{W,4}}{dS} = k_p^2 S(1-S) \quad (3-22)$$

This effect is quadratic dependent on S .

From Eqs (3-21) and (3-22) it can be shown that at the point of inflection the ratio $df_{W,4}/dk_p$ over $df_{W,4}/dS$ is equal to $-1/k_p^2$, and that the ratio of the relative effects, Eq. (3-21) over Eq. (3-22), is equal to $-1/(k_p-1)$.

As for $f_{W,1}$ S in $f_{W,4}$ can be replaced by \mathbf{q}/\mathbf{f}_p or by $\mathbf{q}/(1-\mathbf{r}_d/\mathbf{r}_s)$. Then the following effects can be given:

$$\frac{\mathbf{q}}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{q}} = \frac{k_p^2(\mathbf{f}_p - \mathbf{q})^2}{\mathbf{f}_p^2} \quad (3-23)$$

$$\frac{\mathbf{f}_p}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{f}_p} = - \frac{\mathbf{q}}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{q}} \quad (3-24)$$

and

$$\frac{\mathbf{q}}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{q}} = \frac{k_p^2 \mathbf{r}_s (\mathbf{r}_s (1-\mathbf{q}) - \mathbf{r}_d) \mathbf{q}}{(\mathbf{r}_s - \mathbf{r}_d)^2} \quad (3-25)$$

$$\frac{\mathbf{r}_d}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{r}_d} = \frac{\mathbf{r}_d}{\mathbf{r}_s - \mathbf{r}_d} \frac{\mathbf{q}}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{q}} \quad (3-26)$$

$$\frac{\mathbf{r}_s}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{r}_s} = - \frac{\mathbf{r}_d}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{r}_d} = - \frac{\mathbf{r}_d}{\mathbf{r}_s - \mathbf{r}_d} \frac{\mathbf{q}}{f_{W,4}} \frac{df_{W,4}}{d\mathbf{q}} \quad (3-27)$$

The effects with respect to k_p are not given, as they follow simply from Eq. (3-21) by replacing S by \mathbf{q}/\mathbf{f}_p or by $\mathbf{q}/(1-\mathbf{r}_d/\mathbf{r}_s)$, respectively.

3.3 Soil temperature reduction function f_T

The relative change of f_T at relative change in Q_{10} is given by

$$\frac{Q_{10}}{f_T} \frac{df_T}{dQ_{10}} = \frac{(T - T_{ref})}{10} \quad (3-28)$$

This effect is independent on Q_{10} and is linearly dependent on T .

The relative change of f_T at relative change in T_{ref} is given by

$$\frac{T_{ref}}{f_T} \frac{df_T}{dT_{ref}} = -\frac{T_{ref} \ln(Q_{10})}{10} \quad (3-29)$$

This effect is linearly dependent on T_{ref} and is independent on T .

The relative change of f_T at relative change in T is given by

$$\frac{T}{f_T} \frac{df_T}{dT} = \frac{T \ln(Q_{10})}{10} \quad (3-30)$$

This effect is linearly dependent on T .

In Appendix C the sensitivity of the double Q_{10} function by Hénault and Germon (2000) is presented.

When the Arrhenius type reduction function , Eq. (2-16), is used, the following effects are obtained. The relative change of f_T at relative change in A is given by

$$\frac{A}{f_T} \frac{df_T}{dA} = T - T_{ref} \quad (3-31)$$

This effect is independent on A and is linearly dependent on T .

The relative change of f_T at relative change in T_{ref} is given by

$$\frac{T_{ref}}{f_T} \frac{df_T}{dT_{ref}} = -T_{ref} \ln(A) \quad (3-32)$$

This effect is linearly dependent on T_{ref} and is independent on T .

The relative change of f_T at relative change in T is given by

$$\frac{T}{f_T} \frac{df_T}{dT} = T \ln(A) \quad (3-33)$$

This effect is linearly dependent on T .

3.4 Example: table

In Table 3-1 some numerical examples of effects for the reduction functions are given. Per parameter default values were used as listed in the legend of Table 3-1. The effects were computed for two sets of environmental conditions. The most extreme effects are observed in the water reduction function, especially for the function given by Eq. (2-6).

Table 3-1. Relative change of the reduction functions at relative change in parameters for a) $[NO_3-N] = 20 \text{ mg N kg}^{-1}$; $S = 0.675$; $T = 10 \text{ }^{\circ}\text{C}$ en b) $[NO_3-N] = 100 \text{ mg N kg}^{-1}$; $S = 0.85$; $T = 15 \text{ }^{\circ}\text{C}$. The following default values for the parameters were used: $K_{MM} = 22 \text{ mg N kg}^{-1}$, $w_1 = 0.62$, $w_2 = 1.74$, $\phi_p = 0.5 \text{ cm}^3 \text{ cm}^{-3}$, $\rho_d = 1.25 \text{ g cm}^{-3}$, $\rho_s = 2.5 \text{ g cm}^{-3}$, $T_{ref} = 20 \text{ }^{\circ}\text{C}$, $Q_{10} = 2.5$.

	a					b				
	f_N	$f_{w,1}$	$f_{w,3}$	$f_{w,4}$	f_T	f_N	$f_{w,1}$	$f_{w,3}$	$f_{w,4}$	f_T
K_{MM}	-0.52					-0.18				
$[NO_3-N]$	0.52					0.18				
w_1		-16.78					-1.85			
w_2		-3.36					-0.87			
f_p, r_s		-21.35					-6.43			
S, q, r_d		21.35					6.43			
a			-5.73					-3.43		
f_p, r_s			-4.84					-3.65		
S, q, r_d			4.84					3.65		
k_p				-6.76					-1.44	
f_p, r_s				-14.04					-8.16	
S, q, r_d				14.04					8.16	
Q_{10}					-1					-0.5
T_{ref}					-1.83					-1.83
T					0.92					1.37

3.5 Example: graphic

Because most of the effects are non-linear and dependent on the soil's environmental conditions, the effect is not constant. Therefore, the effects have been visualised in 3D contour plots in Figures 3-1 to 3-3.

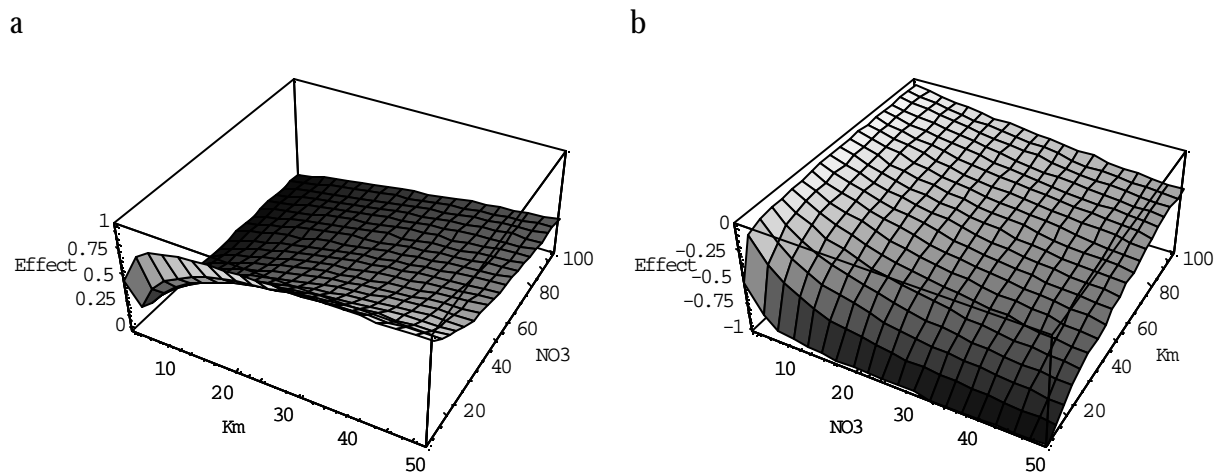
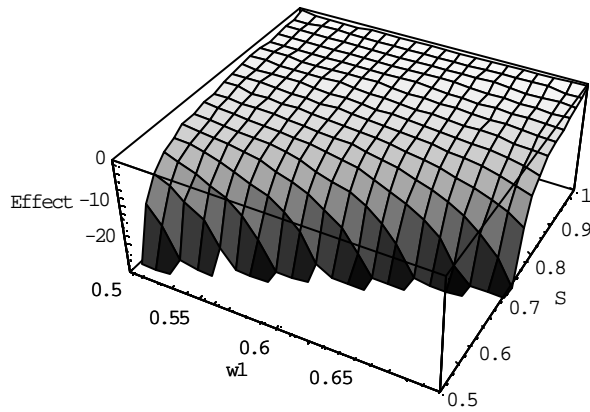


Figure 3-1. a) Relative change in f_N (Effect) at relative change in K_{MM} at varying $[NO_3-N]$ and b) Effect at relative change in $[NO_3-N]$ at varying K_{MM} .

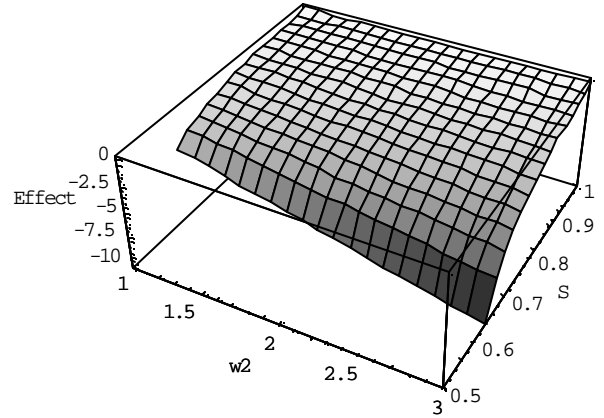
From Figure 3-1 it appears that for low $[\text{NO}_3\text{-N}]$ nitrate-N contents the effects are relatively large. Especially when K_{MM} is not large, both K_{MM} and $[\text{NO}_3\text{-N}]$ need to be determined with great accuracy.

From Figure 3-2 it is clear that the effect is very large when S is close to w_1 . Because the effects on f_W are large (with respect to those on f_N and f_T) it is necessary that both S and w_1 are determined with great accuracy.

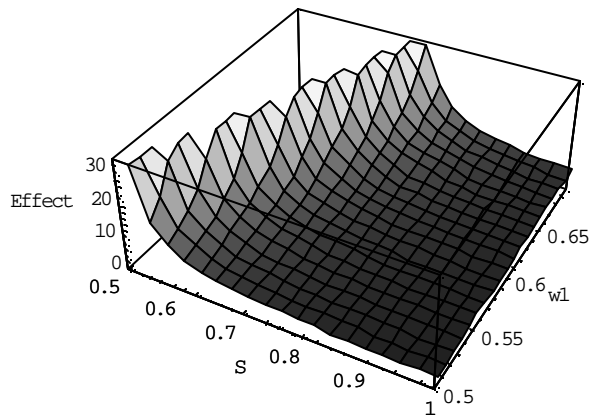
a



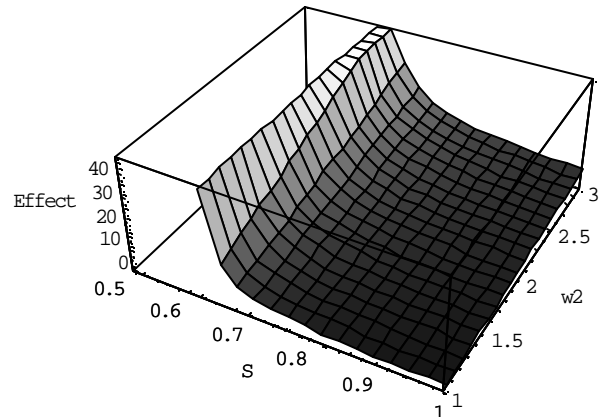
b



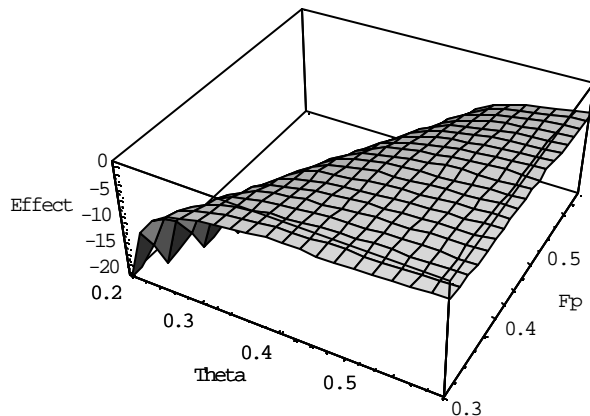
c



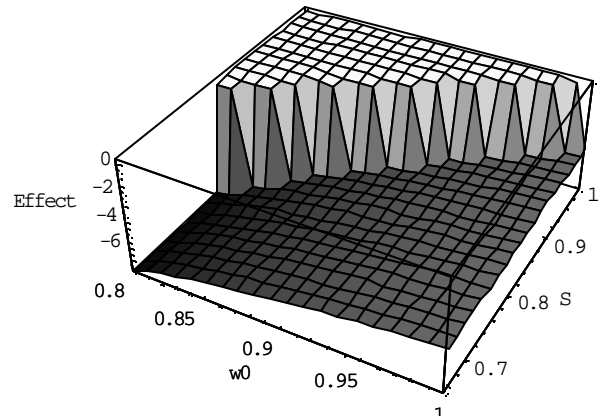
d



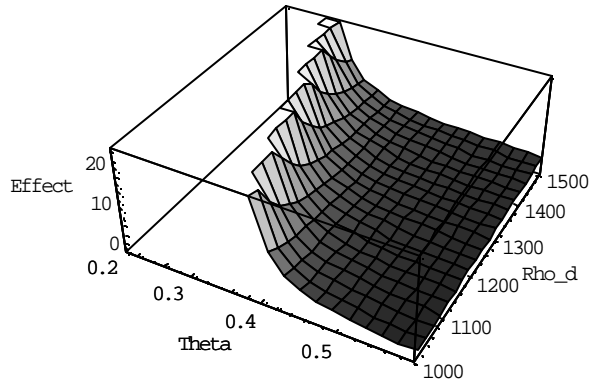
e



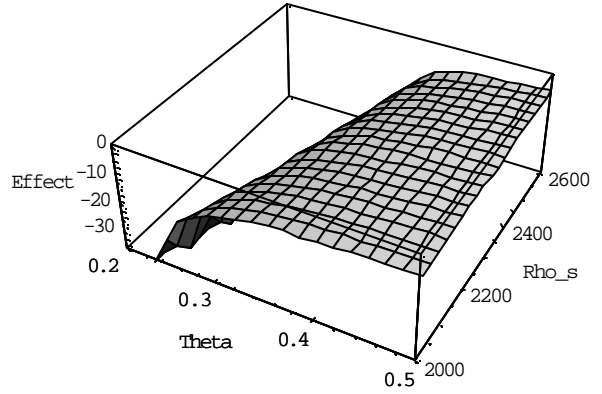
f



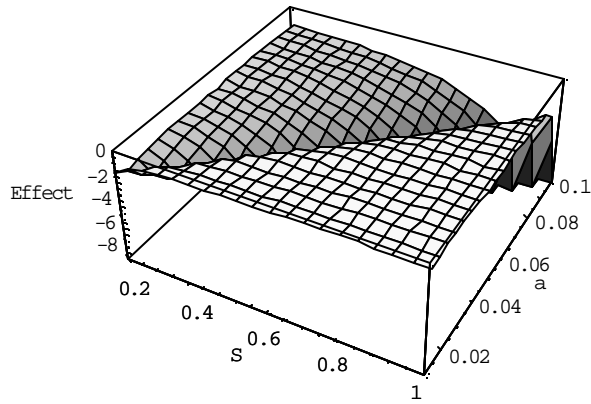
g



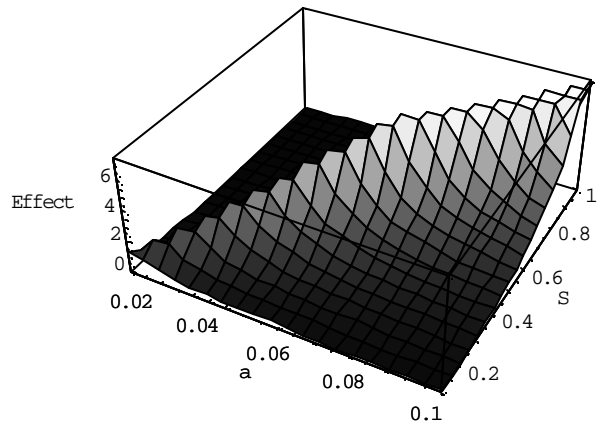
h



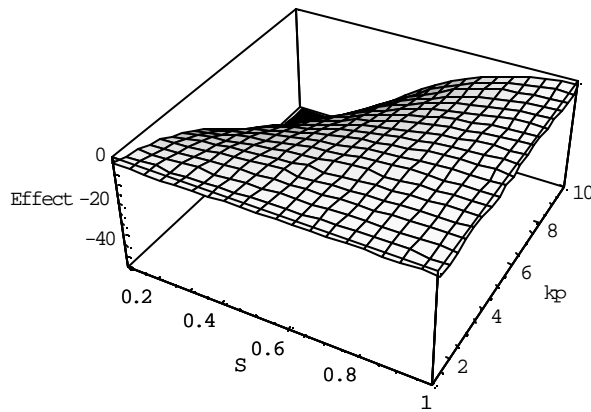
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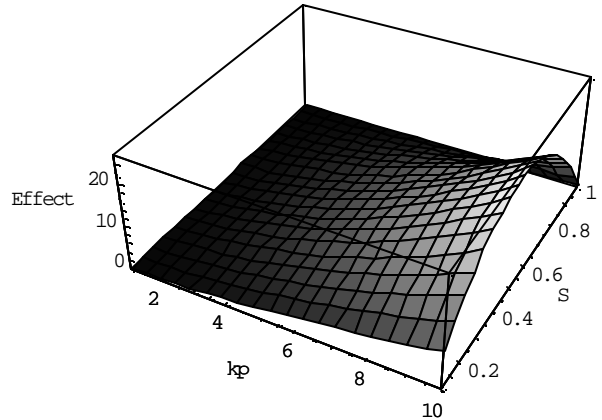
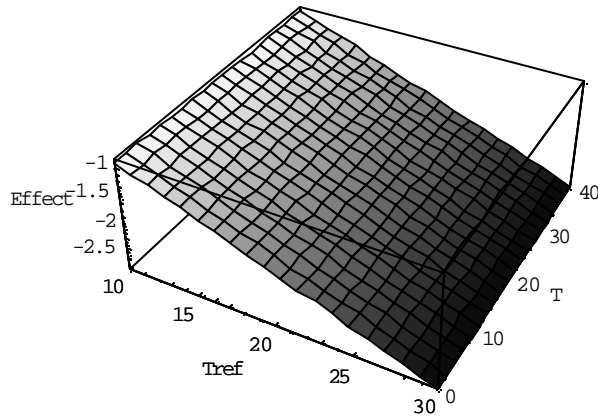
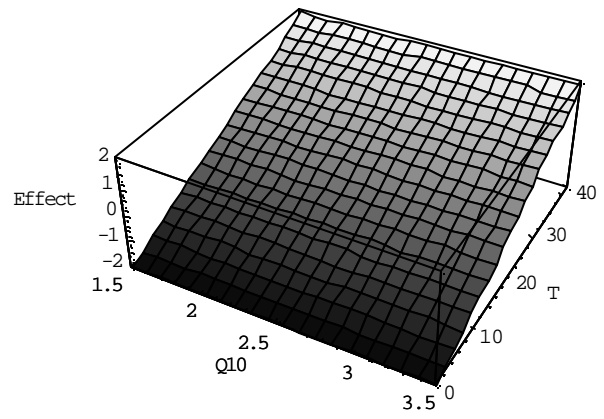


Figure 3-2. For Eq. (2-8): a) Relative change in $f_{w,1}$ (Effect) at relative change in w_1 at varying S , b) Effect at relative change in w_2 at varying S , c) Effect at relative change in S at varying w_1 , d) Effect at relative change in S at varying w_2 , e) Effect at relative change in θ at varying ϕ_p , f) Effect at relative change in w_0 at varying S , g) Effect at relative change in θ at varying ρ_a , and h) Effect at relative change in θ at varying ρ_s . Where needed the following default values were used: $w_0 = 1$, $w_1 = 0.62$, $w_2 = 1.74$. In plots e), f) and g) zones representing over-saturation occur and should be disregarded: in e) θ must be lower than ϕ_p , in f) and g) θ must be lower than $(1-\rho_a/\rho_s)$. For Eq. (2-12): i) Effect at relative change in a at varying S , and j) Effect at relative change in S at varying a . For Eq. (2-13): k) Effect at relative change in k_p at varying S , and l) Effect at relative change in S at varying k_p .

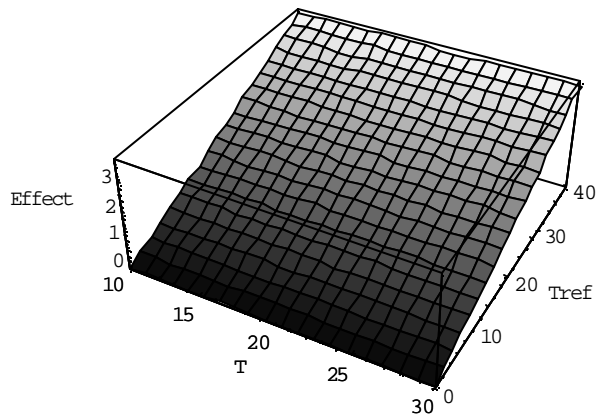
a



b



c



d

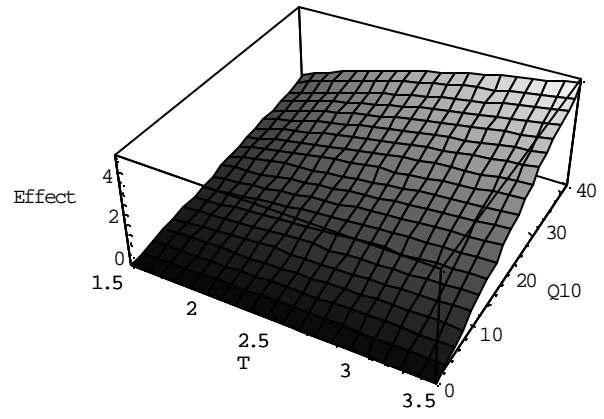


Figure 3-3. a) Relative change in f_T (Effect) at relative change in T_{ref} at varying T , b) Effect at relative change in Q_{10} at varying T , c) Effect at relative change in T at varying T_{ref} , en d) Effect at relative change in T at varying Q_{10} . Where needed the following default values were used: $T_{ref} = 20\text{ }^{\circ}\text{C}$, $Q_{10} = 2.5$.

In general, the effects of w_i en S , and thus also f_p , are large. That means that these quantities need to be determined with great accuracy. It needs to be mentioned here that s and w_i refer to a degree of saturation (water-filled pore space). In most cases the volumetric water content q (mL cm^{-3}) or gravimetric water content w_g (g g^{-1}) is determined. Next, S is computed from q by dividing by the porosity f_p ($\text{cm}^3 \text{cm}^{-3}$), which thus needs to be known:

$$S = \frac{q}{f_p} \quad (3-34)$$

When S is computed from w_g multiplication with dry bulk density r_d (g cm^{-3}) and division by f_p occurs, which thus needs to be known:

$$S = \frac{w_g}{f_p} \frac{r_d}{r_w} \quad (3-35)$$

where r_w is the density of water, mostly considered constant (1.0 g cm^{-3}).

In many cases f_p is computed from r_d in which case a constant density of the solid phase r_s is assumed, for example, $r_s = 2.65 \text{ g cm}^{-3}$:

$$f_p = 1 - \frac{r_d}{r_s} \quad (3-36)$$

All these intermediate steps introduce additional inaccuracies, and thus should be kept to a minimum.

In other cases either r_s or f_p are obtained from pedo-transfer functions. That should be avoided because these are inaccurate.

3.6 Example: random conditions

For a set of default parameter values the relative denitrification rate D_a/D_p is computed for 10000 randomly chosen values of soil conditions, i.e. nitrate content, water content, temperature. The default values were (c.f. Hénault and Germon, 2000): $K_{MM} = 22 \text{ mg N kg}^{-1}$, $w_0 = 1$, $w_1 = 0.62$, $w_2 = 1.74$, $Q_{10} = 2.5$, and $T_{ref} = 20^\circ\text{C}$. Uniform random drawings took place in the following ranges: $0 < [\text{NO}_3\text{-N}] < 200 \text{ mg N kg}^{-1}$, $0.62 < S < 1$, and $0 < T < 20^\circ\text{C}$. In Figure 3-4 D_a/D_p is shown per soil condition.. From Figure 3-4 it is evident that the majority of the D_a/D_p ratios are small. In Figure 3-4d the relative frequency distribution and cumulative frequency distribution of D_a/D_p is given. The maximum of the relative frequency distribution occurs at $D_a/D_p = 0.15$. At $D_a/D_p = 0.15$ the cumulative frequency equals about 70%; i.e. in 70% of the cases $D_a/D_p < 0.15$. Note that the frequency distribution near $D_a/D_p = 0$ shows also a maximum.

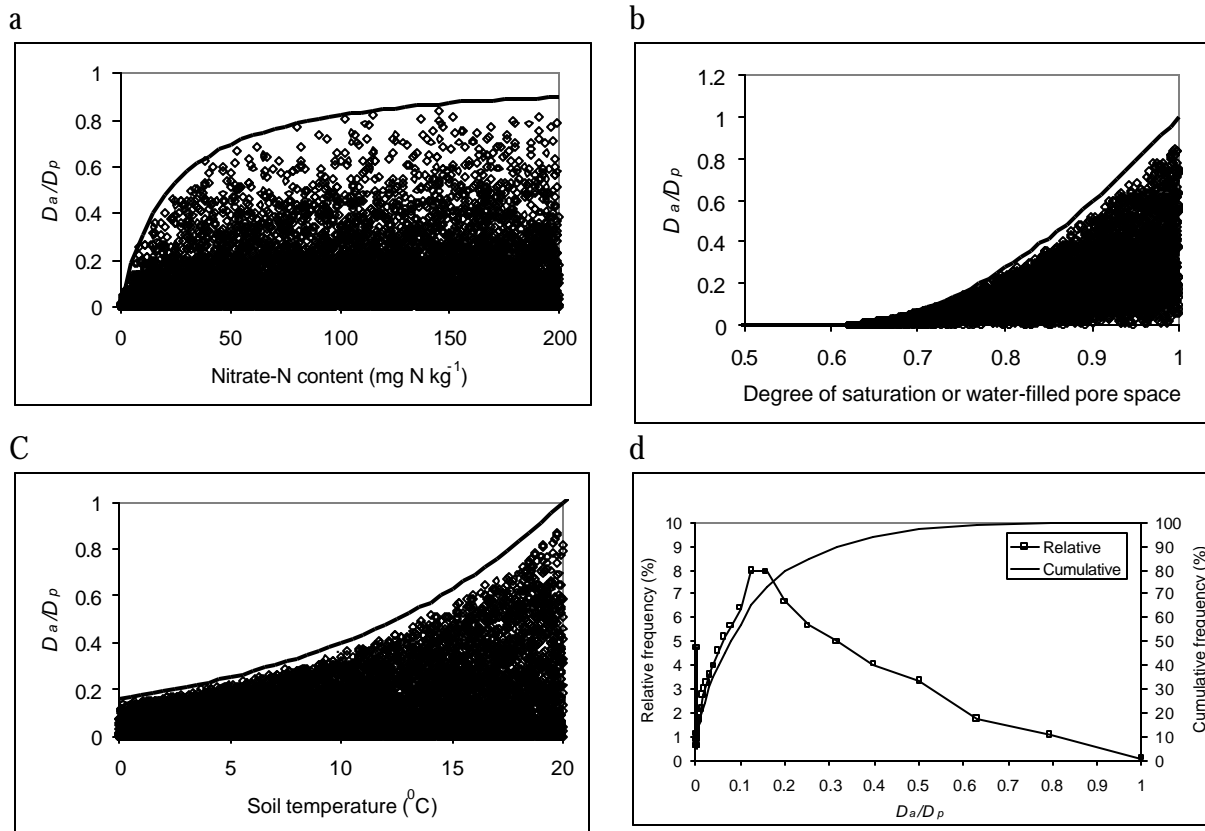


Figure 3-4. Relative denitrification rate D_a/D_p as a function of 10000 randomly drawn soil conditions: a) nitrate-N content, b) degree of saturation (water-filled pore space), and c) soil temperature. The solid lines in a), b) and c) represent the reduction functions Eqs. (2-5), (2-6), (2-13) for parameters $K_{MM} = 22 \text{ mg N kg}^{-1}$, $w_0 = 1$, $w_1 = 0.62$, $w_2 = 1.74$, $Q_{10} = 2.5$, $T_{ref} = 20^\circ\text{C}$. In d) the relative and cumulative frequency distributions of D_a/D_p are shown.

3.7 Example: Monte-Carlo analysis

For randomly chosen combinations of soil conditions and randomly chose combinations of parameters in the reduction functions, the effect of changes in the parameters on denitrification have been analysed.

At first, the analysis was carried out for effects of errors in the parameters of the nitrate reduction function, power water reduction function, and temperature reduction function. The analysis is based on one set of 1000 randomly drawn soil conditions. For parameters K_{MM} , w_1 , w_2 and Q_{10} 100 realisations were taken in any combination, yielding 10^8 realisations in total; $w_0 = 1$ in all cases. In all cases drawings were done from uniform distributions in the wide range [minimum, maximum] as given in Table 3-2. The data set of Ryden (1983; as given by Hénault and Germon, 2000) did not give an indication to use a normal or log-normal distribution for any of the soil conditions. Table 3-3 presents the statistics of the computed D_a for situations when only one parameter was changed (100 realisations) or when all four parameters were changed (10^8 realisations). Variations in the parameter w_1 results in the largest differences in computed D_a (high coefficient of variation). The coefficient of variation in the situation when all four parameters were changed is larger than any of the coefficients of variation in case only a single parameter was changed. This situation is different from the one that is discussed next, since the ranges from which the parameters were drawn were not equal in a relative sense. Expressed as relative denitrification rate D_a/D_p , then mean, minimum and maximum in Table 3-3 are 8.0%, 2.0% en 25.0%, respectively.

Secondly, the analysis was done for all parameters in the three reduction functions. For practical reasons, less realisations per parameter were used: 250 soil conditions and 25 parameter conditions. Since T_{ref} is a pre-defined temperature to which D_p refers, it has less sense to include T_{ref} in the analysis. In Table 3-4 analogous results are presented when the maximal spreading in K_{MM} , w_1 , w_2 and Q_{10} equals 5% with respect to the defaults in Table 3-2. This results to a somewhat smaller D_a accompanied with a drastic lowering of the coefficient of variation. If K_{MM} , w_1 , w_2 and Q_{10} can be determined with an error of 5%, this implies that D_a can be computed with a standard deviation of about 5%. Expressed as relative denitrification rate D_a/D_p , then mean, minimum and maximum in Table 3-4 are 7.1%, 6.2% en 8.1%, respectively. This 1:1 relation appears to be valid also for other maximal errors in the parameters; Table 3-4b gives the results in case the parameters were drawn from a 25% range.

Table 3-2. Default, minimum and maximum values per parameter and soil conditions as used in the Monte-Carlo analysis.

Parameter	Default	Minimum	Maximum
K_{MM} mg N kg ⁻¹	25	5	45
[NO ₃ -N] mg N kg ⁻¹		0	50
w_1	0.6	0.4	0.8
w_2	1.75	1.0	2.5
S		0.35	1
T_{ref} °C	20	15	25
Q_{10}	2.5	1.5	3.5
T °C		5	25
D_p g N ha ⁻¹ d ⁻¹	8000		

Table 3-3. Mean actual denitrification rate D_a ($g\ N\ ha^{-1}\ d^{-1}$) with standard deviation, coefficient of variation (%), minimum and maximum values for situations where parameters K_{MM} , w_1 , w_2 are changed together or independently. For 1000 combinations of soil condition per parameter 100 different (combinations of) values were used.

Varied parameters	Mean	Standard deviation	Coefficient of variation	Minimum	Maximum
K_{MM}, w_1, w_2, Q_{10}	647.7	283.6	43.8	147.3	2282.6
K_{MM}	619.7	163.0	26.3	420.3	958.6
w_1	581.3	178.4	30.7	293.7	860.5
w_2	592.6	105.7	17.8	449.0	786.5
Q_{10}	580.3	34.2	5.9	541.4	652.6

Table 3-4. As Table 3-3, but now temperature reduction function parameters are also included. The parameters were changed in a range around their default values of a) $\pm 5\%$ or b) $\pm 25\%$. For practical reasons, the number of random soil conditions was 250, and for each parameter (not T_{ref}) 25 different (combinations of) values were used. When T_{ref} is included, the numbers between brackets should be read.

Varied parameters	Mean	Standard deviation	Coefficient of variation	Minimum	Maximum
a)					
K_{MM}, w_1, w_2, Q_{10} (+ T_{ref})	564.8 (557.3)	26.4 (37.8)	4.7 (6.8)	496.0 (453.2)	635.7 (689.8)
K_{MM}	563.9	8.9	1.6	549.2	574.7
w_1	569.6	27.8	4.9	523.2	603.0
w_2 (T_{ref})	564.8 (572.4)	11.7 (34.5)	2.1 (6.0)	545.6 (516.1)	579.1 (614.7)
Q_{10}	562.8	5.3	0.9	554.3	569.3
b)					
K_{MM}, w_1, w_2, Q_{10} (+ T_{ref})	591.4 (568.0)	141.3 (201.7)	23.9 (35.5)	298.0 (175.4)	1056.7 (1569.4)
K_{MM}	578.7	46.1	8.0	506.6	637.5
w_1	603.8	13.3	23.1	371.9	770.9
w_2	585.7	61.0	10.4	491.9	664.9
(T_{ref})	(641.6)	(183.3)	(28.6)	(369.4)	(885.7)
Q_{10}	574.6	28.9	5.0	532.6	614.3

3.8 Conclusions

- In Eq. (2-20) D_a is only equal to D_p when all three reductions functions equal one: at excess amounts of nitrate-N, at saturation (anaerobic conditions) and at reference temperature. It is possible that $D_a > D_p$ i.e. at excess amounts of nitrate-N, at saturation, and at temperatures larger than the reference temperature (where D_p is measured at). In most cases, however, one will observe $D_a < D_p$ and the ratio D_a/D_p will always be smaller than the smallest of the reduction functions. Thus, the soil conditions that leads to the smallest value of its reduction function determines D_a / D_p .
- In general, the effects of errors in w_1 and S on D_a are large. That means that these quantities should be determined with great accuracy. Because these two quantities are not measured directly but computed from water content and porosity, this means that both water content and porosity needed to be determined with great accuracy. Additional sources of error are introduced in situations where porosity is estimated from dry bulk density of the soil and the density of the solid phase, or from pedo-transfer functions.
- Low values of K_{MM} and $[NO_3-N]$ need to be determined with great accuracy.

- For a set values of parameters in the reduction functions (Hénault en Germon, 2000) it appears that for randomly chosen soil conditions (nitrate-N content, degree of saturation, soil temperature) the de relative denitrification rate D_a/D_p in 70% of the cases is smaller than 0.15.
- When for randomly chosen soil conditions the parameter values in the reduction functions (only nitrate, water) are varied, it appears that again w_1 has the largest influence. The coefficient of variation of the computed relative denitrification rate D_a/D_p is about equal to the maximal deviation of the parameters. If the parameters can be determined with 10% accuracy, this means that the coefficient of variation in the computed relative denitrification rate D_a/D_p (for all combinations of soil conditions) is about 10%.

4 Reduction function parameters: optimisation on existing data sets

As mentioned at the end of Chapter 2, the parameters in the reduction functions can be optimised using existing data sets. In this chapter a few examples are given. In all cases the denitrification model

$$D_a = D_p f_N f_W f_T \quad (4-1)$$

was used. The following reduction functions were used:

- nitrate the Michaelis-Menten function (Eq. (2-5)),
- temperature the Q_{10} function (Eq. (2-13)),
- water three functions were considered, either Eq. (2-6), Eq. (2-8), or Eq. (2-12).

Optimisations were carried out by minimising the sum of squared differences between predicted and observed actual denitrification, i.e.

$$SSQ = \sum_{i=1}^N (P_i - O_i)^2 \quad (4-2)$$

where

SSQ	sum of squared differences
N	number of observations
P	predicted D_a
O	observed D_a

As it appeared to be difficult (if at all possible) to find a unique set of parameters, several methods, c.q. software, was used for the optimisation: Mathematica[®] (Wolfram, 1999), the amoeba routine of Press *et al.* (1992), the bcoah routine of the IMSL[®] library (Visual Numerics, 1997; see Appendix D), and the solver tool of Microsoft[®] Excel. Results obtained with the last method will be given here.

The data sets considered here were not primarily obtained for validation of Eq. (4-1). That means that not always all the information needed in Eq. (4-1) was available. For example, mostly the volumetric water content was measured but porosity was not measured. For that reason assumptions needed to be made and are explained in each subsection.

The following soil types are considered: loam soil overlying a clay (section 4.1), a dry and a wet sand (section 4.2), peat (section 4.3), anaerobic sandy peat (section 4.4), and a heavy loam (section 4.5).

4.1 Loam soil: the Ryden data set

The data set of Ryden (1983; as given in Hénault and Germon, 2000) refers to a loam soil overlying a clay. Gravimetric water content data were converted to volumetric water contents assuming an average dry bulk density of 1.4 g cm^{-3} and a density of the solid phase equal to 2.6 g cm^{-3} resulting in a porosity of about $0.46 \text{ cm}^3 \text{ cm}^{-3}$. The potential denitrification rate was estimated by Hénault and Germon (2000) as $D_p = 7194 \text{ g ha}^{-1} \text{ d}^{-1}$. Figure 4-1 shows the comparison between measured and simulated actual denitrification rates D_a . The simulated data refer to the computed D_a after optimisation. In total 46 data were available.

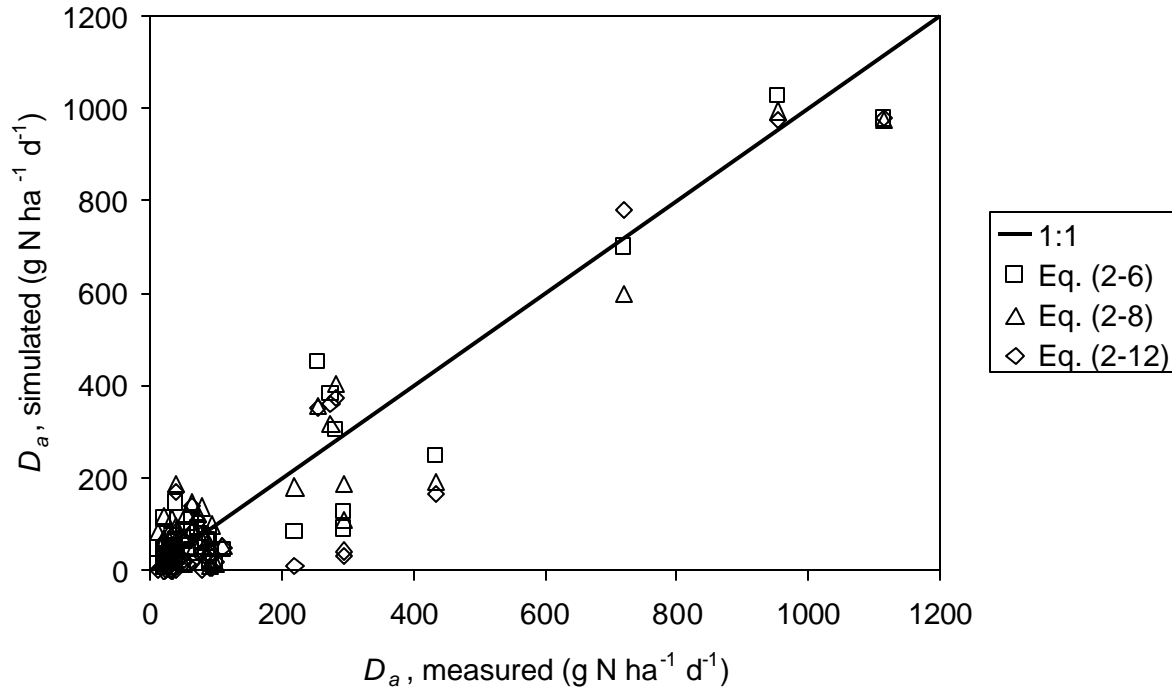


Figure 4-1. Comparison between measured and predicted actual denitrification D_a for the Ryden data set for three cases of water reduction functions: power function Eq. (2-6), arctangent function Eq. (2-8), exponential polynome Eq. (2-12).

Figure 4-1 shows the comparison between measured and simulated D_a for the three water reduction functions considered. The comparison is relatively good. In Table 4-1 the estimated parameters are given as well as the slopes of the regression lines (with intercept equal to zero) through these data. The regressions coefficients belonging to these regression lines are relatively high, indicating that the denitrification model works good on these data. Note that relatively high estimates for the Q_{10} parameter were obtained.

Since for the Ryden data set D_p was estimated by Hénault and Germon (2000), an additional optimisation was carried out in which D_p was estimated as well. This did not result in extremely different estimates for the parameters (Table 4-1).

Table 4-1. Optimised parameters occurring in the reduction functions for six data sets: D_p ($g\ N\ ha^{-1}\ d^{-1}$), K_{MM} ($mg\ N\ kg^{-1}$), w_1 , w_2 , a , k_p , Q_{10} . The regression line without intercept through the data is given by the slope RC and the goodness of this regression is given as R^2 .

Soil type	D_p	K_{MM}	w_1	w_2	a	k_p	Q_{10}	RC	R^2
Loam	7194 ^a	15.50	0 ^d	5.94			3.93	0.928	0.899
	6278	15.09	0 ^d	5.66			3.47	0.926	0.898
	7194 ^a	21.50			0.085		3.12	0.907	0.883
	11956	33.33			0.087		3.85	0.929	0.896
	7194 ^a	22.89				7.19	3.44	0.892	0.861
	5322	21.60				6.69	2.62	0.891	0.858
Dry sand	17350 ^b	22.84	0 ^d	6.39			3.11 ^b	0.635	0.341
	17350 ^b	8.00			0.342		3.11 ^b	0.325	-0.371
	17350 ^b	142.5				3.37	3.11 ^b	0.583	0.280
Wet sand	9796 ^b	4.38	0.33	3.69			3.11 ^b	0.798	0.757
	9796 ^b	8.42			0.0827		3.11 ^b	0.847	0.728
	9796 ^b	3.45				6.26	3.11 ^b	0.839	0.838
Peat		135.3	0 ^d	10.15			3.32	0.553	0.291
		70.60			0.100		2.71	0.723	0.382
		345.5				9.87	2.5 ^a	0.401	0.171
Sandy peat		69.9	c	c	c	c	2.44	0.933	0.743
Heavy loam	2679	22.58	0 ^d	1 ^d			4.99	0.787	0.757
	2682	33.96	0 ^d	1 ^d			3 ^e	0.788	0.754
	22599	15.39			0.098		3.33	0.756	0.725
	6314	6.12				5.73	8.78	0.540	0.608
	4176	26.78				4.85	3 ^e	0.561	0.653
^a fixed value ^b determined from a separate parameter optimisation (see text for explanation) ^c cannot be determined since data refer to anaerobic ($f_w = 1$) measurements ^d lower bound during optimisation ^e upper bound during optimisation									

4.2 Dry and wet sand: the De Marke data set

Corré (1996) measured denitrification on sandy soils of the experimental farm “De Marke”, both for a dry and a wet parcel (both permanent pasture). Table 4-2 gives some general information of both parcels. Measurements were carried out on 20 cm soil samples of the 0-20 cm soil layer. Potential denitrification data were obtained from another study at the same experimental farm “De Marke” (Gorissen *et al.*, 2001).

Table 4-2. Properties of the dry parcel (9) and wet parcel (17) at experimental farm “De Marke”. Groundwater level class is characterised by the average highest groundwater level (GHG) and average lowest groundwater level (GLG).

	Parcel 9 (dry)	Parcel 17 (wet)
Soil profile (Dekkers, 1992)	podzol weak loamy, very fine to moderately fine sand	podzol weak loamy, very fine to moderately fine sand
Groundwater table depth class (Dekkers, 1992)	VII (VIId) GHG 80-140 GLG 180-250	V (Vbo) GHG 25-40 GLG 120-180
Dry bulk density (kg m^{-3}) (W. Corré, pers. comm.)	1340	1430

4.2.1 Data preparation

Data for D_a ($\text{g N ha}^{-1} \text{ d}^{-1}$) and $\text{NO}_3\text{-N}$ (mg N kg^{-1}) were digitally available. Other data were obtained from graphs in Corré (1996). In the following sub-sections details of data preparation are given. It is obvious that the more preparation with corresponding assumptions are needed, the greater will be the errors and uncertainties.

Water content and degree of saturation

Water content was available as gravimetric water content w_g . The degree of saturation S was computed from Eq. (3-35). The porosity f that is needed in Eq. (3-35) was computed according to Eq. (3-36). For mineral soils $r_s = 2650 \text{ kg m}^{-3}$ is a good average value. The dry bulk density r_d is given in Table 4-2; no information was available of r_d of the individual samples.

For about the first two-third of the measurements, w_g was digitally available. These data were compared with those read from the graph. Not all data were comparable, which could not be attributed to false readings from the graph. This represents another source of uncertainty.

Temperature reduction function

Gorissen *et al.* (2001) measured denitrification at a high $\text{NO}_3\text{-N}$ levels under anaerobic conditions, and at governing soil temperature; this was done at three times in a year. Although Gorissen *et al.* (2001) call this potential denitrification, this is not equal to D_p as then the measurements need to have been done at one reference temperature (i.e. 20°C). However, these measurements can be used for calibrating the temperature reduction function. Measurements were only done in a wet parcel (parcel 17-2). Table 4-3 presents the measured denitrification at the given incubation temperatures for the two depths 5 cm and 20 cm. Measurements were done in soil samples of 5 cm height, and here transformed to denitrification rates from a 20 cm soil layer. This transformation is needed since Corré (1996) measured denitrification in 20 cm soil samples. Therefore, an average denitrification rate was obtained at 10 cm from the data of Gorissen *et al.* (2001) through linear interpolation.

Table 4-3. Denitrification rate ($\text{g N ha}^{-1} \text{ d}^{-1}$ per 20 cm soil layer) according to Gorissen *et al.* (2001) for parcel 17-2 of experimental farm “De Marke” at three incubation temperatures at high nitrate content and under anaerobic conditions for soil depths 5 cm and 20 cm. The average for soil depth interval 0-20 cm is also given (see text for explanation).

Temperature ($^{\circ}\text{C}$)	Soil depth		
	5 cm	20 cm	0-20 cm
6	2288	147	1574
14	10888	3612	8463
20	19492	3700	14228

The Q_{10} value was optimised at 3.11 for imposed reference temperature of $T_{\text{ref}} = 20^{\circ}\text{C}$. This is somewhat larger than the expected range of 2 to 3. Measurements were carried out at three times during a year. We assumed that D_p does not change in time. However, for example, Hénault and Germon (2000) and Wheatley and Williams (1989) showed that this is not necessarily true. Finally, measurements by Gorissen *et al.* (2001) were carried out six years later than those of Corré (1996). During this period, D_p may have changed due to changes in soil fertility.

Potential denitrification

Corré (1996) measured denitrification in anaerobic soil samples at governing soil temperature without addition of nitrate (he called this ‘potential denitrification’, but this is not the same as the definition for D_p). These measurements were used to estimate D_p as follows. In Eq. (4-1) we know D_a and f_W ($f_W = 1$), and D_p and the parameter K_{MM} in f_N need to be determined; f_T was already calibrated in the previous sub-section ($Q_{10} = 3.11$ en $T_{\text{ref}} = 20^{\circ}\text{C}$). There were four measurements and four unknowns (D_p and K_{MM} per parcel). However, we assumed that K_{MM} was the same for both parcels. The two values for D_p and the value for K_{MM} were optimised.

Soil temperature

For both parcels one average soil temperature at 10 cm depth per measurement time was available. According to Corré (1996) soil temperature did not differ between the two parcels.

4.2.2 Results and discussion

Potential denitrification

A fairly good agreement between measured anaerobic denitrification and fitted denitrification could be obtained with a single K_{MM} and two D_p values (Table 4-4).

Table 4-4. Measured denitrification rate ($\text{g N ha}^{-1} \text{ d}^{-1}$) at two times in parcels 9 and 17 and computed denitrification rate after optimisation of the parameters K_{MM} (mg N kg^{-1}) and D_p ($\text{g N ha}^{-1} \text{ d}^{-1}$), which values are given as well.

	Parcel 9		Parcel 17	
	Measured	Computed	Measured	Computed
October 1994	1730	1729	630	609
March 1995	1797	1798	152	211
K_{MM}		8		8
D_p		17350		9796

The value for K_{MM} is lower than the one given by Hénault and Germon (2000; 22 mg N kg^{-1}). The value for D_p for parcel 17 is about half the value obtained by Gorissen *et al.* (2001; see Table 4-3). The value for D_p for parcel 9 is about two times that of parcel 17.

For comparison, K. Zwart (unpublished data) measured potential denitrification in disturbed soil samples (0-20 cm soil layer) for a dry (*cf.* parcel 9) and a wet (*cf.* parcel 17) location on experimental farm “De Marke”. These were $4.06 \text{ mg N kg}^{-1} \text{ d}^{-1}$ en $4.27 \text{ mg N kg}^{-1} \text{ d}^{-1}$, respectively.

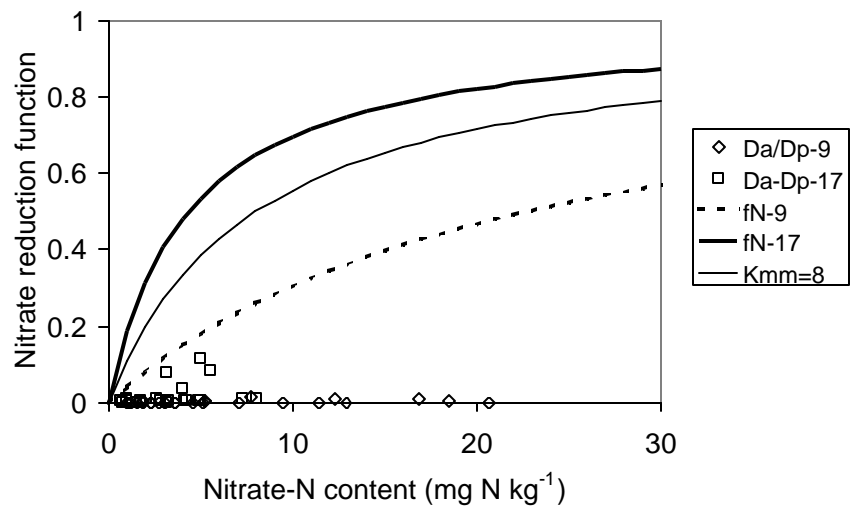
Since disturbed soil samples were used, a direct comparison is not pure. After conversion via dry bulk density (Table 4-2) and layer thickness of 20 cm, these values are equal to $10880 \text{ g N ha}^{-1} \text{ d}^{-1}$ en $12212 \text{ g N ha}^{-1} \text{ d}^{-1}$, respectively. These are of the same order as those given in Table 4-4.

Parameter optimisation

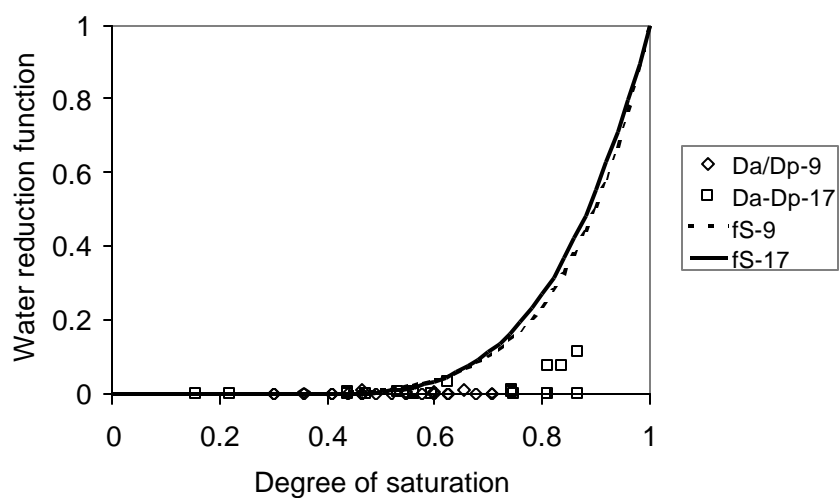
Via parameter optimisation the parameters K_{MM} , w_1 en w_2 were determined (Table 4-1). The values for D_p , Q_{10} and T_{ref} as determined above were used.

The values for K_{MM} differed between the two parcels (Figure 4-2a). For illustration purposes, Figure 4-2a also shows the nitrate reduction function for $K_{MM} = 8 \text{ mg N kg}^{-1}$, the value that was obtained during the optimisation for D_p . The parameter values for the water reduction function differ between the two parcels. However, when plotted graphically, the two water reduction functions differ hardly (Figure 4-2b). Figure 4-2 shows the optimised reduction functions (lines) together with the relative denitrification D_a/D_p (symbols). It is clear that D_a/D_p is always very low. Apparently, at no occasion the circumstances were such that a high denitrification rate resulted. This, of course, influences the reliability of the estimates of the parameters.

a



b



c

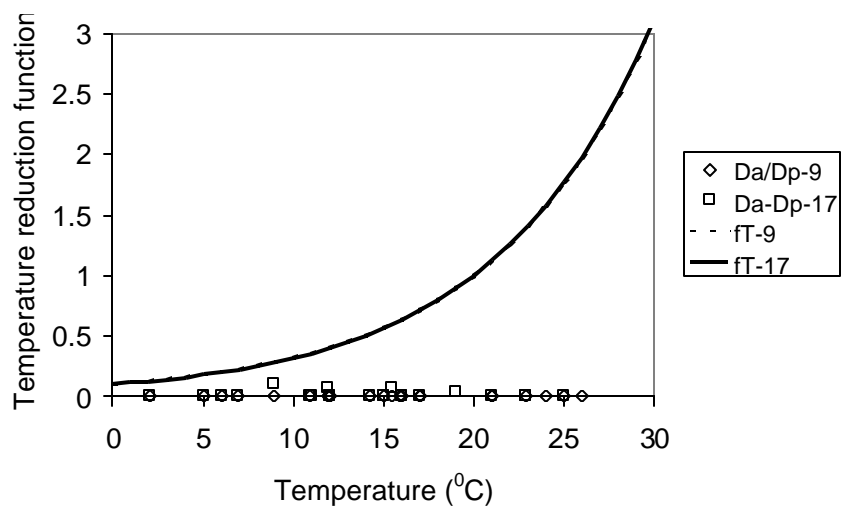
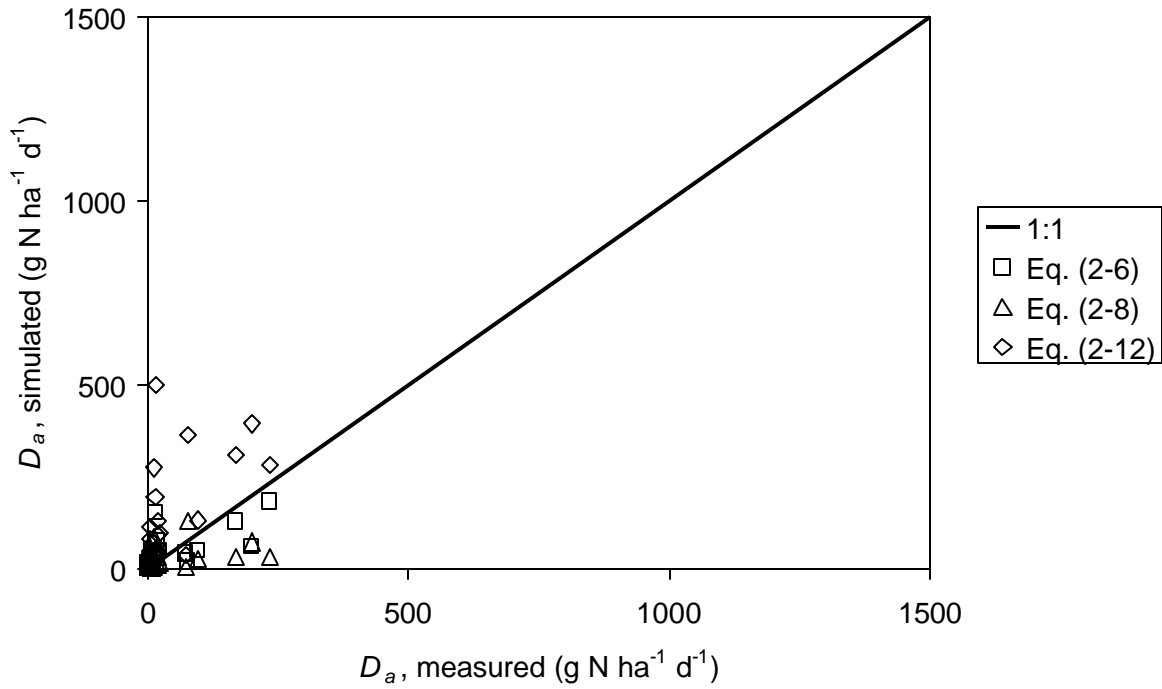


Figure 4-2. Reduction functions (lines) and relative denitrification D_a/D_p (symbols) for parcels 9 (dry) and 17 (wet) for a) nitrate, b) degree of saturation, and c) temperature. The thin line in a) is the nitrate reduction function for $K_{MM} = 8 \text{ mg N kg}^{-1}$, which was used for the determination of D_p . This situation refers to the case where Eq. (2-6) was used.

Figure 4-3 presents the comparison between measured and fitted D_a for the dry parcel 9 (Figure 4-3a) and the wet parcel 17 (Figure 4-3b). The comparison is best for the wet parcel 17. The spreading for the dry parcel 9 is large (low R^2 in Table 4-1). Note that D_a for the dry sand is much smaller than that for the wet sand.

a



b

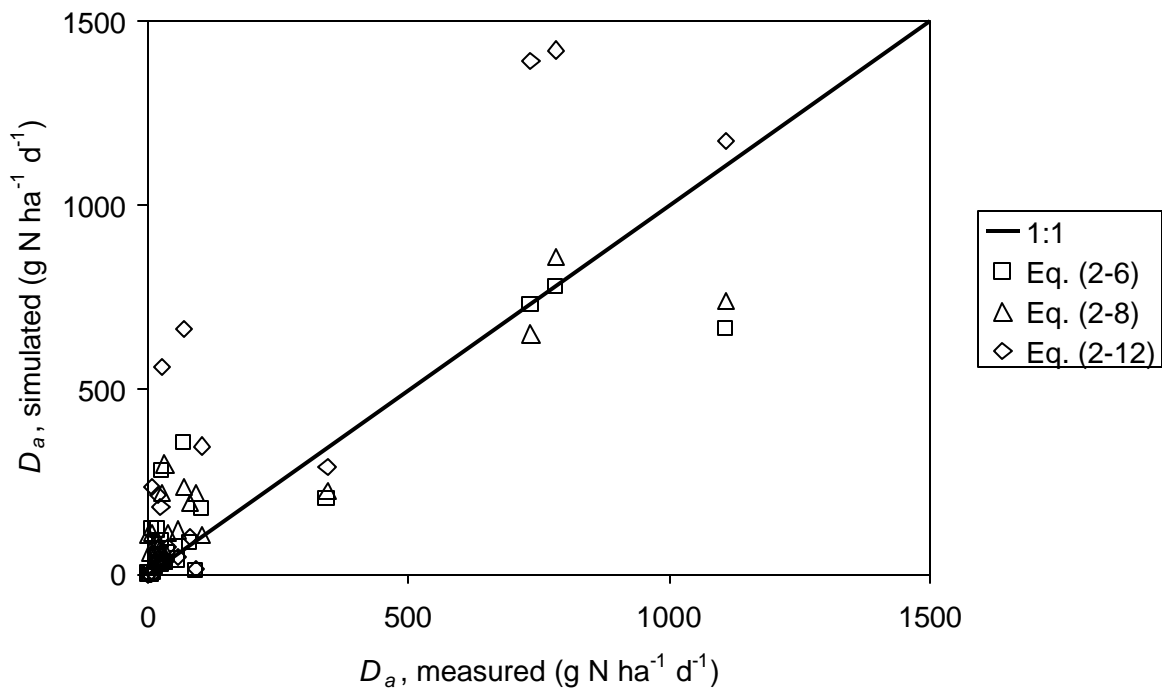


Figure 4-3. Comparison between measured and predicted actual denitrification D_a for the a) dry and b) wet sand data sets from the “De Marke” data set for three cases of water reduction functions: power function Eq. (2-6), arctangent function Eq. (2-8), exponential polynome Eq. (2-12).

4.3 Peat: the Velthof data set

Velthof (1997) measured denitrification in peat soils (three measurement dates, in total 120 data). Actual denitrification was measured together with water content, nitrate content and dry bulk density for the soil layer 0-20 cm. Measurements were carried out at the average soil temperature during sampling. Porosity was not measured at the sampling locations. From neighbouring fields data for organic matter content, clay content and sand + silt content was available, so that the density of the solid phase of the peat soil was estimated from

$$r_s = \frac{1}{\frac{H}{1470} + \frac{L}{2750} + \frac{Z+S}{2660}} \quad (4-3)$$

where

H	organic matter content	g g^{-1}
L	clay content ($< 2\mu\text{m}$)	g g^{-1}
$Z+S$	sand + silt content	g g^{-1}
1470	density of solid organic matter	kg m^{-3}
2750	density of solid clay minerals	kg m^{-3}
2660	density of solid sand and silt particles	kg m^{-3}

Porosity was computed from dry bulk density and the density of the solid phase. Potential denitrification was also estimated from data available from the neighbouring plots. On average D_p was $37320 \text{ g N ha}^{-1} \text{ d}^{-1}$. Appendix E gives an indication that this value is acceptable based on estimated organic matter decay.

The optimisations based on the Velthof data set did not result in good agreement between measured and predicted denitrification (Table 4-1; Figure 4-4).

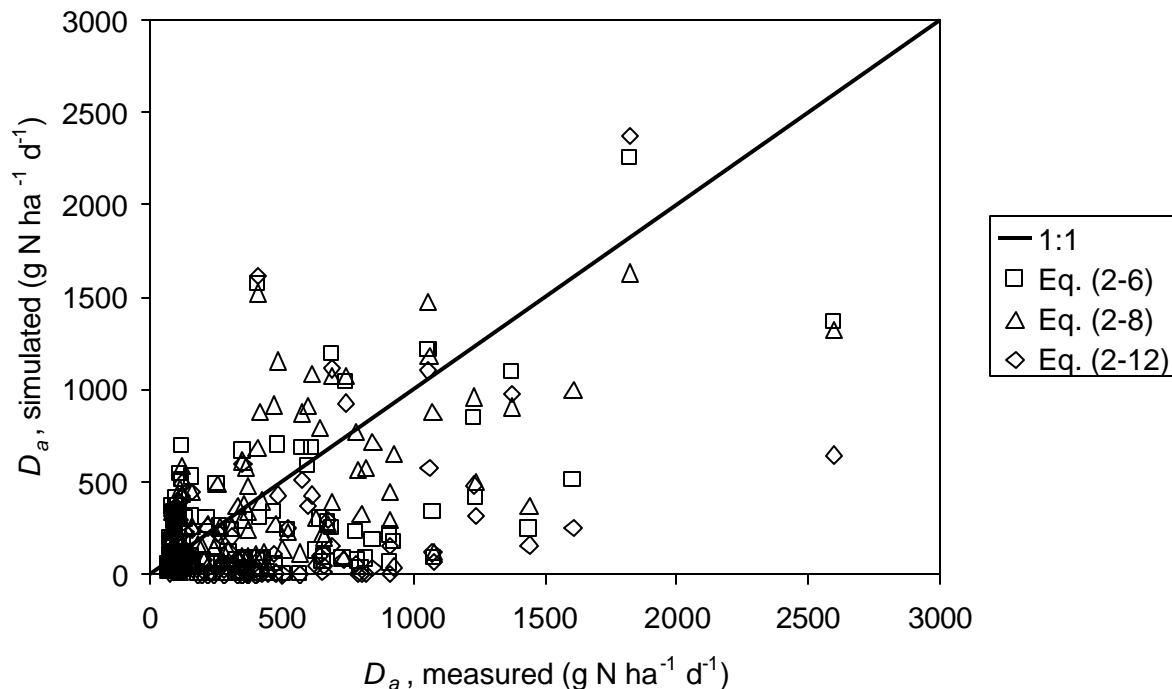


Figure 4-4. Comparison between measured and predicted actual denitrification D_a for the Velthof data set for three cases of water reduction functions: power function Eq. (2-6), arctangent function Eq. (2-8), exponential polynome Eq. (2-12).

Part of this lack of agreement may be attributed to the assumptions made to obtain porosity and potential denitrification. When using the exponential water reduction function (Eq. (2-12)) optimisation yielded an extreme low value for Q_{10} and a very large value for K_{MM} . Therefore, Q_{10} was fixed at 2.5 (Table 4-1).

4.4 Anaerobic sandy peat: the Meijer anaerobic data set

Meijer (2000) measured denitrification on disturbed anaerobic sandy peat samples at three temperatures and at different nitrate contents. Potential denitrification rates were taken from another study on the same soil (C. van Beek, personal communication). Since measurements were carried out under anaerobic conditions, $S = 1$ and thus $f_w = 1$. That means that the water reduction function parameters cannot be optimised. Unfortunately, the nitrate content of the samples at time of sampling were not measured. The nitrate content in the samples was raised with 0, 10, 50 or 90 mg N kg⁻¹. The control samples, i.e. without extra N added, were used to estimate the initial NO₃-N content of the soil. For Q_{10} fixed at 2.5, a parameter optimisation was carried out for K_{MM} and the nitrate contents at the four depth intervals. The correspondence between fitted and measured D_a was good (Figure 4-5). These estimated initial nitrate contents were then used as initial nitrate contents for all samples at the same sampling depth and then these were raised with the treatment values 10, 50 or 90 mg N kg⁻¹. For these samples the final parameter optimisation results were obtained.

The optimisations based on the Meijer data set did result in a fairly good agreement between measured and predicted denitrification (Table 4-1; Figure 4-6). Apparently, the fact that saturated conditions were used eliminated the great uncertainties in the effect of water content on denitrification, especially in peaty soils.

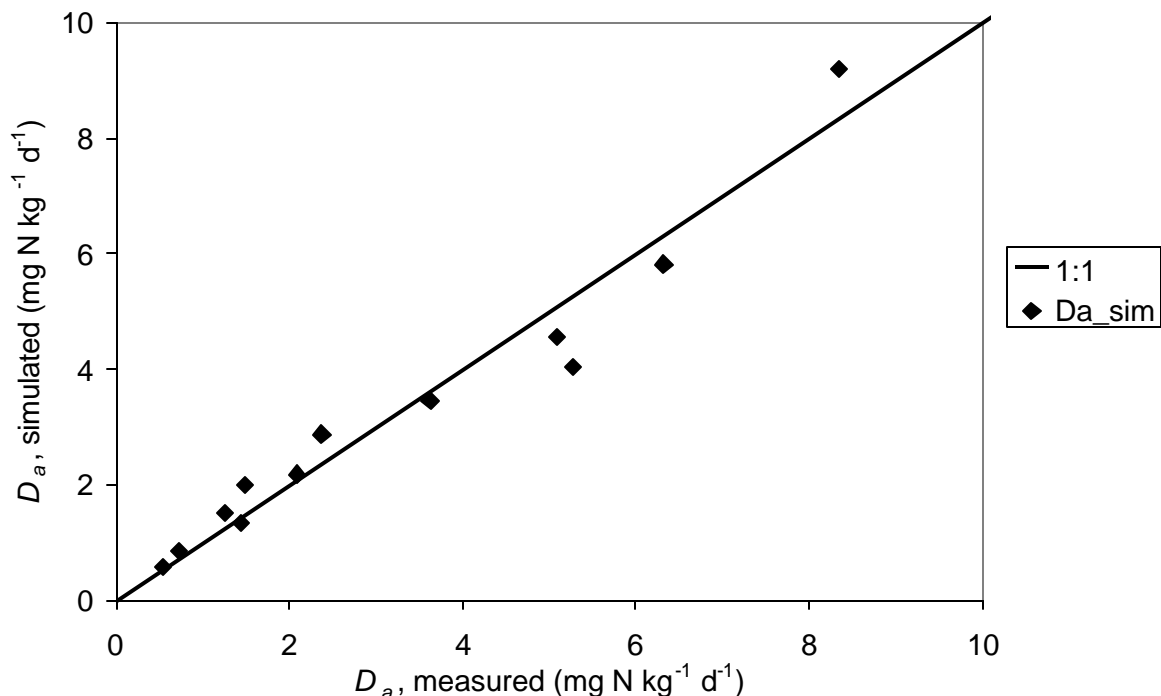


Figure 4-5. Comparison between measured and predicted actual denitrification D_a for the Meijer anaerobic data set for the determination of the initial nitrate content.

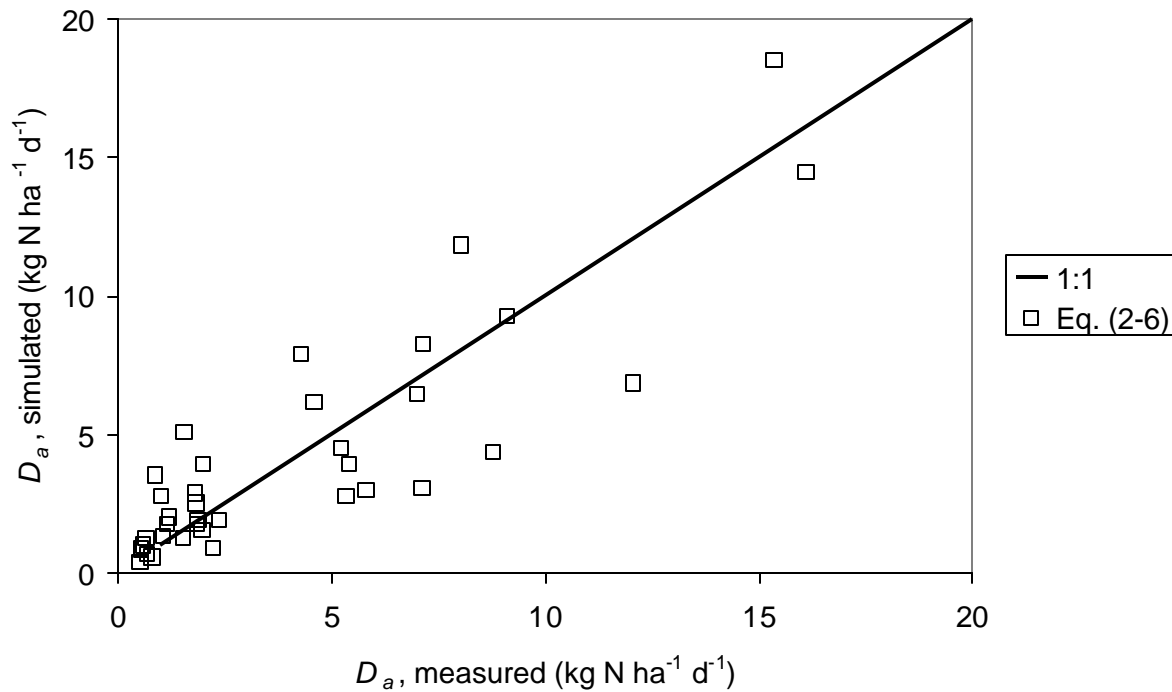


Figure 4-6. Comparison between measured and predicted actual denitrification D_a for the Meijer anaerobic data set.

The estimated value for Q_{10} was very close to the assumed value of 2.5 for which the initial nitrate contents were estimated. The estimated value for K_{MM} was larger than the value of 23 mg N kg⁻¹ for which the initial nitrate contents were estimated. From this, one can conclude that the estimation procedure for the initial nitrate content was a rough approximation. The initial nitrate contents were estimated as: 9.4, 7.8, 45.3, 16.6 mg N kg⁻¹ for layers 0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm.

4.5 Heavy loam: the Corré data set

For a well-drained calcareous heavy loam soil, Corré (1995) measured actual denitrification together with nitrate content, water content and gave temperatures at which the measurements were carried out. In total 60 data were available (five measurement dates, six measurement depths of 20 cm interval each, two locations). In order to compute degree of saturation, the porosity was computed based on a single measurement of dry bulk density and an estimated (according to Eq. (4-3)) density of the solid phase.

Corré (1995) did not measure D_p according to the definition used in this report. For deeper soil layers he measured denitrification under anaerobic conditions at governing nitrate and temperature conditions. These data were not used in the parameter optimisation. In the following analysis it was assumed that D_p decreases exponentially with depth. D_p for the top soil layer (0-20 cm) was estimated during the parameter optimisation besides the parameters of the reduction functions. D_p for depths 20-40 cm, 40-60 cm, 60-80 cm, 80-100 cm and 100-120 cm were, respectively, 0.40, 0.16, 0.06, 0.025, 0.01 times D_p of the top soil layer.

The optimisations based on the Corré data set did not result in good agreement between measured and predicted denitrification (Table 4-1; Figure 4-7). Part of this lack of agreement may

be attributed to the unknown potential denitrification rate, and to the fact that porosity was not measured but estimated. The obtained parameter sets were not able to predict the anaerobic data set of Corr   (1995) (data not shown). This is another indication that there is a great uncertainty in the value of the optimised parameters.

In two cases the fit for Q_{10} yielded extremely high values. Therefore, this fits were run another time with a maximum allowable value of 3 (Table 4-1).

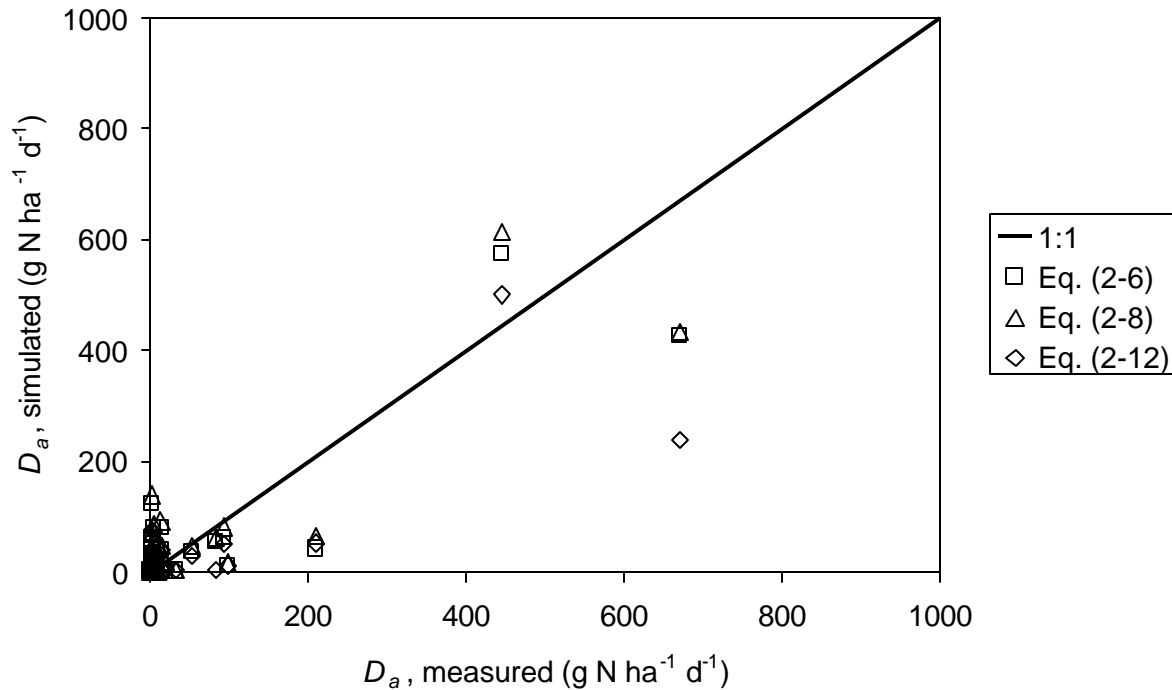


Figure 4-7. Comparison between measured and predicted actual denitrification D_a for the Corr   data set for three cases of water reduction functions: power function Eq. (2-6), arctangent function Eq. (2-8), exponential polynome Eq. (2-12).

4.6 Conclusions

Based on the experience with the limited amount of data sets above, the following conclusions are drawn. Parameter optimisation did not result in an perfect fit between measured and computed denitrification. The best results were obtained for a loam soil (section 4.1). Extremely bad results were obtained for a dry sand (section 4.2). Parameter optimisation itself was also difficult, indicating that it was difficult to obtain an unique set of parameters. To demonstrate this aspect, Figure 4-8 presents SSQ as a function of parameter values for w_1 and w_2 for a given set of values of K_{MM} and Q_{10} . The large white area in the middle of this picture refers to small values of SSQ . It is evident that there is no clear minimum of SSQ in this w_1 - w_2 plane. This implicates that w_1 and w_2 are highly correlated. Thus, one of these two parameters need to be determined independently. Also for the arctangent and exponential polynome water reduction functions, the parameter planes show no clear minimum.

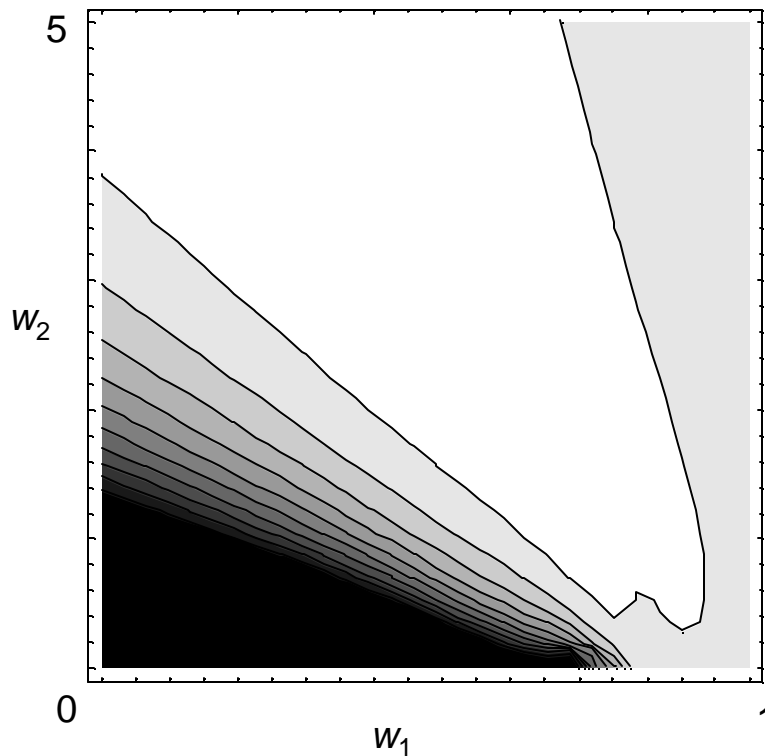


Figure 4-8. Example of the w_1 - w_2 parameter plane showing the sum of squared differences (SSQ) for the loam data set (with $K_{MM} = 22 \text{ mg N kg}^{-1}$, $Q_{10} = 2.5$). The white region indicates a small value of SSQ.

One reason for the difficulties in parameter optimisation must attributed to the fact that the measured actual denitrification D_a was always very small (except for the anaerobic sandy peat data set) compared to the potential denitrification D_p (Table 4-5).

Table 4-5. Average of measured actual denitrification rates of the data sets used in this chapter D_a ($\text{g N ha}^{-1} \text{ d}^{-1}$) and ratio of this average D_a to potential denitrification rate D_p .

Soil type	Average D_a	D_a/D_p
Loam	144	0.020
Dry sand	41	0.002
Wet sand	166	0.017
Peat	412	0.012
Sandy peat		0.475
Heavy loam	31	0.043

This was, for example, shown for the sandy soils in section 4.2 (Figure 4-2). It is difficult to determine the envelop reduction functions when most data points (i.e. D_a/D_p) are close to zero. If this will most likely be the case, then parameter optimisation based on measurements should not be used for calibration of the reduction functions. Instead, specific calibration of the reduction function must be carried out. For example, calibration of the nitrate reduction function must be carried out using anaerobic soil samples at $T_{ref} = 20^\circ\text{C}$ with different levels of initial nitrate-N content. Calibration of the water reduction function must be carried out using soil samples high in nitrate-N content at $T_{ref} = 20^\circ\text{C}$ with different degrees of saturation. Calibration of the temperature reduction function must be carried out using anaerobic soil samples high in nitrate-N content at different temperatures.

It is not possible to point out what water reduction function (Eq. (2-6), Eq (2-8) or Eq. (2-12)) appears to be best based on the data sets used in this chapter, since the differences between the mutual fitted denitrification rates were small in all cases.

For a proper validation of the denitrification model determine the following detailed information on each sample on which D_a is measured, i.e. D_a , volumetric water content (from gravimetric method on soil samples in a sampling ring of exact known volume), porosity, nitrate content, temperature; determine D_p as a function of time in the same soil (not adjacent fields that can have had different organic matter input histories).

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Appendix A Examples of denitrification descriptions in the literature.

Below an overview is given of denitrification descriptions in existing simulation models. The models are given in no specific order. See Table of Contents to find page number of an specific model searched for.

NEMIS

Hénault & Germon (2000) described actual denitrification as

$$D_a = D_p f_N f_W f_T$$

where

D_a	actual denitrification rate	kg N ha ⁻¹ d ⁻¹
D_p	potential denitrification rate	kg N ha ⁻¹ d ⁻¹
f_N	dimensionless reduction function for nitrate content in soil	
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The dimensionless reduction function f_N was calibrated against field data to yield

$$f_N = \frac{[\text{NO}_3^-]}{K_m + [\text{NO}_3^-]} = \frac{[\text{NO}_3^-]}{22 + [\text{NO}_3^-]}$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	mg N kg ⁻¹
K_m	Michaelis-Menten half-saturation constant	mg N kg ⁻¹

The dimensionless reduction function f_W was taken from Grundmann & Rolston (1987) (empirical)

$$f_W = \begin{cases} \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \\ 0 & S < w_1 \end{cases} = \left[\frac{S - 0.62}{0.38} \right]^{1.74}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
w_1	threshold value for S , below which $f_W = 0$
w_2	empirical exponent determining the steepness of the relationship

The dimensionless reduction function f_T was taken from Stanford *et al.* (1975^b)

$$f_T = \begin{cases} \exp \left[\frac{(T - 11) \ln 89 - 9 \ln 2.1}{10} \right] & T < 11^\circ \text{C} \\ \exp \left[\frac{(T - 20) \ln 2.1}{10} \right] & T \geq 11^\circ \text{C} \end{cases}$$

where

T	temperature	°C
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Requirements

Measurements of D_p (defined as denitrification rate from undisturbed soil columns, at $T = 20^\circ \text{C}$, under water saturated conditions with high nitrate contents e.g. 200 mg N kg⁻¹ soil),

measurements (or simulations) of volumetric water content, dry bulk density or porosity, nitrate content, soil temperature.

Additional information

Calibration and validation was done against independent data sets. Model was compared to predictions by model of Parton *et al.* (1996). Simple sensitivity analysis indicated that NEMIS is very sensitive to dry bulk density (from which porosity was calculated, from which S was calculated), NEMIS was sensitive to the rupture temperature (here $T = 11^\circ\text{C}$) in f_T . NEMIS was rather insensitive to K_m and to soil nitrate content (but the measurement of this quantity is not precise!). NEMIS predictions are proportional to potential denitrification rate D_p .

SONICG

Bril *et al.* (1994) described actual denitrification as (based on experimental data of Mahli *et al.*, 1990)

$$D_a = -\frac{4}{5} \frac{dC}{dt} f_N f_W$$

where

D_a	actual denitrification rate	$\text{kg ha}^{-1} \text{ d}^{-1}$
dC/dt	carbon degradation rate	$\text{kg ha}^{-1} \text{ d}^{-1}$
4/5	conversion factors from moles to electron equivalents	

In the description of dC/dt a temperature reduction function is included.

The dimensionless reduction function f_N is a Michaelis-Menten function with no explicit value for K_m .

$$f_N = \frac{[\text{NO}_3^-]}{K_m + [\text{NO}_3^-]}$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	mol N kg^{-1}
K_m	Michaelis-Menten half-saturation constant	mol N kg^{-1}

The dimensionless reduction function f_W is given by

$$f_W = \begin{cases} \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \\ 0 & S < w_1 \end{cases}$$

The form of f_W is related to the decrease of the oxygen supply rate by gas diffusion, which is a function of gas-filled pore space. The exact form of f_W can depend on soil type and on soil water hysteresis (Sexstone *et al.*, 1988; Groffman and Tiedje, 1988). Based on Figure 3.5 of Bril *et al.* (1994) the parameters w_1 and w_2 are: $w_1 = \sqrt[3]{(1/3)}$ (~ 0.577) and $w_2 = 2.0$.

Additional information

The maximum amount of nitrate that can be denitrified per day is limited in the model to 25% of the amount present.

This model was used in combination with models for the description of carbon degradation and nitrification.

This model was based on data from Mahli *et al.* (1990), who gave Michaelis-Menten constant in the range 117-138 mg N kg^{-1} . These values are presumably used in SONICG

De Willigen (2000) used this concept in the NUTMON nitrogen balance computations, with $K_m = 0.008 \text{ mol kg}^{-1}$ ($= 112 \text{ mg N kg}^{-1}$), $w_1 = 0.7$ and $w_2 = 2.5$.

NITDEN

Conijn & Heinen (2001) slightly adapted the description of denitrification of Bril *et al.* (1994; SONICG) to

$$D_a = DPR f_N f_w f_T f_e$$

where

DPR potential denitrification rate of the soil expressed in electron equivalents mmol electrons cm^{-3} (soil) d^{-1}

Total denitrification is expressed as total electron production accepted either by NO_3 or by N_2O . The dimensionless reduction function f_N is a Michaelis-Menten function

$$f_N = \frac{\left(0.8 \frac{[\text{NO}_3^-]}{14M_w} + 0.4 \frac{[\text{N}_2\text{O}]}{28M_w} \right)}{K_{m2} + \left(0.8 \frac{[\text{NO}_3^-]}{14M_w} + 0.4 \frac{[\text{N}_2\text{O}]}{28M_w} \right)}$$

where

NO_3	nitrate concentration	mg cm^{-3}
N_2O	total nitrous oxide concentration	mg cm^{-3}
M_w	wet mass of unit volume of soil	g cm^{-3}
14	molar mass of nitrogen	g mol^{-1}
28	$= 2 \times 14$	g mol^{-1}
0.4	dimensionless electron equivalent ratio of N_2O	
0.8	dimensionless electron equivalent ratio of NO_3	
K_{m2}	Michaelis-Menten half-saturation constant: amount of source in terms of both NO_3 and N_2O corrected for their electron equivalents	mmol N g^{-1} (wet soil)

The dimensionless reduction function f_w is given by

$$f_w = \begin{cases} \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \\ 0 & S < w_1 \end{cases}$$

The dimensionless reduction function f_T was described as

$$f_T = \begin{cases} 0 & T < 0^\circ\text{C} \\ \frac{t_1 T^{t_2}}{(1 + t_3 T^{t_4}) f_{T=20}} & T \geq 0^\circ\text{C} \end{cases}$$

where

t_1, t_3	empirical constant	$(^\circ\text{C})^{-1}$
t_2, t_4	dimensionless empirical constant	

As NO_3 and N_2O compete for the electrons produced during decay of organic matter an additional reduction function f_e is used, given by

$$f_e = \frac{\frac{[\text{NO}_3^-]}{14} + \frac{2[\text{N}_2\text{O}]}{28}}{4\frac{[\text{NO}_3^-]}{14} + 2\frac{[\text{N}_2\text{O}]}{28}} e^{f_{pH}}$$

where

- e dimensionless parameter that accounts for the sink strength of N_2O in consuming electrons relative to that of NO_3
- f_{pH} dimensionless reduction function for the pH of the soil

The dimensionless reduction function f_{pH} is given by

$$f_{pH} = \text{MAX} \left[p_1, 10^{\frac{pH - p_2}{p_3}} \right]$$

where

- MAX function that yields the maximum values of its arguments
- p_1 minimum value of f_{pH}
- p_2 pH at which the $f_{pH} = e$
- p_3 dimensionless curve shape parameter

Conijn & Heinen (2001; in Heinen & de Willigen (2001) their Table 15-21) gave the typical values and possible ranges for the parameters in this model (see Table A-1).

Table A-1. Typical values (with range and units) of the parameters appearing in the model NITDEN.

Parameter	Typical value	Range	Units
K_{m2}	0.008	0.0008 – 0.08	mol kg ⁻¹ (wet soil)
w_1	0.5	0.2 – 0.8	dimensionless
w_2	2.5	1.0 – 5.0	dimensionless
t_1	0.00376	< not given >	dimensionless
t_2	1.75	< not given >	dimensionless
t_3	$6.0 \cdot 10^{-7}$	< not given >	dimensionless
t_4	4.0	< not given >	dimensionless
e	1000	100 – 100000	dimensionless
p_1	0.25	0.0 – 1.0	dimensionless
p_2	6.5	1.0 – 9.0	dimensionless
p_3	3.0	4.0 – 9.0	dimensionless

Additional information

This denitrification model was used in combination with nitrification and N_2O emission description in order to describe the N_2O dynamics in soils. It was used as a subroutine in the FUSSIM2 model of Heinen and de Willigen (1998, 2001). Later, Conijn (2002) introduced some changes to the NITDEN model.

ANIMO

In the model ANIMO (Groenendijk & Kroes, 1999) aerobic (oxic) and anaerobic (anoxic) zones are considered. In aerobic zones no denitrification occurs. Under (partial?) anaerobic conditions the model ANIMO describes denitrification by a zero order rate or a first order rate expression. At high nitrate concentrations the oxygen requirement for organic decomposition is the rate limiting process, while at low nitrate concentrations the nitrate concentration will be rate limiting. The rate limiting process leading to the highest nitrate concentration at the end of a time interval is subsequently selected as the denitrification loss of nitrate.

The zero order denitrification function is given by

$$D_a = -0.58 \frac{24}{30} \frac{14}{12} f_{hetero} \frac{dC}{dt}$$

where

D_a	actual denitrification rate	$\text{g N g}^{-1} \text{d}^{-1}$
0.58	assumed carbon content of organic material	g C g^{-1}
24/30	the oxidation of 1 mol C requires 24/30 mol NO_3	$\text{mol N mol}^{-1} \text{C}$
14	molar mass of N	$\text{g N mol}^{-1} \text{N}$
12	molar mass of C	$\text{g C mol}^{-1} \text{C}$
f_{hetero}	dimensionless factor to account for the reduced organic matter transformation rates when only nitrate oxygen is available	
dC/dt	organic matter decomposition rate coefficient	d^{-1}

From several field validation studies it appeared that $f_{hetero} = 0.5$.

The first order denitrification function is given by

$$D_a = k_d f_N$$

where

D_a	actual denitrification rate	$\text{g N cm}^{-3} \text{d}^{-1}$
k_d	first order rate constant (model input)	d^{-1}

The dimensionless reduction function f_N is simply equal to the nitrate content in the soil, i.e.

$$f_N = q[\text{NO}_3 - \text{N}]$$

where

q	volumetric water content	mL cm^{-3}
$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	g N mL^{-1}

Additional information

Groenendijk & Kroes (1999) give an expression for dC/dt in which several classes of organic matter pools can be distinguished, and in which the dissolved organic matter concentration, the content of root exudates and the content of organic material present in humus/biomass pool is considered.

The soil consists of aerobic and anaerobic zones. The aerated soil fraction is computed by considering oxygen diffusion in an idealised pore-aggregate system.

Grundmann and Rolston

Grundmann & Rolston (1987) defined denitrification as

$$D_a = k f_w f_N f_T [C]$$

where

D_a	actual denitrification rate	$\text{mg N m}^{-3} \text{d}^{-1}$
k	denitrification rate coefficient	$\text{kg mg}^{-1} \text{C d}^{-1}$
$[C]$	water soluble organic carbon concentration	mg C kg^{-1}

A typical value for k was $7.35 \cdot 10^{-4} \text{ kg soil mg}^{-1} \text{C d}^{-1}$.

The function f_N is given simply as the nitrate concentration

$$f_N = [\text{NO}_3^-]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration	mg N m^{-3}
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The dimensionless water reduction function f_w is given by

$$f_w = \begin{cases} \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \\ 0 & S < w_1 \end{cases}$$

Grundmann & Rolston fitted w_1 and w_2 as 0.62 and 1.735, respectively.

These authors also showed that f_w differs for different soil depths. At given S , f_w is less for deeper depths.

No expression for f_T was given as it was assumed to be equal to 1.

CANDY

Franko *et al.* (1995) describe denitrification in the model CANDY as a first order decay process according to

$$D_a = kf_w f_N f_T [C]$$

where

D_a	actual denitrification rate	kg N ha ⁻¹ d ⁻¹
k	denitrification rate coefficient	kg ⁻¹ C ha d ⁻¹
[C]	carbon content of the biologically active soil organic matter	kg C ha ⁻¹
f_N	“reduction” function for nitrate content in soil	kg N ha ⁻¹
f_w	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The f_N is given by the nitrate content of the soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate content in soil	kg N ha ⁻¹
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The reduction function for water content in soil is given by (according to McGechan and Wu, 2001)

$$f_w = \begin{cases} 0 & q \leq q_d \\ \frac{q - q_d}{q_{FC} - q_d} & q_d < q \end{cases}$$

where

q	volumetric water content	%
q_d	threshold q below which $f_w = 0$	%
q_{FC}	q at field capacity	%

The threshold value q_d is given by

$$q_d = 0.627q_{FC} - 0.0267q_{FC}e_{pv}$$

where

e_{pv}	relative pore volume (relative to what?)	% (?)
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The reduction function for temperature in soil is given by a Q_{10} relationship (according to McGechan and Wu, 2001)

$$f_T = \begin{cases} Q_{10}^{0.1(T-35)} & T \leq 35^\circ\text{C} \\ 1 & 35^\circ\text{C} < T \end{cases}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	°C

CERES

Denitrification in the CERES model (Godwin & Jones, 1991) is described as

$$D_a = kf_w f_N f_T C \Delta z$$

where

D_a	actual denitrification rate	kg N ha ⁻¹ d ⁻¹
k	denitrification rate coefficient: $k = 6 \cdot 10^{-5}$?
C	total water extractable carbon in soil layer	µg C g ⁻¹
Δz	thickness of soil layer	m

The dimensionless water reduction factor f_w is given by

$$f_w = \begin{cases} 0 & q < q_1 \\ 1 - \frac{q_s - q}{q_s - q_1} = \frac{q - q_1}{q_s - q_1} = \frac{S - w_1}{1 - w_1} & q_1 \leq q \end{cases}$$

where

q_s	volumetric water content at saturation	cm ³ cm ⁻³
q_1	threshold value of volumetric water content below which $f_w = 0$	cm ³ cm ⁻³
S	degree of saturation q/q_s	
w_1	threshold value of S below which $f_w = 0$; $w_1 = q_1/q_s$	

Godwin & Jones (1991) gave for w_1 a value of 0.6.

The function f_N is given simply as the nitrate concentration

$$f_N = [\text{NO}_3^-]$$

where

$[\text{NO}_3\text{-N}]$	nitrate concentration	µg N g
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The temperature function f_T is given by

$$f_T = 0.1 \exp(0.0467T)$$

where

T	soil temperature	°C
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The total water extractable C is estimated from

$$C = 24.5 + 0.0031C_s$$

where

C_s	58% of the stable humic fraction
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Later, when CERES is implemented in DSSAT, Godwin and Singh (1998) used a different expression to compute total water extractable C, i.e. according to

$$C = 24.5 + 0.0031fH + 0.4CH$$

where

f	conversion factor to allow for bulk density and layer thickness
H	mass of stable or 'humus' organic matter in soil layer
CH	mass of carbohydrate fraction of organic matter in soil layer

Boundary-line model, 1

Denitrification according to Elliott & de Jong (1993) is described by their so-called boundary-line model, given as

$$\ln D_a = \ln D_{a,m} f_w f_a f_N f_c f_T$$

where

D_a	actual denitrification rate	$\text{g N ha}^{-1} \text{ d}^{-1}$
$D_{a,m}$	maximum denitrification rate	$\text{g N ha}^{-1} \text{ d}^{-1}$
f_w	reduction function for water-film thickness	
f_a	reduction function for air porosity	
f_N	reduction function for nitrate content	
f_c	reduction function for total organic C	
f_T	reduction function for maximum daily air temperature	

Note that denitrification here is based on its natural logarithm. Based on scatter diagrams of relative denitrification, $\ln D_a / \ln D_{a,m}$ against water-film thickness WFT (mg cm^{-2}), air porosity AP (%), organic carbon C (mg C g^{-1}), nitrate content N ($\mu\text{g g}^{-1}$) and maximum daily temperature T ($^{\circ}\text{C}$), boundary lines below which all data were lying were drawn; this explains the name boundary-line model. The boundary-line is a trend line empirically fitted to experimental data. Point falling below the boundary line are assumed to be subject to limitations other than the soil property being examined. Once the boundary line has been established, the f -values can be obtained for any level of the soil property. These lines were approximated by the following analytical expressions.

$$f_w = \begin{cases} 1 & WFT > 1.2 \\ -2.8355WFT^3 + 6.9852WFT^2 - 4.0649WFT + 0.7036 & 0.4 \leq WFT \leq 1.2 \\ 0 & WFT < 0.4 \end{cases}$$

$$f_a = \begin{cases} 1 & AP < 25 \\ -0.04AP + 2 & 25 \leq AP \leq 50 \\ 0 & AP > 50 \end{cases}$$

$$f_c = \begin{cases} 7.906 \cdot 10^{-7} C^4 + 1.021 \cdot 10^{-4} C^3 - 4.766 \cdot 10^{-3} C^2 + 0.102C + 0.003 & C < 25 \\ 0.0425C + 0.724 & C \geq 25 \end{cases}$$

$$f_N = \begin{cases} 0.032(\ln N)^3 - 0.249(\ln N)^2 + 0.896(\ln N) + 0.032 & \ln N < 2.2 \\ 0.0229(\ln N) + 0.886 & \ln N \geq 2.2 \end{cases}$$

$$f_T = \begin{cases} 1 & \text{if } f_T > 1 \\ -0.0011T^2 + 0.00667T - 0.0424 & \\ 0 & \text{if } f_T < 0 \end{cases}$$

Boundary-line model, 2

Bergstrom and Beauchamp (1993) also used a boundary-line model. They compute denitrification from

$$D_a = D_{a,m} f_a f_N f_r d$$

where

D_a	actual denitrification rate	$\text{g N ha}^{-1} \text{ d}^{-1}$
$D_{a,m}$	maximum measured denitrification rate	$\text{g N ha}^{-1} \text{ d}^{-1}$
f_a	reduction function for air porosity	

f_N	reduction function for nitrate content
f_r	reduction function for respiration rate
d	the denitrifying enzyme activity (DEA) fraction

The parameter d is the measured DEA divided by the maximum measured DEA value. It accounts for variation in enzyme content and number of denitrifiers among the soil samples. Instead of respiration rate, the authors used also mineralizable C content, i.e. f_r was replaced by f_C . The authors concluded that in their samples nitrate never was limiting, no boundary line for f_N could be obtained, i.e. $f_N = 1$. The boundary lines are given by

$$f_a = \begin{cases} 1 & a < 0.247 \\ 0.0167a^{-2.89} & 0.247 \leq a \leq 0.514 \\ 0 & a > 0.514 \end{cases}$$

$$f_r = \begin{cases} 0 & r < 0.319 \\ 1.93r - 0.615 & 0.319 \leq r \leq 0.837 \\ 1 & r > 0.837 \end{cases}$$

$$f_C = \begin{cases} 0 & C < 0.294 \\ 2.66C - 0.78 & 0.294 \leq C \leq 0.67 \\ 1 & C > 0.67 \end{cases}$$

where

a	air-filled porosity	
r	respiration rate	$\mu\text{g CO}_2\text{-C g}^{-1} \text{ h}^{-1}$
C	mineralizable C content	$\mu\text{g CO}_2\text{-C g}^{-1} \text{ h}^{-1}$

DAISY

Hansen *et al.* (1990, 1991) consider two denitrification functional relationships. The actual denitrification rate is then set equal to the lowest of the two calculated processes. The first process is given by

$$D_{a,1} = \left[\sum_{i=1}^n q A_i D \frac{C}{\Delta r_i} \right] V^{-1} = K_d [\text{NO}_3^- - \text{N}]$$

where

$D_{a,1}$	actual denitrification rate determined by transport of $\text{NO}_3\text{-N}$ to anaerobic micro-sites	$\text{kg N m}^{-3} \text{ s}^{-1}$
q	volumetric water content	$\text{m}^3 \text{ m}^{-3}$
D	diffusion coefficient	$\text{m}^2 \text{ s}^{-1}$
A_i	surface area of micro-sites	m^2
V	soil volume	m^3
C	concentration of $\text{NO}_3\text{-N}$ in soil solution	kg N m^{-3}
$[\text{NO}_3\text{-N}]$	concentration of $\text{NO}_3\text{-N}$ in soil	kg N m^{-3}
K_d	empirical constant	s^{-1}
Δr_i	diffusion distance to micro-sites	m
n	number of micro-sites	

The basic idea is that nitrate diffuses to the micro-sites. This process is lumped in the empirical constant K_d , for which the authors gave the following typical value: $K_d = 0.1 \text{ d}^{-1}$.

The second process is given by

$$D_{a,2} = D_p f_W$$

where

$D_{a,2}$	actual denitrification rate determined by actual microbial activity at anaerobic micro-sites	$\text{kg N m}^{-3} \text{ s}^{-1}$
D_p	potential denitrification rate of soil	$\text{kg N m}^{-3} \text{ s}^{-1}$
f_W	dimensionless reduction function for water content	

This second process assumes that there is ample $\text{NO}_3\text{-N}$ supply towards the micro-sites, so that the actual denitrification rate is determined by the actual denitrification activity.

The dimensionless reduction function for water content f_W was taken from Rolston *et al.* (1984):

$$f_W = \begin{cases} 0 & S \leq f_2 \\ f_1 \frac{S - f_2}{f_3 - f_2} & f_2 < S < f_3 \\ f_1 + (1 - f_1) \frac{S - f_3}{1 - f_3} & f_3 < S \leq 1 \end{cases}$$

where

S	dimensionless degree of saturation (q/q_s)	
q	volumetric soil water content	$\text{m}^3 \text{ m}^{-3}$
q_s	volumetric soil water content at saturation or porosity	$\text{m}^3 \text{ m}^{-3}$
f_1, f_2, f_3	dimensionless empirical constants	

Hansen *et al.* (1990) gave the following values for f_1, f_2, f_3 : $f_1 = 0.2$, $f_2 = 0.8$, and $f_3 = 0.9$. The function f_W consists of two linear parts (broken-line relationship). Parameter f_2 represents S below which $f_W = 0$, f_3 represents S where the two linear parts intersect, and f_1 is the slope of the first (left) linear part and $(1-f_1)$ is the slope of the second (right) linear part.

Hansen *et al.* (1990) gave also an expression for D_p

$$D_p = a f_T \frac{d\text{CO}_2}{dt}$$

where

D_p	potential denitrification rate of soil	$\text{kg N m}^{-3} \text{ s}^{-1}$
a	empirical constant	$\text{kg N kg}^{-1} \text{ C}$
f_T	dimensionless reduction function for temperature	
$d\text{CO}_2/dt$	CO_2 evolution rate	$\text{kg C m}^{-3} \text{ s}^{-1}$

The authors gave a typical value for a as $a = 0.1 \text{ kg N kg}^{-1} \text{ C}$.

The dimensionless reduction function for temperature is given by

$$f_T = \begin{cases} 0 & T \leq 2 \\ 0.15(T - 2) & 2 < T \leq 6 \\ 0.10T & 6 < T \leq 20 \\ \exp(0.47 - 0.027T + 0.00193T^2) & 20 < T < 40 \end{cases}$$

where

T temperature $^{\circ}\text{C}$

The boundary line approach was used by Schmidt *et al.* (2000) to predict N_2O fluxes (not denitrification) based on soil nitrate content, water filled pore space, soil temperature.

SOILN

Johnsson *et al.* (1987; 1991) describe denitrification, under the assumption that easily metabolizable organic matter is freely available, as,

$$D_a = D_p f_N f_W f_T$$

where

D_a	actual denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
D_p	potential denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
f_N	dimensionless reduction function for nitrate concentration in soil solution	
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The authors gave a typical value for D_p as $0.1 \text{ g N m}^{-2} \text{d}^{-1}$

The dimensionless reduction function for water content in soil is given by

$$f_W = \begin{cases} 0 & q \leq q_d & S < b \\ \left(\frac{q - q_d}{q_s - q_d} \right)^a = \left(\frac{S - q_d / q_s}{1 - q_d / q_s} \right)^a = \left(\frac{S - b}{1 - b} \right)^a & q_d < q \leq q_s & b < S < 1 \end{cases}$$

where

q	actual volumetric water content	$\text{m}^3 \text{m}^{-3}$
q_s	volumetric water content at saturation (or porosity)	$\text{m}^3 \text{m}^{-3}$
q_d	threshold volumetric water content	$\text{m}^3 \text{m}^{-3}$
a	dimensionless empirical curve shape parameter	
b	dimensionless empirical curve shape parameter = q_d / q_s	

Johnsson *et al.* (1987) used $a = 2$ and $(q_s - q_d) = 0.1$ resulting in b being a function of q_s : $b = (q_s - 0.1) / q_s$. Johnsson *et al.* (1991) calibrated the b parameter as $b = 0.58$ ($q_d = 0.26$, $q_s = 0.45$). They compared their f_W relationship with that of Grundmann & Rolston (1987) and observed very close correspondence.

The dimensionless reduction function for nitrate concentration in soil solution is given by

$$f_N = \frac{[\text{NO}_3^- - \text{N}]}{k_m + [\text{NO}_3^- - \text{N}]}$$

where

$[\text{NO}_3^- - \text{N}]$	nitrate concentration in soil solution	mg N L^{-1}
k_m	Michaelis-Menten half saturation constant	mg N L^{-1}

For k_m the authors gave a typical value of $k_m = 10 \text{ mg N L}^{-1}$.

The temperature reduction function is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T - T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	°C
T_{ref}	reference T where $f_T = 1$	°C

A Q_{10} equal to 3 was used and $T_{ref} = 20$ °C.

The SOILN model was used by others, e.g. Bergström *et al.* (1991), Eckersten and Jansson (1991), Larocque and Banton (1994). Van Grinsven and Makaske (1993) used SOILN for grassland and grazing studies, and adapted SOILN but not the denitrification equations.

SOILN-modified

Vold *et al.* (1999) modified the denitrification description of the SOILN model (SOILNNO model in McGeachan and Wu, 2001). An additional reduction function for respiration rate is included. Thus, the SOILN denitrification model is then given by

$$D_a = D_p f_N f_W f_T f_C$$

where the reduction function f_C is given by an Michaelis-Menten type function

$$f_C = \frac{dCO_2/dt}{dCO_2/dt + K_C}$$

where

dCO_2/dt	C mineralization rate	g C kg ⁻¹ d ⁻¹
T	Michaelis-Menten half-saturation constant for C mineralization rate	g C kg ⁻¹ d ⁻¹

NGAS

Parton *et al.* (1996) presented the NGAS model in which total denitrification is computed and split in N₂ and N₂O production. Their model was calibrated against a data set of Weier *et al.* (1993). Total denitrification is given by

$$D_a = \min[F_d(NO_3), F_d(CO_2)] f_W$$

where

D_a	actual denitrification rate	g N ha ⁻¹ d ⁻¹
\min	operator that yields the minimum value of its arguments	
$F_d(NO_3)$	the maximum total N gas flux for a given soil NO ₃ level assuming high respiration rates	g N ha ⁻¹ d ⁻¹
$F_d(CO_2)$	the maximum total N gas flux for a given soil respiration rate assuming high NO ₃ levels	g N ha ⁻¹ d ⁻¹
f_W	dimensionless reduction function for water content in soil	

The F_d variable resembles some potential denitrification rate at given nitrate (and respiration rate). Based on the data of Weier *et al.* (1993), the $F_d(NO_3)$ variable is given by

$$F_d(NO_3) = 11000 + \frac{40000 \arctan(0.002p(NO_3 - 180))}{p}$$

where

NO ₃	nitrate content	µg N g ⁻¹
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Based on the data of Weier *et al.* (1993), the $F_d(\text{CO}_2)$ variable is given by

$$F_d(\text{CO}_2) = \frac{24000}{1 + \exp\left(\frac{200}{0.35\text{CO}_2}\right)} - 100$$

where

CO_2 soil respiration rate kg C ha⁻¹ d⁻¹

Based on the literature Parton *et al.* (1996) gave two functions for f_w , one for loam and sandy loam soils, and one for clay soils. For loam+sandy loam f_w can be described by

$$f_w = \begin{cases} 1 & 0.9 \leq S \\ \left[\frac{S - w_1}{0.9 - w_1} \right]^{w_2} & w_1 < S < 0.9 \\ 0 & S \leq w_1 \end{cases}$$

where

S dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
 w_1 threshold value for S , below which $f_w = 0$
 w_2 empirical exponent determining the steepness of the relationship

It is remarkable to notice that already for near saturated conditions, $S > 0.9$, the function f_w equals 1, while in other functions $f_w = 1$ for $S = 1$. Based on data read from their graph, the parameters were calibrated as: $w_1 = 0.55$ and $w_2 = 2.134$.

For clay soils some sigmoidal function for f_w was given

$$f_w = ab^{-cb^{-ds}}$$

where

S dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
 a, b, c, d empirical parameters

Based on data read from their graph, the parameters were calibrated as: $a = 3.149$, $b = 36.919$, $c = 23.695$ and $d = 1.326$.

In general, denitrification in clay soils is less reduced at some value for S than in loam+sandy loam soils.

The effect of soil temperature was not explicitly considered in the denitrification model.

The NGAS model was used by e.g. Mummey *et al.* (2000). A similar approach was used by Del Grosso *et al.* (2000).

LEACHM(N)

In the LEACHM model (originally developed by Wagenet and Hutson, 1989; here I used the description given by Ramos and Carbonell, 1991) describes denitrification as a first order decay process. In analogy with other models it can be stated as

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
k_d	denitrification rate constant	d^{-1}
f_N	“reduction” function for nitrate content in soil	g N m^{-2}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is the actual $\text{NO}_3\text{-N}$ content in the soil

$$f_N = [\text{NO}_3 - \text{N}]$$

No reduction based on water content is used, thus $f_W = 1$.

The temperature reduction function is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T - T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference T where $f_T = 1$	$^{\circ}\text{C}$

Ramos and Carbonell (1991) used for k_d values in the range 0.001 d^{-1} (soil layer 60-100 cm) to 0.005 d^{-1} (soil layer 0-30 cm), and $Q_{10} = 2.3$; no value for T_{ref} was given.

Later, Sogbedi *et al.* (2001) presented the LEACHMN description of denitrification as

$$D_a = D_p f_N f_W f_T$$

where

D_a	actual denitrification rate	$\text{mg N L}^{-1} \text{d}^{-1}$
D_p	potential denitrification rate	$\text{mg N L}^{-1} \text{d}^{-1}$
f_N	“reduction” function for nitrate concentration in soil solution	mg N L^{-1}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is given by a Michaelis-Menten function

$$f_N = \frac{[\text{NO}_3 - \text{N}]}{K_m + [\text{NO}_3 - \text{N}]}$$

where

$[\text{NO}_3\text{-N}]$	nitrate concentration in soil solution	mg N L^{-1}
K_m	Michaelis-Menten half-saturation constant	mg N L^{-1}

The reduction functions f_W and f_T were assumed to be the same as used in the SOILN model of Johnsson *et al.* (1987). The dimensionless reduction function for water content in soil is given by

$$f_W = \begin{cases} 0 & q \leq q_d \quad S < b \\ \left(\frac{q - q_d}{q_s - q_d} \right)^a & q_d < q \leq q_s \quad b < S < 1 \\ \left(\frac{S - q_d / q_s}{1 - q_d / q_s} \right)^a & \\ \left(\frac{S - b}{1 - b} \right)^a & \end{cases}$$

where

q	actual volumetric water content	$\text{m}^3 \text{m}^{-3}$
q_s	volumetric water content at saturation (or porosity)	$\text{m}^3 \text{m}^{-3}$

q_d	threshold volumetric water content	$\text{m}^3 \text{m}^{-3}$
a	dimensionless empirical curve shape parameter	
b	dimensionless empirical curve shape parameter = q_d / q_s	

The temperature reduction function is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T-T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference T where $f_T = 1$	$^{\circ}\text{C}$

Sogbedi *et al.* (2001) used $K_m = 10 \text{ mg L}^{-1}$, $Q_{10} = 2$. Values for k_d were adjusted to fit data; the range of values for k_d was 0.003 d^{-1} (loamy sand, low fertiliser application) to 0.28 d^{-1} (clay loam, high fertiliser application). Other parameter values were not explicitly given.

SWATNIT

In the SWATNIT model (Vereecken *et al.*, 1990; 1991) denitrification is described as a first order decay process. In analogy with other models it can be stated as

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate, i.e. loss of N from soil solution	$\text{mg N L}^{-1} \text{d}^{-1}$
k_d	denitrification rate constant	d^{-1}
f_N	“reduction” function for nitrate content in a unit volume of soil	mg N L^{-1}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is the actual $\text{NO}_3\text{-N}$ content in a unit volume of soil

$$f_N = [\text{NO}_3 - \text{N}]$$

The dimensionless reduction function f_W was given by

$$f_W = \begin{cases} \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \\ 0 & S < w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
w_1	threshold value for S , below which $f_W = 0$
w_2	empirical exponent determining the steepness of the relationship

The temperature reduction function is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T-T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference T where $f_T = 1$	$^{\circ}\text{C}$

Vereecken *et al.* (1991) used $k_d = 0.01 \text{ d}^{-1}$. No values were given for w_1 , w_2 , Q_{10} and T_{ref} .

WANISIM

In the WANISIM model (Antonopoulos and Wyseure, 1998) denitrification is described as a first order decay process. In analogy with other models it can be stated as

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate, i.e. loss of N from a unit volume of soil	$\text{mg N L}^{-1} \text{ d}^{-1}$
k_d	denitrification rate constant	d^{-1}
f_N	“reduction” function for nitrate concentration in soil solution	mg N L^{-1}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is the actual $\text{NO}_3\text{-N}$ concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

The same dimensionless reduction function f_W as used by Johnsson *et al.* (1987) is used, given by

$$f_W = \begin{cases} 0 & q \leq q_d \quad S < b \\ \left(\frac{q - q_d}{q_s - q_d} \right)^a = \left(\frac{S - q_d / q_s}{1 - q_d / q_s} \right)^a = \left(\frac{S - b}{1 - b} \right)^a & q_d < q \leq q_s \quad b < S < 1 \end{cases}$$

where

q	actual volumetric water content	$\text{m}^3 \text{ m}^{-3}$
q_s	volumetric water content at saturation (or porosity)	$\text{m}^3 \text{ m}^{-3}$
q_d	threshold volumetric water content	$\text{m}^3 \text{ m}^{-3}$
a	dimensionless empirical curve shape parameter	
b	dimensionless empirical curve shape parameter	

The temperature reduction function is given by a relationship of the form

$$f_T = A^{(T - T_{ref})}$$

where

A	increase factor	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference T where $f_T = 1$	$^{\circ}\text{C}$

Antonopoulos and Wyseure (1998) used $A = 1.083$, $T_{ref} = 20^{\circ}\text{C}$.

MELEF

Morell *et al.* (1996) described denitrification as a first order irreversible decay process as

$$D_a = k_d f_N f_H f_T$$

where

D_a	actual denitrification rate, i.e. loss of N from a unit volume of soil	$\text{mg N L}^{-1} \text{ d}^{-1}$
k_d	denitrification rate constant	d^{-1}
f_N	“reduction” function for nitrate concentration in soil solution	mg N L^{-1}
f_H	dimensionless reduction function for total water head in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is the actual $\text{NO}_3\text{-N}$ concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$$[\text{NO}_3\text{-N}] \quad \text{nitrate concentration in soil solution} \quad \text{mg N L}^{-1}$$

Instead of a reduction function based on water content, a reduction function f_H based on total head is used. However, it is not explicitly given.

The dimensionless reduction function for temperature in soil is given by

$$f_T = A \exp \left[-\frac{E_a}{RT} \right]$$

where

A	dimensionless constant	
E_a	activation energy	J mol^{-1}
R	universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
T	absolute temperature	K

Morell *et al.* (1996) gave $E_a = 55000 \text{ J mol}^{-1}$ and $A = 1754.5$.

NICCE

Van Dam and van Breemen (1995) describe denitrification as potential denitrification reduced by soil moisture potential, soil temperature and nitrate concentration using Michaelis-Menten kinetics. No explicit equations of the reduction functions were given. It is remarkable to notice that instead of reduction due to water content, here reduction due to pressure head is used. This is probably related to two types of description of microbial activity (e.g. in mineralisation models; e.g. Whitmore and Heinen, 1999): one driven by water content and one driven by pressure head.

NUCM

Sogn and Abrahamsen (1997) describe denitrification as a first order decay process

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate, i.e. loss of N from a unit volume of soil	$\text{mg N L}^{-1} \text{d}^{-1}$
k_d	denitrification rate coefficient at $T = 20^\circ \text{C}$	d^{-1}
f_N	“reduction” function for nitrate concentration in soil solution	mg N L^{-1}
f_W	dimensionless reduction function for total water head in soil	
f_T	dimensionless reduction function for temperature in soil	

The function f_N is the actual $\text{NO}_3\text{-N}$ concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$$[\text{NO}_3\text{-N}] \quad \text{nitrate concentration in soil solution} \quad \text{mg N L}^{-1}$$

No reduction based on water content is used, i.e. $f_W = 1$.

The dimensionless reduction function for temperature in soil is given by

$$f_T = A^{(T - T_{ref})}$$

where

A	dimensionless constant	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference temperature	$^{\circ}\text{C}$

Sogn and Abrahamsen (1997) used $A = 1.07$ and $T_{ref} = 15^{\circ}\text{C}$. Note that this reference temperature differs from the temperature at which k_d was determined (20°C).

IMPACT

Andrews *et al.* (1997) describe denitrification as a first order decay process

$$D_a = \begin{cases} 0 & T_{30} < 10^{\circ}\text{C} \\ k_d f_N f_W f_T & T_{30} \geq 10^{\circ}\text{C} \end{cases}$$

where

D_a	actual denitrification rate, i.e. loss of N from a unit volume of soil	$\text{kg N ha}^{-1} \text{ d}^{-1}$
k_d	denitrification rate coefficient at $T = 21^{\circ}\text{C}$	d^{-1}
f_N	“reduction” function for nitrate content in soil	kg N ha^{-1}
f_W	dimensionless reduction function for total water head in soil	
f_T	dimensionless reduction function for temperature in soil	
T_{30}	soil temperature at 30 cm depth	$^{\circ}\text{C}$

The function f_N is the actual $\text{NO}_3\text{-N}$ content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	kg N ha^{-1}
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No reduction based on water content is used, i.e. $f_W = 1$.

The dimensionless reduction function for temperature in soil is given by

$$f_T = A^{(T - T_{ref})}$$

where

A	dimensionless constant	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference temperature	$^{\circ}\text{C}$

Andrews *et al.* (1997) used $k_d = 0.1 \text{ d}^{-1}$, $A = 1.07$ and $T_{ref} = 21^{\circ}\text{C}$.

NITS

Birkinshaw and Ewen (2000) used an approach similar to the DAISY model (Hansen *et al.*, 1990) to describe denitrification; see elsewhere. Only the dimensionless temperature reduction function is different, here given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T - T_{ref})}$$

where

Q_{10}	increase factor for a 10°C increase in temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference T where $f_T = 1$	$^{\circ}\text{C}$

Birkinshaw and Ewen (2000) used $T_{ref} = 30^{\circ}\text{C}$.

WHNSIM

Huwe and Totsche (1995) describe denitrification as a zero-order or first-order decay process

$$D_a = \begin{cases} k_d f_N f_W f_T (SC) q & [\text{NO}_3 - \text{N}] \leq C_s \\ k_d C_s f_W f_T (SC) q & [\text{NO}_3 - \text{N}] > C_s \end{cases}$$

where

D_a	actual denitrification rate, i.e. loss of N from a unit volume of soil	$\text{g N cm}^{-3} \text{d}^{-1}$
k_d	denitrification rate coefficient at $T = 21^\circ \text{C}$	d^{-1}
f_N	“reduction” function for nitrate content in soil	g N cm^{-3}
f_W	dimensionless reduction function for total water head in soil	
f_T	dimensionless reduction function for temperature in soil	
C_s	threshold value for nitrate content above which zero-order kinetics applies and below which first-order kinetics applies	g N cm^{-3}
SC	concentration of soluble organic matter	
q	volumetric water content	mL cm^{-3}

SC can be computed from the easily mineralisable organic matter (OM) according to $SC = 0.58116OM/q$.

The function f_N is the actual $\text{NO}_3\text{-N}$ content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	g N cm^{-3}
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The reduction function for water content is given by (Huwe, 1993)

$$f_W = \begin{cases} 0 & S \leq w_1 \\ \frac{S - w_1}{1 - w_1} & w_1 < S \end{cases}$$

where

S	degree of saturation
w_1	threshold value of S below which $f_W = 0$; $w_1 = 0.9$

The reduction function for temperature is given by (Huwe, 1993)

$$f_T = \begin{cases} 0 & T < 0^\circ \text{C} \\ 0.1 + \frac{0.9T}{T + \exp(9.54 - 0.3T)} & 0^\circ \text{C} \leq T < 35^\circ \text{C} \end{cases}$$

where

T	soil temperature	$^\circ \text{C}$
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In a second approach the WHNSIM model describes denitrification as

$$D_a = \begin{cases} k_d^* f_N \text{MIN}(f_W, f_T, f_{pH}) q & [\text{NO}_3 - \text{N}] \leq C_s \\ k_d^* C_s \text{MIN}(f_W, f_T, f_{pH}) q & [\text{NO}_3 - \text{N}] > C_s \end{cases}$$

where

f_{pH} dimensionless reduction function for pH of the soil
 MIN function that results the minimum value of its argument

k_d^* is computed from

$$k_d^* = 0.06 + 0.026C_t$$

where

C_t total C content

The reduction function for water content is given by (Huwe, 1993)

$$f_w = \begin{cases} 0 & S \leq w_1 \\ \frac{S - w_1}{1 - w_1} & w_1 < S \end{cases}$$

where

S degree of saturation
 w_1 threshold value of S below which $f_w = 0$; in this case S at field capacity

The reduction function for pH is given by (Huwe, 1993)

$$f_T = \begin{cases} 0 & pH \leq 5 \\ pH - 5 & 5 < pH < 6 \\ 1 & 6 \leq pH \leq 8 \\ 9 - pH & 8 \leq pH < 9 \\ 0 & 9 \leq pH \end{cases}$$

where

pH soil pH

LASCAM-NP

Viney *et al.* (2000) describe denitrification as a first-order decay process

$$D_a = k_d f_N f_w$$

where

D_a actual denitrification rate, i.e. loss of N from a unit volume of soil mg N kg⁻¹ d⁻¹
 k_d denitrification rate coefficient d⁻¹
 f_N “reduction” function for nitrate content in soil mg N kg⁻¹
 f_w dimensionless reduction function for total water head in soil

The function f_N is the actual NO₃-N content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$ nitrate content in soil mg N kg⁻¹

A step reduction based on water content is used. This can be modelled by

$$f_w = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^0 & S \geq w_1 \end{cases}$$

where

S dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
 w_1 threshold value for S , below which $f_w = 0$

A value of $w_1 = 0.9$ was used.

No temperature effect is considered.

MATHILD

Lafolie (1991) describes denitrification as a first-order decay process

$$D_a = k_d f_N f_w f_T$$

where

D_a actual denitrification rate, i.e. loss of N from a unit volume of soil solution mg N L⁻¹ d⁻¹
 k_d denitrification rate coefficient d⁻¹
 f_N “reduction” function for nitrate concentration in soil solution mg N L⁻¹
 f_w dimensionless reduction function for total water head in soil
 f_T dimensionless reduction function for temperature in soil

The function f_N is the actual NO₃-N concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$ nitrate content in soil mg N L⁻¹

The same dimensionless reduction function f_w as used by Johnsson *et al.* (1987) is used, given by

$$f_w = \begin{cases} 0 & q \leq q_d & S < b \\ \left(\frac{q - q_d}{q_s - q_d} \right)^a = \left(\frac{S - q_d / q_s}{1 - q_d / q_s} \right)^a = \left(\frac{S - b}{1 - b} \right)^a & q_d < q \leq q_s & b < S < 1 \end{cases}$$

where

q actual volumetric water content m³ m⁻³
 q_s volumetric water content at saturation (or porosity) m³ m⁻³
 q_d threshold volumetric water content m³ m⁻³
 a dimensionless empirical curve shape parameter
 b dimensionless empirical curve shape parameter

The temperature reduction function is given by a Q_{10} relationship

$$f_T = A^{(T - T_{ref})}$$

where

A increase factor
 T soil temperature °C
 T_{ref} reference T where $f_T = 1$ °C

Lafolie (1991) used $A = 1.072$. See also Lafolie *et al.* (1997).

NLEAP

Shaffer *et al.* (1991) describe denitrification in the NLEAP model as a loss of nitrogen during a time step t according to

$$D_a = k_d f_N f_T (t_{wet} + f_W (t - t_{wet}))$$

where

D_a	actual denitrification $\text{NO}_3\text{-N}$ loss during time t	mg N kg^{-1}
k_d	denitrification rate coefficient	d^{-1}
f_N	“reduction” function for nitrate content in soil	mg N kg^{-1}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	
t_{wet}	number of wet days for rainfall or irrigations during time t	d
t	time	d

The rate coefficient k_d is a function of organic matter content, soil drainage class, type of tillage, presence of manure, tile drainage, type of climate and occurrence of pans as described by Meisinger and Randall (1991); Table A-2 shows how to determine k_d .

Table A-2. Approximate N denitrification estimates for various soils. See footnote for adjustments due to tillage, manure N, irrigation, drainage, and special soil conditions (from: Meisinger and Randall (1991), their Table 5-7).

	Soil drainage classification				
Soil organic matter content	Excessively well drained	Well-drained	Moderately well-drained	Somewhat poorly drained	Poorly drained
%	% of inorganic N denitrified [#]				
< 2	2-4	3-9	4-14	6-20	10-30
2-5	3-9	4-16	6-20	10-25	15-45
> 5	4-12	6-20	10-25	15-35	25-55
[#] : Adjust for tillage, manure, irrigation, and special soils as follows: no-tillage: use one class wetter drainage manure N: double all values tile drainage: use one class better drainage paddy culture: use values under poorly drained irrigation or humid climate: use value at upper end of range (semi-)arid nonirrigated sites: use values at lower end of range soils with compacted very slowly permeable layer below plow depth (but above 1.2 m): use one class wetter drainage					

The function f_N is simply given as the nitrate content of the soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	mg N kg^{-1}
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The dimensionless reduction function for water content in soil is given by

$$f_W = \begin{cases} 1 & \text{if raining or irrigation} \\ a \exp(bS) & \text{if not raining or irrigation} \end{cases}$$

where

S	water filled pore space
a, b	dimensionless curve shape parameters

Values for a and b are: $a = 0.000304$, $b = 8.15$ (with S given as a fraction in range [0,1]).

The dimensionless reduction function for temperature is given by

$$f_T = A \exp(BT)$$

where

T	soil temperature	$^{\circ}\text{C}$
A	dimensionless curve shape parameter	
B	curve shape parameter	$^{\circ}\text{C}^{-1}$

Values for A and B are: $A = 0.07$, $B = 0.076 \text{ } ^{\circ}\text{C}^{-1}$.

Xu *et al.* (1998) used an adapted denitrification model in the NLEAP model. Denitrification is the sum of wet- and dry-period denitrification during a time step, according to

$$D_a = k_d f_N f_T t_{wet} + k_d f_N f_T f_W (t - t_{wet})$$

Recently, the NLEAP model is accessible through internet (Shaffer *et al.*, 2001; <http://nleap.usda.gov/nresearch.html>).

The NLEAP model has been translated to the graphic-based STELLA[®]-II platform, and is called NLOS (NLEAP on STELLA[®]) (Bittman *et al.*, 2001).

SUNDIAL

Bradbury *et al.* (1993) compute denitrification at weekly intervals. Denitrification can only occur in the top 0-25 cm soil layer (where 80% of the organic matter entering the soil each year is decomposed). Their formulation can be given as

$$D_a = k_d f_N f_w$$

where

D_a	actual denitrification rate	$\text{kg N ha}^{-1} \text{ week}^{-1}$
k_d	denitrification rate coefficient	week^{-1}
f_N	“reduction” function for nitrate content in soil	kg N ha^{-1}
f_W	dimensionless reduction function for pressure head in soil	

The denitrification rate coefficient k_d is computed from the CO_2 evolution rate (as modelled by the SUNDIAL model) according to

$$k_d = k_d^* \frac{W}{5}$$

where

k_d^*	denitrification factor	$(\text{kg C ha}^{-1})^{-1}$
W	CO_2 -C released from soil in specific soil layer	$\text{kg CO}_2\text{-C ha}^{-1} \text{ week}^{-1}$

The function f_N is simply given as the nitrate content of the soil

$$f_N = \begin{cases} 0 & [\text{NO}_3 - \text{N}] \leq N_{resN} \\ [\text{NO}_3 - \text{N}] & [\text{NO}_3 - \text{N}] > N_{resN} \end{cases}$$

where

$[\text{NO}_3\text{-N}]$	nitrate content in soil	kg N ha ⁻¹
N_{resN}	nitrate content in soil below which denitrification does not occur	kg N ha ⁻¹

The reduction function f_w is given by

$$f_w = \frac{y_f - y_c}{y_f}$$

where

y_f	water held in specific soil layer between field capacity and -15 bar	cm
y_f	calculated water deficit in specific soil layer	cm

No temperature adjustment on denitrification is applied, since the CO₂ evolution depends on temperature.

O'Leary and Conor (1996^{ab}) used the same concept.

RESAM

De Vries *et al.* (1988; 1994; 1995; see also Kros, 2002) described denitrification as a first order decay process

$$D_a = k_d f_N f_{GHG} f_{pH}$$

where

D_a	actual denitrification rate	mol N m ⁻² yr ⁻¹
k_d	denitrification rate coefficient	yr ⁻¹
f_N	“reduction” function for nitrate concentration in soil solution	mol N m ⁻²
f_{GHG}	reduction function for water, based on average highest groundwater level (GHG)	
f_{pH}	dimensionless reduction function for pH	

The function f_N is given as the nitrate concentration in soil solution for the given soil layer expressed as the concentration (mol m⁻³) times thickness of the layer (m)

$$f_N = [\text{NO}_3 - \text{N}] q \Delta z$$

where

$[\text{NO}_3\text{-N}]$	nitrate concentration in soil solution	mol N m ⁻³
q	volumetric water content	m ³ m ⁻³
Δz	thickness of soil layer	m

The function f_N represents the nitrate content in a soil layer per unit soil surface (mol m⁻²).

The reduction function f_{GHG} is given by

$$f_{GHG} = 1 - \frac{1}{1 + \exp(-6(GHG - 0.9))}$$

where

GHG	average highest groundwater level	m
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The reduction function f_{pH} is given by

$$f_{pH} = \begin{cases} 0 & pH \leq 3.5 \\ \frac{pH - 3.5}{3} & 3.5 < pH < 6.5 \\ 1 & pH \geq 6.5 \end{cases}$$

where

pH soil pH

RENLEM

Kragt and de Vries (1989) described denitrification as a first order decay process

$$D_a = k_d f_N f_W f_T f_{pH} f_C$$

where

D_a	actual denitrification rate	$\text{g N m}^{-2} \text{ yr}^{-1}$
k_d	denitrification rate coefficient at optimal conditions, i.e. $pH > 7$, $T = 30^\circ\text{C}$, water saturated, no carbon deficiency	$\text{m}^3 \text{ m}^{-3} \text{ d}^{-1}$
f_N	“reduction” function for nitrate concentration in soil solution	mol N m^{-2}
f_W	dimensionless reduction function for water content	
f_T	dimensionless reduction function for soil temperature	
f_{pH}	dimensionless reduction function for pH	
f_C	dimensionless reduction function for carbon (based on ratio soluble (carbon):(potential C-consumption through denitrification))	

The function f_N is given as the nitrate concentration in soil solution times thickness of the layer (m)

$$f_N = [\text{NO}_3 - \text{N}] \Delta z$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	g N m^{-3}
Δz	thickness of soil layer	m

No explicit formulations for f_W , f_{pH} , and f_C were not presented, only references to literature were given. f_T is calculated from the Arrhenius equation assuming a constant average soil temperature in the winter and summer periods of about 7°C and 12°C , respectively. f_{pH} is zero for $pH < 3$ and has an optimum for $pH = 7$.

Breeuwsma *et al.* (1991) gave pedo-transfer expressions for k_d according to

$$\text{sand } k_d = 0.41C - 0.35MLW$$

$$\text{clay } \log k_d = 0.41 - 0.049L + 0.20C$$

where

C	organic carbon content	%
L	clay content	%
MLW	mean low water level	m

Note that the rate constant has units $\text{m}^3 \text{ m}^{-3} \text{ yr}^{-1}$, where the volume per volume units refer to volumetric water content. These would not occur in k_d if the function f_N was expressed as the nitrate concentration in soil solution for the given soil layer expressed as the concentration (mol m^{-3}) times thickness of the layer (m) (see e.g. the RESAM model).

EPIC

The description of denitrification as used in the EPIC model was taken from Marchetti *et al.* (1997; original publication of the EPIC model by A.N. Sharply and J.R. Williams (1990), USDA-ARS Technical Bulletin 1768). The $\text{NO}_3\text{-N}$ lost during a time step t is computed from

$$D_a = \begin{cases} 0 & S < 0.9 \text{ or } T \leq 0^\circ\text{C} \\ f_N(1 - \exp(-1.4f_Tf_Ct)) & S \geq 0.9 \text{ and } T > 0^\circ\text{C} \end{cases}$$

where

D_a	$\text{NO}_3\text{-N}$ lost during a time step t	mg N kg^{-1}
t	time	d
S	degree of saturation, q/q_s (dimensionless)	
1.4	coefficient	d^{-1}
T	soil temperature	$^\circ\text{C}$
f_N	“reduction” function for nitrate content in soil	mg N kg^{-1}
f_T	dimensionless reduction function for soil temperature	
f_C	dimensionless reduction function for soil organic carbon content	

The function f_N is given as the nitrate content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate N content in soil	mg N kg^{-1}
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The function f_T is given as

$$f_T = \frac{T}{T + \exp(9.93 - 0.312T)}$$

where

T	soil temperature	$^\circ\text{C}$
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The function f_C is given as

$$f_C = C$$

where

C	soil organic C content	%
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This denitrification model can be written as

$$D_a = f_N f_W (1 - \exp(-1.4f_Tf_Ct))$$

where a step reduction function based on water content f_W can be used, given as

$$f_W = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^0 & S \geq w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
w_1	threshold value for S , below which $f_W = 0$

with $w_1 = 0.9$.

And, where the temperature reduction function is given by

$$f_T = \begin{cases} 0 & T \leq 0 \text{ } ^\circ\text{C} \\ \frac{T}{T + \exp(9.93 - 0.312T)} & T > 0 \text{ } ^\circ\text{C} \end{cases}$$

CROPSYST

The description of denitrification as used in the CROPSYST model was taken from Marchetti *et al.* (1997; original publication of the CROPSYST model C.O. Stöckle and R. Nelson (1995), Washington State University, Pullman, WA). The $\text{NO}_3\text{-N}$ lost during a time step t is computed from

$$D_a = \begin{cases} 0 & S \leq S_{FC} \\ f_N (1 - \exp(-k_{d,15} f_W f_T t)) & S > S_{FC} \end{cases}$$

where

D_a	$\text{NO}_3\text{-N}$ lost during a time step t	mg N kg^{-1}
t	time	d
$k_{d,15}$	denitrification rate constant at $T = 15 \text{ } ^\circ\text{C}$	d^{-1}
S	degree of saturation, q/q_s (dimensionless)	
S_{FC}	degree of saturation at field capacity, q_{FC}/q_s (dimensionless)	
f_N	“reduction” function for nitrate content in soil	mg N kg^{-1}
f_T	dimensionless reduction function for soil temperature	
f_C	dimensionless reduction function for soil organic carbon content	

For $k_{d,15}$ a value of 0.01 d^{-1} was used.

The function f_N is given as the nitrate content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate N content in soil	mg N kg^{-1}
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The function f_T is given as

$$f_T = \begin{cases} 0.67 \exp(0.43(t - 10)) & T \leq 10 \text{ } ^\circ\text{C} \\ \exp(0.08(t - 15)) & T > 10 \text{ } ^\circ\text{C} \end{cases}$$

where

T	soil temperature	$^\circ\text{C}$
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The function f_W is given by

$$f_W = \exp(0.304 + 2.94(q_s - q) - 47(q_s - q)^2)$$

where

q	volumetric water content	mL cm^{-3}
q_s	volumetric water content at saturation	mL cm^{-3}

CREAMS

The description of denitrification as used in the CREAMS model was taken from Marchetti *et al.* (1997; original publication of the CREAMS model W.G. Knisel (1980), USDA-SEA Conservation Research Report 26, Washington, DC). The $\text{NO}_3\text{-N}$ lost during a time step t is computed from

$$D_a = \begin{cases} 0 & S \leq S_{FC} \\ f_N (1 - \exp(-f_{Ta,kd}(t - 0.5))) & S > S_{FC} \end{cases}$$

where

D_a	$\text{NO}_3\text{-N}$ lost during a time step t	mg N kg^{-1}
f_N	“reduction” function for nitrate content in soil	mg N kg^{-1}
$f_{Ta,kd}$	dimensionless reduction function for air temperature and denitrification rate coefficient	

The function f_N is given as the nitrate content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate N content in soil	mg N kg^{-1}
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The function $f_{Ta,kd}$ is given as

$$f_{Ta,kd} = \exp(0.0693T_a + \ln(k_d) - 2.4255)$$

where

T_a	air temperature	$^{\circ}\text{C}$
k_d	denitrification rate coefficient	d^{-1}

The denitrification rate coefficient k_d is related to soil organic C according to

$$k_d = 24(0.011C + 0.0025)$$

where

C	soil organic C	%
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This denitrification model can be written as

$$D_a = f_N f_W (1 - \exp(-f_{Ta,kd}(t - 0.5)))$$

where a step reduction function based on water content f_W can be used, given as

$$f_W = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^0 & S \geq w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)	
w_1	threshold value for S , below which $f_W = 0$, $w_1 = q_{FC}/q_s$	
q_{FC}	volumetric water content at field capacity	mL cm^{-3}
q_s	volumetric water content at saturation	mL cm^{-3}

See also the description of CREAMS-NT in which a different description of denitrification was used.

CREAMS-NT

The description of denitrification in the CREAMS model was altered by Deizman and Mostaghimi (1991) in a study to simulate N transformations and transport following application of organic waste. Denitrification is described by a first-order decay process according to

$$D_a = k_d f_N f_W f_T f_{pH}$$

where

D_a	$\text{NO}_3\text{-N}$ lost during a time step t	$\text{mg N kg}^{-1} \text{ d}^{-1}$
k_d	denitrification rate coefficient at reference temperature T_{ref} ($^{\circ}\text{C}$)	
f_N	“reduction” function for nitrate content in soil	mg N kg^{-1}
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	
f_{pH}	dimensionless reduction function for pH in soil	

The rate coefficient k_d was determined from Stanford *et al.* (1975^a), i.e. from extractable glucose-C (an index for readily decomposable C sources)

$$k_d = 0.188C - 0.00093$$

where

C	extractable glucose-C	mg C g^{-1}
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The function f_N is given as the nitrate content in soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3\text{-N}]$	nitrate N content in soil	mg N kg^{-1}
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A step reduction function based on water content f_W is used, given as

$$f_W = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^0 & S \geq w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)	
w_1	threshold value for S , below which $f_W = 0$, $w_1 = q_{FC}/q_s$	
q_{FC}	volumetric water content at field capacity	mL cm^{-3}
q_s	volumetric water content at saturation	mL cm^{-3}

The temperature reduction function is given as

$$f_T = A^{(T - T_{ref})}$$

where

A	increase factor for soil temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{ref}	reference soil temperature	$^{\circ}\text{C}$

The pH reduction function is given as

$$f_{pH} = \begin{cases} -0.527 + 0.129pH & 4.1 \leq pH \leq 4.8 \\ -3.942 + 0.84pH & 4.8 \leq pH \leq 5.8 \\ 0.745 + 0.032pH & 5.8 \leq pH \leq 8.0 \\ 7.0 - 0.75pH & 8.0 \leq pH \leq 9.2 \\ 1.414 - 0.143pH & 9.2 \leq pH \leq 9.9 \end{cases}$$

where

pH soil pH

Deizman and Mostaghimi (1991) used: $A = 1.08$, $T_{ref} = 35$ °C.

GLEAMS

The description of denitrification as used in the GLEAMS model was taken from Marchetti *et al.* (1997; original publication of the GLEAMS model R.A. Leonard, W.G. Knisel and D.A. Still (1987), Trans. ASAE 30:1403-1428). The NO_3 -N lost during a time step t is computed from

$$D_a = \begin{cases} 0 & S \leq S_{FC} + 0.1(1 - S_{FC}) \\ f_N(1 - \exp(-k_d f_W f_T t)) & S > S_{FC} + 0.1(1 - S_{FC}) \end{cases}$$

where

D_a	NO_3 -N lost during a time step t	mg N kg ⁻¹
k_d	denitrification rate coefficient	d ⁻¹
f_N	"reduction" function for nitrate content in soil	mg N kg ⁻¹
f_T	dimensionless reduction function for soil temperature	
f_W	dimensionless reduction function for water content	

The denitrification rate coefficient k_d is related to soil organic C according to

$$k_d = 24(0.022C + 0.0042)$$

where

C soil organic C %

The function f_N is given as the nitrate content in soil

$$f_N = [NO_3 - N]$$

where

$[NO_3-N]$ nitrate N content in soil mg N kg⁻¹

The function f_T is given as

$$f_T = \frac{T}{T + \exp(9.93 - 0.312T)}$$

where

T soil temperature °C

The reduction function based on water content f_w is given as

$$f_w = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
w_1	threshold value for S , below which $f_w = 0$
w_2	exponent, $w_2 = 1$

with

$$w_1 = S_{FC} + 0.1(1 - S_{FC})$$

where

S_{FC}	degree of saturation at field capacity, $S_{FC} = q_{FC}/q_s$	
q_{FC}	volumetric water content at field capacity	mL cm^{-3}
q_s	volumetric water content at saturation	mL cm^{-3}

The concepts of GLEAMS were used in the WATRCOM model of Parsons *et al.* (1998).

ADAPT

The ADAPT model (Desmond *et al.*, 1995) is an adapted version of the GLEAMS model that includes surface runoff and subsurface drainage.

NCSOIL (and NCSWAP)

In the model NCSOIL (Molina *et al.*, 1983) denitrification is considered, however, no clear formulation was given. The authors state: “At water saturation denitrification occurs with a rate proportional to the amount of energy available, as measured by the sum of the rates of decomposition of C residues, pool I, and pool II. ... denitrification can be ... activated for water content lower than the saturation level. Boundary conditions arise when immobilization competes with ... denitrification for nitrate. When the initial nitrate supply is not sufficient to supply both denitrification and immobilization, the C flow rates are recomputed with a nitrate level reduced by the nitrate demand for denitrification. Following this correction, precedence is given to immobilization over denitrification”. In NCSOIL processes are affected by soil temperature and soil water content. According to Rodrigo *et al.* (1997) the reduction function for water content can be given as

$$f_w = \begin{cases} 0 & S \leq f_2 \\ f_1 \frac{S - f_2}{f_3 - f_2} & f_2 < S < f_3 \\ f_1 + (1 - f_1) \frac{S - f_3}{1 - f_3} & f_3 < S \leq 1 \end{cases}$$

where

S	dimensionless degree of saturation (q/q_s)	
q	volumetric soil water content	$\text{m}^3 \text{m}^{-3}$
q_s	volumetric soil water content at saturation or porosity	$\text{m}^3 \text{m}^{-3}$
f_1, f_2, f_3	dimensionless empirical constants	

Rodrigo *et al.* (1997) showed a graph from which the following values for f_1 , f_2 , f_3 can be derived: $f_1 = 0.9$, $f_2 = 0.6$, and $f_3 = 0.8$. The function f_W consists of two linear parts (broken-line relationship). Parameter f_2 represents S below which $f_W = 0$, f_3 represents S where the two linear parts intersect, and f_1 is the slope of the first (left) linear part and $(1-f_1)$ is the slope of the second (right) linear part.

The NCSWAP model (Clay *et al.*, 1985) contains the NCSOIL model.

NUCSAM

In the model NUCSAM (Kros, 2002) denitrification is described as a first order decay process according to

$$D_a = k_d f_N f_W f_{pH}$$

where

D_a	actual denitrification rate	$\text{mol N ha}^{-1} \text{ yr}^{-1}$
k_d	denitrification rate coefficient at optimal conditions	yr^{-1}
f_N	“reduction” function for nitrate content in soil	mol N ha^{-1}
f_W	dimensionless reduction function for water	
f_{pH}	dimensionless reduction function for pH	

A typical value for k_d was given as 10 yr^{-1} .

The function f_N is given as the nitrate concentration in soil solution times thickness of the layer (m)

$$f_N = q [\text{NO}_3 - \text{N}] \Delta z 10^4$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	mol N m^{-3}
q	volumetric water content	$\text{m}^3 \text{ m}^{-3}$
Δz	thickness of soil layer	m
10^4	area conversion	$\text{m}^2 \text{ ha}^{-1}$

The function f_W is based on the mean spring water-table and is given by

$$f_W = \begin{cases} f_{W, \max} & MSW \leq 0 \text{ m} \\ f_{W, \max} - (f_{W, \max} - f_{W, \min}) \frac{MSW}{z_d} & 0 < MSW < z_d \\ f_{W, \min} & MSW \geq z_d \end{cases}$$

where

MSW	mean spring water table	m
z_d	when MSW is below depth z_d $f_W = f_{W, \min}$	m
$f_{W, \max}$	maximum value for f_W	
$f_{W, \min}$	minimum value for f_W	

The function f_{pH} for the mean soil pH is given by

$$f_{pH} = \begin{cases} 0 & pH \leq 3.5 \\ \frac{pH - 3.5}{3} & 3.5 < pH < 6.5 \\ 1 & pH \geq 6.5 \end{cases}$$

where

pH mean soil pH mol N m⁻³

SMART2

Kros (2002) describes denitrification as a fraction of the net nitrate input in the soil according to

$$D_a = f_d \left(NO_{3,in} - NO_{3,ru} + NH_{4,ni} - \frac{NO_{3,in}}{N_{in}} N_{im} \right) f_W f_{pH} f_T$$

where

D_a	denitrification	mol ha ⁻¹ yr ⁻¹
f_d	denitrification fraction	
$NO_{3,in}$	gross input flux of NO ₃	mol ha ⁻¹
$NO_{3,iru}$	root uptake flux of NO ₃	mol ha ⁻¹
$NH_{4,ni}$	nitrification flux	mol ha ⁻¹
N_{in}	total N gross input flux	mol ha ⁻¹
N_{im}	total N immobilisation flux	mol ha ⁻¹
f_W	dimensionless reduction function for water	
f_{pH}	dimensionless reduction function for pH	
f_T	dimensionless reduction function for soil temperature	

The function f_W is based on the mean spring water-table and is given by

$$f_W = \begin{cases} f_{W,max} & MSW \leq 0 \text{ m} \\ f_{W,max} - (f_{W,max} - f_{W,min}) \frac{MSW}{z_d} & 0 < MSW < z_d \\ f_{W,min} & MSW \geq z_d \end{cases}$$

where

MSW	mean spring water table	m
z_d	when MSW is below depth z_d $f_W = f_{W,min}$	m
$f_{W,max}$	maximum value for f_W	
$f_{W,min}$	minimum value for f_W	

The function f_{pH} for the mean soil pH is given by

$$f_{pH} = \begin{cases} 0 & pH \leq 3.5 \\ \frac{pH - 3.5}{3} & 3.5 < pH < 6.5 \\ 1 & pH \geq 6.5 \end{cases}$$

where

pH mean soil pH mol N m⁻³

The temperature reduction function is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T - T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	K
T_{ref}	reference T where $f_T = 1$	K

A Q_{10} equal to 1.6 was used and no value for T_{ref} was given.

STOTRASIM

Feichtinger (1996) describes denitrification in the model STOTRASIM as

$$D_a = k_d f_N f_W f_T f_C$$

where

D_a	actual denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
k_d	denitrification rate coefficient	d^{-1}
f_N	“reduction” function for nitrate content in soil	g N mL^{-1}
f_W	dimensionless reduction function for water	
f_T	dimensionless reduction function for pH	
f_C	“reduction” function for carbon content	

The function f_N is given as the nitrate concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	g N mL^{-1}
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The function f_C is given as the carbon content of organic matter

$$f_C = C$$

where

C	carbon content of organic matter	g g^{-1}
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The function f_T is given by

$$f_T = \begin{cases} \frac{T}{30} & 0 \leq T \leq 30 \\ 1 & 30 < T < 40 \\ 1 - \frac{0.8}{20}(T - 40) & 40 \leq T \leq 60 \end{cases}$$

where

T	soil temperature	$^{\circ}\text{C}$
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The reduction function f_W is given by a linear response, but is a function of T : at increased temperatures f_W is larger at a given degree of saturation. The function f_W can be given by

$$f_W = \left(\frac{S - w_1}{1 - w_1} \right)^{w_2}$$

where

S	degree of saturation
w_1	threshold value for S , below which $f_W = 0$; being a function of T
w_2	empirical exponent determining the steepness of the relationship

In STOTRASIM $w_2 = 1$, and w_1 is a function of soil temperature T . For $10^{\circ}\text{C} \leq T \leq 40^{\circ}\text{C}$, Feichtinger (1996) gave w_1 as

$$w_1 = 0.9 - \frac{(T - 10)}{100}$$

DRAINMOD-N

As an alternative to coupling DRAINMOD to CREAMS or GLEAMS, Brevé *et al.* (1997) extended DRAINMOD to include nitrogen dynamics. Denitrification is described by a first-order process according to

$$D_a = k_d f_N f_W f_T f_z$$

where

D_a	actual denitrification rate	$\text{g N m}^{-3} \text{d}^{-1}$
k_d	denitrification rate coefficient	d^{-1}
f_N	“reduction” function for nitrate content in soil	g N m^{-3}
f_W	dimensionless reduction function for water	
f_T	dimensionless reduction function for soil temperature	
f_z	dimensionless depth reduction function	

Brevé *et al.* (1997) gave the following typical values for k_d : 0.004 to 1.08 d^{-1} .

The function f_N simply the nitrate-N content of the soil

$$f_N = q [\text{NO}_3^-]$$

where

$[\text{NO}_3\text{-N}]$	nitrate concentration in soil solution	mg N L^{-1}
q	volumetric water content	L L^{-1}

The function f_W is given by

$$f_W = \begin{cases} 0 & S < w_1 \\ \left[\frac{S - w_1}{1 - w_1} \right]^{w_2} & S \geq w_1 \end{cases}$$

where

S	dimensionless water filled pore space, defined as volumetric water content of the soil divided by the porosity (which is a function of the dry bulk density)
w_1	threshold value for S , below which $f_W = 0$
w_2	empirical exponent determining the steepness of the relationship

Brevé *et al.* (1997) explicitly used $w_2 = 2$.

The dimensionless reduction function f_T is given by a q_{10} function

$$f_T = Q_{10}^{0.1(T - T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	temperature	$^{\circ}\text{C}$
T_{ref}	reference temperature where $f_T = 1$	$^{\circ}\text{C}$

The dimensionless reduction function f_z is given by an empirical relationship that reflects the decrease of organic matter with depth

$$f_z = \exp(-az)$$

where

a	empirical factor	cm^{-1}
z	depth	cm

Brevé *et al.* (1997) gave the following typical values for α : 0.02 to 0.05 cm⁻¹.

HERMES and MINERVA

Denitrification in the HERMES (Kersebaum, 1995) and MINERVA (Kersebaum and Beblík, 2001) models is described as

$$D_a = D_p f_N f_W f_T$$

where

D_a	actual denitrification rate	g N ha ⁻¹ d ⁻¹
D_p	potential denitrification rate	g N ha ⁻¹ d ⁻¹
f_N	dimensionless reduction function for nitrate content in soil	
f_W	dimensionless reduction function for water	
f_T	dimensionless reduction function for pH	
f_C	“reduction” function for carbon content	

The function f_N is given by a Michaelis-Menten type function

$$f_N = \frac{[\text{NO}_3 - \text{N}]^2}{[\text{NO}_3 - \text{N}]^2 + K_m}$$

where

$[\text{NO}_3 - \text{N}]$	nitrate content in top 30 cm layer of soil	kg N ha ⁻¹ 30 cm ⁻¹
K_m	Michaelis-Menten half-saturation constant	(kg N ha ⁻¹ 30 cm ⁻¹) ²

Note that here the quadratic nitrate content is used.

The function f_W is given as

$$f_W = 1 - \exp\left(-\left(\frac{S}{S_{crit}}\right)^r\right)$$

where

S	degree of saturation
S_{crit}	degree of saturation at which $f_T = 1 - 1/e$
r	power constant, with $r = 6$

The function f_T is given as

$$f_T = 1 - \exp\left(-\left(\frac{T}{T_{crit}}\right)^s\right)$$

where

T	soil temperature	°C
T_{crit}	soil temperature at which $f_T = 1 - 1/e$	°C
s	power constant, with $s = 4.6$	

Kersebaum (1995) gave the following typical parameter values (for a loam soil): $D_p = 1274$ g ha⁻¹ d⁻¹, $K_m = 74$ (kg N ha⁻¹ 30 cm⁻¹)², $S_{crit} = 0.77$, and $T_{crit} = 15.5$ °C.

DAYCENT

Denitrification in the DAYCENT¹ model (Parton *et al.*, 2001; Del Grosso *et al.*, 2001) is described similarly as in the NGAS model (Parton *et al.*, 1996). The only difference is found in the reduction function for water content. It is given as a sigmoidal function according to

¹ DAYCENT is the daily time step version of the CENTURY model.

$$f_w = 0.5 + \frac{\arctan(0.6p(0.1S - a))}{p}$$

where

S	degree of saturation	%
a	S at point of inflection	%

The parameter a is a function of soil gas diffusivity at field capacity D_{FC} and soil respiration rate CO_2 .

$$a = 0.90 - M(CO_2)$$

where M is a multiplier that is a function of soil gas diffusivity at field capacity D_{FC} and can be computed from

$$M = 0.36 - 3.05 * \min[0.113, D_{FC}]$$

Based on repacked soil data, Del Grosso *et al.* (2000) concluded that this inflection point occurs at lower values of S for coarser soils (see Table A-3). For intact soils the authors concluded that for loam soils the point of inflection was not much influenced by the respiration rate, while for clay soils the point of inflection moved towards lower values of S with increasing respiration rates (see Table A-3).

Table A-3. Degree of saturation (%) where the point of inflection occurs of the DAYCENT water reduction function.

Repacked soils			Intact soils			
Coarse	Medium	Fine	Loam, low CO_2	Loam, high CO_2	Clay, low CO_2	Clay, high CO_2
63%	75%	85%	89%	81%	85%	53%

EXPERT-N

The EXPERT-N model (Priesack *et al.*, 2001) is a modular system in which several processes can be selected. The modules that are used are mostly based on existing models. N transformations are described based on relationships either from the CERES model or from the LEACHN model (see the descriptions of these models elsewhere).

According to documentation on the internet², the EXPERT-N model (can also?) considers processes on a yearly basis. Denitrification can be considered as a constant fraction of some net N input, or can be computed from a kinetic formulation. In both cases denitrification only occurs when N deposition exceeds the sum of net N uptake in crop + net N immobilisation in root zone.

Constant denitrification fraction

Denitrification is computed according to

$$D_a = \begin{cases} 0 & N_{dep} < N_u + N_i \\ f_d(N_{dep} - N_u - N_i) & N_{dep} \geq N_u + N_i \end{cases}$$

where

D_a	actual denitrification rate	eq ha ⁻¹ yr ⁻¹
N_{dep}	N deposition	eq ha ⁻¹ yr ⁻¹
N_u	net N uptake by crop	eq ha ⁻¹ yr ⁻¹
N_i	net N immobilisation in root zone	eq ha ⁻¹ yr ⁻¹
f_d	constant denitrification fraction $0 \leq f_d \leq 1$	

² see <http://www.gsf.de/ufis/ufis/modell38/gle185.html>

In practice, $0.1 \leq f_d \leq 0.8$.

Kinetic denitrification formulation

Denitrification is computed according to

$$D_a = \begin{cases} 0 & N_{dep} < N_u + N_i \\ k_d f_N f_W f_T f_{pH} & N_{dep} \geq N_u + N_i \end{cases}$$

where

D_a	actual denitrification rate	eq ha ⁻¹ yr ⁻¹
k_d	potential denitrification rate	eq ha ⁻¹ yr ⁻¹
f_N	dimensionless reduction function for nitrate content in soil	
f_W	dimensionless reduction function for water content	
f_T	dimensionless reduction function for soil temperature	

A value of $k_d = 1710$ eq ha⁻¹ yr⁻¹ is used.

The function f_N is given by a Michaelis-Menten type relationship

$$f_N = \frac{(N_{dep} - N_u - N_i)}{K_m + (N_{dep} - N_u - N_i)}$$

where

N_{dep}	N deposition	eq ha ⁻¹ yr ⁻¹
N_u	net N uptake by crop	eq ha ⁻¹ yr ⁻¹
N_i	net N immobilisation in root zone	eq ha ⁻¹ yr ⁻¹
K_m	Michaelis-Menten half-saturation constant	eq ha ⁻¹ yr ⁻¹

A value of $K_m = 2900$ eq ha⁻¹ yr⁻¹ is used.

The reduction function f_W is given by

$$f_W = \frac{5.96S}{0.96 + S}$$

where

S	degree of saturation (based on volumetric water content)
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The function f_T is given by (hard to read from internet document, presumably an Arrhenius type relationship as stated below)

$$f_T = 10^{5660 \left(\frac{1}{T_{ref}} - \frac{1}{273+T} \right)}$$

where

T	soil temperature	°C
T_{ref}	reference soil temperature	K

For T_{ref} a value of 281 K is used.

The reduction function f_{pH} is given by

$$f_{pH} = 5.15 - 2.7808pH + 0.408pH^2$$

where

pH	pH of soil
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It is suggested to use $pH = 5$, in which case f_{pH} would be 1 according to the internet document; however, this is not in correspondence with the equation just given.

WASMOD

Denitrification in the WASMOD model (Reiche, 1994, 1996) is described by

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate	kg N ha ⁻¹
k_d	denitrification rate coefficient	d ⁻¹
f_N	“reduction” function for nitrate content in soil	kg N ha ⁻¹
f_W	dimensionless reduction function for water content	
f_T	dimensionless reduction function for soil temperature	

The denitrification rate coefficient k_d is computed from the organic carbon content according to

$$k_d = 0.0006 \left(24.5 + 0.0031 \frac{C}{2} \right)$$

where

C	organic C content	g C g ⁻¹
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The function f_N is simply given by the nitrate content of the soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate content in soil	kg N ha ⁻¹
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The reduction function f_W is given by

$$f_W = \begin{cases} 0 & q < q_{FC} \\ 1 - \frac{q_s - q}{q_s - q_{FC}} = \frac{q - q_{FC}}{q_s - q_{FC}} & q_{FC} \leq q \end{cases}$$

where

q_s	volumetric water content at saturation	cm ³ cm ⁻³
q_{FC}	threshold value of volumetric water content below which $f_W = 0$, i.e. q at Field Capacity	cm ³ cm ⁻³

The function f_T is simply given by

$$f_T = 0.1e^{0.046 T}$$

where

T	soil temperature	°C
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Note the great resemblance with the CERES model.

REMM

The REMM (Riparian Ecosystem Management Model) model of Inamdar *et al.* (1999) describes daily denitrification as

$$D_a = k_d d f_A f_T (a f_N + (1 - a) f_C)$$

where

D_a	actual denitrification rate	kg N ha ⁻¹
k_d	denitrification rate under optimal conditions	kg N ha ⁻¹ cm ⁻¹
d	thickness of the soil layer under consideration	cm
f_A	dimensionless reduction function for anaerobiosis	
f_T	dimensionless reduction function for pH	

a	coefficient determining the influence of nitrate on denitrification
f_N	dimensionless reduction function for nitrate availability
f_C	dimensionless reduction function for carbon availability

The function f_A is representative of redox potential and the predisposition of the denitrifying bacteria and is given as

$$f_A = \text{MIN} \left\{ \begin{array}{l} 1 \\ \text{MAX} \left\{ \begin{array}{l} 0.4 \\ b f_A^{t-1} f_W (2 - \exp(-gC)) \end{array} \right\} \end{array} \right.$$

where

f_A^{t-1}	f_A at previous time step	
b	coefficient determining the maximum possible increase in denitrification due to increased redox potential	
f_W	dimensionless reduction function for water content	
?	coefficient relating the amount of C to its affect on anaerobiosis	kg mg^{-1}
C	C available for consumption by denitrification microbes	mg C kg^{-1}

The function f_W is given as

$$f_W = \text{MIN} \left\{ \begin{array}{l} 1 \\ 0.000304 \exp(0.0815S) \end{array} \right.$$

where

S	degree of saturation
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No explicit expression for the function f_T was given. Here we assume that is the same function as the one Inamdar *et al.* (1999) used for describing the carbon dynamics

$$f_T = \left\{ \begin{array}{ll} 0 & T \leq 0 \\ Q_{10}^{0.1(T-T_{opt})} & 0 < T < T_{opt} \\ 1 & T_{opt} \leq T \end{array} \right.$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	$^{\circ}\text{C}$
T_{opt}	optimal temperature	$^{\circ}\text{C}$

The nitrate availability function f_N is given as

$$f_N = \text{MIN} \left\{ \begin{array}{l} 1 \\ \frac{[\text{NO}_3 - \text{N}]}{N_{crit}} \end{array} \right.$$

where

$[\text{NO}_3 - \text{N}]$	nitrate-N content in soil layer	mg N kg^{-1}
N_{crit}	critical nitrate-N content in soil layer below which nitrate is assumed to limit denitrification	mg N kg^{-1}

The function f_C is given by a Michaelis-Menten function

$$f_C = \frac{C}{K_m + C}$$

where

C	C available for consumption by denitrification microbes	mg C kg ⁻¹
K_m	Michaelis-Menten half-saturation constant for C	mg C kg ⁻¹

C is assumed to have a direct effect on the denitrification rate when nitrate is above the critical level.

Inamdar *et al.* (1999) used: $a = 0.19$, $b = 1.5$, $\theta = 0.1$, $T_{opt} = 25$ °C, $N_{crit} = 3$ mg N kg⁻¹, $K_m = 0.01$ mg C kg⁻¹

SWAP

The model SWAP has a solute sink term included in the solute transport equation (Van Dam *et al.*, 1997). This sink term consists of plant uptake and of a transformation part (e.g. decay of pesticides). Transformation is considered as a first order decay process (based on total solute content, i.e. solute dissolved plus solute adsorbed). The process is influenced by soil temperature, soil water content and by a soil-depth function. Denitrification thus can be considered by

$$D_a = k_d f_N f_W f_T f_z$$

where

D_a	actual denitrification rate	g N cm ⁻³ d ⁻¹
k_d	denitrification rate coefficient under optimal conditions	d ⁻¹
f_N	“reduction” function for nitrate content in soil	g N cm ⁻³
f_T	dimensionless reduction function for soil temperature	
f_z	dimensionless reduction function for soil depth	

The function f_N is given by the nitrate content of the soil

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate content in soil	g N cm ⁻³
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The dimensionless reduction function f_W is given by

$$f_W = \text{MIN} \left[\left(\frac{q}{q_{ref}} \right)^B, 1 \right]$$

where

q	volumetric water content	mL cm ⁻³
q_{ref}	q at pressure head –100 cm (field capacity)	mL cm ⁻³
B	empirical exponent determining the steepness of the relationship	

The dimensionless reduction function f_T is given by

$$f_T = \exp(a(T - 20))$$

where

a	parameter	°C ⁻¹
T	temperature	°C

No general functional relationship for f_z is used. The user must supply f_z as a function of soil depth in an input file.

SWMS_2D

In the model SWMS_2D (Šimunek *et al.*, 1994) no specific description for denitrification is included. The user may specify zero- and/or first-order decay for solutes. In that sense zero- and first-order decay due to denitrification can be considered. However, no adaptations due to environmental conditions (e.g. water content, temperature) can be considered.

WAVE

In the WAVE model (Vanclooster *et al.*, 1996; revised version of SWATNIT) denitrification is described as a first order decay process according to

$$D_a = k_d f_N f_W f_T$$

where

D_a	actual denitrification rate	$\text{g N cm}^{-3} \text{d}^{-1}$
k_d	denitrification rate coefficient under optimal conditions	d^{-1}
f_N	“reduction” function for nitrate concentration in soil solution	g N cm^{-3}
f_W	dimensionless reduction function for soil water content	
f_T	dimensionless reduction function for soil temperature	

The denitrification rate coefficient can be computed from

$$k_d = \begin{cases} 0.41C - 0.35MGWL & \text{for sandy soils} \\ 0.51 - 0.049L + 0.20C & \text{for clay soils} \end{cases}$$

where

C	carbon content of the soil	%
$MGWL$	mean groundwater level	m
L	clay content	%

The function f_N is given by the nitrate concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	g N cm^{-3}
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The dimensionless reduction function f_W is given by

$$f_W = \begin{cases} 0 & q \leq q_d \quad S < b \\ \left(\frac{q - q_d}{q_s - q_d} \right)^a = \left(\frac{S - b}{1 - b} \right)^a & q_d < q \leq q_s \quad b \leq S \leq 1 \end{cases}$$

where

q	volumetric water content	mL cm^{-3}
q_s	q at saturation	mL cm^{-3}
q_d	threshold value for q below which $f_w = 0$	mL cm^{-3}
S	degree of saturation, $S = q/q_s$	
b	threshold value for S below which $f_w = 0$, $b = q/q_s$	
a	dimensionless parameter determining the steepness of the function	

In WAVE $b = 0.8$ and $a = 2$.

A Q_{10} temperature reduction function is used

$$f_T = Q_{10}^{0.1(T-T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	°C
T_{ref}	reference T where $f_T = 1$	°C

In WAVE $Q_{10} = 3$, $T_{ref} = 16$ °C.

COUPMODEL

The COUPMODEL (Jansson and Karlberg, 2001) can be seen as an updated and extended version of the SOILN model of Johnsson *et al.* (1987; 1991). Denitrification is computed as

$$D_a = D_p f_N f_W f_T f_z$$

where

D_a	actual denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
D_p	potential denitrification rate	$\text{g N m}^{-2} \text{d}^{-1}$
f_N	dimensionless reduction function for nitrate concentration in soil solution	
f_W	dimensionless reduction function for water content in soil	
f_T	dimensionless reduction function for temperature in soil	
f_z	dimensionless reduction function for soil depth	

With respect to SOILN, an additional reduction function f_z is introduced, and the user can choose between several f_T functions. The authors use $D_p = 0.04 \text{ g N m}^{-2} \text{d}^{-1}$.

The dimensionless reduction function for nitrate concentration in soil solution is given by

$$f_N = \frac{[\text{NO}_3 - \text{N}]}{K_m + [\text{NO}_3 - \text{N}]}$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	mg N L^{-1}
K_m	Michaelis-Menten half saturation constant	mg N L^{-1}

The authors gave a typical value of $K_m = 10 \text{ mg N L}^{-1}$.

The dimensionless reduction function as presented by Jansson and Karlberg (2001) is unrealistic. Presumably the function must be given as

$$f_W = \begin{cases} 0 & q_s - q \geq a \\ \left(\frac{q_s - q - a}{a} \right)^b & q_s - q < a \end{cases}$$

where

q	actual volumetric water content	$\text{m}^3 \text{m}^{-3}$
q_s	volumetric water content at saturation (or porosity)	$\text{m}^3 \text{m}^{-3}$
a	dimensionless range in q (starting at q_s) in which f_w reduces from 1 to 0	$\text{m}^3 \text{m}^{-3}$
b	dimensionless empirical curve shape parameter	

The authors used default values $a = 0.1$ and $b = 10$.

Three possible temperature reduction function can be chosen. The first one is given by a Q_{10} relationship

$$f_T = Q_{10}^{0.1(T-T_{ref})}$$

where

Q_{10}	increase factor for a 10 °C increase in temperature	
T	soil temperature	°C
T_{ref}	reference T where $f_T = 1$	°C

The second one is similar as the Q_{10} function given above, except that for temperatures below a certain threshold temperature a correction is added, according to

$$f_T = \begin{cases} \frac{T}{T_{threshold}} Q_{10}^{0.1(T-T_{ref})} & T < T_{threshold} \\ Q_{10}^{0.1(T-T_{ref})} & T \geq T_{threshold} \end{cases}$$

where

$T_{threshold}$	threshold T below which reduction on Q_{10} relationship occurs	°C
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The third reduction function is the so-called Ratowski function given by

$$f_T = \begin{cases} 0 & T < T_{min} \\ \left(\frac{T - T_{min}}{T_{max} - T_{min}} \right)^2 & T_{min} \leq T \leq T_{max} \\ 1 & T_{max} < T \end{cases}$$

where

T_{min}	minimum T at which Ratowski function equals 0	°C
T_{max}	maximum T at which Ratowski function equals 1	°C

The authors gave default values $Q_{10} = 2$, $T_{ref} = 20$ °C, $T_{threshold} = 5$ °C, $T_{min} = -8$ °C and $T_{max} = 20$ °C.

NITWAT

Denitrification in the model NITWAT (McIssac *et al.*, 1993) is described as

$$D_a = k_d f_N f_W f_T SC$$

where

D_a	actual denitrification rate	mg N L ⁻¹ d ⁻¹
k_d	denitrification rate coefficient	d ⁻¹
f_N	“reduction” function for nitrate concentration in soil solution	mg N L ⁻¹
f_W	dimensionless function for water content	
f_T	dimensionless reduction function for soil temperature	
SC	dissolved C concentration	

The function f_N is given by the nitrate concentration in soil solution

$$f_N = [\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$	nitrate concentration in soil solution	gm N L ⁻¹
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In NITWAT C dynamics is not considered, so that SC is considered to be a constant fraction of the total C concentration according to

$$SC = 0.0087 TOC$$

where

TOC total C concentration

The reduction function for water content is given by (reformulated from original manuscript)

$$f_w = \begin{cases} 0 & S \leq w_1 \\ \frac{S - w_1}{1 - w_1} & w_1 < S \end{cases}$$

where

S degree of saturation

w_1 threshold value of S below which $f_w = 0$; $w_1 = 0.9$

The reduction function for temperature is given by

$$f_T = \begin{cases} 0 & T \leq 0^\circ\text{C} \\ \frac{0.1 + 0.9T}{T + \exp(9.54 - 0.3T)} & 0^\circ\text{C} < T \end{cases}$$

where

T soil temperature $^\circ\text{C}$

Presumably, f_T should be the same as that used in WHNSIM, i.e.

$$f_T = \begin{cases} 0 & T \leq 0^\circ\text{C} \\ 0.1 + \frac{0.9T}{T + \exp(9.54 - 0.3T)} & 0^\circ\text{C} < T \end{cases}$$

APSIM

APSIM is a software system for water and nitrogen dynamics (McCown *et al.*, 1996; Probert *et al.*, 1998). It uses modules that are based on other models. The soil nitrogen module is based on CERES.

Colbourn (1993)

From literature data, Colbourn (1993) derived a denitrification formula of the form

$$D_a = N \exp(0.1S + 0.1T - 8.3)$$

where

D_a	actual denitrification rate	$\text{g N ha}^{-1} \text{ d}^{-1}$
N	nitrate availability in the range [1,100%]	$\text{g N ha}^{-1} \text{ d}^{-1}$
S	degree of saturation in the range [50,100%]	
T	soil temperature	$^\circ\text{C}$

The nitrate availability N was found to be correlated to nitrate-N according to

$$\ln(N) = 0.71 + 0.50[\text{NO}_3 - \text{N}]$$

where

$[\text{NO}_3 - \text{N}]$ nitrate N content in the soil kg N ha^{-1}

This correlation was found for the range $0\text{--}6 \text{ kg N ha}^{-1}$ in the 0-10 cm topsoil

Lippold and Matzel (1992)

Lippold and Matzel (1992) describe denitrification with the following model. In a certain layer during a time step of one day, the nitrate content is decreased by a certain amount D according to

$$D = N - \left[(n-1)f_w k + N^{1-n} \right]^{-\frac{1}{1-n}}$$

where

D	amount of nitrogen lost from a 30 cm soil layer	mg N kg ⁻¹
N	nitrate content in a 30 cm soil layer	mg N kg ⁻¹
f_w	dimensionless reduction function for water content	
k	temperature dependent daily denitrification constant	mg N kg ⁻¹
n	reaction order coefficient that expresses the dependency of denitrification on nitrate content	

For $n = 0$, the equation reduces to $D = -f_w k$.

The temperature dependent daily denitrification constant k follows from

$$k = \exp \left(a + \frac{b}{T} \right)$$

where

a	temperature coefficient determined under anaerobic conditions	
b	temperature coefficient determined under anaerobic conditions	K
T	soil temperature in a 30 cm soil layer	K

The reduction function for water content is the same as that of

$$f_w = \begin{cases} 0 & S < w_1 \\ \frac{S - w_1}{1 - w_1} & w_1 \leq S \end{cases}$$

where

S	degree of saturation
w_1	threshold value for S below which $f_w = 0$; it is equal to the degree of saturation at field capacity

For example, Table A-4 lists the parameters for top 30 cm of three soil types as given by Lippold and Matzel (1992)..

Table A-4. Parameters of the Lippold and Matzel (1992) denitrification model for three soil types.

Parameter	Soil Type		
	Loamy sand	Silty loam	Clay
k (anaerobic)	0.74	0.74	0.45
a	28.88	34.42	34.78
b	-8404	-9999	-10249
n	0	0.2	0.5

CRISP

The CRISP model (Nielsen *et al.*, 1999) describes denitrification to occur only in some anoxic compartment of the soil as considered in their model. Its description is rather poor. It depends on a Michaelis-Menten type reduction function for nitrate content in the anoxic zone. A temperature effect is included. As it is not used for agricultural purposes, it is not further described here.

Others

Some other denitrification functions can be found in

- Shiratani *et al.* (1998): first order decay process, with an Arrhenius-type temperature reduction function.
- Sinclair and Amir (1992) considered denitrification whenever the fraction transpirable water exceeds 1, so that denitrification occurred for the first day or two following rainfall or irrigation. The denitrification rate decreases exponentially with time ($1 - \exp(-0.3t)$). Sinclair and Muchow (1995) extended this concept by including a temperature reduction function based on the work of Stanford *et al.* (1975^b).
- Hermsmeyer and van der Ploeg (1996^{a,b}) consider denitrification as a Michaelis-Menten kinetic process, with adaptation to pH, oxygen and temperature. However, no explicit formulation on how pH, oxygen and soil temperature affect denitrification is given.
- Under flooded conditions Ma *et al.* (1999) described denitrification as a first-order decay process. Since the system is flooded no water content reduction function needed to be considered. No reduction functions for temperature or pH were considered.
- Blackburn (1990) described denitrification in marine sediments as a first-order decay process. Since saturated conditions exist no reduction for water content (or oxygen) was applied. No temperature reduction was considered.
- The BAMO/BAMO2 model (Döring *et al.*, 1993) incorporated denitrification as described in the CANDY model.
- Scholefield *et al.* (1991) did not compute denitrification explicitly. The contribution of denitrification to (denitrification + leaching) was established on assessments of experimental data. The ratio denitrification : (denitrification + leaching) is dependent on soil texture and drainage type according to Table A-5. The ratio denitrification : leaching can be simply computed from these data (say α) from $\alpha / (1 + \alpha)$.

Table A-5. The ratio denitrification : (denitrification + leaching) according to Scholefield *et al.* (1991) for five soil textures.

Drainage	Soil texture				
	sand	sandy loam	loam	clay loam	clay
Poor	0.50	0.55	0.65	0.75	0.80
Moderate	0.15	0.30	0.45	0.55	0.60
Good	0.10	0.15	0.25	0.30	0.35

Appendix B: Sensitivity analysis of the sigmoidal power function.

Equation (2-7) is a four-parameter sigmoidal power function. Its sensitivity, *c.f.* the analysis in chapter 3, is given below, without any comments.

$$\frac{a}{f_w} \frac{df_w}{da} = 1$$

$$\frac{b}{f_w} \frac{df_w}{db} = cb^{-dS} (dS \log[b] - 1)$$

$$\frac{c}{f_w} \frac{df_w}{dc} = -cb^{-dS} \log[b]$$

$$\frac{d}{f_w} \frac{df_w}{dd} = cb^{-dS} dS (\log[b])^2$$

Appendix C: Sensitivity analysis of the NEMIS temperature function.

In the NEMIS model (Hénault and Germon, 2000) the temperature function consists of two parts around a so-called rupture temperature (T_{rup}). It is argued that at lower temperatures other types of microbes are involved than at higher temperatures. The function can be seen as some sort of a double Q_{10} type. It is denoted by $f_{T,1}$ and is given by

$$f_{T,1} = \begin{cases} \exp\left[\frac{(T - T_{rup}) \ln Q_{10,A} - (T_{ref} - T_{rup}) \ln Q_{10,B}}{10}\right] & T < T_{rup} \\ \exp\left[\frac{(T - T_{ref}) \ln Q_{10,B}}{10}\right] & T \geq T_{rup} \end{cases}$$

where

T	soil temperature	$^{\circ}\text{C}$
T_{rup}	rupture temperature where the two parts of f_T meet	$^{\circ}\text{C}$
T_{ref}	reference temperature where $f_T = 1$	$^{\circ}\text{C}$
$Q_{10,A}$	increase factor in f_T of the left part	
$Q_{10,B}$	increase factor in f_T of the right part	

The right part of $f_{T,1}$ is equal to the Q_{10} function given by Eq. (2-13).

The relative change of $f_{T,1}$ at relative change in $Q_{10,A}$ is given by

$$\frac{Q_{10,A}}{f_{T,1}} \frac{df_{T,1}}{dQ_{10,A}} = \begin{cases} \frac{(T - T_{rup})}{10} & T < T_{rup} \text{ } ^{\circ}\text{C} \\ 0 & T \geq T_{rup} \text{ } ^{\circ}\text{C} \end{cases}$$

This effect is independent on $Q_{10,A}$ and is linearly dependent on T in case $T < T_{rup}$.

The relative change of $f_{T,1}$ at relative change in $Q_{10,B}$ is given by

$$\frac{Q_{10,B}}{f_{T,1}} \frac{df_{T,1}}{dQ_{10,B}} = \begin{cases} -\frac{(T_{ref} - T_{rup})}{10} & T < T_{rup} \text{ } ^{\circ}\text{C} \\ \frac{(T - T_{ref})}{10} & T \geq T_{rup} \text{ } ^{\circ}\text{C} \end{cases}$$

This effect is independent on $Q_{10,B}$ and is linearly dependent on T in case $T \geq T_{rup}$.

The relative change of $f_{T,1}$ at relative change in T_{ref} is given by

$$\frac{T_{ref}}{f_{T,1}} \frac{df_{T,1}}{dT_{ref}} = \begin{cases} -\frac{T_{ref} \ln(Q_{10,B})}{10} & T < T_{rup} \text{ } ^{\circ}\text{C} \\ -\frac{T_{ref} \ln(Q_{10,A})}{10} & T \geq T_{rup} \text{ } ^{\circ}\text{C} \end{cases}$$

This effect is linearly dependent on T_{ref} and is independent on T .

The relative change of $f_{T,1}$ at relative change in T_{rup} is given by

$$\frac{T_{rup}}{f_{T,1}} \frac{df_{T,1}}{dT_{rup}} = \begin{cases} -\frac{T_{rup} (\ln(Q_{10,B}) - \ln(Q_{10,A}))}{10} & T < T_{rup} \text{ } ^{\circ}\text{C} \\ 0 & T \geq T_{rup} \text{ } ^{\circ}\text{C} \end{cases}$$

This effect is linearly dependent on T_{rup} in case $T < T_{rup}$ and is independent on T .

The relative change of $f_{T,1}$ at relative change in T is given by

$$\frac{T}{f_{T,1}} \frac{df_{T,1}}{dT} = \begin{cases} \frac{T \ln(Q_{10,A})}{10} & T < T_{rup} \text{ } ^\circ\text{C} \\ \frac{T \ln(Q_{10,B})}{10} & T \geq T_{rup} \text{ } ^\circ\text{C} \end{cases}$$

This effect is linearly dependent on T .

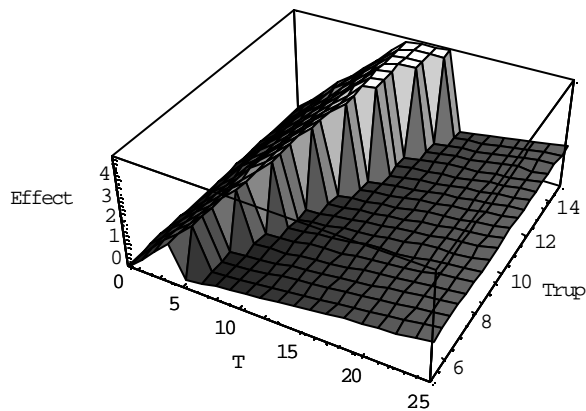
In Table C-1 some numerical values of the effects (*c.f.* Table 3-1) are given.

Table C-1. Relative change of the reduction function $f_{T,1}$ at relative change in parameters for a) $T = 10 \text{ } ^\circ\text{C}$ and b) $T = 15 \text{ } ^\circ\text{C}$. The following default values for the parameters were used: $T_{rup} = 11 \text{ } ^\circ\text{C}$, $T_{ref} = 20 \text{ } ^\circ\text{C}$, $Q_{10,A} = 89$, $Q_{10,B} = 2.1$.

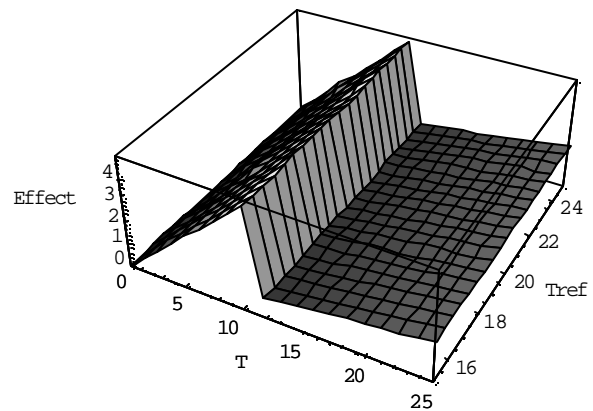
Function	a	b
T_{rup}	-4.12	0
T_{ref}	-1.48	-1.48
$Q_{10,A}$	0.1	0
$Q_{10,B}$	-0.9	-0.5
T	4.49	1.11

In Figure C-1 graphical representation of the effects are given.

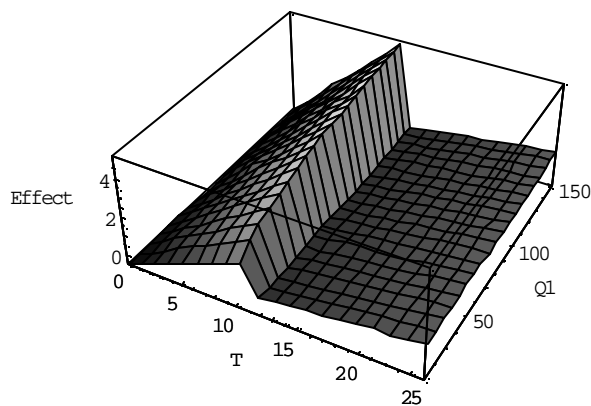
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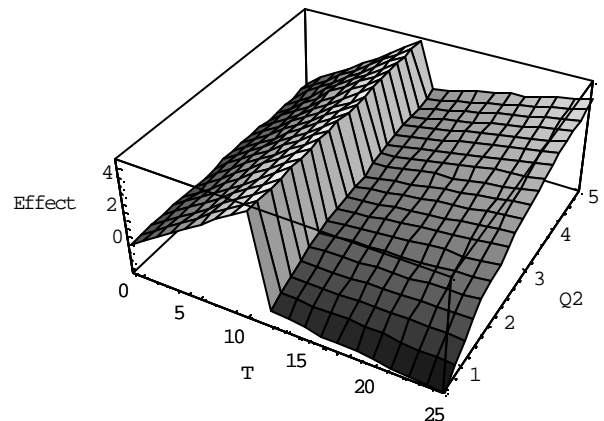
b



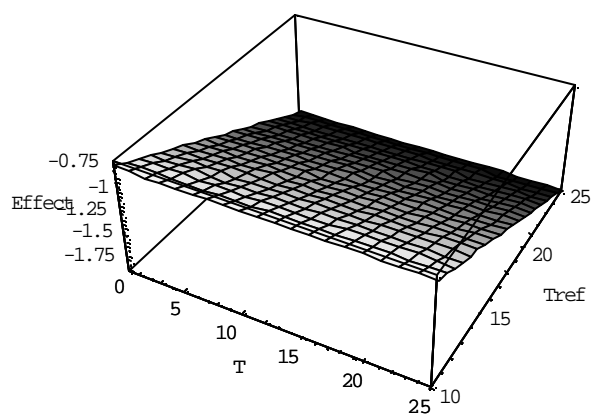
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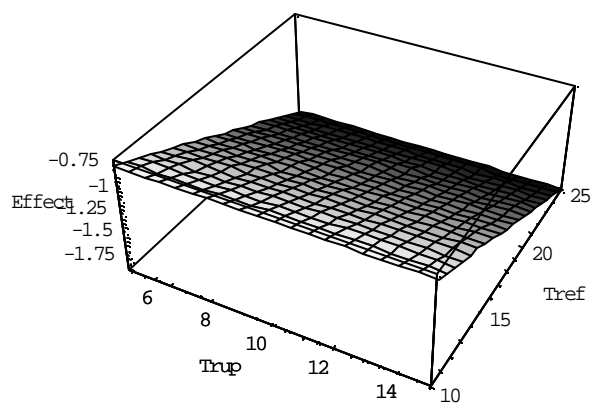
d



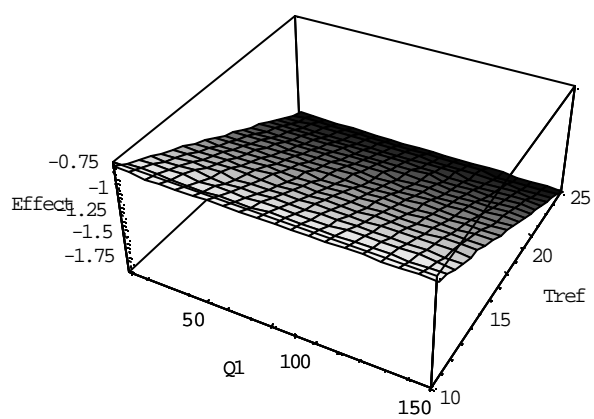
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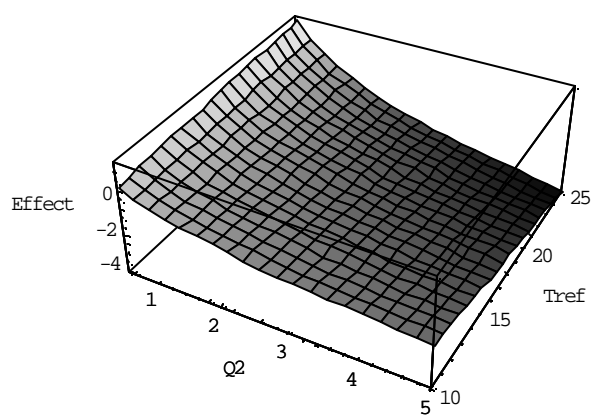
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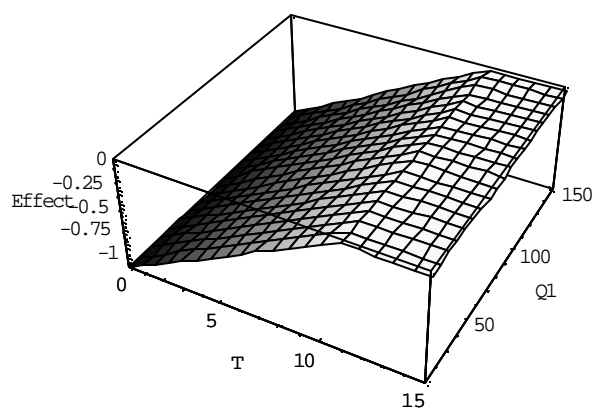
g



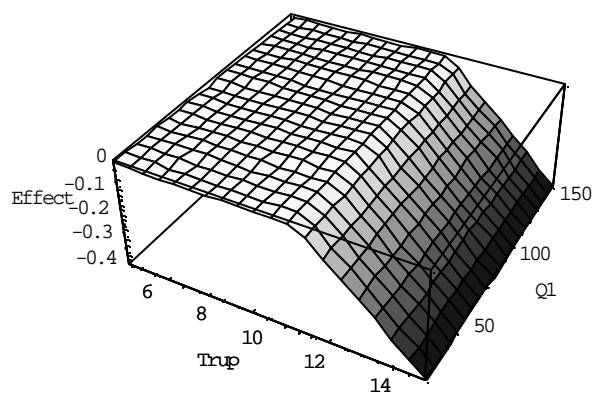
h



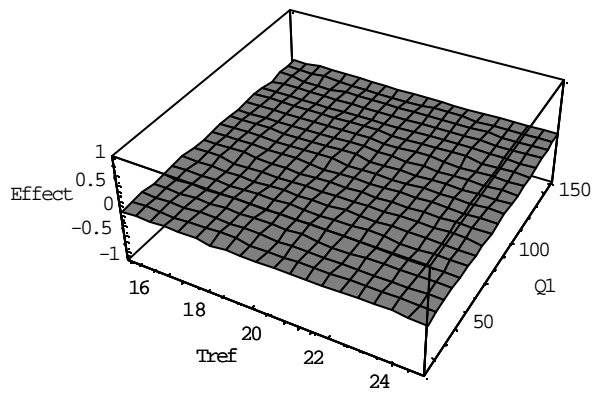
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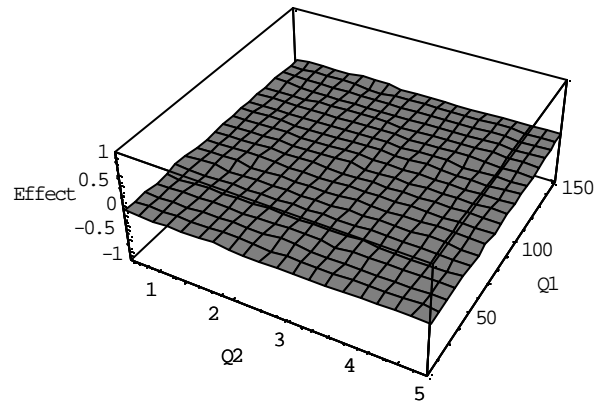
j



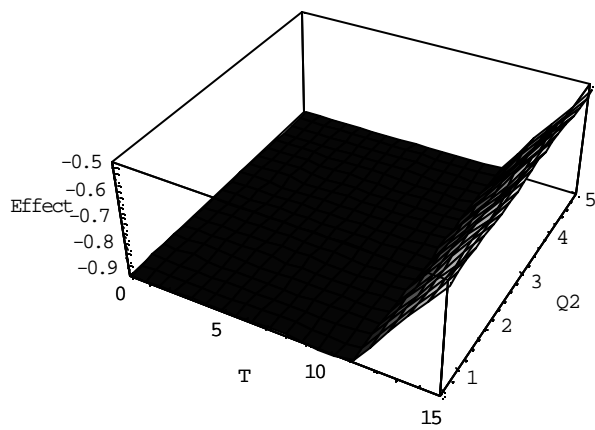
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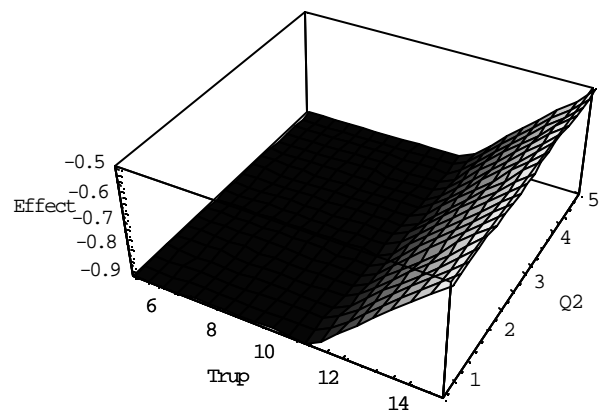
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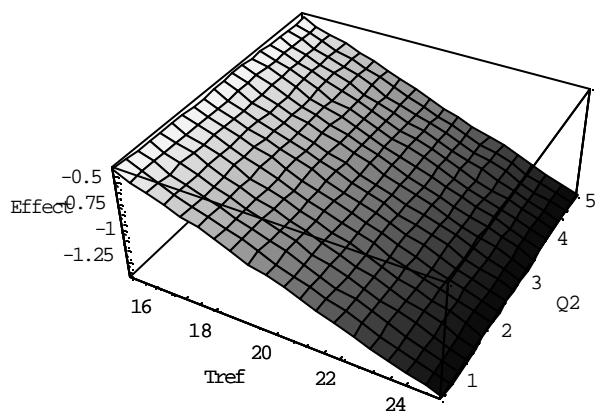
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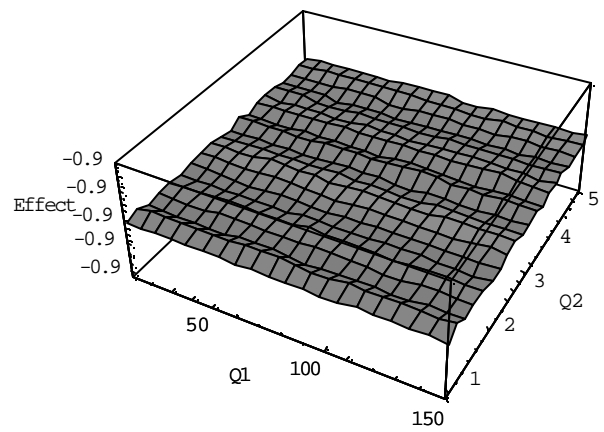
n



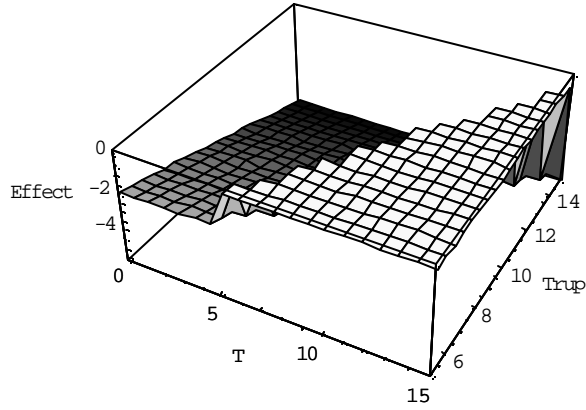
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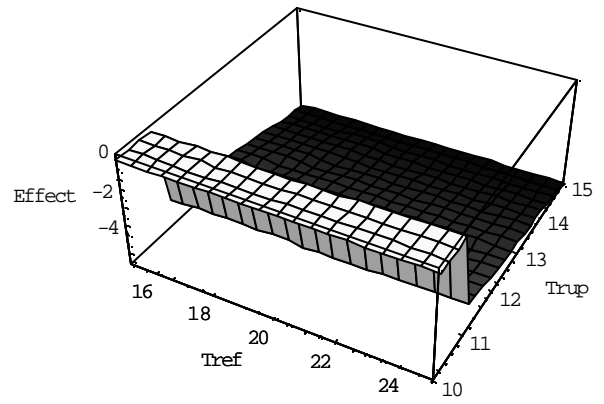
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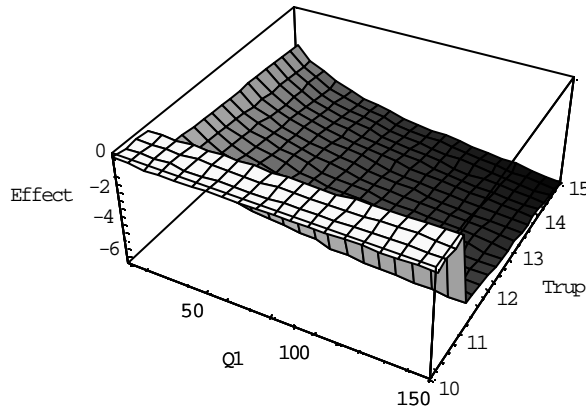
q



r



s



t

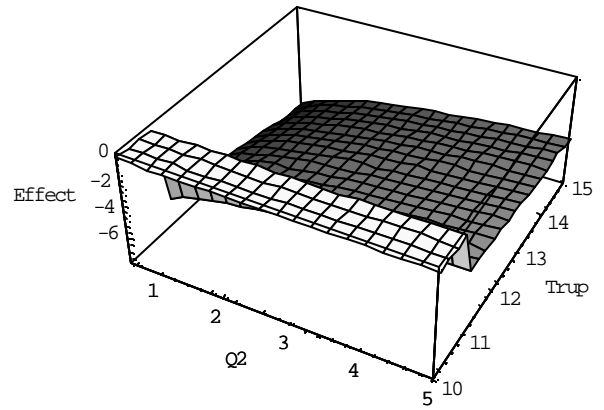


Figure C-1. a) Relative change in $f_{T,1}$ (Effect) at relative change in T at varying T_{rup} , b) idem at varying T_{ref} , c) idem at varying $Q_{10,A}$, d) idem at varying $Q_{10,B}$, e) Effect at relative change in T_{ref} at varying T , f) idem at varying T_{rup} , g) idem at varying $Q_{10,A}$, h) idem at varying $Q_{10,B}$, i) Effect at relative change in $Q_{10,A}$ at varying T , j) idem at varying T_{rup} , k) idem at varying T_{ref} , l) idem at varying $Q_{10,B}$, m) Effect at relative change in $Q_{10,B}$ at varying T , n) idem at varying T_{rup} , o) idem at varying T_{ref} , p) idem at varying $Q_{10,A}$, q) Effect at relative change in T_{rup} at varying T , r) idem at varying T_{ref} , s) idem at varying $Q_{10,A}$, t) idem at varying $Q_{10,B}$. Where needed the following default values were used: $T = 11$ °C, $T_{rup} = 11$ °C, $T_{ref} = 20$ °C, $Q_{10,A} = 89$, $Q_{10,B} = 2.1$.

Figure C-1 shows that: some effects are zero or constant (k,l,p); some effects are identical (e,f,g); some effects are only present at one side of T_{rup} (i,j,q,r,s,t); in some cases there is a clear change in the effect around T_{rup} (a,b,c,d,m,n); Great effects turn up in situations where $Q_{10,A}$ plays a role. This means that both T_{rup} and $Q_{10,A}$ need to be determined at great accuracy.

Appendix D: First and second derivatives of SSQ.

The usage of the bcoah routine of the IMSL[®] library (Visual Numerics, 1997) requires the first and second derivatives, with respect to the parameters to be fitted, of the function to be minimised. For the reduction functions defined in chapter 2, i.e. Eqs. (2-5), (2-6), and (2-13), the derivatives for SSQ as defined by Eq. (4-2) can be derived. Equation (4-2) is recalled here

$$SSQ(K_{MM}, w_1, w_2, Q_{10}) = \sum_{i=1}^N (P_i(K_{MM}, w_1, w_2, Q_{10}) - O_i)^2 \quad (D-1)$$

In general, the first derivative of SSQ to any parameter x is given by

$$\frac{dSSQ(x)}{dx} = \frac{d}{dx} \sum_{i=1}^N (P_i(x) - O_i)^2 = \sum_{i=1}^N \left(2 \frac{dP_i(x)}{dx} (P_i(x) - O_i) \right) \quad (D-2)$$

The derivatives of P to a parameter is simply the derivative of the corresponding reduction function to that parameter (as given in chapter 3) times the other two reduction functions.

The second derivative of SSQ to any set of parameters x and y is given by

$$\begin{aligned} \frac{d^2 SSQ(x, y)}{dx dy} &= \frac{d}{dx} \frac{d}{dy} \sum_{i=1}^N (P_i(x, y) - O_i)^2 \\ &= \sum_{i=1}^N \left(2 \frac{d^2 P_i(x, y)}{dx dy} (P_i(x, y) - O_i) + 2 \frac{dP_i(x, y)}{dx} \frac{dP_i(x, y)}{dy} \right) \end{aligned} \quad (D-2)$$

The derivatives $d^2 P / (dx dy)$ can also be simply obtained. They are given here without any further explanation.

$$\begin{aligned} \frac{d^2 P}{dK_{MM} dK_{MM}} &= P \frac{2}{(K_{MM} + [\text{NO}_3 - \text{N}])^2} \\ \frac{d^2 P}{dw_1 dw_1} &= P \frac{w_2 (S - 1) (1 + S - 2w_1 + w_2 (S - 1))}{(S - w_1)^2 (w_1 - 1)^2} \\ \frac{d^2 P}{dw_2 dw_2} &= P \left(\ln \left(\frac{S - w_1}{1 - w_1} \right) \right)^2 \\ \frac{d^2 P}{dQ_{10} dQ_{10}} &= P \frac{(T - T_{ref})(T - T_{ref} - 10)}{100 Q_{10}^2} \\ \frac{d^2 P}{dK_{MM} dw_1} &= \frac{d^2 P}{dw_1 dK_{MM}} = P \frac{w_2 (S - 1)}{(K_{MM} + [\text{NO}_3 - \text{N}]) (S - w_1) (w_1 - 1)} \\ \frac{d^2 P}{dK_{MM} dw_2} &= \frac{d^2 P}{dw_2 dK_{MM}} = -P \frac{\ln \left(\frac{S - w_1}{1 - w_1} \right)}{(K_{MM} + [\text{NO}_3 - \text{N}])} \\ \frac{d^2 P}{dK_{MM} dQ_{10}} &= \frac{d^2 P}{dQ_{10} dK_{MM}} = -P \frac{(T - T_{ref})}{10 Q_{10} (K_{MM} + [\text{NO}_3 - \text{N}])} \\ \frac{d^2 P}{dw_1 dw_2} &= \frac{d^2 P}{dw_2 dw_1} = -P \frac{(S - 1) \left(1 + w_2 \ln \left(\frac{S - w_1}{1 - w_1} \right) \right)}{(S - w_1) (w_1 - 1)} \end{aligned}$$

$$\frac{d^2 P}{dw_1 dQ_{10}} = \frac{d^2 P}{dQ_{10} dw_1} = -P \frac{w_2 (S-1)(T-T_{ref})}{10Q_{10}(S-w_1)(w_1-1)}$$

$$\frac{d^2 P}{dw_2 dQ_{10}} = \frac{d^2 P}{dQ_{10} dw_2} = P \frac{(T-T_{ref}) \ln\left(\frac{S-w_1}{1-w_1}\right)}{10Q_{10}}$$

Appendix E: D_p estimated from organic matter decay for the Velthof (1997) peat data set.

The Zegveld peat soils are nutrient-rich peat soils. The yearly decay rate of organic matter in these type of soils will be somewhat larger than the 'average' organic matter decay rate of arable soils of 2%, at an average soil temperature of 9 °C to 10 °C. According to K. Zwart (Alterra, pers. comm.) this may be as high as 3% to 4%; I will use 3.5% below. For a Q_{10} type temperature behaviour with say $Q_{10} = 2.5$, the decay rate at 20 °C will thus be

$$2.5 \times 3.5 = 8.75\%.$$

In the Zegveld peat soils, the average C content is 0.19 g C g⁻¹ (Velthof, 1997; his Table 3.1). Thus the average daily C decay rate equals

$$0.0875 \times 0.19 / 365 / 12 = 3.8 \times 10^{-6} \text{ mol C g}^{-1} \text{ d}^{-1}.$$

Suppose potential denitrification is given by the overall chemical equation (J. Dolfing, pers. comm.)



then per mol C 4/5 mol NO₃-N is needed. Thus the average daily N decay rate equals

$$4/5 \times 0.0875 \times 0.19 / 365 / 12 = 3.0 \times 10^{-6} \text{ mol N g}^{-1} \text{ d}^{-1},$$

or

$$4/5 \times 0.0875 \times 0.19 / 365 / 12 \times 14 = 4.3 \times 10^{-5} \text{ g N g}^{-1} \text{ d}^{-1}.$$

This is 43 mg N kg⁻¹ d⁻¹. From a layer of 0-20 cm with an average dry bulk density of 485 kg m⁻³ (Velthof, 1997) this amounts

$$43 \times 485 \times 0.2 \times 10 = 41236 \text{ kg N ha}^{-1} \text{ d}^{-1}.$$

This is very similar to the values measured by Velthof (1997) on two locations: 41340 kg N ha⁻¹ d⁻¹ and 33300 kg N ha⁻¹ d⁻¹.

