Modelação integrada do ciclo Carbono/Azoto no solo

Integrated Nitrogen / carbon cycle modeling in variable saturated soils

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ABSTRACT

Nitrogen contamination of ground and surface waters is a major environmental problem that is recognized in the nitrate directive of the European Union. The use of nitrate fertilizers should be surrounded by precise management practices. However the number of variables that affect nitrate transformations in agricultural or natural soils makes management choices hard to make. The use of computational models can increase the ability to make such choices. This article summarizes the implementation of a soil nitrogen / carbon cycle model, coupled to MOHID system (Chambel-Leitão *et al.*, 2003).

RESUMO

A contaminação com nitratos de águas subterrâneas e superficiais é um problema ambiental reconhecido na directiva dos Nitratos da União Europeia. Como tal o uso de fertilizantes azotados na agricultura deve ser alvo de praticas de gestão criteriosas. No entanto este tipo de gestão não é simples dado a complexidade dos processos que afectam o ciclo azoto no solo pelo que o uso de modelos computacionais pode aumentar essa capacidade de gestão. Este artigo descreve a implementação de um modelo do ciclo integrado carbono / azoto no sistema MOHID que calcula a hidrodinâmica tridimensional para solos não saturados (Chambel-Leitão *et al.*, 2003).

INTRODUCTION

Existing models such as (**EPIC**, Williams et al. 1989; **GLEAMS**, Knisel (1993); **NLEAP**, Shaffer et al. (1991); **NTRM**, Shaffer and Larson (1987); **LEACHM-N**, Wagemet and Hutson (1989); CENTURY, Metherell et al. (1993); and **RZWQM**, USDA (ARS (1992))) use first or zero order kinetics to model the interaction between chemical species. These rates can depend on the concentrations of microbiological populations that perform the transformation or use a simpler approach with constant coefficients. In MOHID, microbial biomass was programmed explicitly, so that specific rates are sensible to physical changes of the soil, such as variation of water contents, temperature, etc.

Another difference between these models is the way soil residue’s carbon and nitrogen pools should be divided and interacts among them. Almost all of the cited models divide soil organic matter into active, slow and passive fractions. However, the way organic matter passes from one compartment to another is different. MOHID was programmed so that these interactions are as generic as possible. Some of the features of this model are:

- Only two soil residues organic matter pools are modelled: a labile and a refractory pool.
- The Carbon / Nitrogen (CN) ratio of both pools is allowed to vary freely during the simulations.
- Introduction of more residues pools into the model is simple

A three-dimensional model for soil water quality like MOHID can face several difficulties, such as large spatial gradients, interactions with soil chemistry and biology. A soil water quality routine must be as flexible as possible in order to respond to all of these interactions. Having this in mind, a particular type of specific rates calculation, Laidler (1969), Shaffer and Dutt (1974); Shaffer (1985), present in Shaffer et. all (1998) was implemented in MOHID.

METHODS

This model uses transitional state rate equations, Laidler (1969), Shaffer and Dutt (1974); Shaffer (1985), present in Shaffer et. all (1998). These equations include Arrhenius temperature response functions, reactive constituent concentrations, and simulate responses to soil oxygen levels, pH, water content and salinity.

Element properties are modeled by first order kinetics following the RZWQM specific rates. For example for Nitrification:

$$K_{nitrification} = f_{aer}\left(\frac{k_b T_{nitrification}}{h_p} A_{nitrification}\right)\exp\left(-\frac{E_a}{R_g T_{nitrification}}\right)\frac{[O_2]^{0.5}}{[\gamma_1 H]^{k_H}} Pop_{Autotrophs}$$

Where $K_{nitrification}$ is the first order nitrification rate $\left[day^{-1}\right]$ and:

f_{aer} - Empirical adimensional parameter

$T_{nitrification}$ - Nitrification temperature $[{}^{\circ}K]$

K_b - Boltzman constant 1.383E-23 $\left[J\ {}^{\circ}K^{-1}\right]$

h_p - Planck constant 6.63E-34 $[J\ s]$

γ - Activity coefficient for monovalent ion

$A_{nitrification}$ -Nitrification rate coefficient $\left[s\ day^{-1} pop^{-1}\right]$

E_a - Activation energy $\left[kcal\ mole^{-1}\right]$

R_g - Universal gas constant 1.99E-3 $\left[kcal\ mole^{-1}\ {}^{\circ}K^{-1}\right]$

k_H - Hydrogen ion exponent for nitrification

$[H]$ - Hydrogen ion concentration $\left[molesH\ m^{3}_{water}\right]$

$[O_2]$ - Oxygen concentration in soil water assuming that soil air O_2 not limited $\left[molesO_2\ m^{-3}_{water}\right]$

$Pop_{autotrophs}$ - Population of autotrophic microbes $\left[\#organisms\ kg\ soil^{-1}\right]$

Anaerobic effects are expressed by f_{aer} that varies from 1 to 0 according to the effective soil water content θ_{ef}. $[O_2]$ is the maximum available dissolved oxygen (in saturation conditions). The rate is affected by Oxygen limitations.

The activation energy, E_a, is the sum of a constant apparent activation energy with the ionic strength times a salinity coefficient. The salinity coefficient and the apparent activation energy are pool specific. This formulation produces an exponential variation with the ionic strength, but will not be implemented in this initial model due to lack of available data. Instead, a medium value for the apparent activation energy is used.

Microbial populations enter explicitly in the specific rate (in the case of nitrification the autotrophic population is present).

The nitrification temperature is equal to the soil temperature when it does not exceed a certain maximum temperature of nitrification. If the soils temperature exceeds this value, the nitrification temperature will follow:

$$T_{nitrification} = 2T_{\max} - soil\ temperature$$

Some environmental effects like anaerobiosis, pH, etc are considered in both the microbial growth and decay. For instance lack of oxygen (expressed by f_{aer}) can stop aerobic organic matter decay or Ammonia nitrification, but at the same time it will also increase the mortality rate of all aerobic pools. This accounts for both the effects of anaerobiosis. On one hand, it stops aerobic decay processes (organic matter decay, nitrification). On the other, microbial populations begin do die off due to anaerobic factors.

For a given property, the variation caused by the biochemical cycle will be the sum of all the variations of related properties. For example, Nitrate is produced by Nitrification, and depleted by immobilization, denitrification, etc

Carbon pools

In a general manner all the existing models for nutrient cycling in soil, use different conceptual models for soil organic matter pools. Almost all of them divide soil organic matter into active, slow and passive fractions. However, the way organic matter passes from one compartment to another is modeled in completely different ways.

At this point, simplified compartments of SOM[1] were used. Two compartments, one of labile and one of refractory Organic matter, were conceived. Both have independent Carbon / Nitrogen ratios. When the microbial biomass dies, it's Carbon and Nitrogen will go to the labile pool. For now, no source terms exists for the refractory pool.

Other carbon pools are:

- Heterotrophic Carbon

[1] Soil Organic matter

- Autotrophic Carbon
- Anaerobic Carbon

The Heterotrophic group includes three different types of organisms: soil fungi, aerobic bacteria, and the aerobic part of the facultative aerobic bacteria. The anaerobic part of this last group is referred as Anaerobic Carbon.

Heterotrophic Carbon accounts for aerobic bacteria, fungi, and the aerobic part of the facultative aerobic bacteria. If anaerobic conditions arise, Heterotrophic Carbon will be diminished while Anaerobic Carbon grows. No explicit simulation is made for facultative aerobic bacteria changing from aerobic processes to anaerobic ones. This would further diminish Heterotrophic Carbon and increase the anaerobic Carbon when transitions occur from dry to wet soil.

Autotrophic Carbon represents the Nitrifying bacteria *Nitrobacter*. *Nitrossomas* action and thus the production of nitrites aren't modeled explicitly.

Nitrogen pools

The simulated Nitrogen pools are:

- Ammonia
- Nitrate
- N gas
- Heterotrophic N
- Autotrophic N
- Anaerobic N
- Refractory N
- Labile N

Soil microbes like other organisms, require a balance of nutrients from which to build their cells and extract energy (Brady et al. 2000). The majority of soil organisms metabolize carbonaceous materials both in order to obtain carbon for building essential organic compounds and to obtain energy for life processes. However, they must also obtain sufficient Nitrogen to synthesize nitrogen containing cellular components, such as amino acids, enzymes and DNA. As so unless storage occurs, carbon and nitrogen uptake rates are intimately related.

For simulation purposes a CN average of 8 (Brady et *al.* 2002) is used for all microbial pools

Autotrophic processes

Autotrophic processes are only limited by the available amount of NH_4^+. The nitrification rate is modeled by first order kinetics following the RZWQM specific rates formulation.

When the autotrophic organisms promote this transformation, they retain part of the denitrified Nitrogen to build their own cell components. This will lead to and increase of the autotrophic Nitrogen mass.

In order to maintain their Carbon / Nitrogen balance, the autotrophic biomass must uptake eight times the value of nitrogen in Carbon. Since Autotrophs use CO_2 as a Carbon source, Nitrification depletes the soils atmosphere of this gas. At the current stage of development, soil CO_2 won't be considered limiting.

Heterotrophic processes

Heterotrophic biomass is considered the start engine of the whole Nitrogen cycle, since they turn the nitrogen contained in the organic residues into their own biomass and later into ammonia.

This process can be limited by the availability of either Nitrogen or Carbon. If no mineral Nitrogen immobilization occurs, the microbial growth is only limited by the amount of available carbon. On the other hand, if mineral N is immobilized, the difference between the Organic Matter and Nitrogen immobilization rates will decide the limiting factor.

The potential (if no N limitation occurs) Organic matter decay rate is modeled according to:

$$K_{Denitrification}\left[NO_3^-\right] \quad \left[\mu g/day/m^3_{water}\right]$$

Where:

$$K_{Denitrification} = f_{anaer}\left(\frac{k_b T_{Denitrification}}{h_p} A_{Denitrification}\right)\exp\left(-\frac{E_a}{R_g T_{Denitrification}}\right)\frac{[O_2]}{[\gamma_1 H]^{k_H}} Pop_{Anaerobic}$$

Only two organic matter pools were modeled, a labile one and a refractory one. The previous equations are for the labile pool, but are also applied to the refractory pool except in this case, different coefficients are used.

The ammonia specific immobilization rate is greater that the Nitrate one, since Nitrogen is more easily segregated from the Hydrogen molecule than from oxygen. The comparison of the potential carbon uptake rate and mineral nitrogen-fixing rate defines the limiting factor.

If carbon uptake is smaller that nitrogen fixing, the organic matter potential decay is the limiting factor and will control the mineral Nitrogen immobilization rate as well as the Heterotrophic population growth.

On the other hand, if the opposite occurs, the nitrogen immobilization rates will control the organic matter decay and consequent microbial growth.

Not all of the decayed biomass will be used for Heterotrophic growth. Most of it will be lost as CO_2 according to predefined carbon efficiency.

The same is assumed for Heterotrophic Nitrogen.

In nature, the process of nitrogen mineralization involves the entire food web, and not just the saprophytic bacteria and fungi that are represented in the model as heterotrophic biomass.

Certain nematode, protozoa and earthworms feed on the saprophytic biomass. As these animals feed, they respire most of the carbon in the microbial cells, using only a small fraction to grow on (or produce eggs). Since the C/N ratio of these animals is not too different from that of their microbial food, and most of the carbon is converted to CO_2, the predators must excrete most of the ingested nitrogen as ammonia. According to Brady et al 2002 this bacterial feeding activity of soil animals may increase the rate of nitrogen mineralization by 100%.

Even thought the importance of predation in nitrogen mineralization is undeniable, a simple approximation is acceptable, since the accumulation of cycle elements by the predatory biomass is negligible. As so at this point, the assumed the breathing efficiency and ammonia excretion, simulate both the Heterotrophs efficiency and the predatory effects. This means that the predatory effects are modeled with first order kinetics without explicit predatory biomass and as so without variations of the predatory specific rate. This should be a point to consider in future work.

Anaerobic processes

During the denitrification processes the anaerobic biomass will retain part of the Nitrogen and release the remaining in gaseous forms of Nitrogen (N_2, N_2O) according to a predefined Nitrogen efficiency. At this point no distinguish is mate between any of the gaseous forms of Nitrogen. Instead a unique property (N_{gas}) is assumed.

Since Nitrate is used as an alternative oxidant for the Organic matter, the decay of Labile and refractory carbon are evaluated from the denitrification rate. Shaffer et al. 1995 proposes a factor of 0.1 to perform this conversion.

If Nitrate supplies are low, hydrogen can be used as an alternative oxidant, giving off carbon in respiration in the form of methane. At this point, this still is not implemented.

The Anaerobic Carbon efficiency was considered equal to the Aerobic one.

It was also assumed that the Anaerobic and anaerobic decay rates are proportional in each pool.

Organic nitrogen uptakes are modeled by the respective pool (labile or refractory) decay rate times the inverse of the respective Carbon / Nitrogen ratio.

A Nitrogen balance is obtained between the obtained Nitrogen and Carbon. Using the nitrogen efficiency proposed by Shaffer et al. 1995, unless organic matter pools have CN ratios as high as 200, no Anaerobic Nitrogen immobilization is required. No data was found in the literature that verified or rejected this theory. As so, in this model, anaerobic pathways are intrinsically mineralizing.

RESULTS

Zero dimensional test runs

A good example of this model versatility is demonstrated with a simple immobilization test. Initial Carbon and Nitrogen pools were established for values similar to those presented by Cameira, 1998, except for the Organic Nitrogen values:

TABLE 1 - **Carbon and Nitrogen Pools initialization**

Nitrogen Pools		**Carbon Pools**	
Ammonia	$7\left[g\ kg_{soil}^{-1}\right]$	Heterotrophic Carbon	$105.26\left[\mu g\ g_{soil}^{-1}\right]$
Nitrogen	$0\left[g\ kg_{soil}^{-1}\right]$	Autotrophic Carbon	$0.11\left[\mu g\ g_{soil}^{-1}\right]$
Heterotrophic Nitrogen	$18.78\left[\mu g\ g_{soil}^{-1}\right]$	Anaerobic Carbon	$1.05\left[\mu g\ g_{soil}^{-1}\right]$
Autotrophic Nitrogen	$0.138\left[\mu g\ g_{soil}^{-1}\right]$	Labile Carbon	$581.12\left[\mu g\ g_{soil}^{-1}\right]$
Anaerobic Nitrogen	$0.131\left[\mu g\ g_{soil}^{-1}\right]$	Refractory Carbon	$23244.78\left[\mu g\ g_{soil}^{-1}\right]$
Labile Nitrogen	$581.12\left[\mu g\ g_{soil}^{-1}\right]$		
Refractory Nitrogen	$2905.6\left[\mu g\ g_{soil}^{-1}\right]$		

This system is placed under heavy Nitrogen stress. The Carbon / Nitrogen ratio of the residues is different from that of the soil fauna (CN of labile OM is as high as 100).

At this first simulation, the soils water levels were considered constant at an aerobic level.

The variation of the different Nitrogen pools are represented in Figure 1- Year long Nitrogen variations

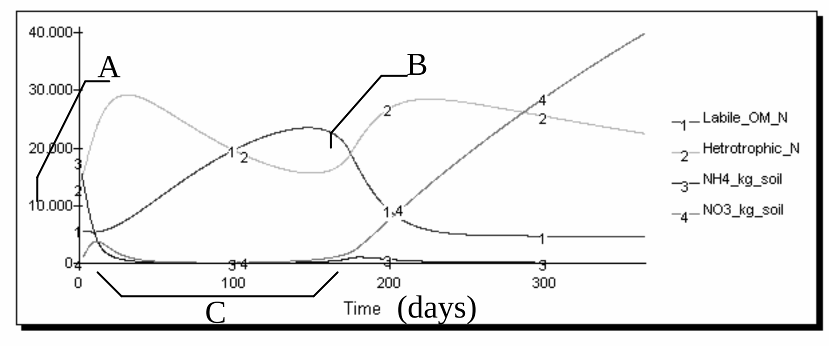
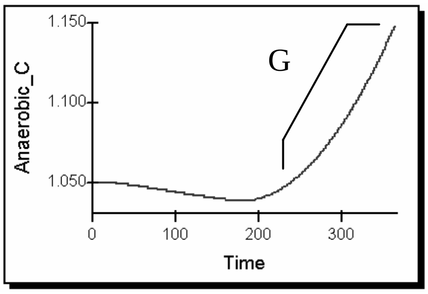


Figure 1- Year long Nitrogen variations

There are clearly two different growth phases for the Heterotrophic biomass. For the first one (A), Heterotrophic Nitrogen (2) is growing, but so is the labile Organic Matter Nitrogen content (1). On the other hand, all the mineral Nitrogen forms (3, 4) disappear from the system, due to Heterotrophic incorporation.



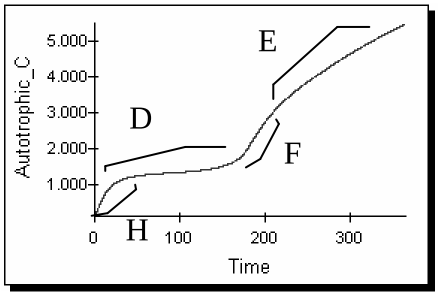


Figure 2 – Anaerobic growth curve

Figure 3 - Autotrophic growth curve

This yields a Nitrogen depression period during which mineral Nitrogen will not be available for soil flora. All the NH_4^+ produced during this period is quickly immobilized by Heterotrophic action. Very little ammonia is available for Nitrification, limiting Autotrophic growth **Figure 3** (D).

It is interesting to note that some competition, between Heterotrophs and Autotrophs for the available Ammonia, occurs in the initial period resulting in some Autotrophic growth **Figure 3** – *(H)*. However, Heterotrophic biomass soon retains most of the Ammonia. Some Nitrate production occurs at residual rate, but Heterotrophic Immobilization quickly drains the soil of this Nitrogen form. In **Figure 1**, Labile Nitrogen is increasing due to biomass death. Microorganism's biomass returns more Carbon than Nitrogen when death occurs. Organic labile Nitrogen is depleted at a reason of 1 part of Nitrogen for each 100 parts of Carbon and is supplied with a reason of 1 part for each eight parts of Carbon, leading to a reduction of labile CN **Figure 4**. In a global perspective, Nitrogen is conserved (denitrification rates are negligible), while Carbon is lost by respiration. Some carbon input exists due to the Autotrophic processes, but this incorporations is much less than Heterotrophic respiration (Heterotrophic populations are 100 times the Anaerobic ones).

The death phase that follows the initial growth period **Figure 1** - (A) is due to Nitrogen limitation. There's not enough mineral Nitrogen to supply the existing Heterotrophic population. However, labile Organic matter CN is getting close to a point where Mineral Nitrogen immobilization won't be limiting. At this point (labile CN near 20) the Heterotrophic Ammonia excretion rate will surpass the Immobilization rate. Immobilization is still needed, but Ammonia levels will grow.

This leads to a situation where Ammonia Immobilization increases its own rate. The more Heterotrophs immobilize, the faster they grow, more ammonia is produced and more they can immobilize which in turn leads to higher Heterotrophic growth rates. The initial period of curve **Figure 1** - (B) correspond to this situation. Autotrophic growth also responds to these ammonia increases **Figure 3** - (F).

Soon the carbon uptake rate will be the limiting factor and the second growth period **Figure 1** - (B) takes place. At this stage more ammonia is produced than immobilized, so Autotrophs can nitrify **Figure 3**- (E). This leads to increasing concentrations of Nitrate, and soon some minimum anaerobic denitrifying activity will take place **Figure 2** - (G).

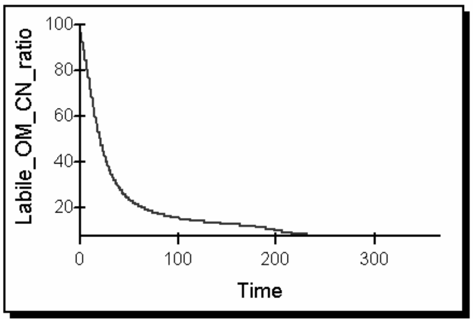
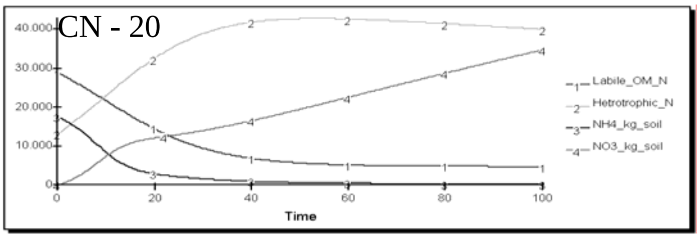


Figure 4- Labile OM CN ratio variations

Repeating the same simulation with and initial labile CN of 20, no Nitrate depression period occurs. Only one Heterotrophic growth curve is present **Figure 5**.

For intermediate CN ratios, both Heterotrophic maximums grow apart and the Nitrate depression period increases (Figure 5).



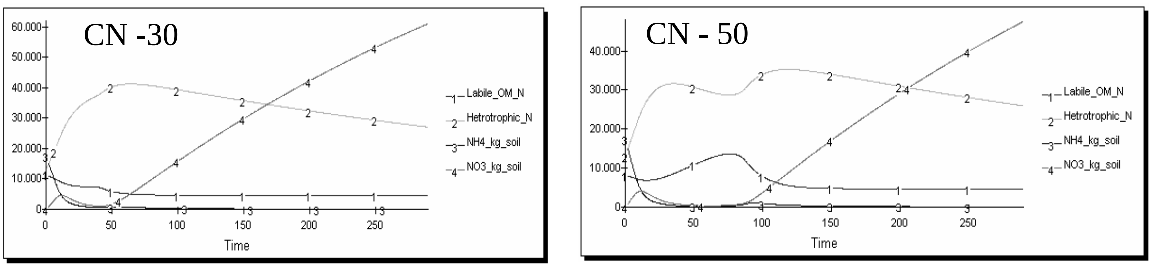


Figure 5- Cycle variations with Labile CN

If Nitrogen stress is greater than a maximum value only one maximum may be present. Refractory Nitrogen also affects the Heterotrophic growth curves distribution, but with less intensity.

Three dimensional test runs

When this complex structure was implemented into MOHID, it was possible to use the previously implemented soil water flow and mass transport routines. For an initial test Nitrogen dynamics was applied to the same soil column described in Chambel Leitão et *al.* (2003). The different Carbon and Nitrogen pools were initialized in a uniform manner according to the values presented in by Cameira (1998), except for the CN ratio of the labile organic matter pool, were a CN ratio of 100 was used.

In order to evaluate the full dimensional capabilities of MOHID, a sloped terrain was used. The next figure shows a cross section and three- dimensional view of the domain.

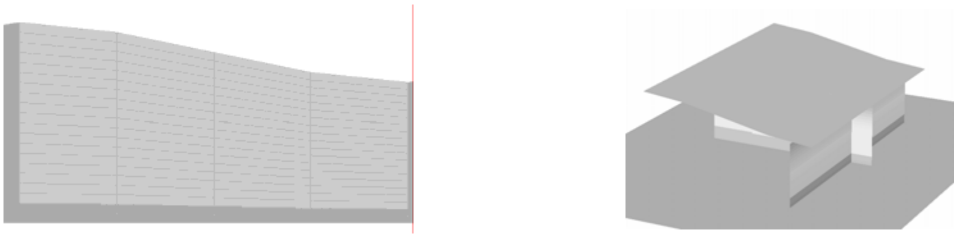


Figure 6 – Sigma vertical descretization and three dimensional view of the domain

Mass Nitrate horizontal fluxes that pass trough a vertical cut perpendicular to the initial picture, were integrated over time do evaluate the importance of horizontal transport.

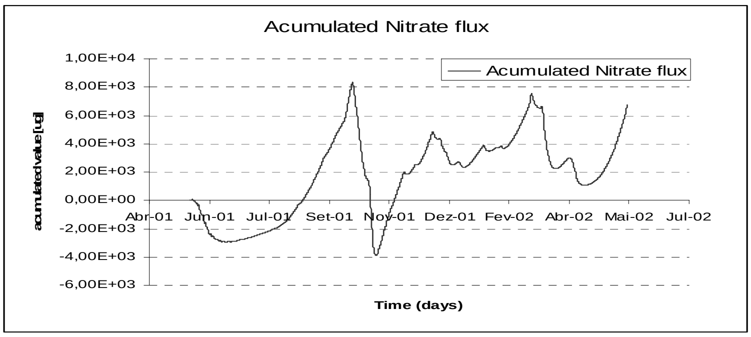


Figure 7 - Horizontal mass fluxes

Negative mass values means that the flux has occurred “down- hill”, while positive values count for ascending mass fluxes. However when compared to the nitrate mass contained in each of the half domains through which these mass fluxes were accounted (around $1E9\mu g$), these effluxes can be considered small.

Leached nitrogen concentrations have values 100 times grater than the horizontal fluxes.

The previous exercises were repeated whit higher CN ratios for the labile Organic matter pool and with a partially covered surface.

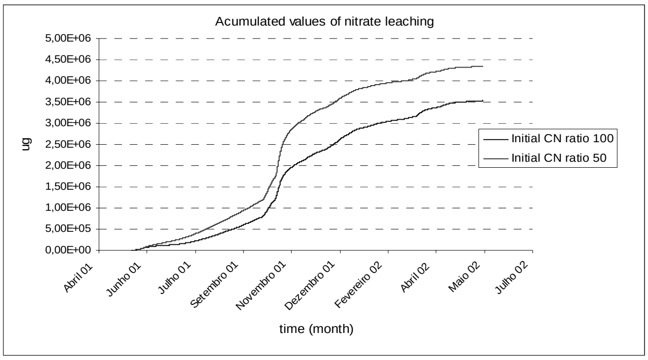


Figure 8 – Accumulated leached values with diferrent initial CN ration

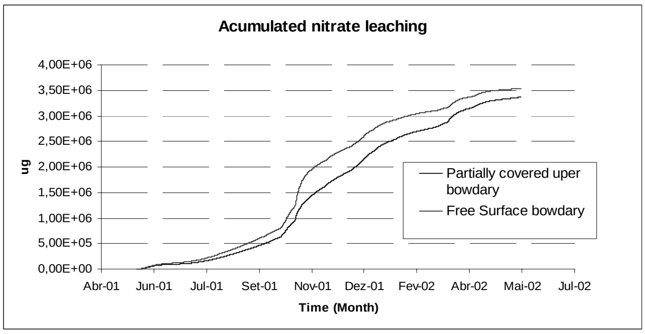


Figure 9 – Acumulated leached values for diferrent

An increase of 18% of leached nitrate occurs for a nitrogen input increases of 100%. The leached values are close to those presented by Cameira (1998), where 30 kg of $NO_3^- - N$ per ha are predicted to leach.

For an irrigated surface decrease of nearly 50%, only a difference of 5% less nitrogen was leached. However spatial distribution of the nitrate levels are somewhat different, when the surface is partially covered due to the different water regimes that affect microbial populations according to their relative positions in the described monolith.

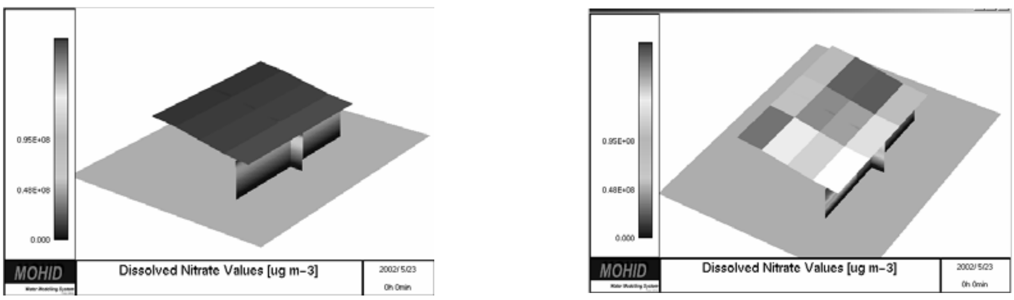


Figure 10 - Comparison of Nitrate levels at the end of the run.

The left hand side of **Figure 10** corresponds to the situation where the whole surface was watered. The image on the right is the situation of partially covered terrain. The cells where the water was added are the ones with the lower concentration (darker colors).

CONCLUSIONS

Water flow and solute transport in unsaturated soil poses an interesting challenge for computational methods. Unlike water flow in streams or oceans, horizontal mixing is very limited, leading to large horizontal heterogeneity and consequent gradients.

In addition, a complex biological structure interacts with soil water and available nutrients creating spatial gradients that horizontal fluxes are not enough to eliminate.

This work attempted to demonstrate that simple terrain variations are enough to invalidate, vertical profiles draw in a single point thus rendering difficult GIS integration of one-dimensional models for micro scale applications (one or less ha).

When developing this model, attention was paid on reducing to the maximum the needs for data entrances. Future implementations should include a similar mechanism to RZWQM, which allows the user to run the model from a standard initial conditions simulating several years of selected cultural practices, which means that the model can initialize it self.

Nutrient and environmental conditions have proven to cause temporal variability in Nitrogen dynamics affecting the microbial populations, thus the choice for a more complicated nutrient cycle that explicitly simulates microbial interactions was successful. The control of nitrogen depression periods in different parts of the terrain is the key to good nitrate management and environmental gains. Another interesting conclusion is that in soil, Nitrogen is the problem that one must follow, but when this problem appears when carbon is the limiting nutrient, thus nitrogen modeling in soil must include parallel carbon cycle modeling.

Field data validation for such a tool is the challenge that must be faced next. At this point, the models runs for realistic values responding accordingly to expected, (leached values of Nitrate are in the same order as those presented in Cameira, 1998) but the ultimate test for any model has to be field data validation.

Implemented soil carbon pools are very simple when compared to other models. This leads to a very flexible model with no restrains on the way residues CN ratios vary, however this may not be a realistic simulation. Predatory food-web sensibility analysis should also be performed.

Zymogenous and Autochthonous biomass pool divisions would also make a good addition to the model, allowing long periods of carbon depression to be modeled without having to explicitly stop death rates.

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