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Carbon, Nitrogen and Phosphorus Soil Cycle Modelling

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Dissertação para Obtenção do Grau de Mestre em

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“Põe quanto és no mínimo que fazes”

Ricardo Reis

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Resumo

O solo fornece suporte físico, água e nutrientes minerais às plantas recebendo destas matéria orgânica na forma de raízes mortas e de detritos. A actividade de produtores secundários que vivem no solo ou os fertilizantes, colocados à superfície ou enterrados, podem ser outras fontes de matéria orgânica. A mineralização realizada por microrganismos regenera nutrientes minerais, que podem ser consumidos pelas plantas fechando o ciclo dos nutrientes, ou lixiviados pelo escoamento da água no solo, tornando-se uma fonte de contaminação dos aquíferos e/ou das águas superficiais. A actividade dos microrganismos no solo resulta num conjunto complexo de processos que dependem da temperatura, da humidade do solo e das proporções dos vários nutrientes.

O objectivo desta dissertação é analisar e modelar os principais processos microbiológicos associados à mineralização da matéria orgânica no solo, nitrificação, desnitrificação, solubilização e fixação do fósforo, descrevendo os ciclos dos seus principais elementos: carbono, azoto e fósforo.

O trabalho dá continuidade ao modelo desenvolvido por Galvão (2002), tendo-lhe sido adicionado o ciclo do fósforo e ainda equações de evolução da temperatura, pH e porosidade do solo.

O modelo foi desenvolvido primeiro em PowerSim, para verificação da consistência da formulação adoptada e posteriormente em FORTRAN 95. Os resultados foram validados por comparação com resultados do modelo RZWQM também implementado no âmbito desta dissertação e por comparação com 2 anos dados (2004-2006) de teor de água, nitrato e amónio obtidos num campo experimental de milho, na zona de Alvalade-Sado no âmbito do projecto AGRO 727 pela Estação Agronómica Nacional.

Palavras-Chave: Solo, Mineralização, Matéria Orgânica, Modelação, Nutrientes

Abstract

Soil is the physical support for plants and the nutrients and the water storage. It receives organic matter primarily from dead roots and wastes, but also from secondary producers activity or fertilizers, added at the surface or buried. The mineralization process by the microorganisms turns available mineral nutrients that may be uptake by the plants, closing the nutrients cycle, or become a source of pollution for aquifers and water lines when they are leached. The microorganisms activity in soil depends on several processes which are affected by temperature, water content and different nutrients proportions.

The aim of this dissertation is to analyze and to model the main microbiological processes related to organic matter mineralization, nitrification, denitrification, and phosphorus solubilization and fixation. The processes will be described according to the cycles of the main elements: carbon, nitrogen and phosphorus.

This work represents the continuation of the developed model by Galvão (2002), with the inclusion of the phosphorus cycle and the ability to respond to temperature, pH and soil porosity variations.

The model was developed in a first step in Powersim, in order to verify the adopted formulation consistency, and after that in Fortran 95. The results validation was made by comparing the model with a version of the RZWQM model. A comparison between the RZWQM and two years (2004-2006) of water content, nitrate and ammonium data was also done. This data was obtained by the Estação Agronómica, from an experimental corn field in Alvalade-Sado in the project Agro 727.

Keywords: Soil, Mineralization, Organic Matter, Modelling, Nutrients

1^{st} Chapter – Introduction

Soil is a complex and important habitat with a lot of meaning for many ecosystems. It's fundamental for plant productivity and it supports the biogeochemical cycles (Naninipieri *et al,* 2003).

In fact, populations living in the soil include macro, micro and mesofauna as well as microflora, which is very diverse. Soil assumes an important role as a mechanical support for plants and a source of nutrients for their uptake.

The microfauna play a crucial role in soil because they exist in most quantity, given that that 80-90% of the reactions which occur in soil are mediated by microbes (Naninipieri *et al*, 2003). This group is very diverse, since 6000 different types of microbes can be found per gram of soil (taking the genome size of Escherichia coli as a unit).

The main process that occurs in the soil is the organic matter decomposition. The heterotrophic population needs organic carbon to grow. As a result of the decomposition, some CO_2 and mineral nutrients, such as the NH_4^+ or soluble phosphorus are released. In fact, heterotrophic will need also some nitrogen, phosphorus and other micronutrients to grow. The proportion of their needs is given by the carbon/nitrogen (CN) and carbon/phosphorus (CP) ratio. So, if there is not enough nitrogen or phosphorus in the substrate they are decomposing, they will immobilize it from the mineral available forms (Quelhas dos Santos, 2001).

Nevertheless, other types of populations play important roles in the soil processes as the autotrophic population which can uptake the carbon that they need from the CO_2 available. These *Chemoautotroph bacteria* (which take energy from chemical reactions) like *Nitrobacter* and *Nitrossomonas* can make the nitrification process where NH_4^+ is transferred into NO_3^- (Metcalf & Eddy, 1978). This happens in aerobic conditions and has a lot of meaning in agriculture, once NO_3^- is easily leached because of its negative charge. This means that if there is a significant population of nitrifying bacteria in soil, fertilizers may be easily spent with no results to plant growth. In some way this NO_3^- leached can reach the lakes and water lines and contribute for the Eutrophication phenomenon, because nitrogen is usually a limitant factor for primary producers growth.

Primary producers need light and nutrients to grow and in aquatic ecosystems, nitrogen and phosphorous are usually the limitative ones. In fact, phosphorus is available from the rocks erosion, not having an atmosphere cycle as carbon or nitrogen. Nitrogen, although available in small quantities too, can be fixed from atmosphere by specific organisms. Ponds and lakes receiving sewage and runoff from fields, fertilized lawns, or other high phosphate/nitrogen sources commonly produce heavy blooms of algae, especially blue-green in the summer. In time this will cause oxygen depletion, killing the consummers in that system (Brewer, 1994).

Ammonia volatilization can be an important process in soil, since the loss of ammonia to the atmosphere can be significant if conditions are favorable. Handling, storage and spreading of manure are the main pathways for this process. Ammonia losses during decomposition may be reduced by: ammonium immobilization, ammonium adsorption and pH control (Kirchmann, 1989).

Other important population is the anaerobic one. This bacteria population can be facultative or strict, i.e, they can operate just in oxygen absence having the ability to change the electron accepter. This is important, because there are places in soil in which the oxygen concentration is low. In these places, these populations can grow up consuming nitrate, using it for respiration process, and stealing it from plants. It's important to note that nitrogen is not being consumed as a substrate, but as a source of energy which is different (Naninipieri *et al,* 2003).

Plants exert a strong influence on composition of microbial communities in soil through rhizodeposition and the decay of litter and roots. The link between plant species and microbial communities in the rhizosphere soil is strict, being the result of co-evolution (Naninipieri *et al*, 2003).

Phosphorus is less available than nitrogen but essential for plant growth. This unavailability happens because phosphorus in the soluble form, which is uptaken by the plants, is usually fixed or adsorbed in soil. However, some microbiological populations can solubilize the fixed phosphorus, turning it available for plants. These bacteria can be seen as a bio-fertilizer, as the plant themselves develop some mechanisms to invite these bacteria to grow near their roots (Horst *et al*, 2001).

As said in the beginning, heterotrophic population needs a carbon source and some nutrients as well. The most important are nitrogen and phosphorus (Stevenson et Cole, 1999). Figure 1 summarizes the cycles of the soil, showing the bacteria role in the organic matter decomposition, nitrification, denitrification and phosphorus solubilization. However, other processes are important to the nutrients concentration is soil such as the nitrogen fixation by some organisms, the rains contribution, the leaching, and the erosion. These external processes are important as well to understand and model correctly the distribution in space and time carbon nitrogen, and phosphorus pools (Stevenson et Cole, 1999). As the processes occurring are both biological and chemical, the abiotic factors, like temperature, moisture and pH will be very important.

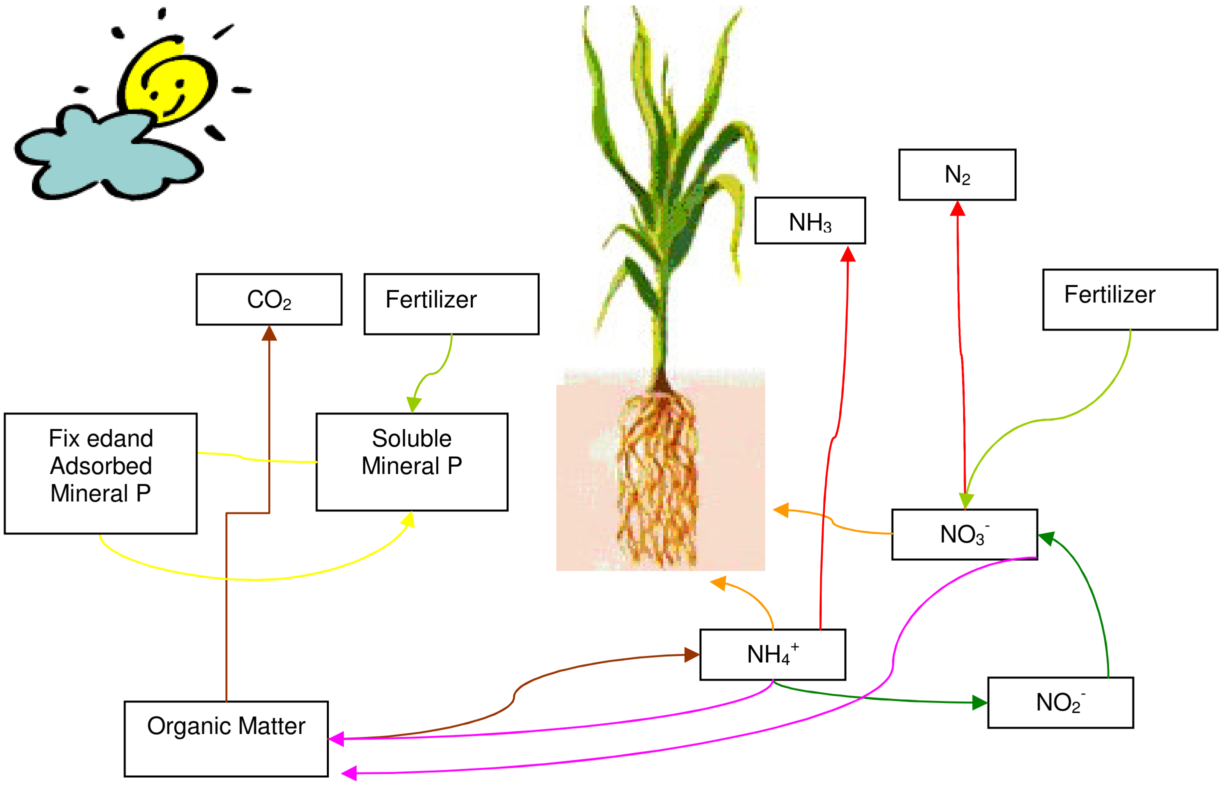

Figure 1 - Soil Processes adapted from Quelhas dos Santos (2001)

After a brief description about the soil importance, the role of the terrestrial and aquatic ecosystems, and the description of the main processes that occur in it, it can be observed that Agriculture will influences the soil processes and is influenced by them.

Agriculture is one of the greatest sources of diffuse pollution, because there is no integrated way ro provide equilibrium between sources and sinks of organic and mineral pools in soil. Too large amounts quantities of fertilizers are sometimes put on soil to improve the plant's growth, but great part of these fertilizers may be never used by plants.

This work was divided in three steps: i) Improvement of the carbon and nitrogen cycle models developed by Galvão (2002) in Mohid and PowerSim; ii) Transformation of the carbon and nitrogen cycles of RZWQM code in to a zero-D (0D) model for a direct comparison with the developed model in PowerSim; iii) Comparison between data of a field experiment (one dimensional) with model results using RZWQM that allows the transport on the vertical axis.

Future work will include the development of advection diffusion equations in Mohid-Land to allow the transport of the nitrogen and phosphorous species. This model already solves the flow in porous media (saturated and non-saturated) in the three dimensions. The development of the advection diffusion equations will allow this model to be calibrated against the data from the mentioned filed experiment. Once the mode is calibrated this it will allow the extrapolation of the results to the watershed.

In the 2nd chapter of the present work it will be done the state of the art of the most important processes that occur in the soil and also a brief view of the current and more important applied models in this area. Chapter 3rd includes the description of the implemented model – Sediment Quality, with the improvements and changes from the last model developed by Galvão (2002) and the first results for the phosphorus cycle. In the next chapter, 4 th, the new model developed will be compared with the RZWQM model, in order to have conclusions about its validation. Some simulations for different environments will also be done, such as temperature, pH, soil porosity and wind variations. In the 5th chapter, RZWQM model will be applied in a specific corn field, and it will be done not only an interpretation of the model results but also, the comparison between the model and the experiment data. The last chapter will summarize the main conclusions and some future work that might be done.

2nd Chapter – State of Art

2.1 - The Soil Processes

In the first chapter it was made a general description of the soil processes. The focus of the present work is the microbial processes that take place in the soil and their importance for the nutrients transformations.

Soil is a support for all the chemical and biological processes, having a solid, liquid and gas composition. In the solid fraction, mineral and organic materials may be found and, regarding the soil texture, the mineral particles can classify the soil texture, among others, in sand, silt or clay.

The composition of the bacteria communities species (obtained with the molecular approach) it's not necessary to determine the nutrient transformations. Instead, an holistic approach can be more efficient (Naninipieri *et al,* 2003) because the system is partitioned into pools with a functional meaning and flows between pools. Nutrients transformations can be obtained with labeled compounds such as ^{14}C, ^{13}C and ^{15}N-enriched and then the distribution of these isotopes between the various pools can be tracked.

Regarding these, it's important to study the system in a pool perspective, observing what happens with each one of the nutrients individually.

For a better and deep knowledge, it's necessary to understand the three cycles of the most important elements in the soil processes: carbon, nitrogen and phosphorus:

2.1.1 - Carbon Cycle

This cycle is a multicompartment system with terrestrial, aquatic and atmospheric components. The organic matter in soil has carbon as the main constituent. The heterotrophic population uptakes the carbon in the soil using part of it for their growth. As a consequence of their inefficiency in incorporating carbon, CO_2 is released to the atmosphere. When they die, the organic carbon of their structure will be joined to the carbon organic matter of the soil where it will also be decomposed.

At this point it's useful to separate the types of organic matter in soil. Usually, organic matter exists in a diverse mix of organic materials in various stages of decomposition (Rühlmann, 1999). They can be distinguished by their decomposition velocity: fast or slow, being active or stable organic matter respectively.

The active organic matter is less available than the stable one, which carries the most significant part of organic matter in soil. Nevertheless, the fast decay organic matter plays a more important and active role in soil dynamics, allowing the possibility of quick changes in nutrients.

Other important characteristic about organic matter is its composition in terms of nitrogen, phosphorus and other minor nutrients. As the heterotrophic population needs specific proportion of these elements to grow, if the organic matter doesn't have enough in its composition, they will have to immobilize the mineral forms. The decision about decomposition or immobilization of the organic matter in the soil will dependend on the CN and CP ratios. It's interesting to note also, the difference between decomposition and mineralization of organic matter; the first refers to the breakdown of fresh organic residues into simpler organic compounds and the second refers to the microbial conversion into mineral compounds (Neitsch *et al*, 2005).

Carbon cycle can be described as it is shown in the Figure 2, where organic carbon is decomposed, resulting in the growth of biomass and the release of CO_2. As it can be seen, organic compounds are first converted into simpler molecules - Monomers. These organic materials are afterwards decomposed and distributed into humic organic matter and biomass growth. From it, new mineralized nutrients are released and uptaken by plants. When biomass dies, their carbon becomes labile organic matter, available for decomposition.

The utilization of organic amendments and fertilizers is increasing with the development of organic farms. Such increase is due to a social need for healthy food produced under conditions to protect the environment and a constant legislative pressure for recycling organic wastes (Thuries *et al*, 2001).

The climate is also an important factor in this cycle because it leads to different plant growth, plant species and also different intensities of microbial activity in the soil and consequently determines the amount organic matter available. Organic carbon mineralization rate, usually measured from the amount of respired CO_2, is affected by external factors like the temperature or moisture as it will be seen in the following chapters (4.4 - Sediment Quality Simulations).

Organic matter can be mineralized in aerobic or anaerobic conditions. If oxygen is available, bacteria will grow and release CO_2, according to Equation 1:

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6H_2O$$

Equation 1 - Aerobic decomposition of organic matter

If O_2 is not available, some bacteria can use other compounds to act as electron acceptor, such as NO_3^- and, in that case, N_2 will be released to the atmosphere as well. If nitrate becomes depleted, then methanogenic bacteria may appear and use CO2 as electron acceptor, releasing CH_4.

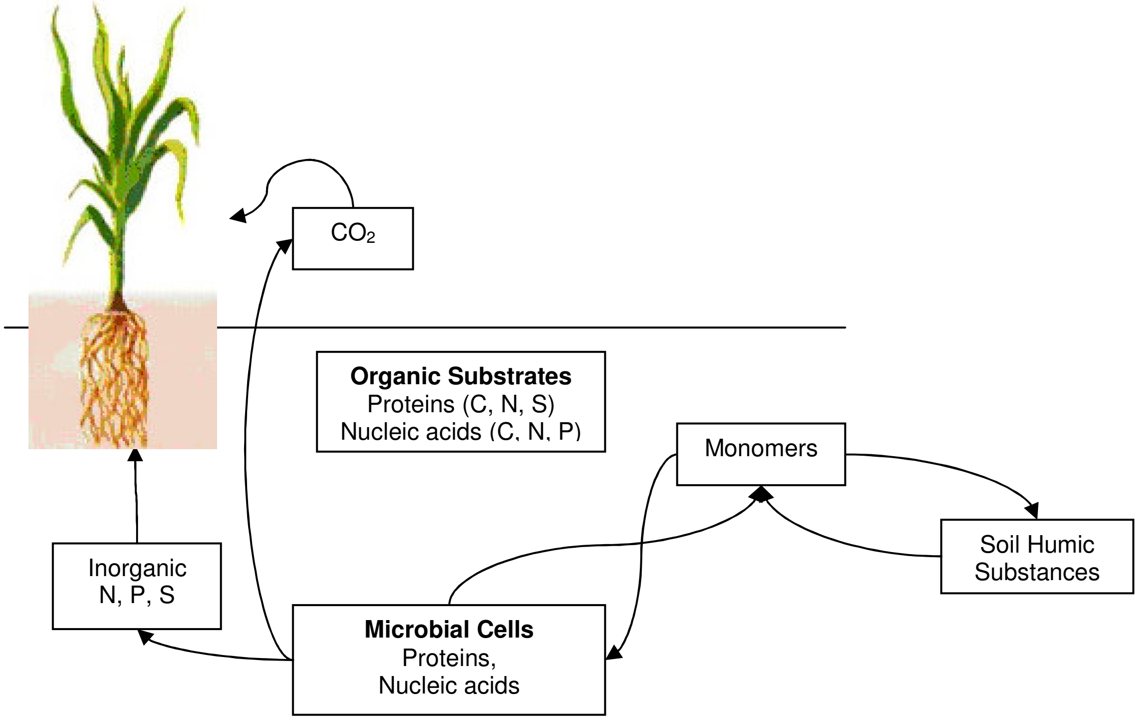

Figure 2 - Carbon cycle adapted from Quelhas dos Santos (2001)

2.1.2 - Nitrogen Cycle

Nitrogen supply and demand is essential to improve the efficiency of nitrogen used in agriculture systems due to both economic and environment concerns (Bremer et Kuikman, 1997).

The nitrogen cycle is more complex than the carbon one, because it may have other sources and sinks for the nitrogen pools. As shown in Figure 3, nitrogen can be added to the soil by fixation through specific bacteria, which are able to take N_2 from the atmosphere for their needs. Also in symbiosis with legume plants, Rhizobium bacteria can do the same. In other way, some nitrogen in NH_4^+, NO_3^- and NO_2^- forms can reach the soil brought through rain water. Once in soil, organic nitrogen is decomposed into inorganic forms that can be uptaken by the plants, or if CN ratio of the substrate is too high, bacteria will immobilize it. Immobilization process may have some influence in agriculture, which means that it's important to know the organic residues characteristics that are put in soil. This process may lead to an even more stress situation for plants, as bacteria are immobilizing the nutrients.

Usually roots increase microbial mineralization because they are a source of organic matter when the plants die. For example, Breland and Bakken, (1991) estimated that barely and ryegrass induced microbial immobilization of 33 to 58 mg N g^{-1} root C by 42 days after planting (Bremer et Kuikman, 1997). The rhizosphere provides optimal conditions to microbial growth (Sanchez *et al*, 2002), but some studies say that the roots also increase immobilization. This difference represents the complex dynamic between the soil and the plants, the nitrogen and carbon dynamics and the different experimental methods used. In the Corn example, this plant takes 70% of its nitrogen from the mineralization occurring in the soil (Sanchez *et al*, 2002).

According to Quelhas dos Santos (2001), the process of N mineralization comports two steps: Aminization in which organic N is used as subtract of microorganism and complex molecules are transformed into amines and amino acids; and in the next step, Amonification, these compounds are transformed into amoniacal salts, and then NH_4^+.

In other relevant process autotrophic bacteria, the nitrifying population, is able to transform NH_4^+ in NO_3^- , in aerobic conditions. They take CO_2 from the atmosphere and grow, using for nitrogen source the NH_4^+. This population is less available and exists in a low number, because they spend energy in fixing CO_2, but they have a survival possibility even if there is no organic carbon in the soil. Nitrification products are nitrite and nitrate that are easily drained out to groundwater, assimilated by plants and bacteria or converted to gaseous N-compounds by denitrification (Daum *et al*, 1998). The bulk of global nitrification is usually attributed to the oxidation of inorganic nitrogenous compounds by *chemolithotrophic* bacteria, but numerous heterotrophic bacteria and fungi have the ability as well, to oxidize a variety of nitrogenous compounds (Castignetti, 1984). Nitrification occurs in two steps: in the first step, NH_4^+ is transformed into NO_2^- by *Nitrossomonas* (Equation 2*)* and then, in the second step NO_2^- becomes NO_3^- by the *Nitrobacter* action (Equation 3) (Castignetti, 1984).

$$NH_4^+ + {}^3\!/_2 O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Equation 2 - Nitrification process: Nitrossomonas transformation

$$NO_2^- + {}^1\!/_2 O_2 \rightarrow NO_3^-$$

Equation 3 - Nitrification process: Nitrobacter transformation

This process is also important to agriculture management, once the plants can take both NH_4^+ and NO_3^- for their growth, but once NO_3^- is negatively charged (and soil particles are also mainly negative) is easily leached, becoming less available.

Denitrifying is another important process in the nitrogen cycle (Equation 4). As said before in the carbon cycle, organic matter can be decomposed in anaerobic conditions. That means that bacteria can use the nitrate available as electron acceptor using it as an energy source and not as a substrate.

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \uparrow \rightarrow N_2O \uparrow \rightarrow N_2 \uparrow$$

Equation 4 - Denitrification process

Denitrification has, as well, a lot of meaning in agriculture. In fact, if oxygen is missing, the fertilizer input is going to be consumed not by plants, but by microorganisms releasing some N_2 to the atmosphere. This happens particularly in rice cultures, where the high levels of water makes oxygen less available.

Urea may be applied to the soil as a fertilizer and becoming a source of ammonium. Nevertheless, ammonia volatilization will be a great sink to this pool, if the pH of the soil becomes basic or if other environmental factors as wind and temperature become favorable (Equation 5).

$$NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O$$

Equation 5 - Ammonia volatilization

Ammonium lost by volatilization may become a serious problem if the fertilizer applied to the soil is added to the surface in the ammonium form. Nevertheless, if the water content is higher, ammonia will return once again to the ammonium form (Equation 6), providing the soil with this nutrient (Quelhas dos Santos, 2001).

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

Equation 6 - Ammonia conversion to ammonium in water presence

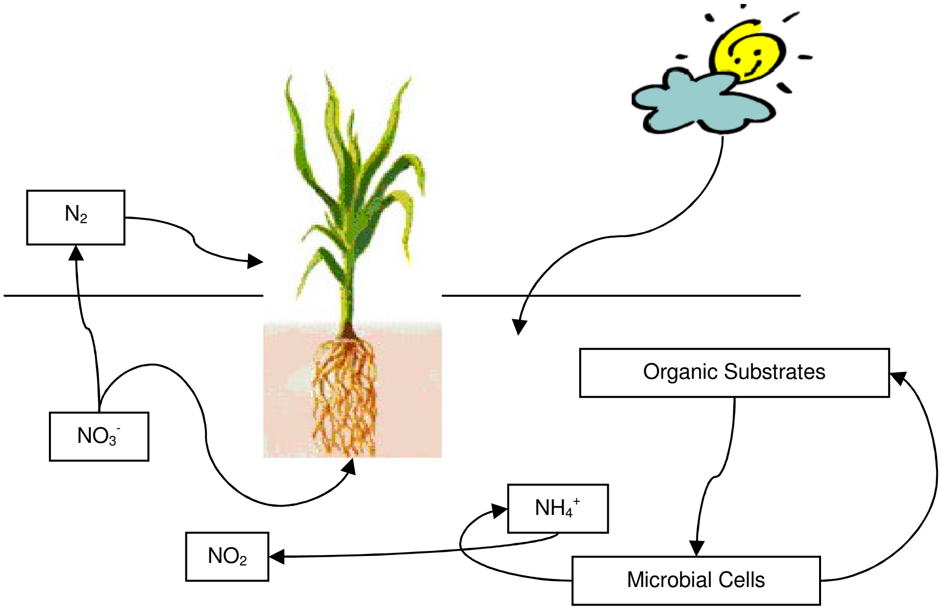

Figure 3 - Nitrogen cycle adapted from Quelhas dos Santos (2001)

2.1.3 - Phosphorus Cycle

Phosphorus is second only to nitrogen as a mineral nutrient required by both plants and microorganisms. Phosphorus in soils is immobilized or becomes less soluble either by absorption, chemical precipitation or both (Johri *et al*, 1999).

In fact, phosphorus can reach the soil by the organic residues decay or erosion. There is no phosphorus source through the rain or by microorganism fixation as in nitrogen cycle. The losses are different too: phosphorus leaves the soil by erosion and it's not easily leached like NO_3^-; although the organic forms can be mineralized and the mineral forms can be immobilized as it happeneds in the nitrogen cycle.

The basic difference between phosphorus cycle and the others mentioned before is that it doesn't have an atmospheric part and has some chemical processes more complex which play an important role in soil like phosphorus solubilization. In fact, plants are only able to uptake the phosphorus in the form of HPO_4^2- and H_2PO4^- and that's why the study of available phosphorus is so important for crops and agriculture. Some studies show that 85-88% of the phosphorus in soil is on the non reactive pool, which means that it is in the fixed or adsorbed form, consequently unavailable for soil transformations (Toor *et al*, 2003). Besides that, the relative immobility of the ion in the soil may cause the phosphate supply to be the limiting factor in plant growths (Johri *et al*, 1999). It's important to know which are the processes that contribute for this element availability in soil, observing the processes that contributes for the phosphorus solubilization, once plants and microorganisms just uptake soluble forms.

In the phosphorus cycle, there are organic forms which can represent 20-80% of the total phosphorus (Curtin *et al*, 2003). Mineralization may turn available some soluble forms, but these can be easily fixed in inorganic unavailable pools. That happens because in acid soils, phosphorus can precipitate in salts, combining with the aluminum and iron ions; in neutral or basic soils, the precipitate occurs with the calcium ions (Ponmurugan et Gopi, 2006). Some of this soluble phosphorus can also be adsorbed and become unavailable.

In other way, some microorganisms may solubilize those inorganic forms (Oberson *et al*, 2001). This is particularly important because if these bacteria can live in the soil, they will act as bio fertilizers, (Igual *et al*, and 2001), turning the phosphorus fertilizer usually fixed in inorganic forms more available. These bacteria, whose name is phosphorus solubilizing bacteria (PSB), can be identified and used for different soil types. At this point it can be understood how important are the soil conditions for the microbial development and their optimal conditions (Oberson *et al*, 2001). The PSB density can vary according to pH, moisture, organic matter or different crops (Ponmurugan *et al*, 2006).

Besides the microorganism metabolism, some plants have the ability to segregate some enzymes that solubilize phosphorus, making it available for them (Helme *et al,* 2001). That's why the soil-plant system has to be the most efficient for providing a sustainable solution (Horst *et al*, 2001).

Summarizing, the different forms of phosphorus in the soil can be a consequence of transport, immobilization, solubilization and mineralization (Horst *et al*, 2001), as it is represented in Figure 4. Present organic phosphorus in soil is mineralized by the heterotrophic population which keeps some of it for their growth. The products of this decomposition are released in soluble phosphorus form available for plants. Nevertheless, this phosphorus mineral pool is easily fixed and adsorbed in soil and becomes unavailable both for plants and microorganisms.

It's important to determine how significant all these processes are in phosphorus cycle in order to adapt the agriculture managements and the fertilizers used to have the best solution. In Agrosystems, for example, plants residues are used to make the nutrients available (Salas *et al*, 2003).

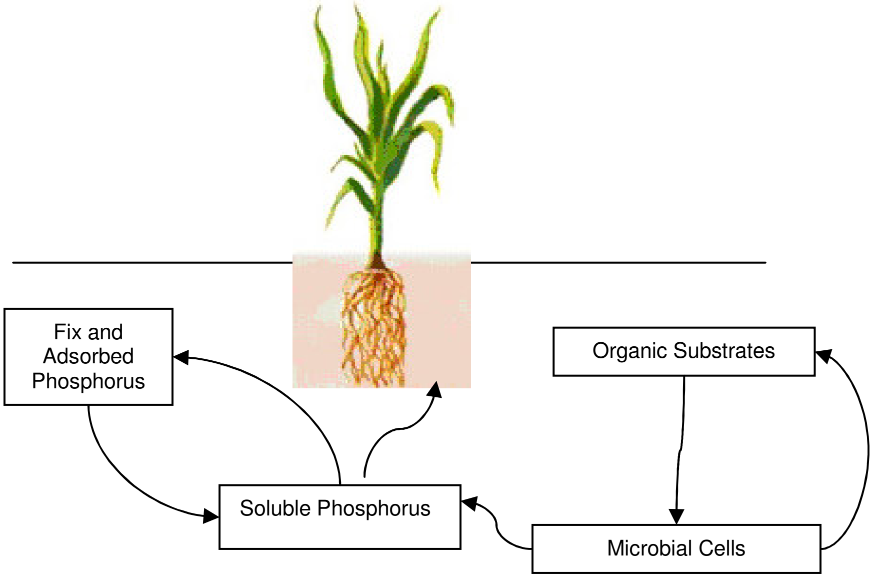

Figure 4 - Phosphorus cycle adapted from Quelhas dos Santos (2001)

2.2 - The Existing Models

Some models can simulate the cycles mentioned before in order to understand the soil dynamic and to predict future behaviors. To model these cycles, it's required to understand the different types of processes that occur in the different steps and, at the same time, describe them mathematically as well as the behavior of the microorganisms and their optimal environment, knowing the ideal conditions and factors that will affect their growth. If the model contemplates more processes it will be more able to represent the reality. However, some simplifications can be made, but it's necessary to know if they are not important in fact. Otherwise, the purpose of the model may not be reached.

There are different models able to simulate the soil processes and the organic matter mineralization and their importance in agriculture and soil uses as has been marked before. Nevertheless, they can be important also to predict environment problems like Eutrophication, when applied to hydrographic basins. The models have different approaches, depending on the purposes and the specific uses. In the next paragraphs a brief summary is made, in order to understand the options adopted during the work.

SWAT (Soil and Water Assessment Tool) was developed to predict the impact of land management practices on water, sediment and agricultural chemical yields in large complex watersheds with varying soils, land use and management conditions, over long periods of time.

This model simulates hydrographic basins processes with crops and organic matter. The modeled cycles for organic matter decay are nitrogen and phosphorus (Neitsch *et al*, 2005).

Summarizing, the SWAT model has 5 different pools of nitrogen, which 3 of them are organic and the other 2 are inorganic. The organic pools include the fresh organic nitrogen that comes from the organic residue and the organic nitrogen in humus substances in the active and stable pool. The model simulates the conversion of the active to stable form, as well as the mineralization of the active form of nitrogen organic pools.

About the nitrogen mineral pools, SWAT has nitrate and ammonium pools, simulating the processes of nitrification and volatilization. Besides that, the process of denitrification is also included.

In order to make this, the model uses some coefficients that are obtained with the environmental factors that enable or disable the bacteria population. No explicit calculation of the bacteria growth is made.

For example, for the mineralization, γ_{temp} is the temperature factor affected by the soil temperature and γ_{wat} is the water factor, affected by the field capacity and available soil water in Equation 7.

$$\gamma_{temp} = 0.9 \frac{T_{soil,ly}}{T_{soil,ly} + \exp\left[9.93 - 0.312 \cdot T_{soil,ly}\right]} + 0.1$$

Equation 7 - Temperature factor used in SWAT

The same approach is made for phosphorus cycle, the difference is that SWAT has 6 different pools of this element, 3 of them organic and 3 of them inorganic. The model simulates the organic forms mineralization, and also the conversion of active inorganic to solution inorganic pools.

The initial inputs are the organic material in the surface and the organic carbon in the soil, and also the initial concentration of phosphorus in the soluble inorganic pools. Some simplifications and considerations are made, such as 15% of the organic residue on the top layer is nitrogen and 3% is phosphorus but they exist just from the surface to the depth of 10mm.

Other inputs are required to relate to the bacteria metabolism such as the coefficients that represent the mineralization, decomposition, nitrification and denitrification rates.

The SWAT model does not simulate the carbon cycle individually and the model does not consider the bacteria populations explicitly. Nevertheless, it monitories many nitrogen and phosphorus types, which helps to understand how these elements become available for plants. It simulates volatilization and fixation, as well as the nitrogen that reaches the soil through the rain.

The other model with some importance in agriculture is the **RZWQM** (Root Zone Water Quality Model), which has a sub model component able to simulate the organic matter and the nitrogen cycles: OMNI. This model includes *Arrehnius* temperature response functions and reactive constituent concentration, and simulates microbial responses to soil oxygen levels, pH, water content and salinity (Shaffer *et al*, 1999).

In RZWQM, nitrogen pools are simulated in organic forms as organic residues, soil organic matter and microbial biomass; and in the mineral forms as NH_4^+, NO_3^-, Urea and N gas as N_2. For carbon pools, a lot of possibilities are considered such as crop organic residues with slow and fast decaying or soil organic matter (humus) with slow, medium and fast decaying. There are also carbon pools for the biomass heterotrophic and autotrophic and for the included.gases CO_2 and CH_4.

The processes simulated in this model are: aerobic decay of organic matter, nitrification, denitrification, urea hydrolysis and methane gas production.

In this model, biomass growth is calculated explicitly and because of that heterotrophic and autotrophic population are modeled as well as the facultative anaerobic biomass, which can produce methane in the absence of oxygen and NO_3.

In this model, the organic matter decay rates and other processes are calculated assuming first order equations in most of the cases (Equation 8). The specific rates of the processes depend on the environmental factors as optimal temperature, pH, and oxygen available (Equation 36) which will be developed in 3.3.2 - Specific Rates.

$$r_{decay} = K_{decay} \times S$$

Equation 8 - Organic Matter Decay rate used in RZWQM

In Hensen *et al*, (1995) it can be found that the organic subtract decomposition can be modeled by different kinetic types, like the *Monod* kinetics which uses some parameters that are affected by the environmental factors such as μ_m and K_s (Equation 9). To limit the number of parameters and the model complexity, zero and first order kinetics are used. Although these approaches are not generally true, they proved to be good approximations once RZWQM is a valid and used model all over the world.

$$\varsigma_n = \frac{\xi_m \cdot \left[NH_4^+\right]}{K_s + \left[NH_4^+\right]}$$

Equation 9 - DAISY Nitrification rate – Monod kinetic

DAISY is a Danish model also used in agriculture. It has three types of organic matter: Added Organic Matter (AOM), Soil organic Matter (SOM) and Biomass Organic Matter (BOM) (Abrahamsen and Hansen, 2000). These different types have a very similar behavior like in RZWQM. Nitrogen processes like nitrification and denitrification are also included. Abiotic factors that have impact in biological processes in soil are included in the specific rates, like in RZWQM but with a different approach.

$$k_x = k_x^* \cdot F_m^C(X_C) \cdot F_m^T(T_D) \cdot F_m^{\psi}(\psi)$$

Equation 10 - DAISY Specific Rate

Specific rates are function of a clay content function $F_m^C(X_C)$, temperature function $F_m^T(T_D)$ and pressure potential function $F_m^{\psi}(\psi)$ (Equation 10). Other differences between the models are related with denitrification processes and oxygen availability. Usually, zero and first order kinetics are used or *Michaelis- Menten* type equation for the oxygen availability. Anaerobic situations depend on how much water is present in the soil. So, anaerobic state can be calculated with a transfer function using a measure of the soil water status as an argument. However, different approaches are made, like the Dutch model ANIMO that calculates the oxygen demand arising from the turnover of the organic matter and the nitrification of ammonium. The vertical transport of oxygen into the soil is simulated by assuming steady-state conditions within each of the model's time steps and by adopting *Fick's* first law (Hensen *et al*, 1995).

RZWQM and DAISY are one dimension models (1D), simulating transport in vertical soil profiles. SWAT has a different approach in which watersheds are composed of small HRU (hydrologic response units) that have the same land cover, soil and management combinations. However, SWAT model simulates the phosphorus cycle including some important processes that neither RZWQM nor DAISY include. Nevertheless RZWQM simulates processes with first order rates and the specific rates have a direct control in the abiotic factors like temperature, pH, water content and soil oxygen. DAISY has empiric functions to evaluate the importance of these factors for the processes and SWAT have functions as well, but for mineralization processes as an example, just water content and temperature effects are taken into account.

For the new tool development (3rd Chapter – Model Bases Implementation), the approach of RZWQM is more adapted because Mohid Land (4.1 - Mohid Land) has the same approach but it is even more complete once it is a three dimensional (3D) model. Besides, the model developed by Galvão (2002) was already based on this, providing a module for organic matter decomposition which included the carbon and nitrogen cycles.

For the development of the last part of the work in which a corn planting was simulated (5th Chapter – RZWQM , RZWQM was more indicated once data available for input and measures were available for different depths.

3rd Chapter – Model Bases Implementation

3.1 - Model Description

The first step of this work was to improve the model developed by Galvão (2002) in order to obtain a better tool that simulates the organic matter decomposition in the soil and also other important processes.

The new model description is shown in this chapter with the inclusions and changes that were made. A schematic model is in the APPENDIX A – Model Structure, while in the next points, a brief explanation is given about the system pools as well as the sources and sinks related with the processes that were modeled. The equations adopted for every process are also decrypted and in the last point of this chapter some simulations in PowerSim are shown and discussed.

To improve the model, some inclusions and amendments were made in order to join more advantages from models as RZWQM and SWAT, allowing a more consistent modelling of the soil processes. The main changes of the work are summarized below:

- Inclusion of the phosphorus cycle with immobilization by the heterotrophic population and solubilization/fixation and adsorption of the mineral phosphorus pool.
- Inclusion of methane gas released in anaerobic conditions, hydrolysis of urea and ammonia volatilization.
- Results variations of the model with temperature, pH, wind, soil type (porosity) and salinity
- Verification and correction of all the processes equations, comparing them with the RZWQM's source code. The first equations used by Galvão (2002) in the previous organic matter decomposition model were taken from Shaffer *et al* (1999). In this work the RZWQM source code (2007) was available, allowing a deeper and more complete study.

3.2 - System Elements Definition

The model supports both organic and inorganic pools. Almost all of the models include for the organic pools, a small pool which has a rapid turnover time (dynamic, active, labile pool) containing relatively young carbon with a mean age of less than a few decades and a large pool that turns over slowly (stable, passive, refractory) characterized by very old carbon with a mean age of more than several hundred years (Ruhlmann, 1999).

Galvão (2002) adopted three organic matter pools: a fast organic matter decay pool, a slow organic matter decay pool and the biomass pool. To make this simplification, some assumptions needed to be done, as the fact that when biomass dies it becomes part of the fast organic matter decay pool.

Models like RZWQM and SWAT consider more pools for organic matter (2.2 - The Existing Models) which allow them to separate organic residues in the soil from humus. With the approach of Galvão (2002) there is no distinction between these types of organic matter.

According to the Holistic approach, these three types of organic matter will be distributed in the three nutrients considered: carbon, nitrogen and phosphorus.

Galvão (2002) used also three inorganic pools: ammonium, nitrate and carbon dioxide. This last one was just the one excreted by the heterotrophic. In fact, the CO_2 to be consumed by the autotrophic was assumed to be always available.

Because of the new model improvements, some inorganic pools were also added: mineral phosphorus pools and methane, urea and ammonia. Table 1 summarizes the considered pools:

Table 1 - Organic and inorganic pools

Organic Pools	Biomass	Aerobic Het (C, N, P)
		Autotrophic (C, N, P)
		Anaerobic Het (C, N, P)
	Labile organic matter (C,N,P)	
	Refractory organic matter (C,N,P)	
Inorganic Pools	NO_3^-	
	NH_4^+	
	Inorganic soluble phosphorus	
	Fixed/adsorbed Phosphorus	
	CO_2	
	N_2	
	CH_4	
	Urea	
	NH_3	

3.3 - Simulated Processes Definition

After a study about the main and significant microbiological and chemical processes that take place in soil and their mean in agriculture (developed in 2.1 - The Soil Processes), the identification for each pool of the sources and sinks was done.

In Table 2, Table 3 and Table 4, flows for carbon, nitrogen and phosphorus cycle are represented:

Table 2 - Sources and sinks in the carbon cycle

Level	Flows	
	Source	**Sink**
Aerobic heterotrophic carbon	- Decomposition of labile OM - Decomposition of refractory OM	- Aerobic excretion of CO_2 - Death
Autotrophic carbon	- CO_2 uptake	- Death
Anaerobic heterotrophic carbon	- Decomposition of labile OM - Decomposition of refractory OM	- Anaerobic excretion of CO_2 - Death
CO_2	- Aerobic and anaerobic Excretion	
CH_4	- Anaerobic excretion	
Refractory organic matter carbon		- Decomposition by aerobic het - Decomposition by anaerobic het
Labile organic matter carbon	- Aerobic and anaerobic heterotrophic death - Autotrophic death	- Decomposition by aerobic het - Decomposition by anaerobic het

Table 3 - Sources and sinks in the nitrogen cycle

Level	Flows	
	Source	**Sink**
Aerobic heterotrophic nitrogen	- Decomposition of labile OM - Decomposition of refractory OM - NH_4+ Immobilization - NO_3^- Immobilization	- Aerobic excretion of NH_4^+ - Death
Autotrophic nitrogen	- NH_4^+ Uptake	- Death
Heterotrophic anaerobic nitrogen	- Decomposition of labile OM - Decomposition of refractory OM - Denitrification - NO_3^- consumption	- Anaerobic excretion of NH_4^+
NO_3^-	- Nitrification - excretion of NO_3^-	- Denitrification - Anaerobic Het consumption - Denitrification - excretion of N gas - Immobilization
NH_4^+	- Aerobic and anaerobic Het Excretion - Urea Hydrolysis	- Nitrification - excretion of NO_3^- - Immobilization - Nitrification - Autotrophic growth - NH_3 Volatilization
Refractory Organic Matter Nitrogen		- Decomposition by aerobic Het - Decomposition by anaerobic Het
Labile Organic Matter Nitrogen	- Aerobic and anaerobic Death - Autotrophic Death	- Decomposition by aerobic Het - Decomposition by anaerobic Het
N_2 (gas)	- Denitrification - Excretion of N(gas)	
Urea		- Urea Hydrolysis
NH_3	- NH_3 Volatilization	

Table 4 - Sources and sinks in the phosphorus cycle

Level	Flows	
	Source	**Sink**
Aerobic heterotrophic phosphorus	- Decomposition of labile OM - Decomposition of refractory OM - Soluble phosphorus immobilization	- Aerobic excretion soluble phosphorus - Death
Autotrophic phosphorus	- Soluble phosphorus uptake	- Death
Anaerobic heterotrophic phosphorus	- Decomposition of labile OM - Decomposition of refractory OM	- Anaerobic excretion soluble phosphorus - Death
Mineral soluble phosphorus	- Aerobic heterotrophic excretion - Anaerobic heterotrophic excretion - Solubilization	- Autotrophic uptake - Immobilization - Fixation/Adsorption
Mineral fix/adsorbed phosphorus	- Fixation/Adsorption	- Solubilization
Refractory organic matter phosphorus		- Decomposition by aerobic het - Decomposition by anaerobic het
Labile organic matter phosphorus	- Aerobic and anaerobic Het Death - Autotrophic Death	- Decomposition by heterotrophic - Decomposition by anaerobic

The aerobic and anaerobic excretion are a sink in the heterotrophic biomass because they cannot incorporate all nutrients into their growth and so, as a consequence, some flows in the CO_2, orthophosphates and NH_4^+ pools appear. The excretion dependens on the bacterias efficiency in transforming the organic elements into organic biomass.

Other interesting issue is related to the mass conservation: total carbon, nitrogen and phosphorus is always the same. They may be distributed into different pools (organic or inorganic) and in terrestrial or atmospheric parts, but the total mass is conserved. That is easily observed with a look over the different sources and sinks of the pools. For example, organic matter decay is the source for biomass growth, but it is a sink for the Labile and Refractory organic matter,

In APPENDIX B, C and D the PowerSim implementation is shown where all these flows may be identified and related to the pools.

3.3.1 - Flow Equations Definition

3.3.1.1 - Aerobic Heterotrophic Processes

Heterotrophic aerobic biomass uses the organic carbon as carbon source and from this up take biomass growth occurs and mineralized organic compounds are released. But microorganism's populations need as well nitrogen and phosphorus in smaller quantities to survive. That is why the carbon/nitrogen and the carbon/phosphorus ratios are defined. If the organic matter available has the enough nitrogen and phosphorus, mineralization processes happen. Otherwise, to assimilate the organic carbon, they will immobilize nitrogen and phosphorus in the mineral form, incorporating them into their growth.

The previous model developed by Galvão (2002) represented this immobilization phenomenon just for nitrogen. Now, the phosphorus immobilization was included too.

Equation 11 represents the potential biomass growth while Equation 12 defines the potential immobilization rate. This last potential immobilization rate was developed before for the nitrate and the ammonium. In the current model, the same potential is calculated for phosphorus.

$$P_{Adecay} = [OM] \times K_{Adecay}$$

Equation 11 - Potential aerobic organic matter decay rate

P_{Adecay} - Potential aerobic decay $\mu g / g_{soil} / day$

$[OM]$ - Total organic matter (Labile and Refractory) $\mu g / g_{soil}$

K_{Adecay} - Aerobic Decay Specific Rate day^{-1}

$$P_{\mathrm{Im}\_P} = [P_{sol}] \times K_{\mathrm{Im}ob\_P}$$

Equation 12 - Potential phosphorus immobilization rate

$P_{\mathrm{Im}ob\_P}$ - Potential phosphorus immobilization $\mu g / m^3 water / day$

P_{sol} - Soluble mineral phosphorus $\mu g / m^3 water$

$K_{\mathrm{Im}ob\_P}$ - Phosphorus immobilization specific Rate day^{-1}

Nevertheless, not always the maximum rates are applied. In fact, depending on the immobilization limits these processes may occur at potential rate or not.

The decision regarding if there is a mineralization or immobilization process is made according to Equation 13 and Equation 14.

$$\frac{1}{CN_{het}} \cdot (P_L + P_R) > \frac{P_L}{CN_{lab}} + \frac{P_R}{CN_{ref}}$$

Equation 13 - Decision for nitrogen immobilization

$$\frac{1}{CP_{het}} \cdot (P_L + P_R) > \frac{P_L}{CP_{lab}} + \frac{P_R}{CP_{ref}}$$

Equation 14 - Decision for phosphorus immobilization

P_L - Labile organic matter potential decay $\mu g / g_{soil} / day$

P_R - Refractory organic matter potential decay $\mu g / g_{soil} / day$

CN_{Lab} - Carbon nitrogen ratio of labile organic matter

$CN_{\mathrm{Re}f}$ - Carbon nitrogen ratio of refractory organic matter

CN_{het} - Carbon nitrogen ratio of heterotrophic biomass population

CP_{Lab} - Carbon phosphorus ratio of labile organic matter

$CP_{\mathrm{Re}f}$ - Carbon phosphorus ratio of refractory organic matter

CP_{het} - Carbon phosphorus ratio of heterotrophic biomass population

These equations translate the CN and the CP ratios importance for the organic matter and the biomass which will decompose it. If Equation 13 or Equation 14 are verified, that means that the CN or CP ratios of the organic matter are too high for the biomass population and, as a consequence, they will need to immobilize some of the mineral nitrogen or phosphorus.

In the previous model, only the nitrogen immobilization was accounted, but with the phosphorus cycle introduction, it's necessary to know if there would be any phosphorus immobilization, even if the biomass doesn't need to immobilize nitrogen.

For both nutrients, the model will consider two phases in immobilization situation: the first when the potential decaying is smaller than the potential immobilization by the heterotrophic, which means that organic matter decay is the limiting process; and the other when the decaying potential is greater than the immobilization potential which will influence the biomass growth. These limit situations are represented by Equation 15 and Equation 16. These limits, that decide the type of growth and the type of immobilization related to the nitrogen nutrient, were developed by Galvão (2002) and now the same is applied to the phosphorus cycle.

$$P_L\left(\frac{1}{CN_{het}}-\frac{1}{CN_{Lab}}\right)+P_R\left(\frac{1}{CN_{het}}-\frac{1}{CN_{\mathrm{Re}\,f}}\right)<P_{\mathrm{Im}\,ob\_NO3}+P_{\mathrm{Im}\,ob\_NH4}$$

Equation 15 - Decision for nitrogen immobilization limit

$$P_L\left(\frac{1}{CP_{het}}-\frac{1}{CP_{Lab}}\right)+P_R\left(\frac{1}{CP_{het}}-\frac{1}{CP_{\mathrm{Re}\,f}}\right)<P_{\mathrm{Im}\,ob\_P}$$

Equation 16 - Decision for phosphorus immobilization limit

$P_{\mathrm{Im}\,ob\_NH4}$ - Potential ammonium immobilization $\mu g/m^3 water/day$

$P_{\mathrm{Im}\,ob\_NO3}$ - Potential nitrate immobilization $\mu g/m^3 water/day$

$P_{\mathrm{Im}\,ob\_P}$ - Potential phosphorus immobilization $\mu g/m^3 water/day$

These equations summarize the fact that the rates of immobilization and biomass growth may be different, even if nitrogen or phosphorus immobilization is happening., As mentioned before, if the organic matter is the limiting situation, biomass growth will be the potential (Equation 11) but the immobilization rate will be a *Real* one, ruled by the Equation 17 (for both nitrogen and phosphorus):

$$R_{I_{Phosphorus}}=\left[P_L\left(\frac{1}{CP_{hete}}-\frac{1}{CP_{lab}}\right)+P_R\left(\frac{1}{CP_{hete}}-\frac{1}{CP_{\mathrm{Re}\,f}}\right)\right]$$

Equation 17 - Real soluble phosphorus immobilization

Otherwise if the immobilization is the limitation, bacteria will grow with a rate below the potential – *Real Growth* given by Equation 18 or Equation 19 . In this case, immobilization will be the highest one - potential.

$$R_{aerobicdecay}=\frac{P_{\mathrm{Im}\,ob\_NO3}+P_{\mathrm{Im}\,ob\_NH4}}{\left(\frac{1}{CP_{hete}}-\frac{1}{CP_{lab}}\right)+\left(\frac{1}{CP_{hete}}-\frac{1}{CP_{ref}}\right)}$$

Equation 18 - Real organic matter decay rate - nitrogen immobilization situation

$$R_{aerobicdecay} = \frac{P_{\mathrm{Im}\,ob\_P}}{\left(\frac{1}{CP_{hete}} - \frac{1}{CP_{lab}}\right) + \left(\frac{1}{CP_{hete}} - \frac{1}{CP_{ref}}\right)}$$

Equation 19 - Real organic matter decay rate - phosphorus immobilization situation

As it can be noted, a lot of possibilities are included for the biomass growth and immobilization rates, when phosphorus cycle is added. To summarize these mineralization/immobilization situations, Table 5 and Table 6 indicate all the possibilities.If Equation 13 and Equation 14 are verified, immobilization situation will be ON or OFF. Besides that, the potential or real growth and immobilization will be dependent if Equation 15 and Equation 16 are true or false.

Table 5 - Equations for heterotrophic growth

		IMOBILIZATION (P) ON		**IMOBILIZATION (P) OFF**
		LIMIT ON	**LIMIT OFF**	
IMOBILIZATION (N) ON	**LIMIT ON**	SPECIAL CASE	REAL N	REAL N
	LIMIT OFF	REAL P	POTENTIAL	POTENTIAL
IMOBILIZATION (N) OFF		REAL P	POTENTIAL	POTENTIAL

For the Special Case situation, the model will compare the two limited growths and will decide which immobilization (nitrogen or phosphorus) is being more limitative.

Table 6 - Equations for immobilization situations

		IMOBILIZATION (P) ON		**IMOBILIZATION (P) OFF**
		LIMIT ON	**LIMIT OFF**	
IMOBILIZATION (N) ON	**LIMIT ON**	N - POTENTIAL	N - POTENTIAL	N- POTENTIAL
		P - POTENTIAL	P - REAL	P - 0
	LIMIT OFF	N - REAL	N - REAL	N - REAL
		P - POTENTIAL	P - REAL	P - 0
IMOBILIZATION (N) OFF		N - 0	N - 0	N - 0
		P - POTENTIAL	P - REAL	P - 0

Heterotrophic populations needs have some cost. Although they uptake the carbon essential to survive from the organic matter, some of it will be transformed into carbon dioxide. The same happens with the organic nitrogen and phosphorus that become respectively NH_4^+ and soluble phosphorus.

Equation 20 represents the rate at which they release mineralization phosphorus products. It is applied as well to CO_2 and ammonium. Nevertheless, in the carbon cycle there is no immobilization source for CO_2.

$$R_{exc\_P} = \left(\frac{R_{total\_Aer\_decay}}{CP_{hete}} + R_{totalI\,\mathrm{Im}\,ob\_P} \right) \times Ef_{hete}$$

Equation 20 - Soluble mineral phosphorus aerobic excretion rate

R_{exc_P} - Mineral soluble phosphorus excretion rate $\mu g / m^3 water / day$

$R_{total\_Aer\_decay}$ - Total organic matter aerobic decay rate $\mu g / g_{soil} / day$

$R_{totalI\,\mathrm{Im}\,ob\_P}$ - Potential phosphorus immobilization $\mu g / m^3 water / day$

Ef_{hete} - Heterotrophic population efficiency in organic matter decay

3.3.1.2 - Anaerobic Heterotrophic Processes

The anaerobic heterotrophic population is very similar with the one mentioned previously; the difference is that they just act in oxygen's absence. This happens because the previous model, developed by Galvão (2002), simulated just the strict anaerobic bacteria. This particular type of bacteria uses nitrate as an electron acceptor and from this process nitrogen gas is released. In some situations, when nitrate becomes unavailable for the consumption, the bacteria may take some dioxide carbon and the result is the release of methane gas.

The potential denitrification rate, given by Equation 21, will depend of the nitrate concentration and, as not all of the organic matter decaying is converted into biomass growth, it will also be dependent of the population efficiency.

$$R_{total\_Ana\_decay} = \left[NO_3^-\right] \times K_{des} \times Ef_{des}$$

Equation 21 - Anaerobic organic matter decay rate

The remainder, not conduced to biomass growth, is released as nitrogen gas - Equation 22. Nevertheless is important to note that the organic matter decaying process has its own efficiency and from this fact, NH_4^+, CO_2 and soluble phosphorus are excreted as well.

$$R_{Ngas} = \left[NO_3^-\right] \times K_{des} \times \left(1 - Ef_{des}\right)$$

Equation 22 - Anaerobic released of N gas

$R_{total\_Ana\_decay}$ - Total organic matter anaerobic decay rate $\mu g / g_{soil} / day$

$[NO_3^-]$ - Nitrate $\mu g / m^3 water$

K_{des} - Denitrification specific rate day^{-1}

R_{Ngas} - N gas excretion rate $\mu g / m^3 water / day$

Ef_{des} - Anaerobic heterotrophic population efficiency in nitrate consumption

These equations were present in the previous model of Galvão (2002). With the inclusion of phosphorus cycle, anaerobic heterotrophic bacteria will also consume some phosphorus. That is counted with the Equation 21 affected by the CP ratio of the organic Matter. No immobilization processes were counted here because that process was not included before. According to the same source, Galvão (2002), there is not enough information about anaerobic immobilization and because of that, phosphorus immobilization was not included.

If in an anaerobic situation, nitrate becomes depleted, bacteria will have to arrange another solution and so, they will start to uptake some CO_2 as electron acceptor and will release CH_4. In fact, this process is more complex but, in order to simplify the model, it's assumed that bacteria breathe only CO_2, and the result is the biomass growth and the methane gas released. Details are explained in 2.1.1 - Carbon Cycle. From the consumption of this electron acceptor, methane is produced - Equation 23 and the remaining part is used for the biomass processes - Equation 24. These equations were adapted from Shaffer *et al*, (1999).

$$R_{CH4} = [OM] \times K_{CH4} \times (1 - Ef_{CH4})$$

Equation 23 - Methane production rate in nitrate absence

$$R_{Total\_ana\_decay} = [OM] \times K_{CH4} \times Ef_{CH4}$$

Equation 24 - Anaerobic organic matter decay in nitrate absence

$R_{total\_Ana\_decay}$ - Total organic matter anaerobic decay rate $\mu g / g_{soil} / day$

$[OM]$ - Total organic matter $\mu g / m^3 water$

K_{CH4} - Methane production specific rate day^{-1}

R_{CH4s} - Methane excretion rate $\mu g / m^3 water / day$

Ef_{CH4} - Anaerobic heterotrophic population efficiency in producing methane

3.3.1.3 - Autotrophic Processes

This biomass is characterized by the fact that they do not need an organic carbon source, because they can use the carbon present in the dioxide carbon. This makes this population not dependent on the available carbon in the soil. Nevertheless they use the ammonium available and transforme it into nitrate, in the nitrification processes. This has a great importance in Agriculture once ammonium available for plants uptake may become nitrate. That could be a problem because nitrate is easily leached and become less available for plants and at the same time is capable to contribute to the water lines contamination.

Nitrification process is modeled as a first order reaction, which means that will depend on the ammonium concentration in time - Equation 25. Once again, these equations were used from the previous model, developed by Galvão (2002). The same happened here, as in anaerobic population: autotrophic microorganisms will need to uptake some phosphorus and that is simulated with the CP ratio (Equation 26).

$$R_{uptakeN} = \left[NH_4^+\right] \times K_{nit} \times Ef_{nit}$$

Equation 25 - Nitrogen uptake rate by autotrophic

$$R_{uptakeP} = \frac{\left[NH_4^+\right] \times K_{nit} \times Ef_{nit}}{CP_{auto}}$$

Equation 26 - Phosphorus uptake rate by autotrophic

$R_{uptakeN}$ - Ammonium uptake rate by autotrophic $\mu g / m^3 water / day$

$\left[NH_4^+\right]$ - Ammonium $\mu g / m^3 water$

K_{nit} - Nitrification specific rate day^{-1}

Ef_{nit} - Autotrophic population efficiency in nitrification process

$R_{uptakeP}$ - Phosphorus uptake rate by autotrophic $\mu g / m^3 water / day$

CP_{auto} - Carbon phosphorus ratio of autotrophic population

3.3.1.4 - Phosphorus Inorganic Processes

As it was said in *2.1 - The Soil*, phosphorus dynamic in inorganic pools is different from nitrogen. This element is easily fixed and adsorbed by chemical processes, becoming unavailable for plant uptake or biomass growth.

Literature reports that this is, in reality, one big problem for plants and consequently for agriculture economy. The opposite process, phosphorus solubilization is not so easy to occur. Otherwise, some bacteria that live near the roots may do that job

The model may not simulate the solubilizing bacteria, but uses the SWAT approach of these processes (2.2 - The Existing Models), assuming that the flow from soluble to fixed phosphorus is 10 times higher than the opposite flow, which is shown in Equation 27 and Equation 28. These equations were taken from Neitsch *et al* (2005).

$$R_{P\_sol\_fix} = \left[P_{sol} - P_{fix} \times \left(\frac{PAI}{1 - PAI} \right) \right]$$

Equation 27 - Conversion rate from soluble to fixed phosphorus

$$R_{P\_fix\_sol} = 0.1 \left[P_{sol} - P_{fix} \times \left(\frac{PAI}{1 - PAI} \right) \right]$$

Equation 28 - Converse rate from fixed to soluble phosphorus

$R_{P\_sol\_fix}$ - Conversion rate from mineral soluble to mineral fixed phosphorus pool $\mu g / m^3 water / day$

$R_{P\_fix\_sol}$ - Conversion rate from mineral fixed to soluble phosphorus pool $\mu g / m^3 water / day$

P_{sol} - Mineral phosphorus soluble pool $\mu g / m^3 water$

P_{fix} - Mineral phosphorus fixed pool $\mu g / m^3 water$

PAI - Phosphorus available index

These equations use the concept of PAI (Phosphorus Available Index) defined in SWAT model by Equation 29.

$$PAI = \frac{P_{sol,f} - P_{sol,b}}{fert_{\min P}}$$

Equation 29 - Phosphorus available index

PAI - Phosphorus available index

$P_{sol,f}$ - Mineral soluble phosphorus after fertilization $\mu g / m^3 water$

$P_{sol,b}$ - Mineral soluble phosphorus before fertilization $\mu g / m^3 water$

$fert_{\min P}$ - Mineral phosphorus soluble fertilizer $\mu g / m^3 water$

This parameter will help to define the ability of the soil to keep some soluble phosphorus. If enough soluble phosphorus is available after fertilization, PAI will be closer to 1, while in the soils where fixation of phosphorus is expected, PAI will be more close to 0.

3.3.1.5 - Urea Hydrolysis and Ammonia Volatilization

Urea $\left(CO(NH_2)_2\right)$, is converted into NH_4^+ by the process of Hydrolysis in which the involved enzyme is *Urease*. This activity in soil does not appear to be a function of microbial population size or water content, and it's also modeled by first order equations (Shaffer *et al*, 1999). As Urea may be added to the soil as a fertilizer, this process may become a source of ammonium in soil (Equation 30).

$$R_{Urea} = \left[NH_4^+\right] \times K_{Urea}$$

Equation 30 - Urea hydrolysis rate

R_{Urea} - Urea hydrolysis rate $\mu g / m^3 water / day$

K_{Urea} - Urea hydrolysis specific rate day^{-1}

Ammonia volatilization is the reaction occurring at the soil surface, mainly in basic soils, in which ammonium is depleted. Because of that, this phenomenon is modeled by first order reaction (Equation 31). This process was not included in the previous model, but the source of the equations is the same, Shaffer *et al* (1999).

$$R_{vol} = \left[NH_4^+\right] \times K_{vol}$$

Equation 31 - Ammonia volatilization rate

Ammonia volatilization specific rate will depend on some parameters as the ammonia partial pressure, pH, temperature and wind, shown in Equation 32.

$$K_{vol} = X_{KG} \times Tf \times \left(P_{NH3} - Pa_{NH3}\right)$$

Equation 32 - Ammonia volatilization specific rate

R_{vol} - Ammonia volatilization rate $\mu g / m^3 water / day$

$[NH_4^+]$ - Ammonium $\mu g / m^3 water$

K_{vol} - Ammonia volatilization specific Rate day^{-1}

X_{KG} - Coefficient of wind and depth effect

Tf - Coefficient of temperature effect

P_{NH3} - Partial pressure of NH_3 atm

Pa_{NH3} - Partial ambient pressure of NH_3 atm

NH_3 partial pressure will be given by Equation 33.If the Ammonia pressure is equal to the environmental one, no volatilization will occur. This specific rate is dependent of two factors that take in count temperature and wind effect (Equation 34 and Equation 35).

$$P_{NH_3} = \frac{EK \times [NH_4^+]}{[H^+]}$$

Equation 33 - Ammonia partial pressure

$$Tf = TK \times e^{\left(\frac{-6}{R_g \times T}\right)}$$

Equation 34 - Temperature effect in ammonia volatilization

$$X_{KG} = X_{K_1} \times \log(W) \times e^{(X_K)}$$

Equation 35 - Wind effect in ammonia volatilization

$[H^+]$ - Hydrogen mol / L

$[NH_4^+]$ - Ammonium mol / L

EK - Equilibrium constant

Tf - Coefficient of temperature effect

TK - General decomposition constant

Rg - Universal gas constant $Kcal / mole / K$

T - Temperature K

X_{KG} - Coefficient of wind and depth effect

X_K - Depth constant

X_{K1} - Volatilization constant

W - Wind km/day

3.3.2 - Specific Rates

In the previous point, used equations for each process were shown. In the model developed by Galvão (2002) these processes were modeled by first order equations, like in the RZWQM. At this point a description of the specific rates used for each process is given, showing the environmental parameters that will affect the microbiological activities.

The main factors affecting the soil processes are: temperature, pH, salinity, and water content. New specific rates that were adopted are different from those who were implemented in Galvão (2002). The changes happened because in this work the source code of RZWQM (2007) was available and could be studied.

As seen in 3.3.1 - Flow Equations, each process has a specific rate. However, an exhaustive description is not needed. The Equation 36 referres to the organic matter aerobic decay and for the other processes similar specific rates were adopted.

$$K_{Adecay} = f_{aer} \times \left(\frac{K_b \cdot T_p}{h_p} \times A_{Adecay} \right) \times e^{\left(\frac{-Ea}{Rg \times T_p} \right)} \times \frac{[O_2]}{[H^+]^{Khn}} \times Het_{pop} \times Adj$$

Equation 36 - Aerobic labile organic matter specific rate

f_{aer} - Aerobic factor

K_b - Boltzman constant $J \cdot K^{-1}$

T_p - Aerobic organic matter decay temperature K

h_p - Planck constant $J \cdot s$

Rg - Universal gas constant $Kcal/mole/K$

A_{Adecay} - Aerobic organic matter decay coefficient

Ea - Apparent activation energy $Kcal \cdot mole^{-1}$

$[O_2]$ - Oxygen concentration in soil, assuming soil air not limited mol/L

$[H^+]$ - Hydrogen mol/L

Khn - Aerobic organic matter exponent for hydrogen ion

Het_{pop} - Heterotrophic population org/g_{soil}

Adj - Coefficient dependent of the soil pH

The soil temperature will affect the biomass activity not only for this process in particular but for others such as nitrification or denitrification (Equation 37).

$$\begin{array}{l} T_{soil} \quad if \quad T_{soil} \le T_p \\ 2 \times T_{\max} - T_{soil} \quad if \quad T_{soil} > T_p \end{array}$$

Equation 37 - Soil process temperature

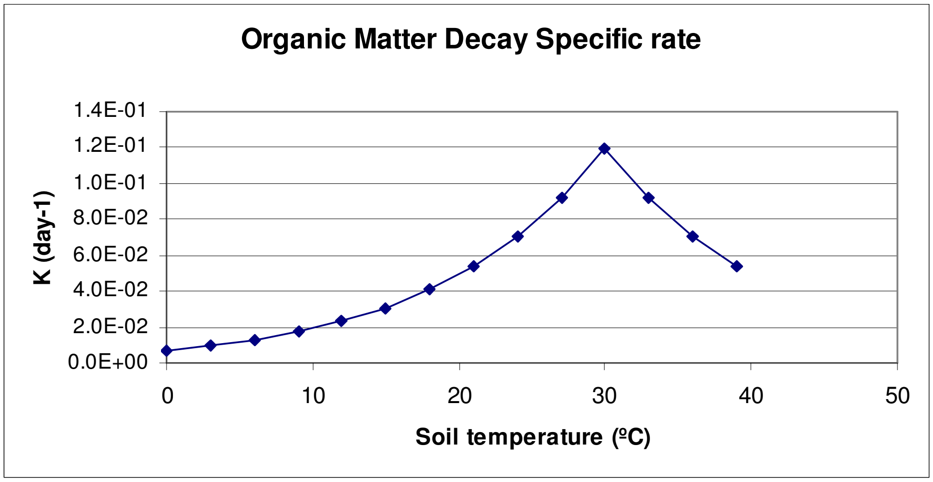

Figure 5 - Temperature effect on organic matter decay specific rate

Specific rate is higher at the optimal temperature of the growth and becomes lower for temperatures values distant from that (Figure 5).

The same happens with pH (Figure 6). The exponent *Khn and the Adj parameter* are affected according to the pH value (Equation 38 and Equation 39).

$$\begin{array}{l} Khn = 0.16665 \quad if \quad pH \le 7 \\ Khn = -0.3333 \quad if \quad pH > 7 \end{array}$$

Equation 38 - Hydrogen coefficient dependence from pH

$$\begin{array}{l} Adj = 1 \quad if \quad pH \le 7 \\ Adj = 3159.7 \quad if \quad pH > 7 \end{array}$$

Equation 39 - Adj coefficient dependence from pH

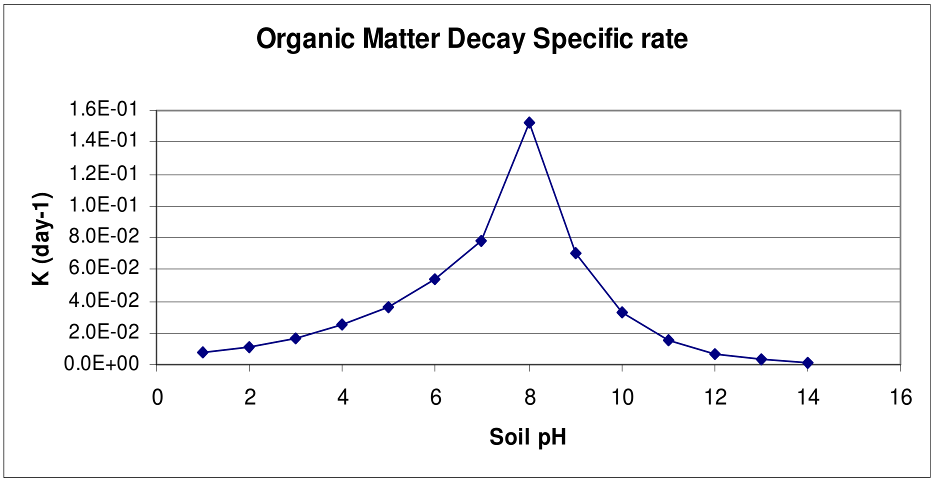

Figure 6 - pH Effects on organic matter specific rate

Other change of this new model is the calculation of the Apparent Activation Energy, while in Galvão (2002) that was an input data. In fact this apparent energy Activation, Ea , is a function of the Ionic Strength (Equation 40). For now, no ion concentrations are being calculated because this model considers only the microbiological processes occurring in soil. Nevertheless, if a chemical model is attached for ions concentration calculation, the ionic strength in soil will vary and with it also this parameter.

$$Ea = E_{0i} + kp \times I$$

Equation 40 - Apparent activation energy

Ea - Apparent activation energy $Kcal \cdot mole^{-1}$

E_{0i} - Referent activation energy $Kcal \cdot mole^{-1}$

kp - Constant coefficient L/mol

I - Ionic strength mol/L

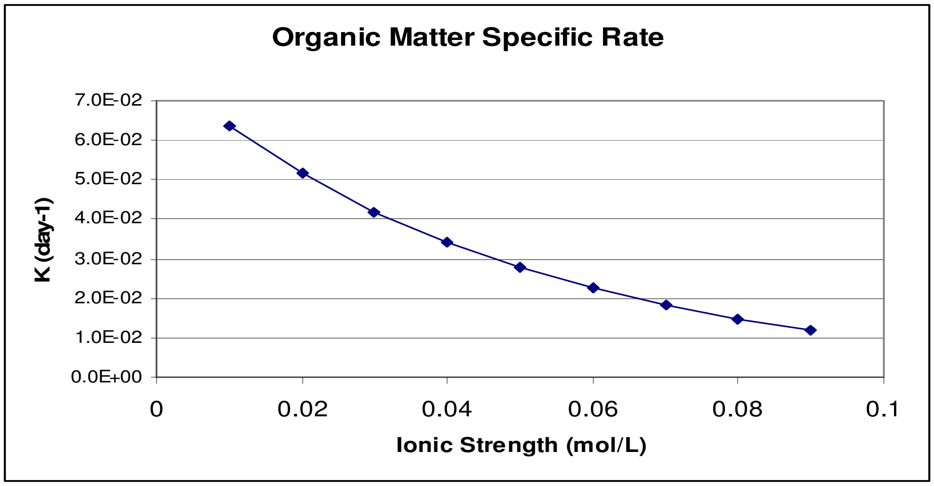

Figure 7 - Ionic strength effect on organic matter specific rate

Figure 7 shows that for a higher Ionic Strength value - a soil with high ions concentration with large charges- the organic matter specific rate will be lower.

Other important issue in biomass environmental conditions is the soil water content. In this model, aerobic and anaerobic environment is modeled by the amount of present water. That means that oxygen flow is not present, which will induce a simplification: there is no oxygen consumption by the different processes, such as organic matter decay or in nitrification. So, the aerobic level of the soil is evaluated by the water content: if the soil has enough water, there is no space for oxygen and anaerobic environment is installed.

Effective water content θ_F ,is calculated with water content and soil porosity (Equation 41), informing about the level of soil saturation .If effective water content is 100%, all of the soil pores are filled with water.

$$\theta_F = \frac{\theta}{\theta_S}$$

Equation 41 - Effective water content

According to the θ_F values, the aerobic f_{aer} and anaerobic f_{ana} factor (present in specific rates equations like Equation 36) is determined. For values between the ones shown in Table 7, is made an interpolation (Shaffer *et al*, 1999).

Table 7 - Aerobic and anaerobic factors from Shaffer et al (1999)

θ_F (%)	f_{aer}
≤ 60	1.00
70	0.40
80	0.10
87 ≥	0.00

θ_F (%)	f_{ana}
≤ 60	0.00
80	0.13
100	1.00

The Soil Oxygen is also present in specific rates. This parameter was one of the input data in Galvão (2002) but, according to Shaffer *et al* (1999), the oxygen concentration will depend on the soil temperature and salinity. Values for the different temperatures and salinities were taken from Metcalf and Eddy (1978). For intermediate values, interpolations are made by the model.

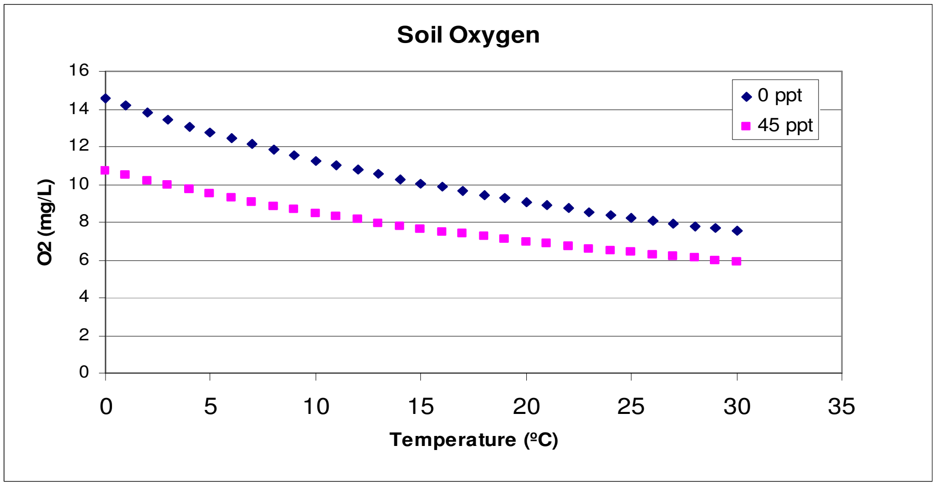

Figure 8 - Salinity influence on dissolved oxygen

Figure 8 shows that dissolved oxygen is lower for higher salinity but that difference becomes less important if temperature increases (Metcalf & Eddy, 1978).

3.4 - Preliminary Results in PowerSim

PowerSim is a software that makes dynamic simulations. The system is designed in a simple way, showing the levels and the flows that affect these levels in time. The interaction is extremely graphic, which allows the user to understand better what's happening in the system. Other advantage is the fact that, in a very easy way, the user can make simulations and observe the data in tables or graphics, taking some conclusions and detecting errors earlier than usual.

In the present work PowerSim was very useful because previously the sources and sinks of carbon, nitrogen and phosphorus had already been identified, allowing now, an easy construction of the model with the pools and their respectively flows.

The previous model developed by Galvão (2002) was also programmed in PowerSim in a first step, and now the new version is being created with the inclusions and changes described before.

The initial values used for these simulations are shown in Table 8 and were taken of the RZWQM source code (2007), Cameira (1999) and Metcalf & Eddy (1978).

Table 8 - Initial PowerSim values of population, organic matter and mineral pools for the simulations

	(mg/Kg soil)
Labile OM	600
Refractory OM	23244.78

	(mg/Kg soil)
NO3-	4.64
NH4+	0.0001
P sol	1.44
P fix	5.8
CO2	0
N2	0

	Population (org/g soil)	**CN**	**CP**
Aerobic het	100 000	8	60
Anaerobic het	10 000	8	60
Autotrophic	1045	8	2000

The next Graphics show the simulation in PoweSim with a CN ratio of 20 and a CP ratio of 80 for Labile Organic Matter.

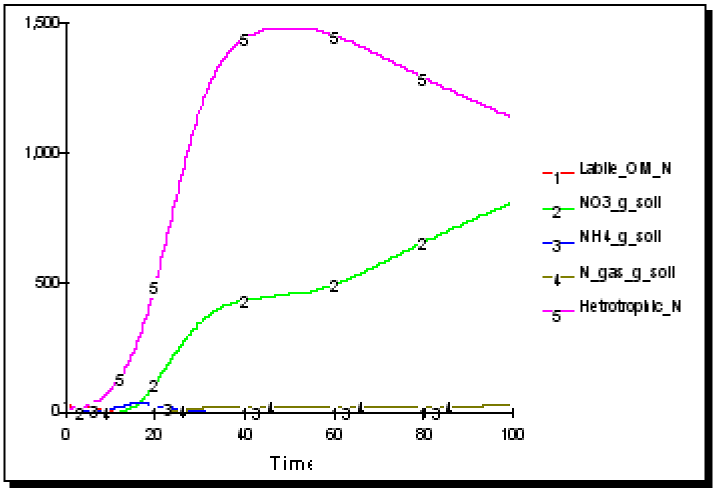

Figure 9 - Nitrogen cycle in mineralization situation

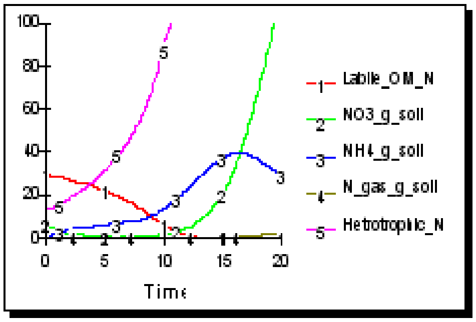

Figure 10 - Detail of Figure 9

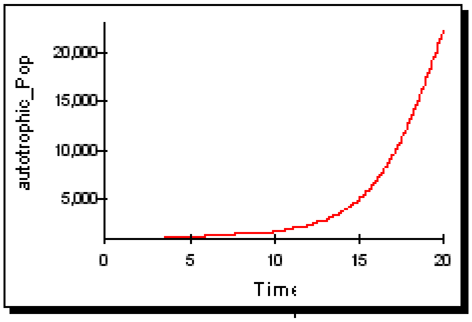

Figure 11 - Autotrophic evolution in mineralization situation

Figure 9 represents a mineralization situation in soil. Galvão (2002) had simulated this too, and the conclusions are the same: population grows because they have enough carbon and they do not need to immobilize nitrogen because the CN ratio of the labile organic matter is low. The new of this simulation is that in fact, mineralization is occurring because CP ratio is 80 which is also a low value and means that biomass does not need to immobilize phosphorus as well. Both nitrate and soluble phosphorus are being produced since there are no immobilization sinks to deplete them. Just like in Galvão (2002), ammonium is, at the beginning, being produced by mineralization (Figure 10), but it is quickly caught by the autotrophic that transforms it into nitrate in nitrification processes to grow up (Figure 11).

For a situation in which CN ratio of the labile organic matter is too high, the bacterial growth will be slower, and in this case, as seen in Galvão (2002) no nitrate is available in soil, because it will be all immobilized (Figure 12). That will lead to the autotrophic death once ammonium is depleted from soil through immobilization and the mineralization is not enough to provide food for them (Figure 13).

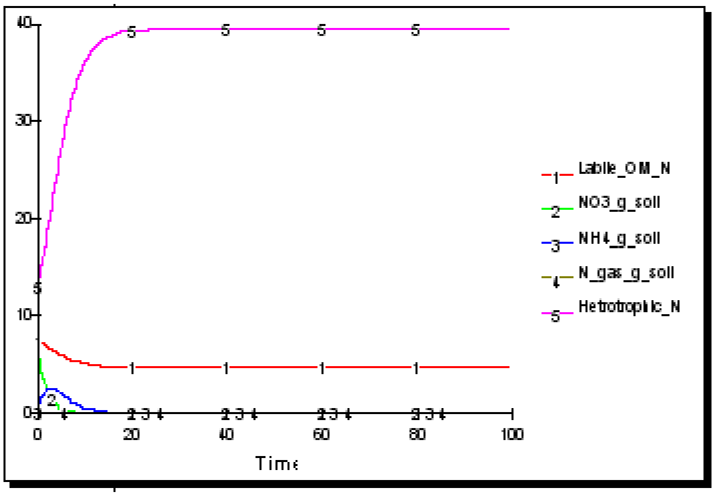

Figure 12 - Nitrogen cycle in immobilization situation

Phosphorus cycle is also affected by this situation. As the mineralization rate is low, soluble phosphorus concentration in soil will also be very low, and mineral phosphorus becomes fixed and unavailable for plants in 60 days (Figure 14).

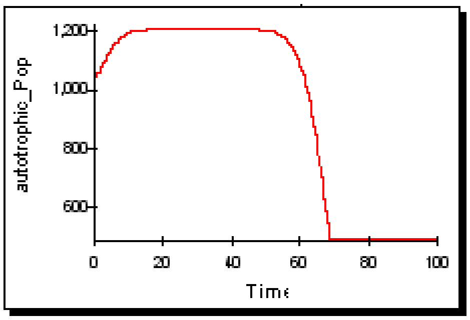

Figure 13 - Autotrophic evolution in immobilization situation

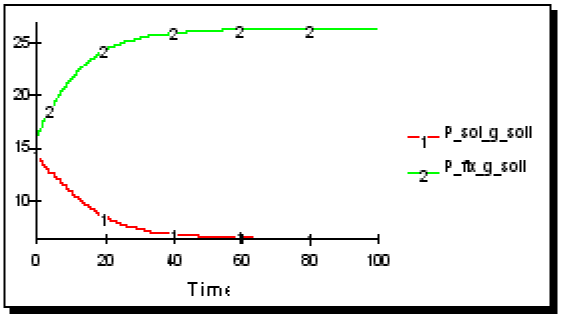

Figure 14 - Phosphorus mineral pools evolution in nitrogen immobilization situation

The next simulation will show a new situation, in which the CN ratio of the organic matter is not limitative, but the CP ratio has a value of 300. In this case, bacteria spend some time immobilizing the soluble phosphorus, growing at a low rate, excreting low concentrations of ammonium and phosphorus. When the CP ratio of the organic matter becomes favorable, biomass is able to grow again at a higher rate as it is shown in Figure 15.

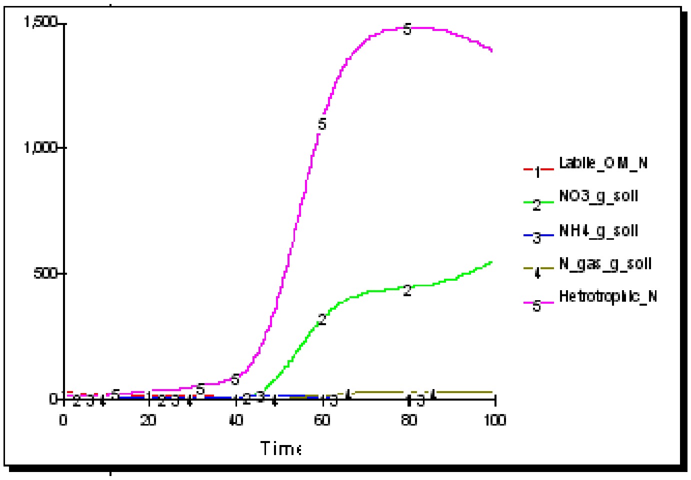

Figure 15 - Nitrogen cycle in phosphorus immobilization situation

Mineral phosphorus shown in Figure 16, is being depleted, because it is being caught for immobilization processes and some part is also fixed. When biomass recovers, this level increases again, but after some time it is fixed.

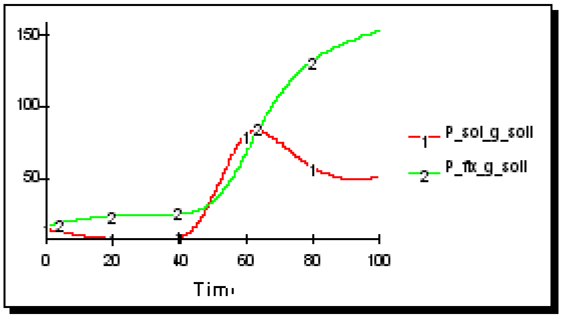

Figure 16 - Phosphorus mineral pools evolution in phosphorus immobilization situation

It’s important also to simulate what happens in an anaerobic situation. Although each simulation has a constant water content value, the fact is that physical and chemical conditions may vary with depth in the soil, such as temperature and water content. This last one may vary with irrigation and rain, which will lead to situations in soil where water content becomes too high and some places become anaerobic.

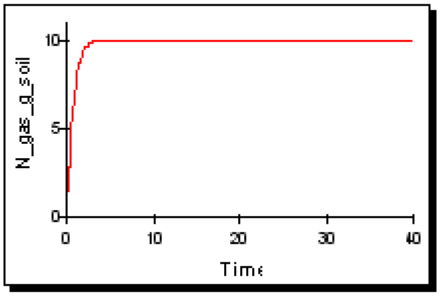

Figure 17 - N gas evolution in anaerobic situation

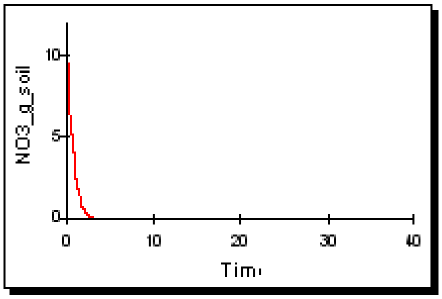

Figure 18 - Nitrate evolution in anaerobic situation

If water content is high enough and nitrate is available to play the role of electron acceptor, then the heterotrophic anaerobic Population is able to grow. In this situation nitrate is depleted, as shown in Figure 18, because it is being consumed and no one is added once there is no nitrification process taking place. From this process, Ngas is also released to the atmosphere - Figure 17. Once again, this simulation had been already done in Galvão (2002) and the results are also similar. With the new additions to the model, phosphorus pools behavior will be watched too. From the mineralization of the organic matter in this anaerobic situation, some ammonium is excreted, but it's not enough to feed autotrophic and, as a consequence, there is no source of nitrate by nitrification, as mentioned before.

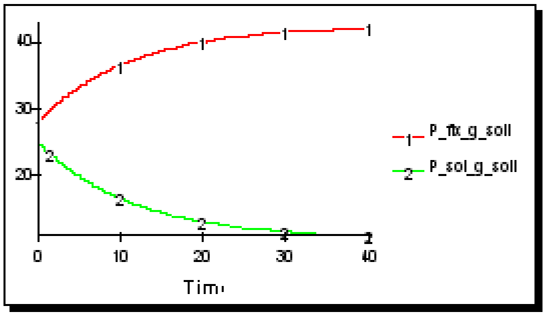

Figure 19 - Phosphorus Mineral pools evolution in anaerobic Situation

Although Mineral soluble phosphorus is not caught for immobilization in this particular simulation, his excretion is very low because anaerobic heterotrophic bacteria are less efficient than the aerobic ones (Figure 19). So, the source of mineral soluble phosphorus by mineralization is not enough and this pool is quickly fixed into mineral fixed phosphorus.

If nitrate is not so abundant in soil, the quick depletion of it, in an anaerobic situation, may lead to a stress condition in which bacteria will excrete methane gas. Under a nitrate value that the model considers too low, nitrate is no longer depleted and bacteria population use carbon dioxide for their needs.

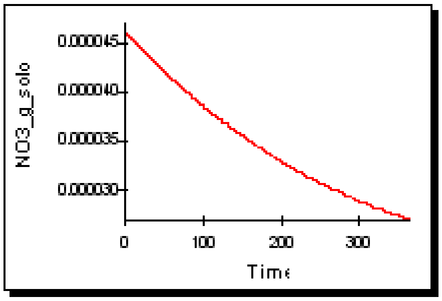

Figure 20 - Nitrate depletion in a stress anaerobic situation

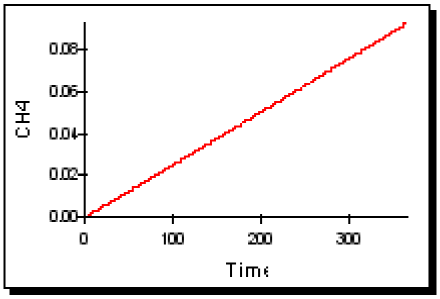

Figure 21 - Methane released in a stress anaerobic situation

Methane gas increases in an anaerobic situation in which nitrate is too low, as shown in Figure 20 and Figure 21.

4th Chapter – Sediment Quality

4.1 - Mohid Land

Mohid land is a sub-model of Mohid in which Drainage network, Overland Flow and Porous Media are modeled (Figure 22). This allows the properties transport in rivers and streams and also the transport through the land and infiltration. According to this, a specific property that reaches the soil, may be transported to the river or be infiltrated.

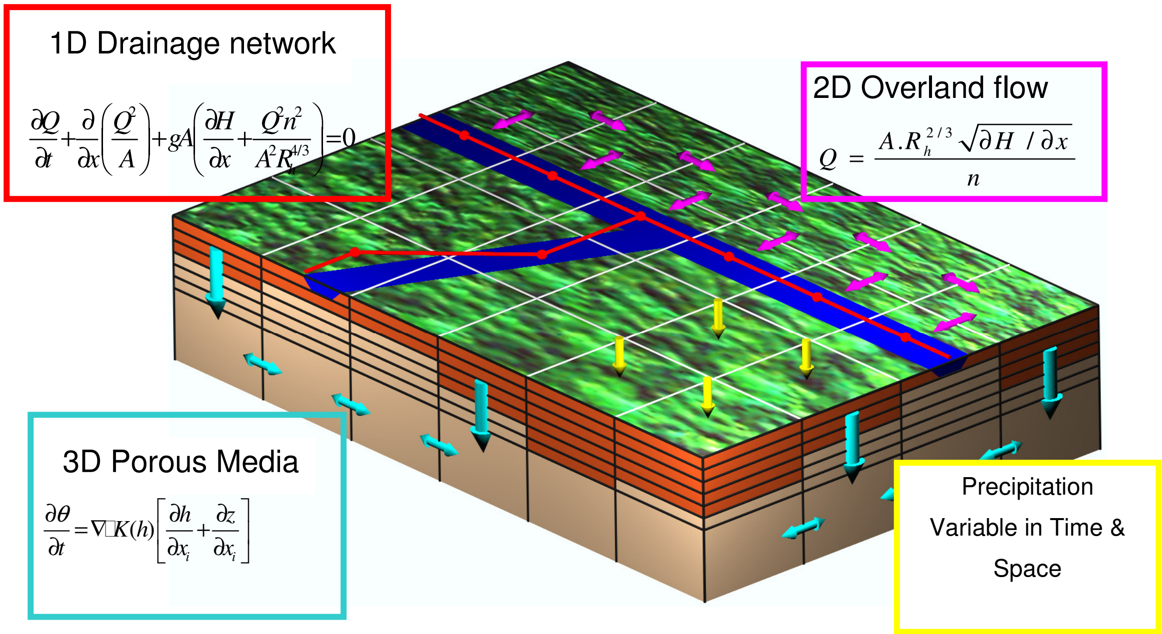

Figure 22 - Mohid Land

Module Drainage Network was developed as a companion module of the catchment model Mohid Land, in order to allow dynamic exchange of water and material carried between the river and the river banks. In normal conditions runoff carries material to the river and during floods the river exports material to the river bank when the level of the water inside the river is higher than on the banks.

Also evapotranspiration is considered in the model as a dynamic boundary condition and is computed as a function of the potential evapotranspiration. Rain is basic data for running the model.

Module PorousMedia describes flow both in the unsaturated (vadoze zone) and saturated zone of groundwater flow.

Flow in the unsaturated zone is described by solving a finite volume model with 3D Richards equation and Vangenuchten retention curves.

Flow in the saturated zone is described solving a finite volume 2D model for the mass balance equations and Darcy law as momentum equation.

Fluid flow is governed by conservation equations for mass, momentum, energy and any additional constituents. The numerical algorithm is based on the finite volume approach and for that reason equations are presented in their integral form. Transport equations are derived directly from conservation principle stated in Equation 42. In case of momentum bottom shear is also deal as diffusive flow.

$$\{AcumulationRate\} = \{FlowIn - FlowOut\}_{Advection} + \{FlowIn - FlowOut\}_{Diffusion} + \{Soures - Sinks\}$$

Equation 42 - Conservation principle

Applying this conservation principle to a generic volume "V" contained into a surface "A" for a generic property with specific (per unit of volume) value *β*, one obtains Equation 43:

$$\frac{\partial}{\partial t}\iiint_V \beta dV + \iint_A \left(\beta\vec{v}.\vec{n}\right)dA = \iint_A \left(\upsilon \cdot \vec{\nabla}\beta\right)\cdot \vec{n} \cdot dA + (\text{Sources - Sinks})$$

Equation 43 - Conservation principle applied to a generic volume

Water properties are described by an advection diffusion equation including a settling term in case of particulate suspended matter. In this case longitudinal diffusion associated to shear diffusion is of the same order of magnitude as advection and has to be considered.

In order to respond to such demands a physical based model, the TempQsim STREAM model, was developed (Galvão *et al*, 2005). This model is currently maintained by Mohid group under the name Mohid River Network (MRN). MRN computes water, sediments and properties transport in a river network. The model is written in Fortran 95 and follows an object oriented programming philosophy with a finite volume approach (Braunschweig *et al*, 2004). The different processes occurring in the river are programmed in different modules. This model has been calibrated for Vène watershed (France) with a special focus on the transport of particulates for the first significant flood events (Obermann, 2007).

An interface between this model and SWAT was also developed in order to simulate agriculture in the catchment using Mohid for simulating the river network and the corresponding sediment transport and biochemistry (Chambel-Leitão *et al*, 2006). SWAT source code was slightly changed so time series of flow / properties are produced for each sub-basin (Chambel-Leitão *et al*, 2007).

The developed module for Organic Matter decomposition – Sediment Quality, may be integrated in this model in order to simulate the properties transport such as nitrate, ammonium and phosphorus into the river and through the soil preventing Eutrophication phenomenons and aquifers contaminations.

4.2 - Sediment Quality Implementation

After the Model Description where are included the new changes and the Preliminary Results - 3rd Chapter – Model Bases Implementation, a Fortran Implementation was made, rebuilding the old existing module- Sediment Quality.

The intention is to have a module able to simulate the main soil processes and then, in a future work, connect this module with a transport model, like Mohid land which will allow the pools variation in space.

For now, Sediment Quality is a zero dimensional tool, which means that variations happen only with time. For each pool is considered an equation with sources and sinks, like Equation 44. An explicit method was used because it has an easier resolution, although it may bring some stability problems (Equation 45). Pools in the time *t+ΔT* are evaluated using the other pools in the time t, which leads to one incognita in each equation. This approach was done before, by Galvão (2002). For this work the new pools and the new processes were added.

$$\frac{\partial\left[NO_3^-\right]}{\partial t} = -K_{IMOB} \times \left[NO_3^-\right] - K_{DES} \times \left[NO_3^-\right] + K_{NIT} \times \left[NH_4^+\right]$$

Equation 44 - Sources and sinks for nitrate pool

If the specific rates become too high during the simulation, stability problems may occur because coefficients become negative. In these cases it should be used a lower ΔT.

$$\left[NO_3^-\right]^{t+\Delta t} = \left[NO_3^-\right]^{t} \cdot \left(1 - \Delta t \times K_{IMOB} - \Delta t \times K_{DES}\right) + \left[NH_4^+\right]^{t} \cdot \left(\Delta t \times K_{NIT}\right)$$

Equation 45 - Explicit method applied to the nitrate pool

After the implementation in Fortran a comparison between these results and the powersim results was made.

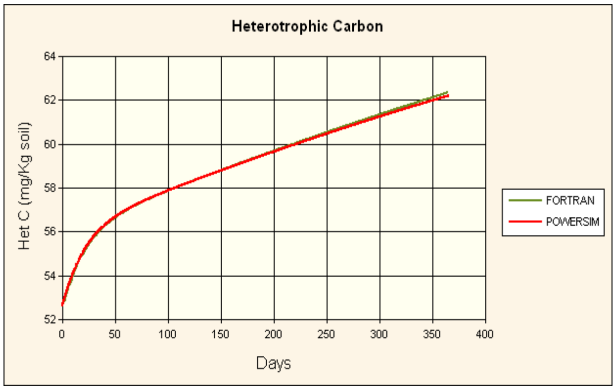

Figure 23 - Sediment Quality - Comparison between PowerSim and Fortran implementation for the ammonium pool

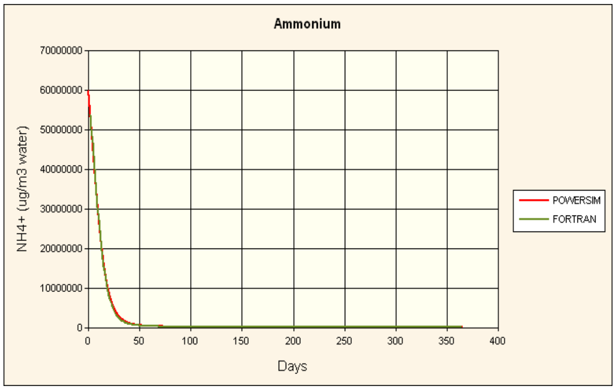

Figure 24 -Sediment Quality - Comparison between PowerSim and Fortran Iimplementation for the heterotrophic pool

Figure 23 and Figure 24 show that the implementation was good and Sediment Quality was making everything that was predictable in the beginning. After PowerSim implementation had been used for detecting conceptual errors, Sediment Quality was able to function, allowing the user to choose inputs more easily.

4.3 - Comparison between Sediment Quality and RZWQM

In the previous points, an implementation of Sediment Quality was made as well as a comparison between Fortran and PowerSim. Now, the module needs validation in order to become consistent and to produce acceptable results. This is very important, because during the modelling some parameters were unknown and may need some calibration. Confronting the model with experimental results should be the best option. Nevertheless, that was not possible because the Sediment Quality model is Zero dimensional, which does not allow hydrodynamic situations for now.

So, as the module was almost all based in RZWQM model, which is a referenced model for agriculture with good results observed, it was tested a comparison with the original model.

RZWQM (2.2 - The Existing Models), allows the user to simulate a lot of situations, having a very extensive input data, but for a comparison with Sediment Quality, RZWQM code was rebuilt and a Zero Dimensional version was specially created.

For this comparison some agreements were made like the adoption efficiencies RZWQM values for biomass population as well as the adoption of processes coefficients values. Other change was related with the RZWQM humus pools initialization with the zero value. As seen before, this model has 5 pools of organic matter and in order to obtain the same situations, some pools were “disable”.

The next graphic shows the variation in time of the fast decay organic matter pool in a situation of mineralization. The models coincide during all the time of simulation. To have the same results also the coefficients in 3.3.2 - Specific Rates were the same.

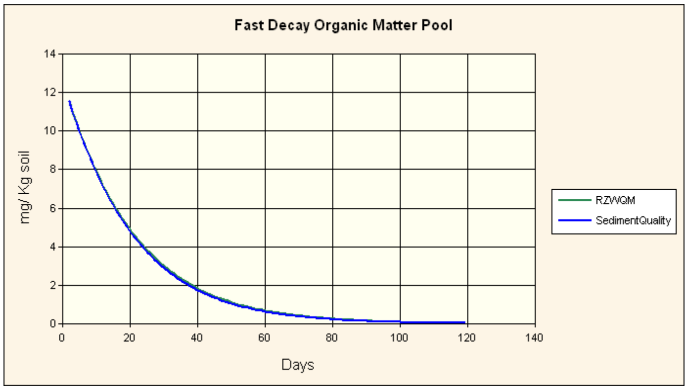

Figure 25 - Comparison between Sediment Quality and RZWQM for the fast decay organic matter pool

The pools tested were referring to organic matter with fast and slow decay and also to the three populations involved in the process as well as to the levels of nitrate and ammonium. The Organic Matter pool with fast decay coincided in both models (Figure 25) as well as the organic matter pool with slow decay; the same happen with Autotrophic population which performs the nitrification process in which nitrate is excreted as shown in Figure 26.

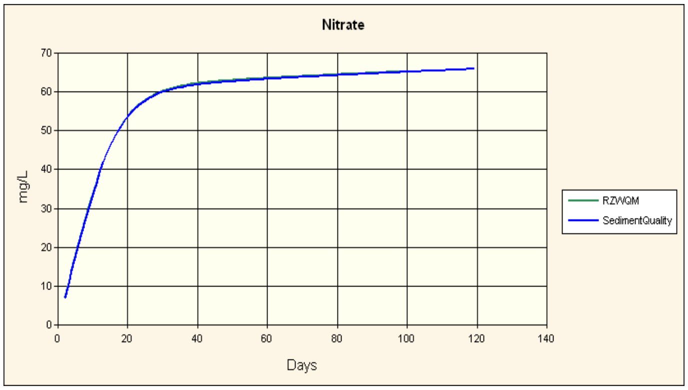

Figure 26 - Comparison between Sediment Quality and RZWQM for the nitrate pool

The results about the anaerobic heterotrophic population biomass were not identical because models are conceptually different. In fact, the RZWQM simulates anaerobic population as being facultative but in the Sediment Quality this population is strict. That means that in Sediment Quality anaerobic population grows just in the presence of high levels of water content (no oxygen) and available nitrate or carbon dioxide playing the role of electron acceptor instead of oxygen. In the RZWQM, there is always an aerobic part of this population, which allows them to grow as if they were heterotrophic aerobic Biomass.

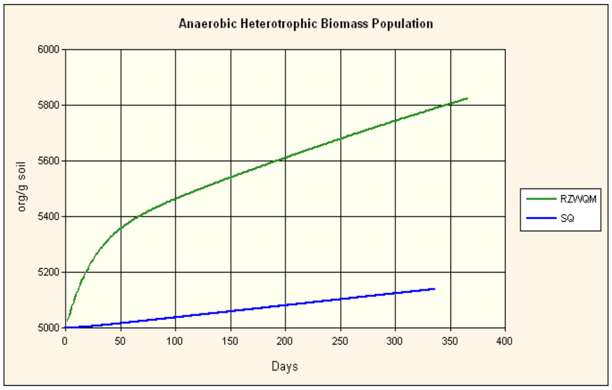

Figure 27 - Comparison between RZWQM and Sediment Quality for the heterotrophic aerobic biomass population

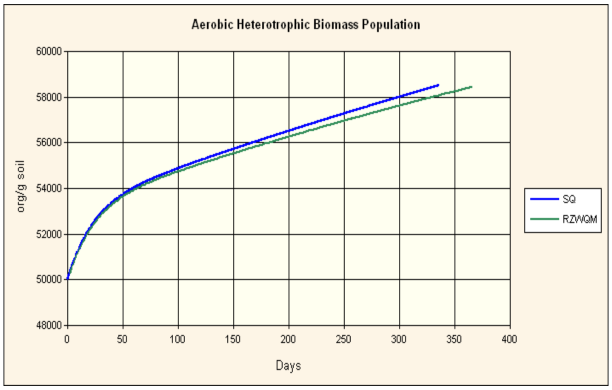

Figure 28 - Comparison between RZWQM and Sediment Quality for the heterotrophic anaerobic biomass population

In Figure 27 and Figure 28 it's shown the difference between the models. As the situation tested was aerobic, in Sediment Quality the anaerobic population is lower than in the RZWQM. In this last model, some parts of these anaerobic microorganisms are behaving as aerobic and that is why the graphic of Figure 27 does not coincide completely. For RZWQM model, some of the aerobic are counted as facultative and so the total heterotrophic aerobic is lower than in Sediment Quality. This may lead to different results in aerobic situations in a first approach. But, as the aerobic part of the facultative in the RZWQM is depleted from the aerobic heterotrophic population, the total biomass that is decaying the organic matter in aerobic conditions is the same in both models. This fact is corroborated by the organic matter graphics, which coincide in both models (Figure 25).

An immobilization situation was also tested. Nevertheless, this immobilization is referring just to nitrogen once the RZWQM is only able to simulate carbon and nitrogen organic matter pools. Changing the CN ratio of the fast decay organic matter from 20 to 80 in both models and with a lower ammonium concentration, some differences were observed. That happens because the immobilization implementation in both models is different.

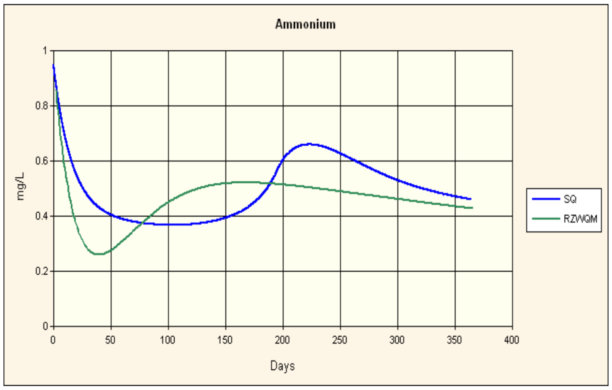

Figure 29 - Comparison between RZWQM and Sediment Quality for the ammonium in immobilization situation

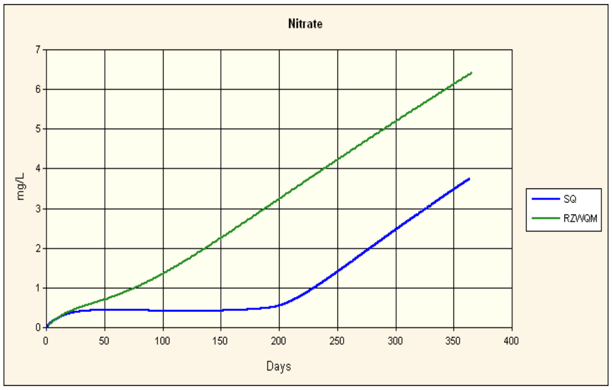

Figure 30 - Comparison between RZWQM and Sediment Quality for the nitrate in immobilization situation

The difference between the models shown in Figure 29 and Figure 30, is related with immobilization limit definition. As seen in 3.3.1 - Flow Equations , nitrogen immobilization will happen if Equation 13 is verified. Nevertheless the type of immobilization is given by Equation 15, where the potential decay rate is compared with the ammonium and nitrate potential immobilization rate, and where is defined which one is the limiting one.

RZWQM also compares CN ratios to see if immobilization is taking place, but the difference is that none nitrate or ammonium potential exist. Model equations make sure that, for the specific immobilization needs of biomass, enough mineral nitrogen is available, like in Equation 46.

$$P_L\left(\frac{1}{CN_{lhet}}-\frac{1}{CN_{lab}}\right)>\left[NH_4^+\right]+\left[NO_3^-\right]$$

Equation 46 - RZWQM immobilization equation

In fact, RZWQM is even more particular, because nitrate immobilization happens just if enough ammonium is available in the soil, which may be observed in Figure 30. While in the beginning in Sediment Quality nitrate is being immobilized, in RZWQM just ammonium was immobilized.

The Sediment Quality approach is more realistic in theory because it compares the mineralization with the immobilization potential in order to decide the immobilization type. This leads to a problem that is connected with the lack of information for immobilization coefficients that are needed for specific rates as seen in Equation 36. Future work will include the comparison of these simulations with fields data to know which is the best option, and at the same time for calibration of immobilization potential coefficients.

4.4 - Sediment Quality Simulations

Although this module is only able to simulate organic matter in soil, without the atmosphere interaction or any crops existing, some important tests may be done.

In 3.4 - Preliminary Results in PowerSim, preliminary results were observed for different CN and CP substrate ratios. In this sub-chapter some tests with Sediment Quality were done changing the environment: temperature, pH, soil porosity, water content and wind.

These tests are important because chemical, physical and biological characteristics of the microhabitats in soil differ in both time and space in soil (Nannipieri *et al*, 2003). Although these tests may be done later in 3 Dimensions, they can be very useful to understand in a first stage how biomass is affected by the environment.

4.4.1 - Soil Temperature Variations

Theoretically, there should be an optimal temperature at which a biological process has a maximum rate (with other environmental factors being constant). This optimum for soil respiration may also depend on the temperature regime of the soil, because of the physiological adaptation of the organisms to their habitat (Fang and MonCrieff, 2001). The next simulations with temperature variations were made for the constant parameters described in Table 9.

Table 9 - Input parameters for the simulation of temperature variations

pH	7.0
Water content (m^3water/m^3soil)	0.3
Soil type	Loam (ρ=1423 Kg/m^3)
Porosity	0.463
Effective Water Content (θF)	64.8%
f_{aer}	0.716
f_{ana}	$5.9\text{x}10^{-2}$

Two conclusions are taken from Figure 31 and Figure 32. In fact, populations have a specific optimum temperature for which growth is the highest; and the response to these temperature variations is different for each population. The optimal temperature is around 30ºC which is consistent with values from MetCalf & Eddy (1978) who said that for *mesofilic* bacteria ideal temperature is 20-40ºC. At lower temperature values, bacteria tend to have a very soft growth. Predictably, if any other restriction of the system is on, they will not be able to survive.

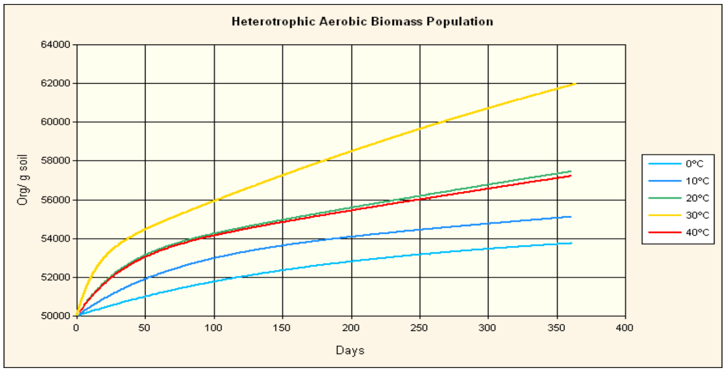

Figure 31 - Temperature influence in the heterotrophic growth

Autotrophic bacteria have the same optimal temperature, but as it is shown in Figure 32, growth may be very different in the first 50 days. For the optimal temperature this growth is very quickly but for 0ºC the growth is constant during the time of simulation. These differences may have important results in the way how nutrients are depleted in the soil.

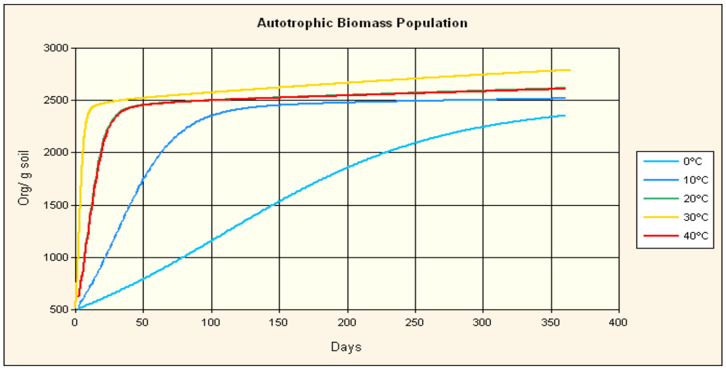

Figure 32 - Temperature influence in the autotrophic growth

If the optimal temperature is reached in the soil, autotrophic will have a great environment to develop nitrification process and ammonium will be quickly depleted, increasing the nitrate level. If some immobilization is occurring the fight between these two populations may be dependent as well on temperature

Literature suggests that soil moisture may affect the magnitude of soil temperature device to the interaction between soil moisture and soil temperature. It is reported that for soil respiration, activation energy may decrease from 84.9 to 39.5 kJ mol^{-1} when a desert soil was wetted (Fang and MonCrieff, 2001).

4.4.2 - Soil pH Variations

The results about pH show in Figure 33 and Figure 34 that biomass has, as it was expected an optimal pH which is 7.0. Nevertheless the biomass behavior is different for pH above and below neutral. According to the model the microorganisms are growing with a higher rate in the acid environments than in the basic ones.

Table 10 - Input parameters for the simulation of pH variations

Temperature (ºC)	20
Water content (m^3water/m^3soil)	0.3
Soil type	Loam (ρ=1423Kg/m3)
Porosity	0.463
Effective Water Content (θF)	64.8%
f_{aer}	0.716
f_{ana}	$5.9\text{x}10^{-2}$

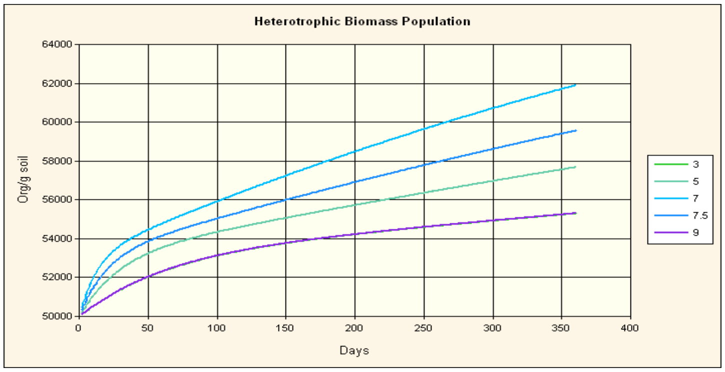

Figure 33 - pH influence in the heterotrophic growth

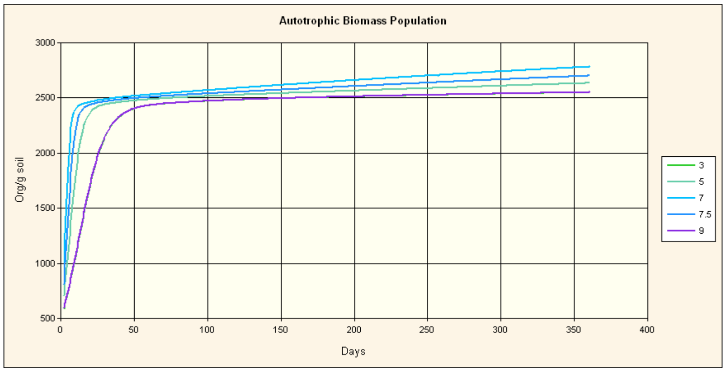

Figure 34 - pH Influence in the autotrophic growth

Biomass shows a very good response to their optimal environment, as it can be seen in the graphics, for pH 7.

The process of ammonia volatilization was already discussed in *3.3.1.5 - Urea Hydrolysis and Ammonia* . Now, it can be seen the differences in the NH_3 released for different pH values. Although this simulation is being done only with time variation, it can be assumed that this simulation in particular is happening in the surface layer, where this phenomenon is more important. This particular situation was simulated for temperature of 10ºC.

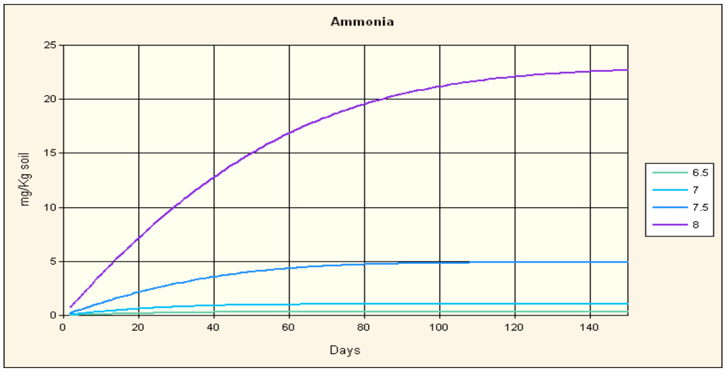

Figure 35 - pH Influence in the ammonia volatilization

As pH is one of the essential parameters that affects this process, these differences in NH_3 released to the atmosphere are expected (Figure 35). It can be seen that for pH 8, a significant amount of ammonia is released. In other way, for pH values lower than 7, this process has no influence in the soil ammonium transformations.

4.4.3 - Effective Water Content Variations

Effective Water Content is given by Equation 41 and so it may vary with the soil water content or with the soil porosity that may be related with the soil type. Both tests were made in order to conclude about this parameters effect in aerobic and anaerobic factor that may also influence the specific rates as the one in Equation 36.

- Soil Porosity Variations

If soil is more porous it will mean that there is more available space for oxygen, leading to an aerobic environment. Different porosity values were tested, related with different soils in this simulation. To simplify the soil characterization,, Pedo-transferences functions from the RZWQM assumed a relationship between the soil type and its porosity. Next tests were made for these porosities (Table 12)

Table 11 - Input parameters for the simulation of soil porosities variations

Temperature (ºC)	20
Water content (m^3water/m^3soil)	0.3
pH	7

Table 12 - Aerobic and anaerobic factors for the different soil types

Soil type	ρ (g/cm3)	Porosity	θ_F	f_{aer}	f_{ana}
Sand	1492	0.437	68.6%	0.563	8.18×10^{-2}
Loam	1423	0.463	64.8%	0.716	5.97×10^{-2}
Clay	1391	0.475	63.15%	0.794	5.22×10^{-2}
Silt	1322	0.501	59.9%	0.975	1.00×10^{-5}

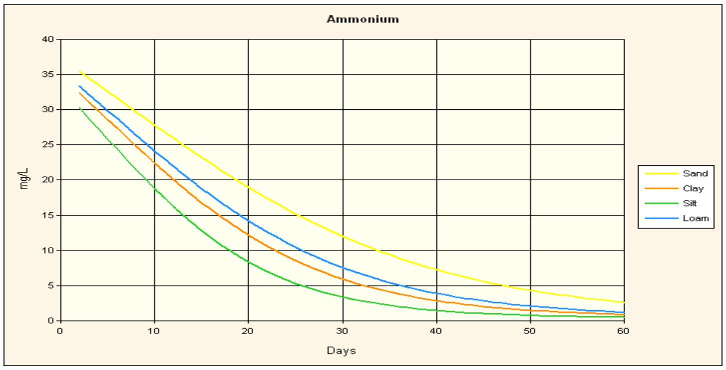

Figure 36 - Effects of the soil type in the ammonium depletion

Figure 36 shows that Sandy soil has an effective water content that provides less aerobic situations, because ammonium is depleted in the softest way. That makes sense, because sand soils have a higher density and as a consequence, less porosity. For the same value of water content, the “holes” are more easily filled and less oxygen is available. The opposite happens with silty soils that have lower densities values and higher porosity. In this case oxygen becomes more available for biomass. In this specific case, it can be concluded that in silty soils, autotrophic have a more aerobic environment and, as a consequence, they deplete ammonium more quickly than in sandy, loam or clay soils. For each soil, the aerobic and anaerobic factors calculated by the model are shown.

- Water Content Variations

Soil Moisture is an important factor across a range of environmental processes, including plant growth, soil biogeochemistry, erosion and land-atmosphere heat and water exchange (Lobell *et al*, 2002).

Table 13 - Input parameters for the simulation of water content variations

Temperature (ºC)	20
Soil type	LOAM
pH	7

Table 14 - Aerobic and anaerobic factors considered for the different water content values

WC (m^3/m^3)	**θ_F**	f_{aer}	f_{ana}
0.15	32.40%	0.405	$1x10^{-5}$
0.2	43.19%	0.6238	110^{-5}
0.3	64.8%	0.7164	$5.97x10^{-2}$
0.35	75.6%	0.3647	0.1440
0.45	97.2%	9.46E-2	0.8372

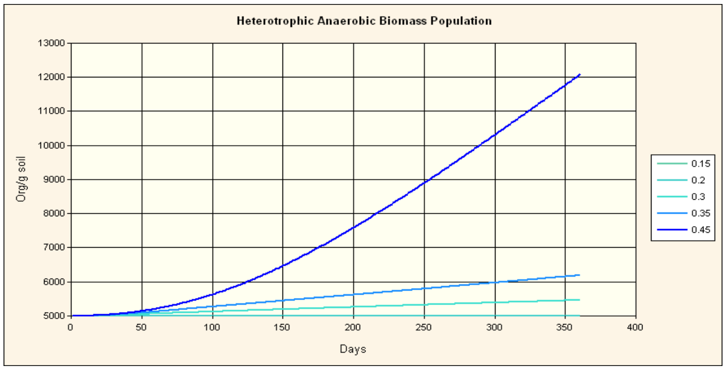

Figure 37 - Effect of water content in the anaerobic growth

In these simulations, the soil type was always loam, but the water content was different from one simulation to another (Table 14). As mentioned before, water content in real situations will vary in the soil, with time and with the space.

For one hand, the water that arrives to the soil comes from rain, which is not homogenous in time; or from irrigation that provides high levels of water content in very specific periods. For the other hand, water content will not be the same for different depths; soil type plays an important role too because of the partition between infiltration and runoff. Different water contents will provide different types of population because of the creation of aerobic or anaerobic environment. It can help to understand what could happen, for example, after an irrigation period.

As it can be seen, in Figure 37, for water content value of 0.35 m^3/m^3 a shy anaerobic population is growing. But, at water content value of 0.45 $m^3/m^{3,}$ this population has an increase that may be interesting, because if this population is present, depletion of nitrate may occur, and organic matter decaying is much more inefficient

High values of water content leads to anaerobic situations in which anaerobic population grows consuming nitrate to their respiration. In the agriculture, this occurance is very important because nitrate can be lost and it is not caught by crops. Nevertheless it is important to predict these situations, because nitrate is not used by plants, even though it will not be leached, contributing for water lines pollution.

It can be seen, in the Figure 38 that, although anaerobic environments factors are increasing with water content, some aerobic processes are still having place. In all simulations, nitrate is increasing because autotrophic are catching ammonium and transforming it into nitrate. For 0.45 m^3/m^3 water content value, this increase is softer because aerobic environment is more restricted. For this last situation, the aerobic environment is not enough to provide nitrate and at the same time there are enough conditions for the anaerobic populations to grow and consume nitrate in the denitrification process. This growth is so important that nitrate is being depleted from soil.

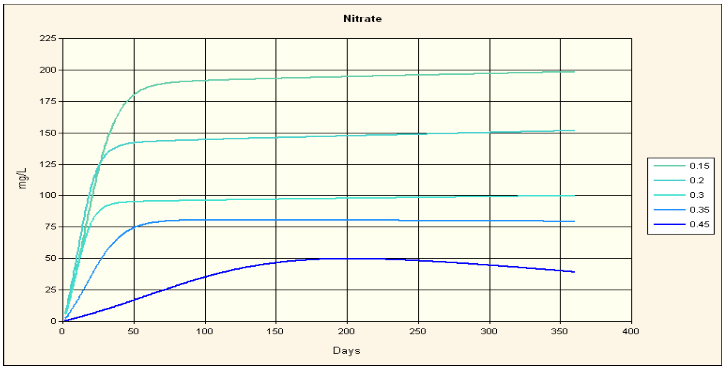

Figure 38 - Effect of water content in the nitrate

The same is expectable with the N gas in Figure 39. The only source of this gas is the denitrification process and so, if anaerobic population is consuming nitrate, some part of the nitrogen will be transferred into the N gas form and will be released to the atmosphere. Once more, at 0.45 m^3/m^3 water content value this increase is significant.

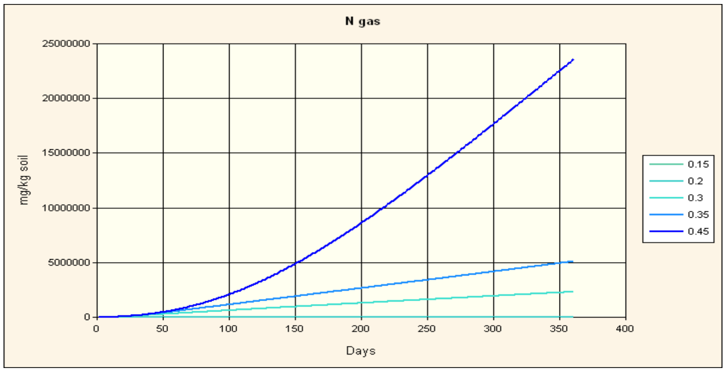

Figure 39 - Effect of water content in the Ngas released to the atmosphere

4.4.4 - Wind Variations

This is not a soil parameter, but it is interesting to observe its influence in ammonia volatilization, once it was said in 3.3.1.5 - Urea Hydrolysis and Ammonia that wind might affect this process.

Table 15 - Input parameters for the simulation of wind variations

Temperature	20
Soil type	LOAM
pH	7

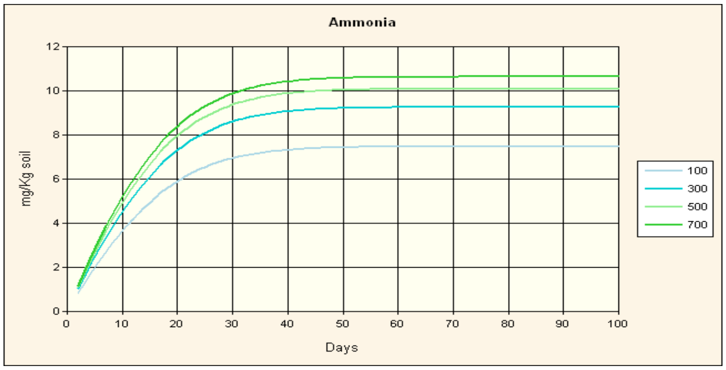

Figure 40 - Effect of wind (km/day) in the ammonia volatilization

Ammonia volatilization shown in Figure 40 is a process that happens at the surface, dependent on chemical reactions. It may be concluded with these simulations, that the wind velocity increases this process, and so ammonium will be more easily depleted from soil in this situation.

5th Chapter – RZWQM Application

5.1 - Project Description

RZWQM (Root Zone Water Quality model) is used all over the world to simulate water movement, nutrients and pesticides over and through the root zone, being primarily a one-dimensional model designed to simulate conditions at a representative point in a field. It has six subsystems that define the simulation program: physical, plant growth, soil chemical, nutrient, pesticide and management processes (Kulmar *et al*, 1999).

The aim of this part of the work is to get a global view of the integrated processes between plant-soil-atmosphere and simulate the impact of nitrogen fertilization in Agriculture. RZWQM simulations were compared with fields data from project Agro 727. In this project, a corn planting was made in Alvalade-Sado under different conditions of nitrogen fertilization and salinity. The purpose of the project was to study the influence of both fertilization and salinity in corn production.

The field was divided into 16 blocks with specific fertilization and salinity (Figure 41). In this Chapter, RZWQM will be used to simulate corn growth during 2 years (2004-2006) in the block where fertilization and salinity had the highest value (A1). In order to have solid conclusions, a global view of the input data is shown in the next sub-chapter.

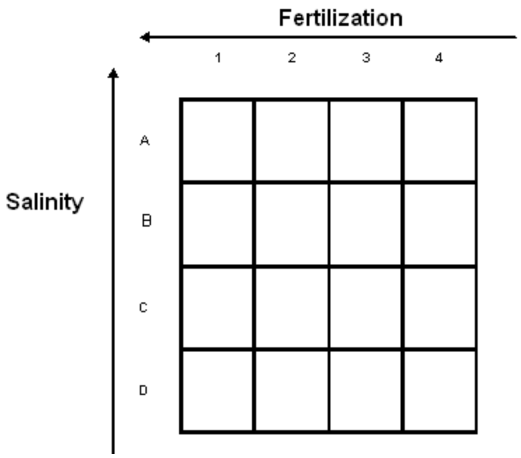

Figure 41 - Agro 727 project field

Future work would include simulating all the situations and comparing them with the fields data. There are not available data for every situation, which increases the advantage in simulating with the RZWQM in order to have conclusions about this issue.

5.2 - Input Data

5.2.1 - Meteorological Data

RZWQM uses temperature, wind and radiation in every day of the year, because these parameters will affect the plant growth, such as the optimal conditions for biomass and water content. This becomes obvious because crop growths are not the same all around the world. Meteorological parameters affect in a strong way agriculture and as a consequence the processes in the soil.

Portugal has a very characteristic weather, resulting from the geographical position and from the sea presence. Input data are shown in Figure 42, Figure 43 and
Figure 44:

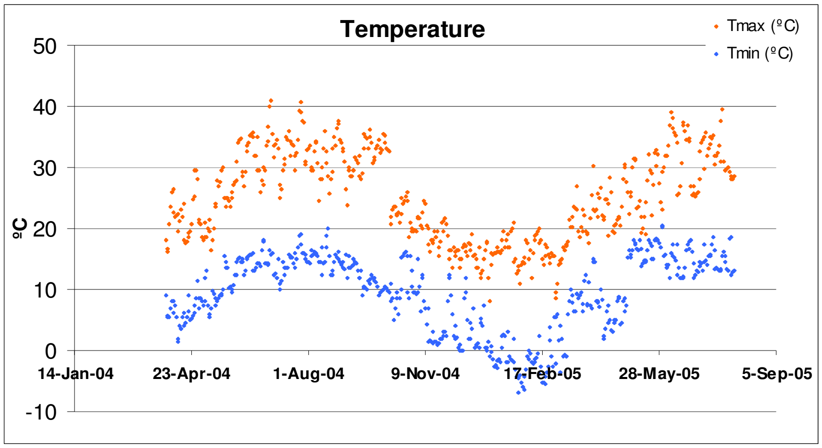

Figure 42 - Temperature input data

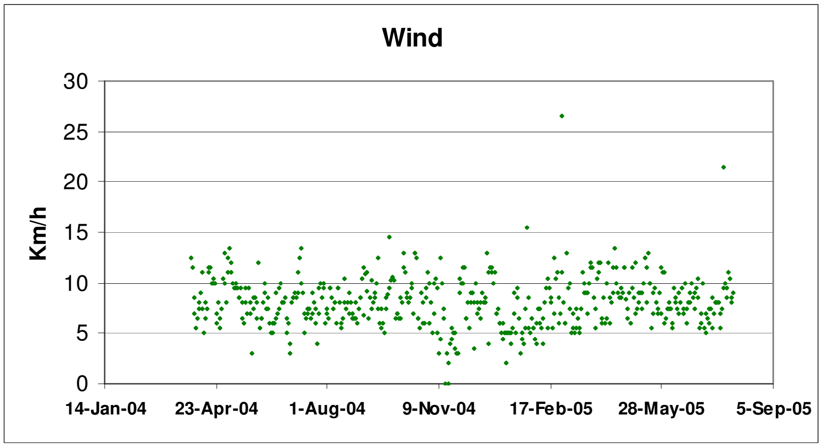

Figure 43 - Wind input data

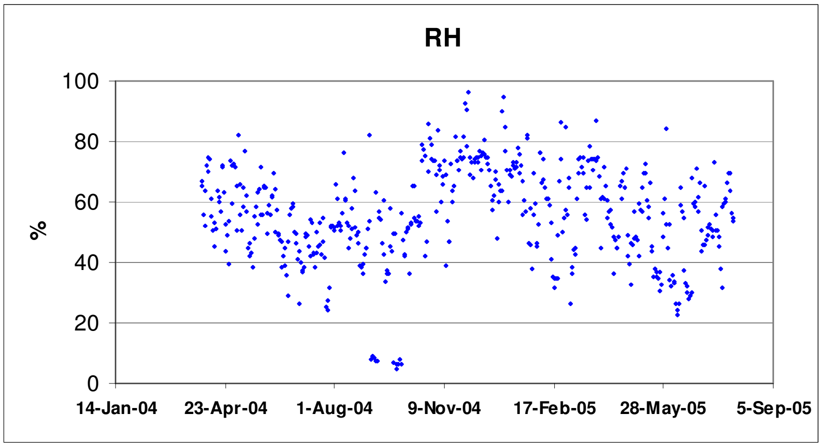

Figure 44 - Relative humidity input data

Temperature variations are typical of Portugal weather, with higher values in summer (June-September) and lower in winter (December-March). Wind variations were very homogeneous in this period with most of the values of the year between 5 and 10 km/h.

The model needed as well radiation values (MJ/m^{2}·day) which were not directly measured, but were calculated considerating that total radiation results from diffuse and direct radion at the surface. Sun hours were also, needed:

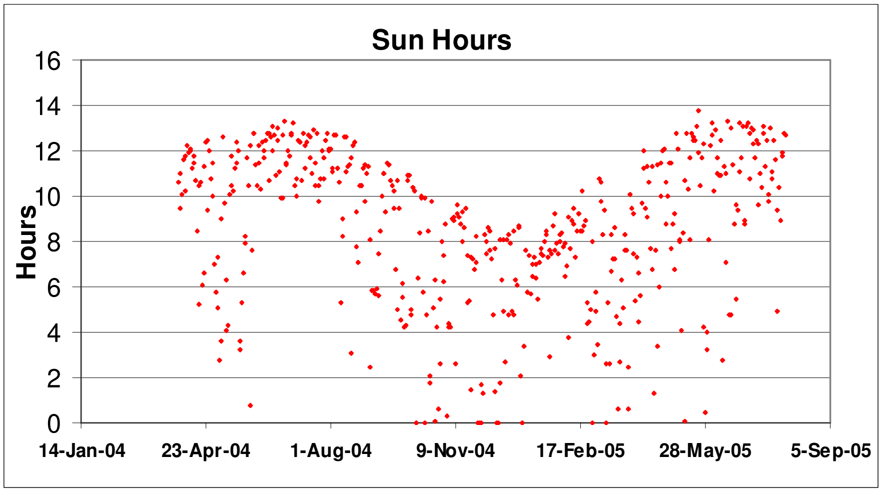

Figure 45 - Sun hours during the simulation time

The last parameter needed by the model was Evapotranspiration. According to Gonçalves *et al*, (2006) the potential evapotranspiration rate was calculated with the Penman-Monteith method, using meteorological values from the metereological station located 10 m from the experimental field (Figure 46).

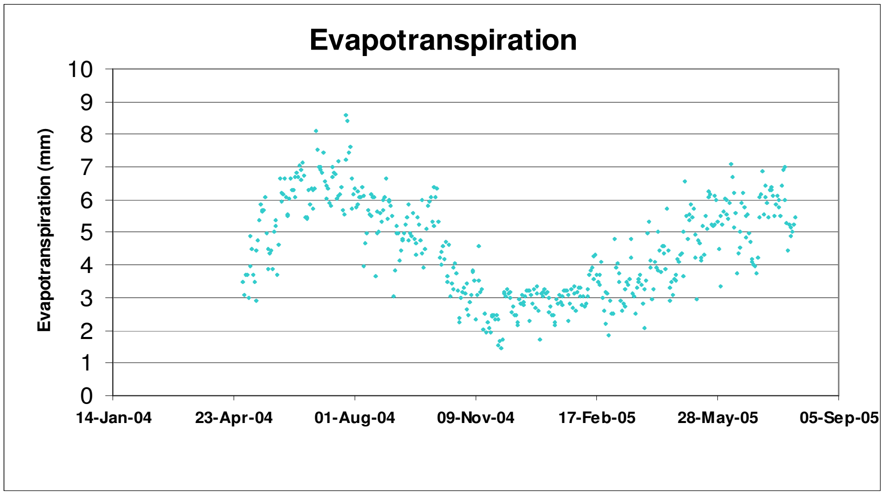

Figure 46 - Evapotranspiration input data

5.2.2 - Rain Data

This is another parameter with a lot of meaning in agriculture in plant growth. Although plants may have different water needs, it is always a stress factor that may determine the plant type. In the soil processes, water will be very important too, because the aerobic and anaerobic processes will depended on the water content and as a consequence nitrate and ammonia availability may vary too.

Data used include the precipitation values (daily) for the time of the simulations:

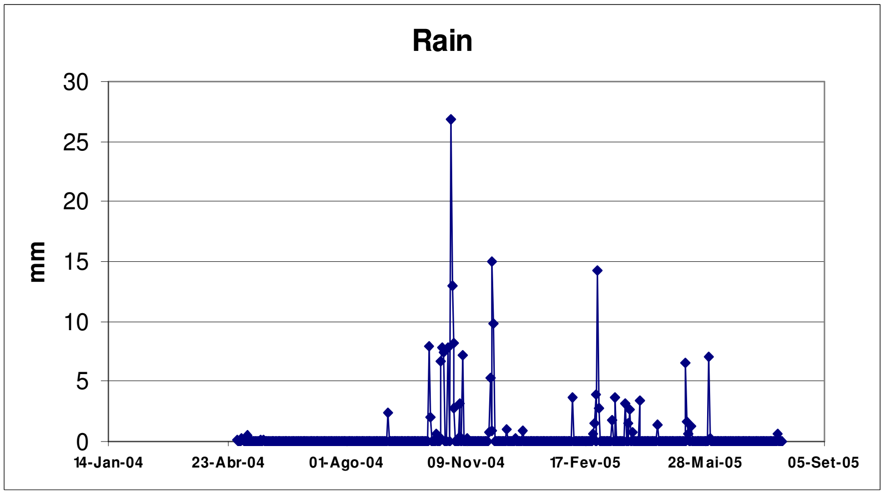

Figure 47 - Rain input data

The model used horary rain values, but the available data just has the daily values (Figure 47). This fact was a limitation of the input data. The highest precipitation event occurred in autumn and others occurred also in winter of 2005. Values are logical for Portugal weather but, in a general way, it was a period with low rain.

5.2.3 - Soil Input Data

The next input is referred to the soil properties such as soil type, and its hydraulic, physic and chemical characteristics.

The soil profile is shown in Table 16 (Gonçalves *et al*, 2006) and the Soil hydraulic properties in Table 17 and Table 18.

Table 16 - Soil profile input data

Soil type	Depth (cm)	Layer	Particle Density(g/cm3)	Bulk Density (g/cm3)	Porosity
Silty loam	30	1	2.650	1.49	0.4377
Silty loam	75	2	2.650	1.51	0.4302
Loam	165	3	2.650	1.61	0.3925

Table 17 - Conductivity curve parameters

	0-30 cm	30-75 cm	75-165 cm
S1	1.530809	1.436503	0.868759344
C1	14.97	93.70	13.69
N1	1.063325	1.47	0.81
C2	102.2568	12.80134	16.52635882
N2	1.497122	1.284656	1.220693476

Table 18 - Water Content curve parameters

	0-30 cm	30-75 cm	75-165 cm
θs	0.421522	0.41302	0.418453532
θr	0.001	0.015	0.027
A1	0.001409	0.002722	0.000923106
S2	1.694875	1.438926	2.06649816
A2	0.159003	0.125292	0.15507975

Table 17 and Table 18 summarize the Brooks and Corey used parameters for the model hydrodynamic. These parameters were calculated from the available laboratory data: the conductivity curve parameters relates the matric suction head with the unsaturated hydraulic conductivity and the water content curve relates the matric suction head with the soil water content

Chemical soil properties were also needed. There were available data, but just for the main ions like sodium, calcium magnesium (measured by atomic absorption spectrophotometry) and chlorine (measured by potentiometry). The other ions values were adopted from the RZWQM default values. The fraction of exchangeable ions was obtained with the modified Melich method.

Table 19 and Table 20 summarize the main chemical properties taken from the project data bases of the Agro 727.

Table 19 - Soil chemistry input data: fraction of exchangeable ions

Layer	**pH**	**Ca^{2+}**	**Na^{+}**	**Mg^{2+}**	**NH_4^{+}**	**Al^{+3}**
1	7	0.924	0.86	0.94	0	0
2	7	0.934	0.77	0.92	0	0
3	7	0.960	0.78	0.95	0	0

Table 20 - Soil chemistry input data:ions concentrations

Layer	**Ca^{2+} µg/g soil**	**Na^{+} µg/g soil**	**Mg^{2+} µg/g soil**	**Cl^{-} µg/g soil**	**HCO_3^{-} µg/g soil**	**SO_4^{2-} µg/g soil**
1	27.00	108.10	14.46	3.207	209.7	2.976
2	42.60	110.40	19.44	2.978	219	2.976
3	30.00	66.70	14.09	2.975	192	2.924

5.2.4 - Organic Matter and Nitrogen Data

Organic matter pools are very important because mineralization and nitrification process may increase ammonium and nitrate concentrations in soil. Also nitrate and ammonium initial levels may play interesting roles, because without fertilizer, plant may be in a stress situation.

RZWQM has different organic matter pools: Organic Residue in the soil, Humus Organic Matter and Biomass. Available data was values for total organic carbon (measured by Potassium dichromate oxidation method) that included all of these pools. The Humus pools were distributed in fast plus medium decomposition and slow decomposition with a percentage of 20-80%. Then the first pool, choosing the option Without Manure, was distributed in Fast and Medium decomposition with a percentage of 10-90% (Table 21). These values were taken from Cameira (1999).

The input is shown in Table 22. For the first layer, it was adopted the values for 0-20 cm, for the second an average between the 20-40 cm values and the 40-60 cm values, and for the last layer, values from 40-60 cm were used

Table 21 - Data bases values for organic matter

Depth(cm)	Organic Carbon	C slow (µgC/g)		C fast + medium	
0 - 20	11770.00	80% of Org Carb	8565.05	20% of Org Carb	2141.26
20 - 40	11160.00	80% of Org Carb	8085.05	20% of Org Carb	2021.26
40 - 60	21300.00	80% of Org Carb	16997.43	20% of Org Carb	4249.36

Depth(cm)	C medium (µg/g)		C fast (µg/g)	
0 - 20	90% of C fast + medium	1927.14	10% of C fast + medium	214.13
20 - 40	90% of C fast + medium	1819.14	10% of C fast + medium	202.13
40 - 60	90% of C fast + medium	3824.42	10% of C fast + medium	424.94

Table 22 - Organic matter input values

Layer	C slow (µgC/g)	C medium (µgC/g)	C fast (µgC/g)
1	8565.05	1927.14	214.13
2	8085.05	1819.14	202.13
3	16997.43	3824.42	424.94

For the biomass population input, a calibration was made in order to adopt the best values for these pools that are very difficult to measure. The first values used, like in Cameira (1999), were the population initial values of the RZWQM. After that, some simulations were made to correct the results.So, the size of the three populations changed based on the evaluation if it was too much or less mineralization and nitrification during the simulations.Table 23 shows the initial values of these populations after calibration.

Table 23 - Soil biomass input data

	Het(org)	Het (µgC/g)
0 – 20 cm	1000000	1052.63
20 – 40 cm	1000000	1052.63
40 – 60 cm	50000	52.63

	Auto (org)	Auto (µgC/g)
0 – 20 cm	100000	10.53
20 – 40 cm	5000	0.53
40 – 60 cm	500	0.05

	Ana (Org)	Ana (µg/g)
0 – 20 cm	5000	0.53
20 – 40 cm	5000	0.53
40 – 60 cm	5000	0.53

The conversion between organisms and carbon content was made with the RZWQM values: 950 org/µg C for aerobic heterotrophic and 9500 org/µg C for both autotrophic and heterotrophic anaerobic population.

Organic matter CN ratio used was the RZWQM default value. For humus pools, values of data available used are in the Table 24.

Table 24 - Soil CN ratio for the organic matter input data

	CN
Transition soil humus pool	8
Stable soil humus pool	10
Fast soil humus pool	11
Aerobic heterotrophic pool	8
Anaerobic heterotrophic Pool	8
Autotrophic Pool	8

Nitrogen and ammonium initial values were measured from a soil sample, and were used in initial input values:

Table 25 - NO_3^- and NH_4^+ Initial Values by layer Input

Layer	**NO_3^- (µg /g soil)**	**NH_4^+ (µg /g soil)**
1	7.28	$5x10^{-5}$
2	5.09	$5x10^{-5}$
3	2.65	$5x10^{-5}$

5.2.5 - Irrigation Data

As a consequence of plants water needs, irrigation in summer must be provided to make sure enough water is available. This will influence the water content in a short period and also in the nitrate and ammonia concentrations.

Irrigation will be different in each block. Although the water is the same, in every block the salt and fertilizer applied is not. Global irrigation (Drip) is shown in Figure 48 and Figure 49, from project databases of Agro 727. Each point represented, is an irrigation event.

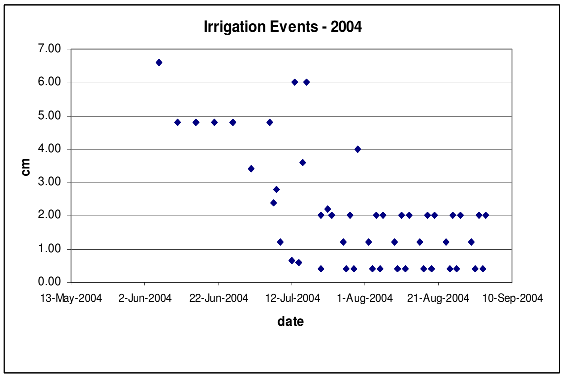

Figure 48 - Irrigation events - 2004

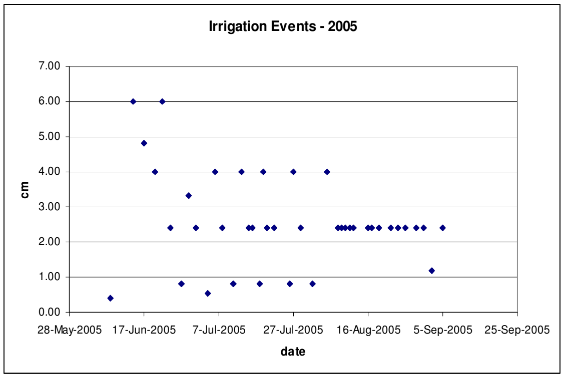

Figure 49 - Irrigation events - 2005

Fertilization was added to the field in the Irrigation Water. That means, that in some irrigation events, nitrogen fertilizer was added (Table 26).

Other important input data was the irrigation water salinity, which is shown in Table 27 (Gonçalves *et al*, 2006). This may affect soil ion concentrations and consequently the behavior of certain pools like nitrate or ammonium, or even affect the biomass growth conditions. Nevertheless this impact was not evaluated here, once the present simulation was done just for the first block, A1.

Table 26 - Fertilization input data

Fertilization Date	Fertilization (kg/ha)	Fertilization NO_3 – N (kg/ha)	Fertilization NH_4 - N(kg/ha)
9-Jul-2004	18.2	9.1	9.1
12-Jul-2004	30.2	15.1	15.1
14-Jul-2004	27.3	13.7	13.7
20-Jul-2004	18.2	9.1	9.1
20-Jul-2004	18.2	9.1	9.1
23-Jul-2004	18.2	9.1	9.1
26-Jul-2004	18.2	9.1	9.1
27-Jul-2004	18.2	9.1	9.1
28-Jul-2004	18.2	9.1	9.1

Table 27 - Irrigation water salinity input data

Block	Ca^{2+} (mg/L)	Na^{+} (mg/L)	Mg^{2+} (mg/L)	Cl^{-} (mg/L)
A1	374.23	175.59	72.47	63.43

Values from Table 27, were adopted from the Project Databases. In fact, for each block it was available the number of eqv/ ha. These values were transformed in these ions according to that they are the most important for water salinity calculation. The other ions concentrations values adopted were theRZWQM default values.

5.2.6 - Plant Data

The experimental field was a corn planting, and that was the plant simulated in the RZWQM. Plant details about growth, water and nitrogen needs, and other parameters as well as its efficiency were adopted from RZWQM database for plants.

The date of planting was 01-May-2004. Details about corn planting are shown in Table 28:

Table 28 - Corn input data

	Plant Density (seeds/ha)	**Row spacing (80cm)**	**Plant Depth (layerIndex)**
Corn	85000	80	2

5.3 - Results and Discussion

Simulations in the RZWQM were made for two years in which corn grew. In order to evaluate the logic of the simulation, next results are shown

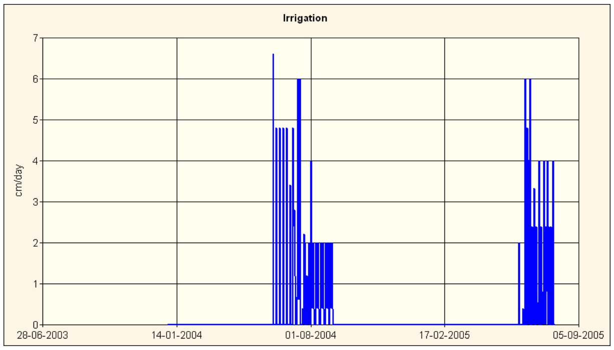

Figure 50 - RZWQM irrigation results

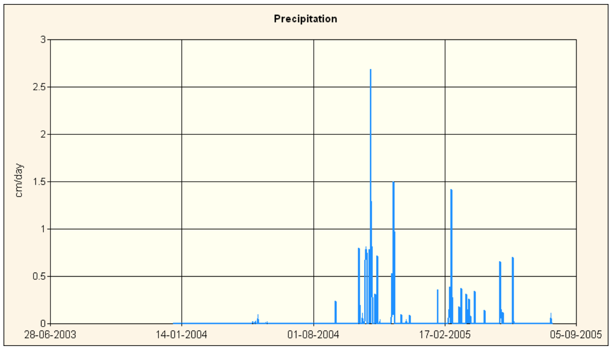

Figure 51 - RZWQM precipitation results

As it was expected, irrigation in Figure 50 had a higher value in summer period, and precipitation generated by the model was similar to the values in input data (Figure 51).

The water in the soil that comes from precipitation and irrigation will infiltrate but not all of it. Some part may leave the surface and reach the water lines, and then becomes no longer important for the soil processes. This partition between Infiltration and Runoff depends of the soil type (mainly its physical characteristics) and the soil coverage, as well as the slope. It can be seen that, in this simulation, water that reaches the field is almost all infiltrated (Figure 52). Nevertheless, some runoff occurred during the irrigation period.

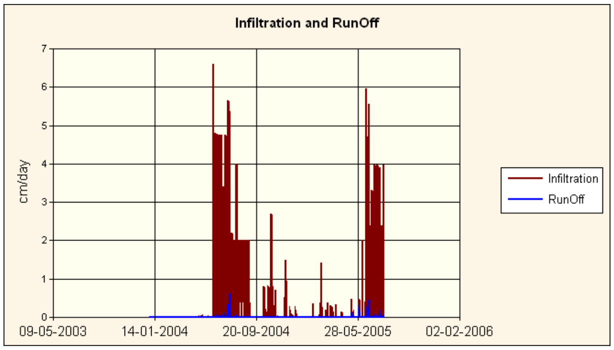

Figure 52 - RZWQM infiltration and runoff results

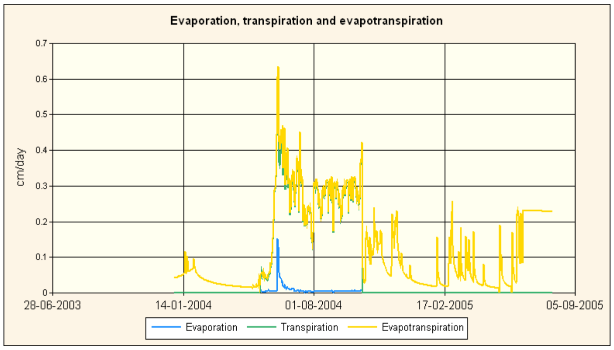

Figure 53 - RZWQM evapotranspiration, transpiration and evaporation results

Other interesting results may be seen, such as the Evapotranspiration, evaporation and transpiration in Figure 53. The planting was made in May and the plants are dead on the end September, which explains transpiration (from corn) appears just in that period.

The model results for nitrate and ammonium at 20, 40 and 60 cm are shown below in Figure 54 and Figure 55. To interpret the model, simulations were divided in 6 different periods where some particular events occurred, changing the levels of these nutrients.

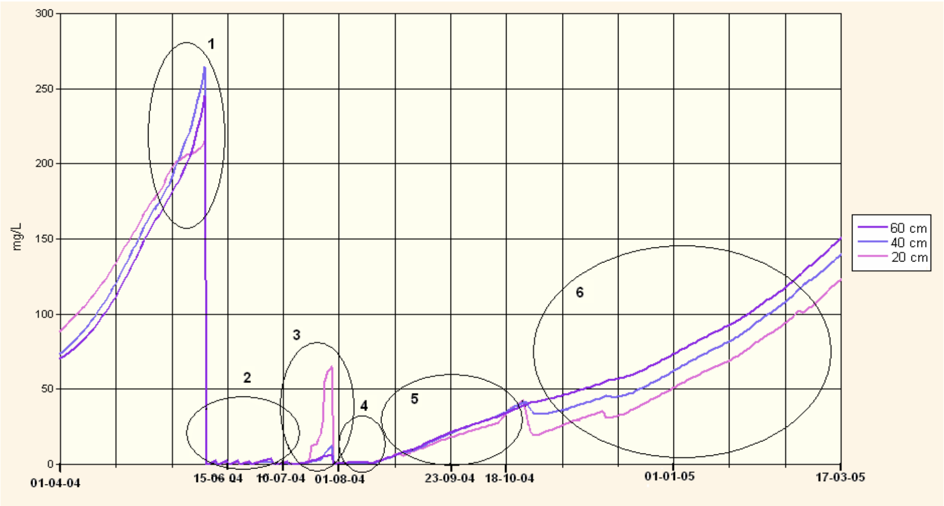

Figure 54 - RZWQM results for nitrate evolution for 20, 40 and 60 cm

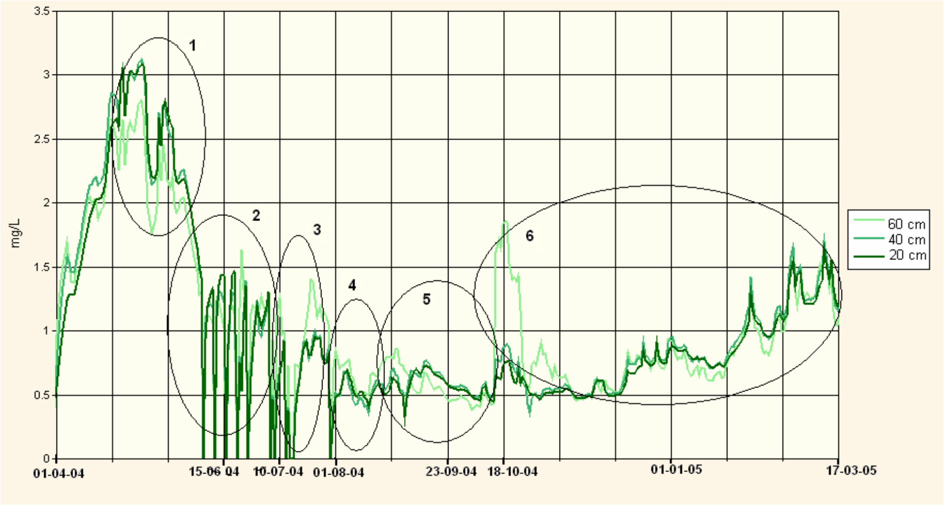

Figure 55 - RZWQM results for ammonium evolution at 20, 40 and 60 cm

1. May 14th – 31st

At 14th May it begins the nitrogen up take by the plants, which were planted in the beginning of May (Figure 56).Once the soil is full of ammonium coming from organic matter mineralization, and nitrate from nitrification, there was no stress for plants. At this time, there were not irrigation events, and so the fact that nitrate being higher at 40 cm or 60 cm (Figure 54) may be explained with the roots, that are growing and up taking nitrogen just from the surface layers.

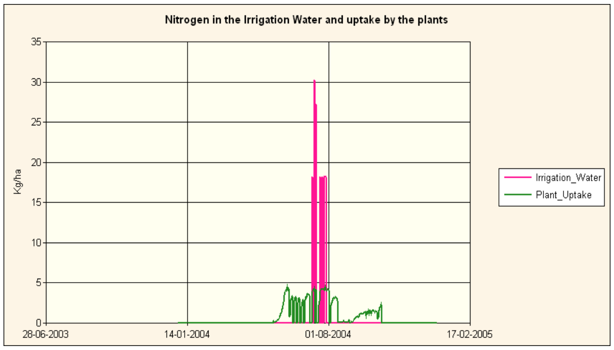

Figure 56 - Nitrogen added in the irrigation water and uptake by the plants

2. June 1st – July 9th

In this period, plants continue to grow and become more exigent for nitrogen, and that’s why both ammonium and nitrate are being depleted. At this time, no fertilizer was added to the soil (Figure 56), so plants are in stress. Roots are now deeper reaching values around 160 cm (Figure 57).

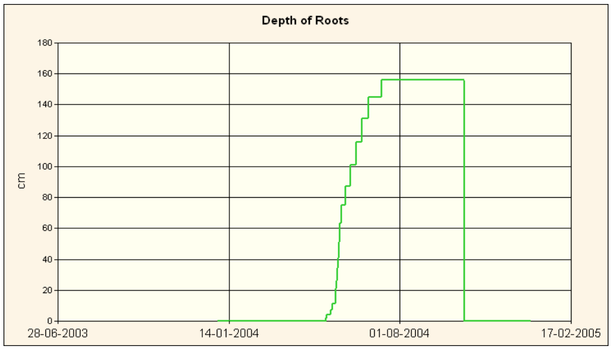

Figure 57 - Depth of roots

3. July 10th – August 1st

This is the fertilization period (Figure 56), in which nitrate and ammonium are added to the soil, providing some nutrients to the plants. In this step, ammonium and nitrate levels increased a little bit, mainly at the surface, once fertilizer is added in the irrigation water form, but are consumed by the plants. Irrigation events make the nitrate be transported but it is quickly consumed by the plants.

Irrigation events in the end of July become less intense (Figure 50) and that's why nitrate fertilizer is being accumulated. Nevertheless, it is transported through the other layers when irrigation events become intense again, as it happens at August 2nd.

4. August 2nd – 20th

In this period, no fertilizer is added, but plants still need to uptake nitrogen (Figure 56), so both nitrate and ammonium become depleted from soil again. The nitrogen inputs in the soil have origin in the mineralization and nitrification processes occurring. Once again, nitrate at 60 cm is higher than at 20 or 40 cm, which is explained by the transport from irrigation water that ends just in the final of August.

5. August 21st – October 14th

During this time plants are dying and consuming much less nitrogen than before (Figure 56). Because of that, both nutrients are being accumulated in the soil (Figure 54 and Figure 55). Some nitrogen continues to be transported and concentrations at 60 cm are higher not only because of the irrigations events but also because the precipitation period begins at this time (Figure 51).

6. October 14th

In this period, dead roots provide a source of fresh organic matter (Figure 58) increasing the level of ammonium and consequently of nitrate. At 27th October, an intense precipitation event made nitrate at the surface be transported and to increase at the deepest layers (Figure 51).

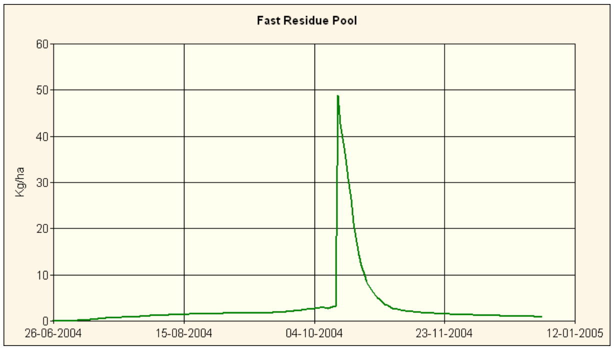

Figure 58 - RZWQM results for the fast residue pool

Some measured data were taken during this experiment. Now they can be compared with the model results. Figure 59, Figure 60 and Figure 61 show the water content measured and simulated for 20, 40 and 60cm.

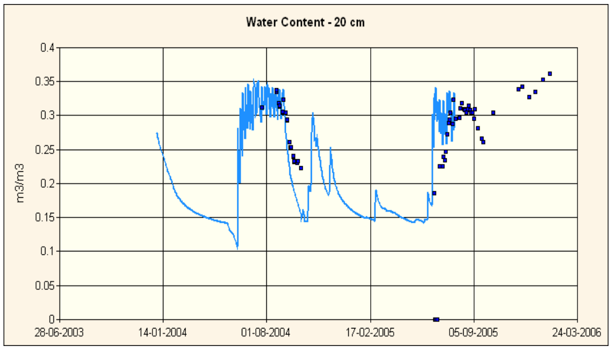

Figure 59 - Model and experimental results for water content - 20 cm

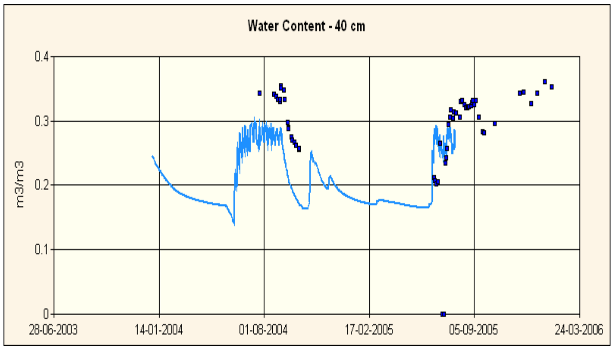

Figure 60 - Model and experimental results for water content - 40 cm

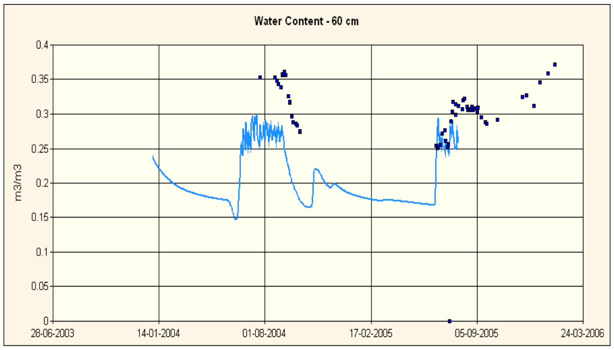

Figure 61 - Model and experimental results for water content - 60 cm

Water content measured is similar to the RZWQM simulations. In fact, water content variations are observed because of the irrigation and precipitation events. During the first year, results from RZWWQM model are higher than the experimental ones, which is not observed at the second year.

The next results (Figure 62, Figure 63 and Figure 64) show the nitrate levels at 20, 40 and 60 cm. As it can be seen, simulation for 20 cm has close results to experimental values, even if some experimental points appear to have higher values than the model, at the beginning of August. Nevertheless, both model and experimental data are in agreement about nitrate increasing in this period.

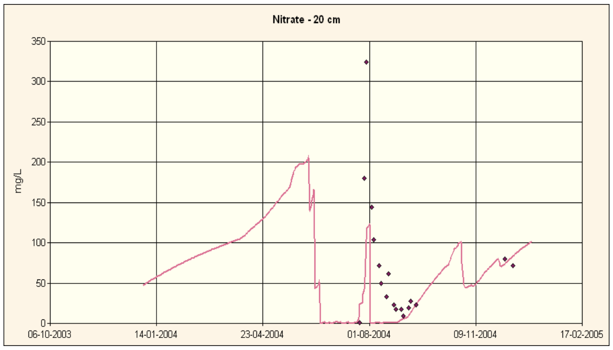

Figure 62 - Model and experimental results for nitrate – 20 cm

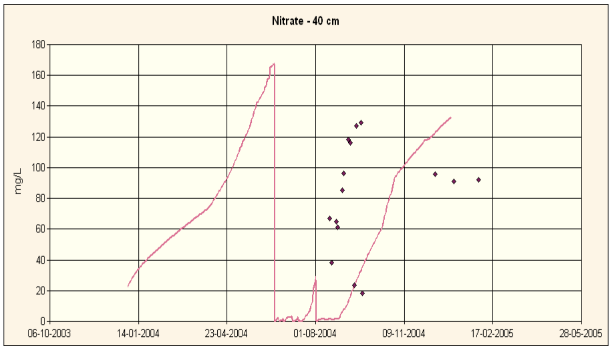

Figure 63 - Model and experimental results for nitrate – 40 cm

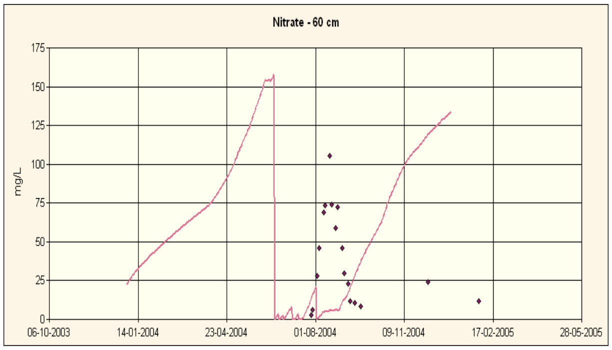

Figure 64 - Model and experimental results for nitrate - 60 cm

Experimental results show, in a general way higher values than the model, especially for 40 and 60 cm in the end of July and begin of August (Figure 63 andFigure 64). Perhaps the model is considering a more exigent plant than in fact exist and because of that more nitrate is being depleted from the deepest layers, where roots are placed

The comparison between experimental and model results for ammonium (Figure 65, Figure 66 and Figure 67) show again higher values in experimental results at some points in August. Once again, corn simulated by the model seems to be exigent with nitrogen needs. It’s important to notice that, as ammonium is not transported through soil, results for 60 cm are more close to the experimental results.

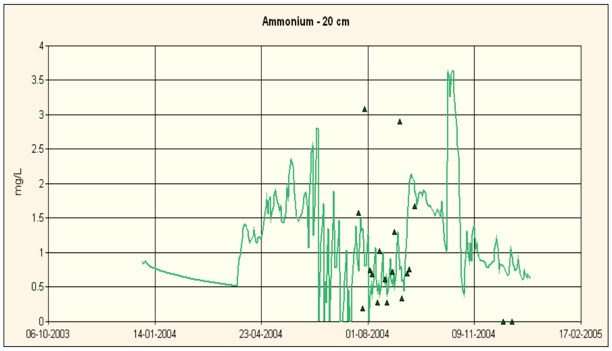

Figure 65 - Model and experimental results for ammonium - 20 cm

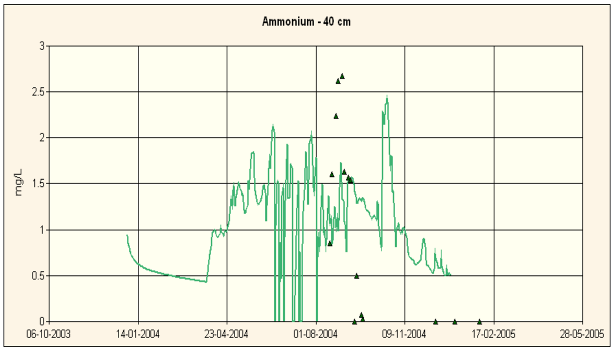

Figure 66 - Model and experimental results for ammonium - 40 cm

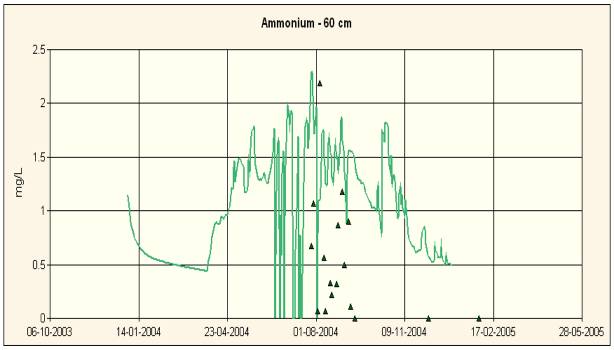

Figure 67 - Model and experimental results for ammonium - 60 cm

Finally, the Figure 68 shows the total organic carbon behavior in the model and the comparison with the only available experimental data. It can be observed by this comparison, that the model is simulating less organic matter in the soil, than the experimental data. That can be very important and explain some of the previous results for nitrate, once the organic matter mineralization is the main process occurring in the soil. If the soil has less organic matter, then the mineralization process will not be as the real one and as a consequence less ammonium and nitrate will be available.

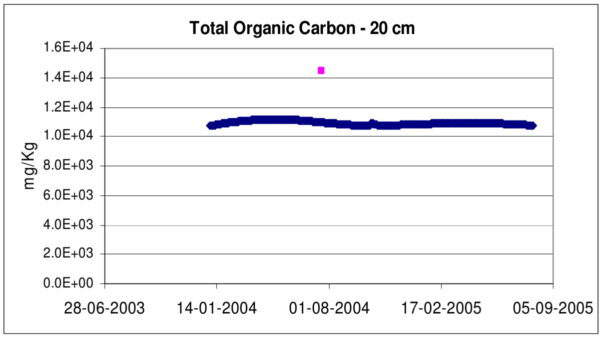

Figure 68 - Total Organic Carbon - 20 cm

The differences between the model and the experimental results may have a lot of origins. That is particularly true for nitrate. In fact, the nitrate concentration is affected by different processes and external inputs as the fertilizers. Some possibilities may be explained or discussed, and should be included in a future work:

- Organic Matter, ammonium and nitrate pools values were available for 20, 40 and 60 cm but the models inputs required initial pools for each layer (30, 75 and 1.65). That may be the origin of the different results in the other depths because soil resource availability may become the main responsible for the community composition through soil profiles (Fierer *et al*, 2003).
- Although it doesn't appear to provoke big differences because water content compared between RZWQM and experimental data were close, rain data input was daily and the model requires horary rain events.
- Biomass population was a result from a calibration process. As it is known, these pools are very difficult to measure. Cameira (1999) used ten years of available data to calibrate the biomass pools. In this simulation calibration was made just with the available meteorological data.
- Corn planting and harvest details, as well as plant needs and efficiency parameters were used from RZWQM data bases. Considering that the model gives lower values than the experimental data, this may be an important issue to analyze in the future.

6th Chapter – Conclusions

The present work had three different moments: Improvement of the module developed by Galvão (2002); comparison between this module with a zero dimensional (0D) version of RZWQM; and a comparison between experimental data from Agro 727 project in Alvalade-Sado with simulations, using RZWQM model.

The aim of the first part was to develop the existing module of the Mohid Land – Sediment Quality, which simulated carbon and nitrogen cycles, created by Galvão (2002). The improvements of this work were the inclusion of phosphorus cycle, allowing a better modelling of the organic matter decay with the junction of phosphorus immobilization process, as had happened before with nitrogen. Also other important processes were added in phosphorus cycle, such as the solubilization and fixation/adsorption that is responsible for the changes in the availability of this nutrient to the plants. Other items were added, such as the methane gas released in anaerobic situations in which nitrate is depleted, the Urea Hydrolysis that is a source of ammonium in soil and the Ammonia volatilization that may, on the contrary, consume ammonium from soil.

Other improvements of this work are related to the model ability to response to temperature, pH and soil porosities variations. That is very important, once in soil different conditions may be found and the behavior of the microorganisms may change depending on the environmental conditions. Simulations done showed that heterotrophic biomass increases if the ideal temperature and pH is reached (Figure 31 and Figure 33). Autotrophic biomass has the same behavior but it seems to be more sensitive to the environmental conditions. Although the optimal pH is the neutral one, the results showed also that for acid pH values the growth is higher than for basic ones (Figure 34).

Other important conclusions were taken from other simulations, such as the impact of different soil porosities tested for different soil types (Figure 36). In soils with more porosity like silt, for the same water content, more oxygen is available, allowing aerobic processes to take place, like mineralization and nitrification, while soils with less porosity like sand may create an anaerobic environment more quickly. Other tests were made to change the effective water content and consequently the aerobiose soil level, such as changing the water content for a constant porosity soil. The anaerobiose level increases with the increase of water content and the result is that anaerobic population has a very good environment to grow (Figure 37) which will lead to an improvement of the denitrification process and as a consequence it will increase also the nitrate consumption and the Ngas released (Figure 38 and Figure 39).

For developing the existing model by Galvão (2002) three steps were followed:

1) Implementation of the changes in PowerSim model, anlysing preliminary simulations, which allowed a first global view of the work and earlier mistakes elimination. That was important to observe the phosphorus responses and the new improvements (3.4 - Preliminary Results in PowerSim);

2) Implementation in Fortran and comparison the result with the PowerSim version. This was made developing the existing module, Sediment Quality in Fortran programmed by Galvão (2002), using his explicit method. The results showed that PowerSim and Fortran matched, which means that the implementation was the same (4.2 - Sediment Quality Implementation). The comparison between the new model with a zero-dimensional (0D) version of RZWQM model showed that the models matched for mineralization situations in mineralization and nitrification processes (Figure 25 and Figure 26). The difference remained for the anaerobic population which in RZWQM was a facultative one, while in Sediment Quality it had been included as a strict population (Figure 28) Besides the fact that the results for this pool have not been the same, this difference is not important because for the aerobic situation simulated, organic matter pools for both models matched (Figure 25), which means that the difference in that population pool was not important. For an immobilization situation, the models didn't match because different equations were used to simulate the search for nitrate and ammonium at immobilization processes (Figure 29 and Figure 30). Although the results are similar, future work will be the comparison of these two alternatives with fields data to know which one is giving better results. Other important issue that may be looked at is that this comparison was made just for nitrogen and carbon pools. Phosphorus cycle added in this model has not been compared with any models or fields data once the developed model is zero dimensional (0D), and as a consequence, this part of the model was not validated. Nevertheless, important conclusions were reached with this work, about the phosphorus importance in nutrients availability. In fact, phoshorus immobilization may induce a lower heterotrophic growth and to interfere with the excreted products from mineralization (Figure 15 and Figure 16).

It's important to say also that the RZWQM source code comparison was very important, because it allowed to correct great part of the equations used in Sediment Quality that were based in Shaffer and al (1999).

The last part of this work was related with the RZWQM simulation of a field in Alvalade-Sado corn plantation. The input data was taken from the Agro 727 project data bases (5.2 - Input Data). The corn planting was made in different conditions of fertilization and salinity. The simulations were done for one particular situation of fertilization and salinity.

RZWQM is One-Dimensional (1D), which allows the transport of nutrients with depth. Besides that, it is able to receive, as an input, the climate, the chemical and physical soil characteristics as well as the used fertilization and type of irrigation.

Experimental data was compared with the simulations results for water content, nitrate and ammonium for the 0-20, 20-40 and 40-60 cm depth, showing reasonable in particulary for the first situation.

Water content variations in model were a response to the irrigation and precipitation events which matched with the experimental data (Figure 59, Figure 60 and Figure 61).

Nitrate, in a general way, is higher in experimental data then in the model (Figure 62, Figure 63 and Figure 64). This may be explained because organic matter results were also not coincident with the experimental data (Figure 68). As the mineralization is the main process in the soil, from it will depend the concentrations of all the other pools. Other explanation for the bad results is related with plants needs for nitrogen. In fact, the plant properties were taken from RZWQM model and may be too much exigent. Future work about this particular chapter will include the solution/improvement of the problems mentioned before, specially related with the organic matter inputs, and simulating the other situations of the project, comparing them with the available fields data and, after a good validation, taking conclusions about the effect of fertilization and salinity in soil in the corn growth.

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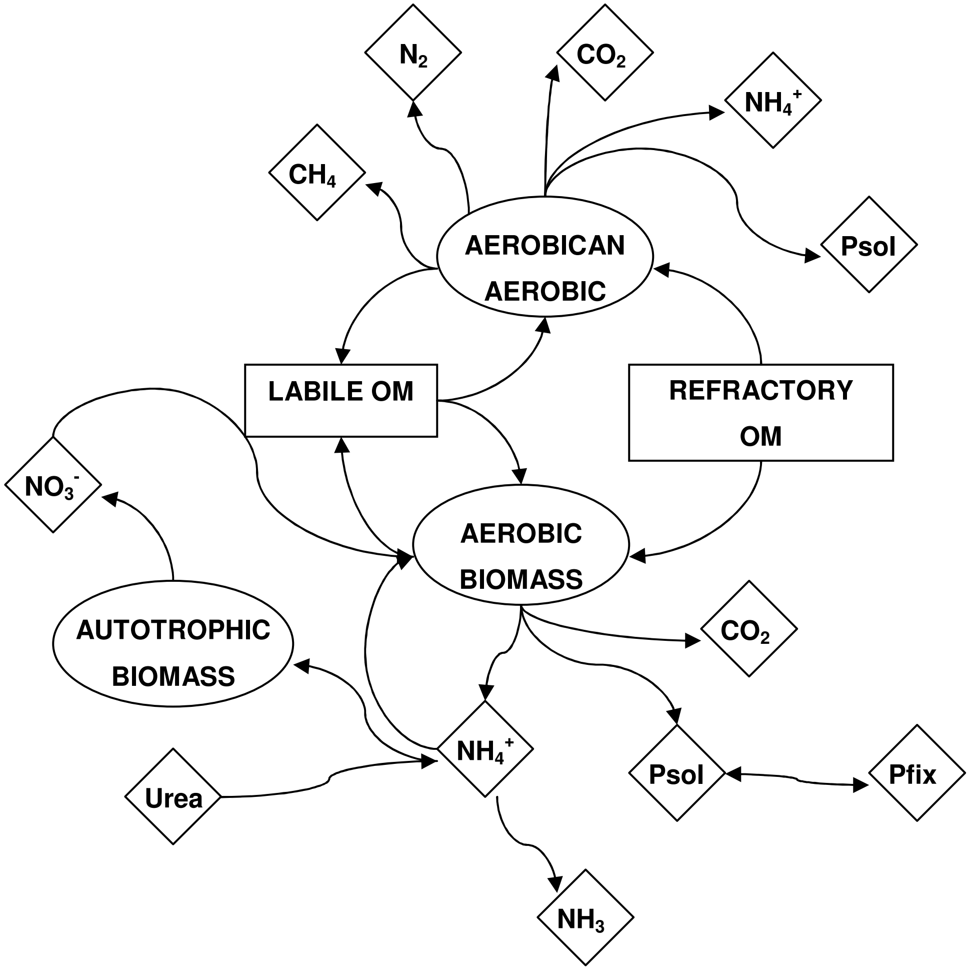
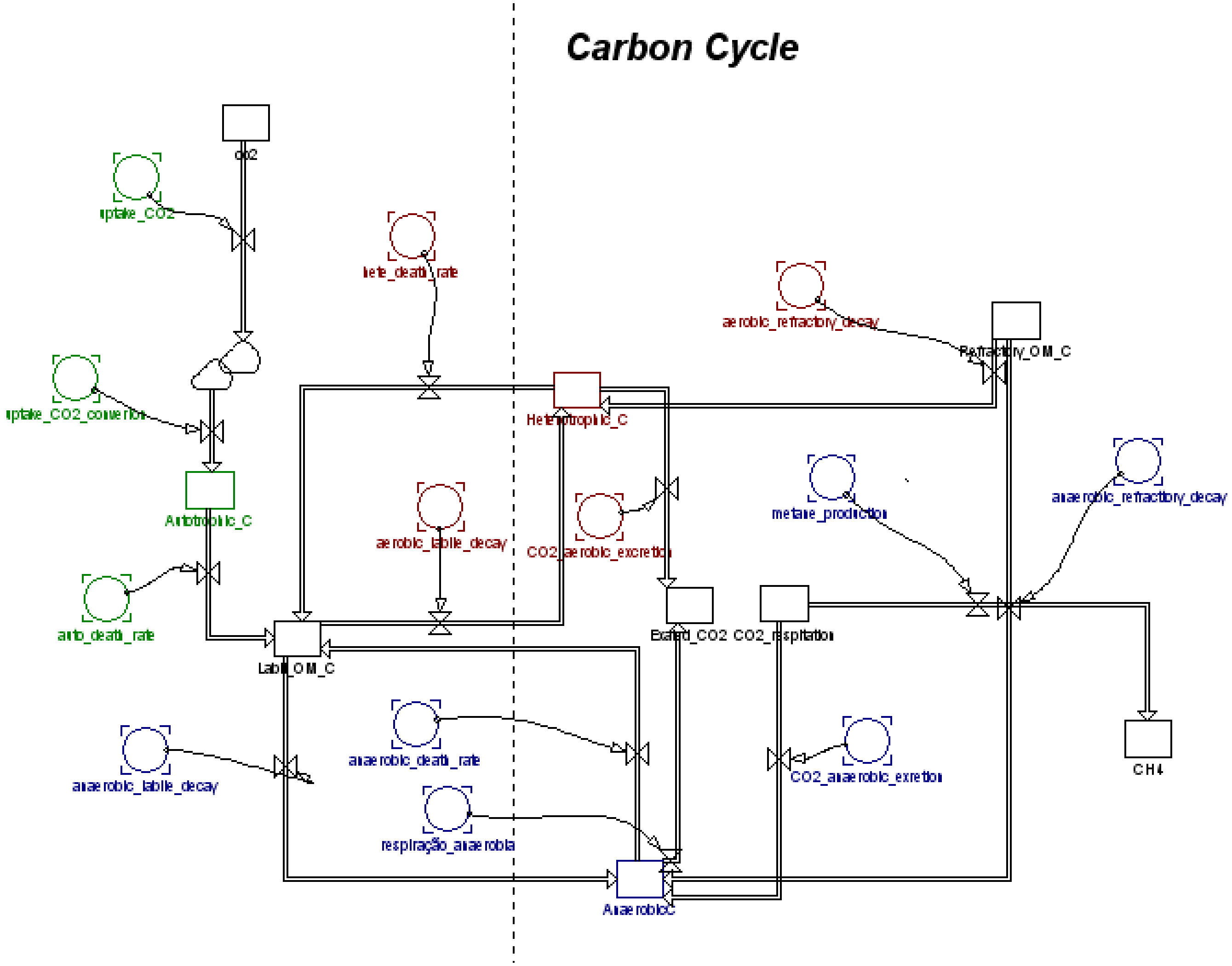
APPENDIX

APPENDIX A – Model Structure

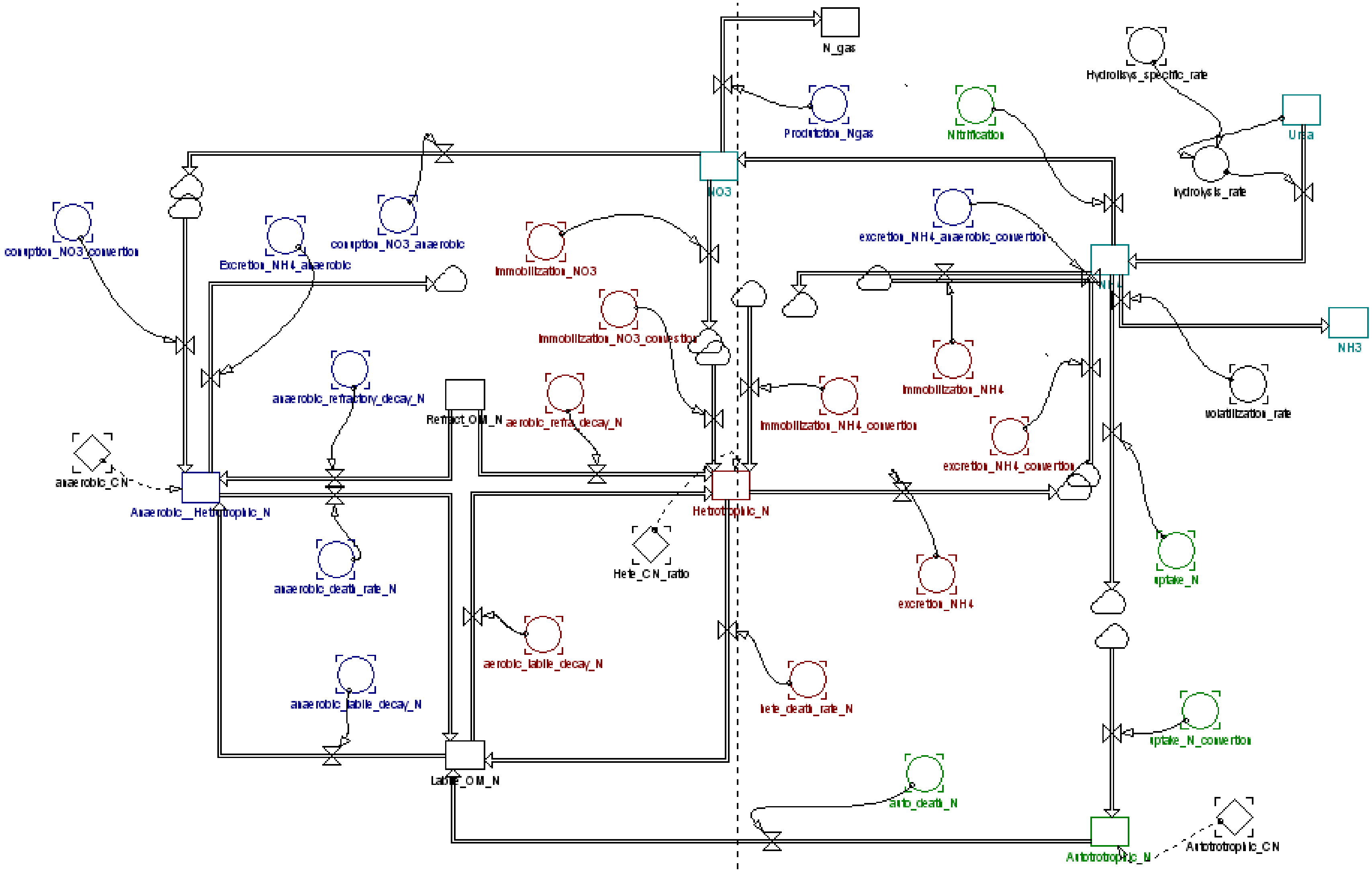


APPENDIX B – Carbon Cycle in POWERSIM

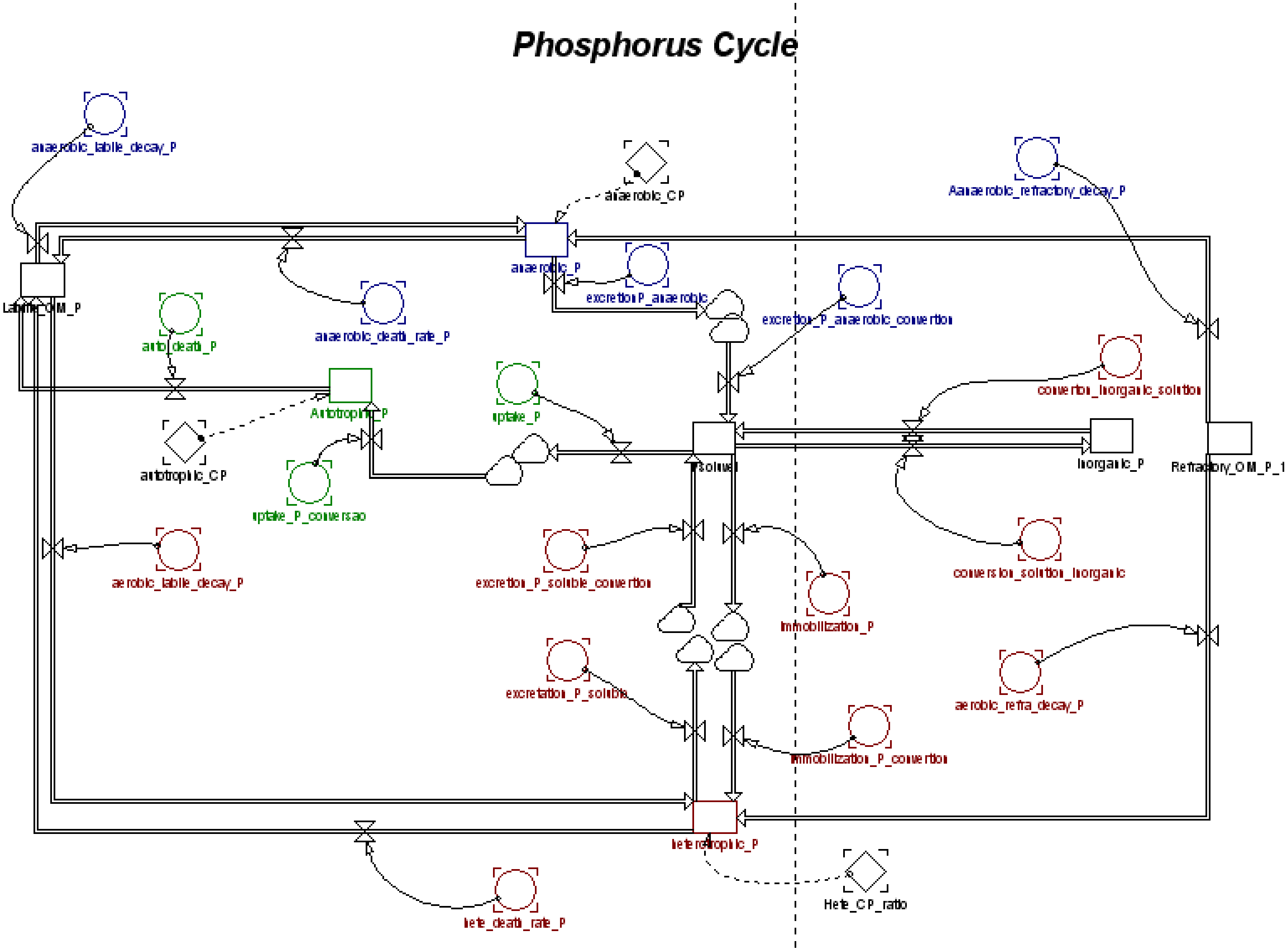


APPENDIX C – Nitrogen Cycle in POWERSIM

Nitrogen Cycle



APPENDIX D – Phosphorus Cycle in POWERSIM



Symbol List

A - Generic area in the conservation principle equation

A_{Adecay} - Aerobic organic matter decay coefficient

Adj - Coefficient dependent of soil pH

CN_{het} - Carbon nitrogen ration of heterotrophic biomass population

CN_{Lab} - Carbon nitrogen ration of labile organic matter

$CN_{\mathrm{Re}\,f}$ - Carbon nitrogen ration of refractory organic matter

CP_{auto} - Carbon phosphorus ratio of autotrophic population

CP_{het} - Carbon phosphorus ratio of heterotrophic biomass population

CP_{Lab} - Carbon phosphorus ratio of labile organic matter

$CP_{\mathrm{Re}\,f}$ - Carbon phosphorus ratio of refractory organic matter

E_{0i} - Referent activation energy $Kcal \cdot mole^{-1}$

Ea - Apparent activation energy $Kcal \cdot mole^{-1}$

Ef_{CH4} - Anaerobic heterotrophic population efficiency in producing methane

Ef_{des} - Anaerobic heterotrophic population efficiency in nitrate consumption

Ef_{hete} - Heterotrophic population efficiency of organic matter decay

Ef_{nit} - Autotrophic population efficiency in nitrification process

EK - Equilibrium constant

f_{aer} - Aerobic factor

f_{ana} - Anaerobic factor

$fert_{\min P}$ - Mineral phosphorus soluble fertilizer $\mu g / m^3 water$

h_p - Planck constant $J \cdot s$

$\left[H^+\right]$ - Hydrogen mol / L

Het_{pop} - Heterotrophic population org / g_{soil}

I - Ionic strength mol / L

K_{Adecay} - Aerobic decay specific rate day^{-1}

K_b - Boltzman constant $J \cdot K^{-1}$

K_{CH4} - Methane production specific rate day^{-1}

K_{decay} - Generic specific rate in RZWQM

K_{des} - Denitrification specific rate day^{-1}

$K_{\mathrm{Im}ob\_P}$ - Phosphorus immobilization specific rate day^{-1}

K_{nit} - Nitrification specific rate day^{-1}

K_s - Half saturation constant in DAISY

K_{Urea} - Urea hydrolysis specific rate day^{-1}

K_{vol} - Ammonia volatilization specific rate day^{-1}

k_x - Decomposition rate in DAISY

k_x^* - Decomposition rate coefficient at standard conditions in DAISY day^{-1}

Khn - Aerobic organic matter exponent for hydrogen ion

kp - Constant coefficient L / mol

$[NH_4^+]$ - Ammonium $\mu g / m^3 water$

$[NO_3^-]$ - Nitrate $\mu g / m^3 water$

$[O_2]$ - Oxygen concentration in soil, assuming soil air not limited mol / L

$[OM]$ - Total organic matter $\mu g / m^3 water$

P_{Adecay} - Potential aerobic decay $\mu g / g_{soil} / day$

P_{fix} - Mineral phosphorus fixed pool $\mu g / m^3 water$

$P_{\mathrm{Im}ob\_P}$ - Potential phosphorus immobilization $\mu g / m^3 water / day$

$P_{\mathrm{Im}ob\_NH4}$ - Potential ammonium immobilization $\mu g / m^3 water / day$

$P_{\mathrm{Im}ob\_NO3}$ - Potential nitrate immobilization $\mu g / m^3 water / day$

P_L - Labile organic matter potential decay $\mu g / g_{soil} / day$

P_R - Refractory organic matter potential decay $\mu g / g_{soil} / day$

P_{sol} - Mineral phosphorus soluble pool $\mu g / m^3 water$

$P_{sol,b}$ - Mineral soluble phosphorus before fertilization $\mu g / m^3 water$

$P_{sol,f}$ - Mineral soluble phosphorus after fertilization $\mu g/m^3 water$

Pa_{NH3} - Partial ambient pressure of NH_3 atm

P_{NH3} - Partial pressure of NH_3 atm

PAI - Phosphorus available index

r_{decay} - Generic rate in RZWQM

R_{CH4s} - Methane excretion rate $\mu g/m^3 water/day$

R_{exc_P} - Mineral soluble phosphorus excretion rate $\mu g/m^3 water/day$

R_{Ngas} - N gas excretion rate $\mu g/m^3 water/day$

$R_{P\_fix\_sol}$ - Conversion rate from mineral fixed to soluble phosphorus pool $\mu g/m^3 water/day$

$R_{P\_sol\_fix}$ - Conversion rate from mineral soluble to mineral fixed phosphorus pool $\mu g/m^3 water/day$

$R_{total\_Aer\_decay}$ - Total organic matter aerobic decay rate $\mu g/g_{soil}/day$

$R_{total\_Ana\_decay}$ - Total organic matter anaerobic decay rate $\mu g/g_{soil}/day$

$R_{totalI\,\mathrm{Im}\,ob\_P}$ - Potential phosphorus immobilization $\mu g/m^3 water/day$

$R_{uptakeP}$ - Uptake phosphorus rate by autotrophic $\mu g/m^3 water/day$

$R_{uptakeN}$ - Uptake ammonium rate by autotrophic $\mu g/m^3 water/day$

R_{Urea} - Urea hydrolysis rate $\mu g/m^3 water/day$

R_{vol} - Ammonia volatilization rate $\mu g/m^3 water/day$

Rg - Universal gas constant $Kcal/mole/K$

S - Generic substrate in RZWQM

T - Temperature K

T_D - Temperature in DAISY ^{o}C

$T_{\max}$ - Maximum temperature that is favorable for bacteria processes

T_p - Aerobic organic matter decay temperature K

$T_{soil,ly}$ - Layer soil temperature in SWAT model

T_{soil} - Soil temperature

Tf - Coefficient from temperature effect

TK - General decomposition constant

V - Generic volume in the conservation principle equation

X_C - Clay content in DAISY $\%$

X_K - Depth constant

X_{K1} - Volatilization constant

X_{KG} - Coefficient of wind and depth effect

W - Wind km / day

Greek Symbols

β - Specific property in the conservation principle equation

γ_{temp} - Temperature factor in SWAT model

Δt - Time step in explicit method

ς_n - Decomposition rate of organic matter in DAISY

θ - Water content

θ_F - Effective water content

θ_S - Porosity

v - Velocity in the conservation principle equation

ξ_m - Maximum specific growth rate in DAISY

ψ - Pressure potential of soil water in DAISY $m\ H_2O$

ρ - Soil density

υ - Diffusivity parameter in the conservation principle equation