Carbon, Nitrogen and Phosphorus Soil Cycle Modelling

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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.

1. 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).

The main process that occurs in soil is the organic matter decomposition where heterotrophic bacteria uses the carbon to grow, releasing some CO_2 and mineral nutrients, such as the NH_4^+ or the soluble phosphorus. Bacterial needs for nitrogen or phosphorus are translated by the carbon/nitrogen and carbon/phosphorus ratio. If there is not enough nitrogen or phosphorus in the substrate, they will immobilize it from the mineral available pools (Quelhas dos Santos, 2001). Plants exert a strong influence on microbial composition of communities in soil through rhizodeposition and the decay of litter and roots (Naninipieri *et al,* 2003). Roots increase microbial mineralization because they are a source of organic matter when 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). In another way, the rhizosphere provides optimal conditions to microbial growth (Sanchez *et al*, 2002).

Mineralization processes in soil may become essential for agriculture, once they produce nutrients for plant uptake. For example, corn plant takes 70% of its nitrogen from the mineralization occurring in the soil (Sanchez *et al*, 2002).

Nevertheless, if the organic matter in the soil has a high CN or CP ratio, immobilization will occur and the nutrients will be uptake by bacteria and not by the plants. The autotrophic bacteria play an important role in the soil as well, once they are able to use the carbon available from the CO_2 of the atmosphere. *Nitrobacter* and *Nitrossomonas* are responsible for nitrification process, in which NH_4^+ is transfer to NO_3^- (Metcalf & Eddy, 1978). This process happens in aerobic conditions and it's very important in agriculture, since NO_3^- is easily leached because of its negative charge. NH_4^+ will be more easily available for plant uptake since it is a positive ion. Nitrate that is leached may contribute for contamination of aquifers or water lines, providing a source of nitrogen in ponds or lakes and blooms of algae may appear (Brewer, 1994).

Denitrification is, as well, an important process for agriculture. In oxygen absence, the added nitrate as fertilizer may be consumed not by plants but by microorganisms, which will release some N_2 to the atmosphere. This happens particularly in rice cultures, where the high water content levels make oxygen less available. The denitrification problem is not just economically important, once fertilizer added is not consumed for plant growth. In fact, intermediate gases from denitrification processes are released to the atmosphere as N_2O.

Ammonia volatilization may also have some importance because it's a sink for ammonium in the soil. The main pathway for nitrogen loss during handling, storage and spreading of manure is ammonia volatilization. The amount of ammonia volatilized is influenced by several factors like temperature, wind variations or pH (Kirchmann, 1989).

Phosphorus is an essential nutrient for plant growth, but they can only uptake it in the soluble forms like HPO_4^{2-} or H_2PO^{4-}. Some studies show that 85-88% of the phosphorus in the soil is in the non reactive pool, which means that it is in the fixed or adsorbed form, consequently unavailable for soil transformations (Toor *et al*, 2003). Mineralization may turn the soluble forms available, but these can be easily fixed into inorganic unavailable pools. This fixation occurs because in acid soils, phosphorus can precipitate in salts, combining with the aluminum and iron ions or, in the neutral or basic soils, the precipitate may occur with the calcium ions (Ponmurugan *et al*, 2006). Some microorganisms may solubilize those inorganic fixed forms (Oberson *et al*, 2001). This is particularly important because if these bacteria are able to live in the soil, they can act as bio fertilizers (Igual *et al*, 2001). The different phosphorus pools in the soil are a consequence of transport, mineralization, immobilization, solubilization and fixation/adsorption (Horst *et al*, 2001).

The aim of the present work is to develop the old model created by Galvão (2002) in order to model the processes in the soil cycles that contribute for the main nutrients transformations. It has three main steps:

- Improvement of the organic matter decomposition model from Galvão (2002) – Sediment Quality; this step included the model redefinition, the research and inclusion of the new equations (RZWQM source code, 2007) and the inclusion of the model ability to respond to temperature, pH, wind and soil porosity variations. In a first step, it was made in an implementation in PowerSim, and later in Fortran 95, using an explicit method.
- Comparison between the reconstructed module with a Zero-dimensional (0 D) version of RZWQM (Root Zone Water Quality Model).
- RZWQM application in a real situation in Portugal, Alvalade-Sado. This last step included the

interpretation of the model results as well as the comparison with the experimental data.

2. MODEL IMPLEMENTATION

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 in soil and other important processes. The improvements 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.

The pools of the system were defined, as well as the flows that affect their concentration in time. Galvão (2002) adopted three pools for the organic matter: the organic matter with fast decay (Labile Organic Matter), the organic matter with slow decay (Refractory Organic Matter) and the biomass population (aerobic heterotrophic, anaerobic heterotrophic and autotrophic populations). Inorganic pools considered were: NO_3, NH_4^+, CO_2 and N_2. With the new improvements other inorganic pools were added, such as soluble and fixed inorganic phosphorus, CH_4, Urea and NH_3.

The processes simulated in this model were: organic matter decomposition (both aerobic and anaerobic) with the release of CO_2, NH_4^+ and inorganic soluble phosphorus. In anaerobic cases CH_4 can be released, depending on the amount of NO_3^- available for consumption. Nitrification, in which NH_4^+ is transformed into NO_3; is also included as well as Ammonia Volatilization process where NH_4^+ is transformed into NH_3; The last one is the Urea Hydrolysis, which represents a source of NH_4^+ in the soil and also the solubilization and fixation of mineral phosphorus pools.

Equations used to simulate these soil processes were affected by a specific rate (1), as it happened in Galvão (2002).

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

(1)

P_{Adecay} is the potential aerobic decay ($\mu g / g_{soil} / day$) ,$[OM]$ is the total organic matter ($\mu g / g_{soil}$) and K_{Adecay} is the aerobic decay specific Rate (day^{-1}).

All the processes modeled in Galvão (2002) were not affected by the phosphorus cycle. The new model includes situations in which heterotrophic population is depending also on the phosphorus levels and not only on the nitrogen ones. This dependence was implemented according to what had been done for nitrogen in the past.

$$\frac{1}{CP_{hete}}(P_L + R_R) > \frac{P_L}{CP_{lab}} + \frac{P_R}{CP_{ref}}$$

(2)

P_R and P_L are the potential refractory and labile organic matter potential decay ($\mu g / g_{soil} / day$)

If (2) is verified, phosphorus immobilization will occur in the soil. Nevertheless, biomass growth and the immobilization type will be determined by equation (3). Model compares the potential rate at which bacteria can decompose organic matter with the potential rate at which they can immobilize phosphorus.

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

(3)

$P_{\mathrm{Im}ob\_P}$ is the phosphorus immobilization potential $\mu g/m^3 water/day$, CP_{Lab} is the carbon phosphorus ration of labile organic matter, $CP_{\mathrm{Re}f}$ is the carbon phosphorus ration of refractory organic matter and CP_{het} is the carbon phosphorus ration of heterotrophic biomass population .

Autotrophic and heterotrophic anaerobic processes equations were adopted from Galvão (2002), with different specific rates (RZWQM source code, 2007) and affected by carbon/phosphorus Ratio.

Ammonia volatilization (4) and Urea Hydrolysis equation (5) used were from Shaffer *et al* (1999).

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

(4)

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

(5)

R_{vol} and R_{Urea} are the ammonia volatilization and urea hydrolysis rate $\mu g/m^3 water/day$

One of the most important improvements in this work was the inclusion of phosphorus solubilization and fixation, naturally occurring in the soil. The model equations ((6) and (7)) used were taken from Neitsch *et al* (2005).

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

(6)

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

(7)

P_{sol} is the mineral soluble phosphorus and P_{fix} is the mineral fix phosphorus($\mu g/m^3 water$);

This simple approach assumes that the conversion from phosphorus soluble to fixed pools is 10 times higher than the conversion from fixed to soluble pools. PAI (*Phosphorus Available Index*) is the parameter that defines the soil ability to solubilize or fix inorganic phosphorus pools.

After the PowerSim implementation, the model was tested and implemented in Fortran 95 using an explicit method. For each pool, sources and sinks were programmed.

3. COMPARISON BETWEEN THE MODEL AND RZWQM

MOHID land is a sub-model of MOHID in which drainage network, overland flow and porous media are modeled.

The new module – Sediment Quality might be, in future work, connected to this model, allowing nutrient transport through soil and surface simulation.

As the current model is zero-dimensional no transport is simulated, becoming impossible to compare it with field data. In order to validate the model, a comparison with a zero-dimensional version of RZWQM was made. Results from this comparison for an aerobic mineralization situation are shown in Figure 1, Figure 2 and Figure 3.

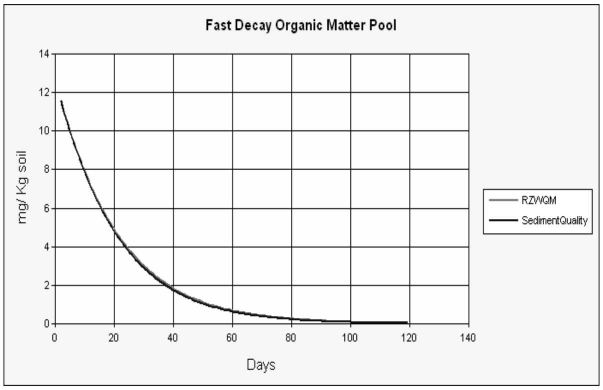

Figure 1 – Comparison between Sediment Quality and RZWQM for fast decay organic matter pool

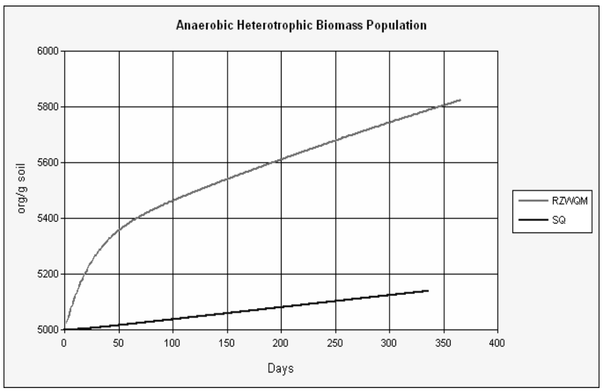

Figure 2 – Comparison between Sediment Quality and RZWQM for anaerobic heterotrophic biomass population

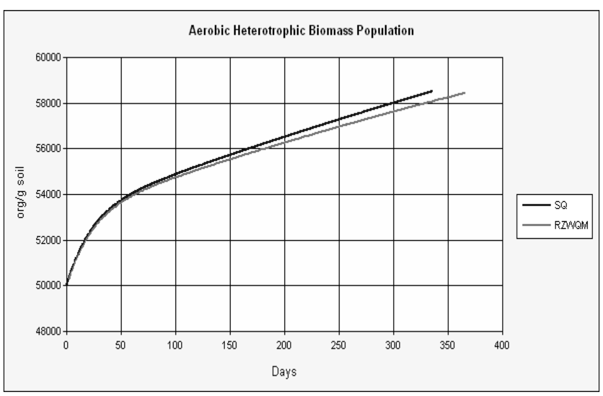

Figure 3 – Comparison between Sediment Quality and RZWQM for the aerobic heterotrophic biomass population

The models matched for organic matter pools but the results differ in the anaerobic population (Figure 2). This happens because RZWQM considers this population type as a facultative one, while in Sediment Quality it is considered as strict one. As a consequence, an aerobic part is growing in the anaerobic pool in RZWQM model. Nevertheless, this aerobic part of the facultative anaerobic population is not included in the aerobic heterotrophic pool, which is observed in Figure 3. Once the results for the organic matter pools matched (Figure 1), this conceptual difference between the models is not important.

For the nitrogen immobilization situation the results are shown in the next figures.

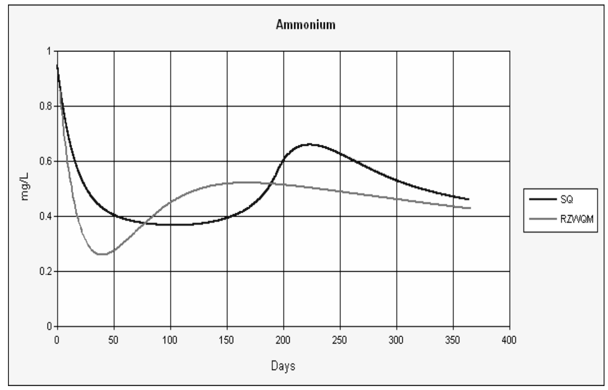

Figure 4 – Comparison between Sediment Quality and RZWQM for ammonium in nitrogen immobilization situation

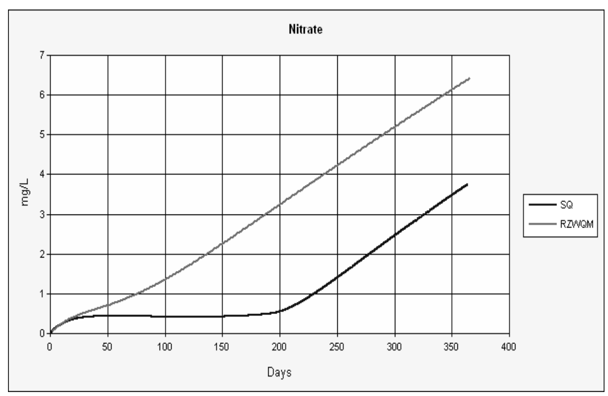

Figure 5 – Comparison between Sediment Quality and RZWQM for nitrate in nitrogen immobilization situation

In this situation, the models didn't match for two reasons: the first is that RZWQM did not use the equation (3) for the decision of the bacterial growth type. In fact, this model compares the bacteria potential organic matter decomposition rate with the available ammonium and not with the immobilization potential, as Sediment Quality does; the second one is that the first step in RZWQM is to check the ammonium availability. Then, if there is enough of it in the soil, bacteria will also immobilize nitrate. This conceptual difference is responsible for the different nitrate evolution in time (Figure 5).

After this comparison, some simulations were done in order to test the model response to temperature, pH, effective water content, soil porosity and wind variations.

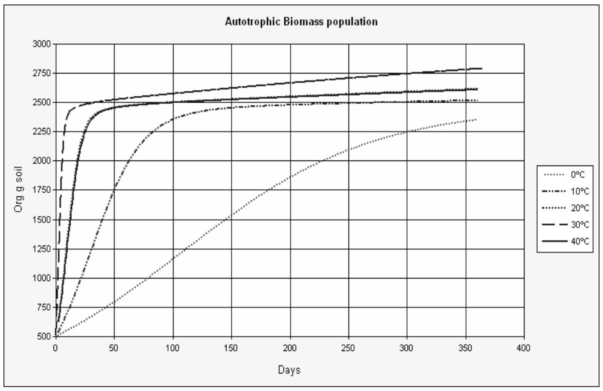

Figure 6 - Temperature influence in the autotrophic growth

Soil temperature variations showed that biomass in the model has an optimal growth temperature (Figure 6). Both heterotrophic and autotrophic populations had the same responses, although autotrophic population seemed to be more sensitive when temperature and pH changed.

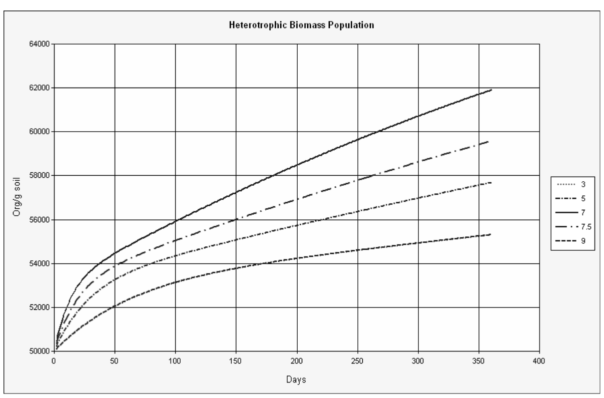

Figure 7 - pH influence in the heterotrophic growth

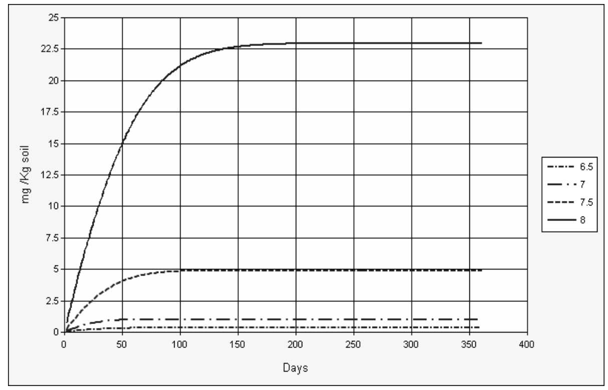

Figure 8 - pH Influence in the ammonia volatilization

The pH variations also showed an optimal pH for biomass growth at the neutral value. Nevertheless, for basic pH values the growth is lower than for acid ones (Figure 7). Ammonia is also affected by pH variations (Figure 8). While, for pH under 7, there is no NH_3 released, at pH equal to 8 this process becomes important for soil nutrients availability.

The effective water content effect is important to determine the level of the soil *aerobiose*. Depending on it, different processes will occur, such as nitrification or denitrification.

The different soil porosities were tested in order to simulate different aerobic factors calculated by Sediment Quality model.

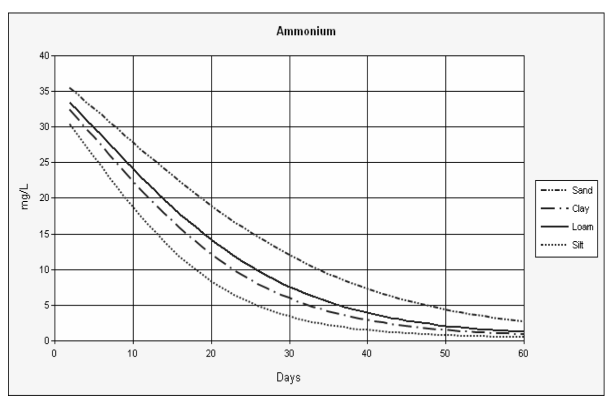

Figure 9 - Effects of the soil type in the ammonium depletion

In a sandy soil, which has a lower porosity value, there will be less space for oxygen, and an *anerobic* environment is more easily created. This can be observed in the ammonium depletion curve of (Figure 9), where nitrification process was not so efficient as it can be in a silty soil, which has a higher porosity. The same effect may be observed if water content varies within the same soil type. In that case, denitrification will be increasing with the decrease of oxygen level in the soil. If this becomes too important the nitrification, which is a source of nitrate, has no conditions to happen, while in the other hand denitrification acts as a nitrate sink, leading to a situation in which nitrate is being depleted, as it can be seen in (Figure 10) for $0.45m^3/m^3$ of water content.

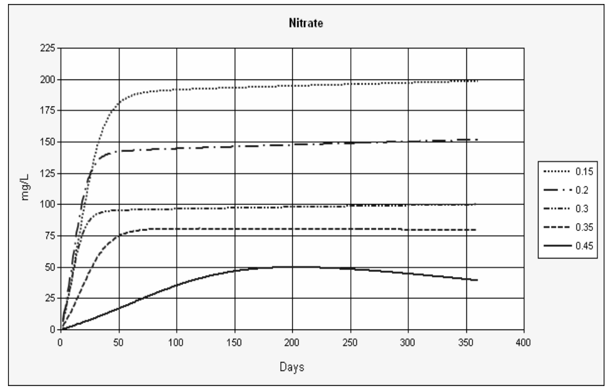

Figure 10 - Effect of water content in the nitrate

Wind variations affect the ammonia volatilization. Figure 11 shows the difference of the gas released for different wind intensities.

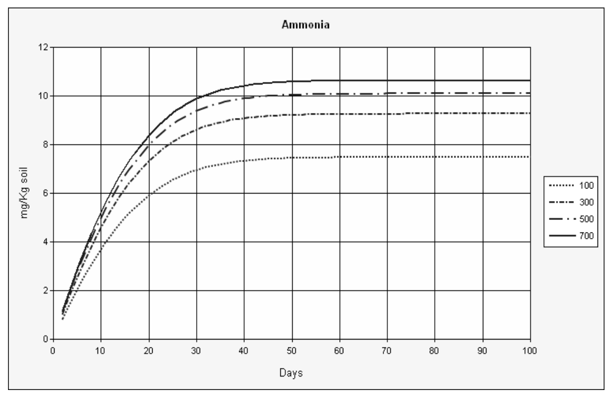

Figure 11 - Effect of wind (km/day) in the ammonia volatilization

4. RZWQM APPLICATION

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 specific part of the work was to get a global view of the integrated processes between plant-soil-atmosphere in agriculture.

RZWQM simulations were compared with experimental data from Agros 727 project, where a corn planting was made in Alvalade-Sado under different conditions of nitrogen fertilization and salinity. The input data used, given by the Estação Agronómica, was: meteorological and rain input, soil profiles and chemical properties. Input values for the different pools were also needed for organic and inorganic pools. For biomass population a calibration process was made, once these pools are very difficult to measure. The fertilization applied (date and amount Kg/ha) in Irrigation Water (Drip) was also an input, as well as the irrigation water salinity.

Results from these simulations showed that model had expectable responses. Different periods were observed in which the nitrate and ammonium behavior was different. Nitrate is depleted from the soil when plants are growing, uptaking it. Nevertheless, it can be accumulated (especially at the surface) during the fertilization period. When plants die, nitrate and ammonium increase in time, but nitrate in particular is transported through the soil because of the irrigation events and the precipitation periods. This accumulation is bigger when dead roots provide a fresh organic matter pool. In this time (October), mineralization and nitrification processes have a lot of influence in soil processes.

The comparison with experimental data for water content is shown in Figure 12.

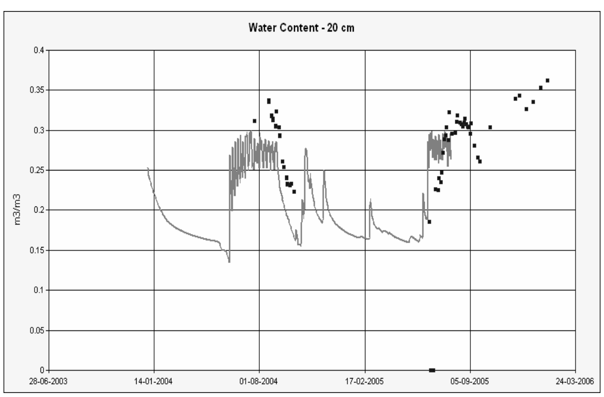

Figure 12 - RZWQM and Experimental Data results for Water content - 20 cm

Tests with nitrate and ammonium pools were also made, in order to compare the model with experimental data (Figure 13 and Figure 14).

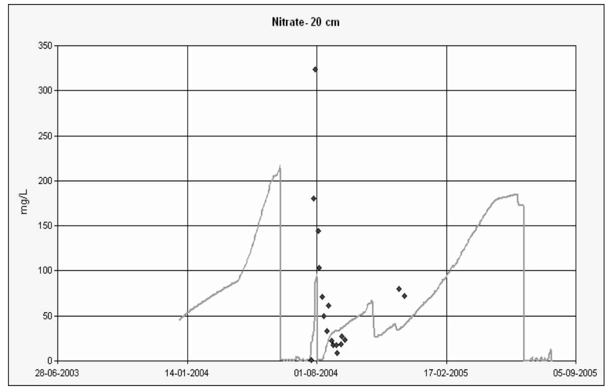

Figure 13 - RZWQM and Experimental Data Results for Nitrate - 20cm

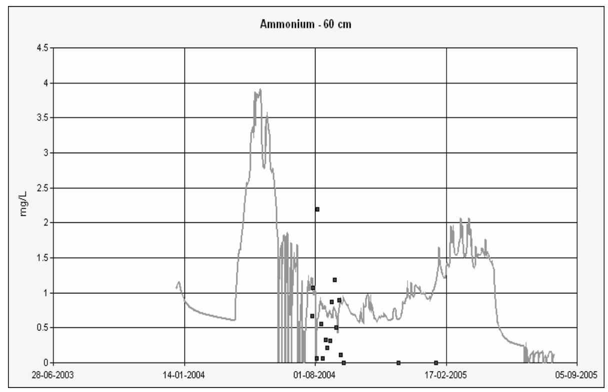

Figure 14 - RZWQM and Experimental Data results for Ammonium - 20 cm

The comparisons between experimental data and the model show that the model gives, in a general way, lower values for nitrate. This may be explained because organic matter mineralization is not correctly simulated by the model (Figure 15), and, in fact, nitrate evolution in time will depend on different processes and external inputs.

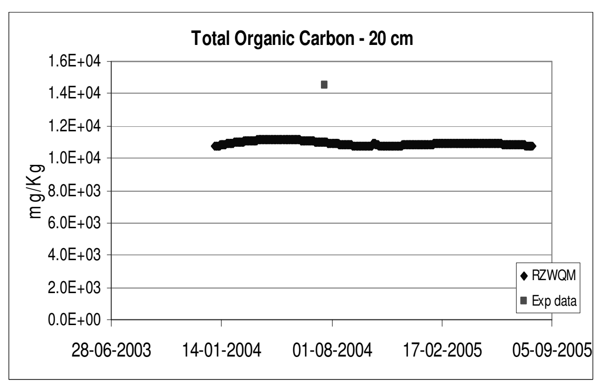

Figure 15 - Total Organic Carbon - 20 cm

5. CONCLUSIONS

This work developed a better tool with the following improvements:

- The inclusion of processes of the phosphorus Cycle, that explain Immobilization phosphorus situations as well as the fixation/ Solubilization processes, that may change phosphorus availability in soil.
- The inclusion of other processes simulated before by RZWQM model that are now included in Sediment Quality, increasing the action area of the model: Ammonia volatilization or Urea hydrolysis may become respectively a sink and a source of ammonium, influencing its availability for bacteria and plants uptake.

The model ability to respond to temperature, pH, soil porosity and wind variations, allowing a better modelling of the soil processes and their optimal environment. This is important once abiotic factors will not be constant in time or in the soil profile. Temperature variations showed that bacteria maximum growth occurs for an ideal temperature and pH. This is true for all the populations simulated, but autotrophic seems to be more sensitive than the others (Figure 6 and Figure 7). pH variations influence as well the Ammonia volatilization process. If pH is above the neutral value, this process is very important in the soil because ammonium will be depleted (Figure 8). Aerobic and anaerobic environment also exert strong influences in soil processes (

- *Figure* 10). Soil porosity variations showed that porous soils have more free space for oxygen ,allowing the development of an aerobic environment (Figure 9).
- The comparison between the model and RZWQM allowed the development of a more consistent tool. To do that, equations of RZWQM source code (2007) were introduced, and the comparison showed good results for the carbon and nitrogen cycle situations in which the approach was the same – Mineralization and Nitrification (Figure 1). In Immobilization, the models did not match, although they had similar curves (Figure 4).

RZWQM simulations in Alvalade – Sado for corn growth allowed a global view of the soil processes that occur in the soil and the fertilization influence.

Simulations for water content showed good results for the comparison with the experimental data. Nitrate and ammonium model results were not so good. The explanation for this result is fact that the model is not simulating organic matter mineralization as it should. Some other possibilities for these differences are the plants specific details related to their nitrogen demand because, in fact, nitrate is affected by different processes and external inputs and that should be taken into acount for future work.

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