MODELLING THE EFFECT OF AGRICULTURAL ACTIVITIES ON GROUNDWATER QUALITY IN THE AQUIFER OF N. MOUDANIA, GREECE

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EXTENDED ABSTRACT

Agricultural activity constitutes one of the most dominant components of global economy, while at the same time it is considered to be the most important anthropogenic source of nitrate contamination in groundwater. In the basin of N. Moudania in northern Greece the intensification of agricultural activities and the increasing use of fertilizers to improve crop productivity in conjunction with the failure to implement appropriate protective measures have contributed to the degradation of the groundwater in the region. Groundwater is used exclusively for the water supply of the region, a fact that renders groundwater protection an issue of high importance, since its quality has to meet the predefined standards, in order not to pose a threat for public health. This study was conducted in order to assess the impact of agricultural activities on the quality of groundwater in the region, as well as to study the influence of various parameters to the transport of nitrate and subsequently to nitrate concentrations in the study area. To this task, a set of several two-dimensional nitrate transport simulation were carried out, using the MT3DMS model, in order to evaluate: (a) the overall impacts of current crop distribution and fertilizer application, (b) the efficiency of proposed protection alternatives on nitrate pollution in the aquifer and (c) the uncertainty of specific parameters, such as effective porosity and denitrification coefficient. The estimation of nitrate loading percolating in the underground aquifer, which depends on the type and the distribution of crops, as well as the groundwater velocity field determined by MODFLOW, are considered to be a prerequisite for the proper application of the transport model. The results highlighted those areas that are affected the most in each simulation and also showed the influence of the various parameters of the transport model, revealing those that have to be taken into consideration thoroughly in future research.

Keywords: groundwater resources management, groundwater pollution, agricultural activities, nitrate contamination, groundwater modelling

1. INTRODUCTION

Nitrogen is considered to be a vital nutrient to enhance plant growth. This fact has contributed to the increased application of nitrogen-based fertilizers in order to improve crop productivity in many rural regions of the world, which has been accompanied by an increase of nitrate concentrations in water resources. The basin of N.Moudania, in the region of Halkidiki in Northern Greece, is a typical agricultural region, which is cultivated and irrigated intensively throughout the year. The significance of the problem lies on the fact that when nitrogen fertilizer application exceeds the plant demand and the denitrification capacity of the soil, nitrogen can leach to groundwater usually in the form of nitrate which is highly mobile with little sorption, causing serious health problems, especially to infants (Almasri & Kaluarachchi, 2007).
In this paper, a two-stage methodological approach was implemented in order to assess the overall impacts of current crop distribution and fertilizer application in the basin of N. Moudania. The first part of this approach emphasizes on the development of a groundwater flow simulation model, using the modular three-dimensional finite-difference groundwater flow model MODFLOW (McDonald and Harbaugh, 1988). Then a set of several nitrate transport simulations was carried out, using the modular three-dimensional multi-species transport model MT3DMS (Zheng & Wang, 1999), in order to study the fate of nitrate when changing the values of various parameters such as effective porosity, dispersivity, denitrification coefficient, and nitrate loading. The results of this approach form a generic image of the nitrate transport process in the study area, so they can be used as a basis for further research regarding nitrate pollution.

2. DESCRIPTION OF THE STUDY AREA

The basin of the study area extends to the Southwest of the prefecture of Halkidiki, occupies an area of 127.22 Km² and is divided into two sub-regions, the hilly area in the North (46.3%) and the flat area in the South (53.7%) (Figure 1) (Latinopoulos et al, 2003). A more comprehensive description of the study area regarding its geomorphology, geology, hydrogeology, hydrologic and climate conditions can be found in Siarkos and Latinopoulos (2013). Agriculture dominates both local economy and land use in the study area. Intensive farming techniques with intensive irrigation are observed throughout the region (Siarkos et al, 2012). This has led to an extensive nitrate contamination in the whole region, as several recent investigations show. Moreover, there is no control in the application of fertilizers, rendering the existing situation even more alarming.

All the settlements in this area rely exclusively on groundwater resources. Specifically, 37 domestic-supply wells are operating (usually at close distance from settlements) and are distributed as follows: St. Panteleimon (3), Zografou (2), Dionisiou (5), Portaria (5), Flogita (7), Simantra (6) and N. Moudania (9) (Figure 1). In the following analysis these wells constitute the critical receptors, which are used in order to both evaluate and compare the results of the various simulations, by observing the nitrate concentrations at them.

3. MODELLING FRAMEWORK

3.1. Groundwater flow model

Groundwater flow simulation was conducted in two steps. A steady-state simulation was first carried out in order to adjust specific model parameters, such as hydraulic conductivity and conductance, as well as to get the initial head values for the transient simulation. A transient-state simulation was then performed in order to adjust the rest of the parameters (e.g. groundwater recharge, storage coefficient), as well as to observe the aquifer response (head distribution) at different time periods under different stresses (recharge and discharge). To this task, pumping (1st May – 30th September, 153 days) and nonpumping (1st October – 30th April, 212 days) periods were considered, since both recharge and discharge receive different values in each period. All the input data of the study area required for the simulations was based upon compiled information derived from Latinopoulos et al (2003).
The model domain was discretized into a single layer finite difference grid of 120 rows and 80 columns, making a total of 6,555 active cells of dimensions 150x150 m. The one layer in the Z-axis represents the semi-confined aquifer, which constitutes the main exploitable aquifer of the study area, whose thickness (250m) was obtained based on well logs and geological sections. Regarding the boundary conditions, the eastern and western boundaries are no-flow boundaries, as there is no hydraulic connection between the aquifer body and the eastern and western regions. The south and north boundaries were both simulated as general head boundaries (GHB), illustrating the lateral groundwater inflows or outflows occurring from them. The south boundary coincides with the sea level (0m), while the north boundary does not coincide with the physical boundary of the aquifer, but, based on observed data, it was set at the isopiezometric contour line of 150m (Figure 1), varying in time as far as the transient simulation is concerned. The various aquifer parameters, such as hydraulic conductivity and storage coefficient were obtained from pumping tests. The values of these parameters were assigned to six distinct zones using the Thiessen Polygon method. Rainfall, irrigation return water and wastewater return water are considered to be the exclusive factors that contribute to the recharge of the aquifer, while the groundwater of the study area is abstracted for domestic, irrigation and livestock purposes. More details about the determination of both recharge and discharge can be found in Siarkos & Latinopoulos (2013).

In this model framework, a two-stage simulation – calibration procedure was followed. First, a quasi-steady state calibration was performed (18 observation wells monitored on September 2001) by using a trial-and-error process of adjusting initial estimates of specific model parameters, such as hydraulic conductivity and conductance (within acceptable ranges) to obtain the best match between simulated and measured water levels. The hydraulic conductivity values ranged between 0.09 and 0.60 m/d, while conductance received a value of 1.1 m²/d in the north boundary and 1.0 m²/d in the south boundary. Then, a transient state calibration was carried out during the one-year period: 1/10/2001 – 30/9/2002. The one-year period was divided into two stress periods, representing the pumping and the nonpumping periods. As before, the transient
calibration (13 observation wells monitored on September 2002) was performed by using a trial-and-error process of adjusting initial estimates of specific model parameters, such as recharge and storage coefficient (within acceptable ranges) until a satisfactory convergence between model results and observed field data was obtained. The recharge values ranged between 0.216 and 0.359 mm/d in the pumping period and between 0.146 and 0.281 mm/d in the nonpumping period, while storage coefficient values ranged between 2.5x10^-2 and 3.75x10^-2. The models generally performed well, but due to the low number of measurements available, an accurate comparison between measured and simulated values was not possible. After the calibration process, the model was run for a 20-year simulation period (2002 - 2022).

3.2. Nitrate fate and transport model

A nitrate transport model developed based on the transient flow model using the same spatial and temporal discretization. Several simulations were performed, depending on the modifications that were made to the various parameters of the transport model. For all the simulations initial and boundary condition were considered constant. More specifically, the distribution of initial nitrate concentrations in the aquifer was undertaken by applying the Kriging method to nitrate concentrations measured at several boreholes at the beginning of the simulations (2001), while regarding the inflow boundaries fixed concentrations of 0 and 3 mg/l (which is equal to natural background concentrations) were assigned to the south and north boundaries, respectively.

Once nitrogen enters the soil, it undergoes several biochemical transformations before leaching to groundwater mostly as nitrate. The main reactions and pathways that the nitrogen undergoes include mineralization, immobilization, nitrification, denitrification, volatilization, crop uptake, and leaching from the soil zone (Almasri & Kaluarachchi, 2007). It has been reported in many studies that approximately 30% to 50% of the applied nitrogen fertilizer leaches to groundwater in the nitrate form (Shamrukh et al., 2001). In this study, 40% of the total nitrogen load was assumed to reach the groundwater system, while a recharge concentration boundary condition was chosen to simulate nitrate leaching. After estimating the nitrogen load by multiplying the fertilizer application rate for each crop with the corresponding fertilized area for each municipal district (Figure 1) and taking into account all the loses due to the aforementioned reactions, the final nitrate load percolating in the groundwater system was estimated. Table 1 presents the nitrate loading entering the groundwater, as well as the final nitrate leaching amount (in mg/l) per municipal district for pumping and nonpumping periods. The higher values of the nitrate load at the nonpumping period result basically from the fact that an annual and not a seasonal nitrate leaching was considered (equal distribution through the year). Furthermore, the recharge is higher during the pumping period.

With regard to the various transport parameters, the longitudinal dispersivity was fixed at a constant value of 25m based on the dependence relation between scale and dispersivity reported in the literature, the ratio of transverse to longitudinal dispersivity was taken as 0.1 and the molecular diffusion was considered to be negligible (Almasri & Kaluarachchi, 2007). Moreover, a uniform effective porosity value of 0.05 was used in the numerical model for the basic simulation. This value corresponds to the geological composition of the aquifer, which consists of alternated beds of sandstones, marls, sands, gravels and red to brick red clays (Latinopoulos et al., 2003).

Finally, since NO₃ does not form insoluble minerals, neither precipitates nor is adsorbed, the only natural way of removing nitrate from aquifers is by reduction, i.e. denitrification which is considered to be the dominant chemical reaction that affects nitrate concentration in the groundwater under anaerobic conditions. Denitrification is basically
modeled by a first order irreversible rate reaction, taking into consideration the half-life time of nitrates which ranges between 1–2.3 years (Shamrukh et al., 2001; Almasri & Kaluarachchi, 2007). For the basic simulation denitrification was considered to be negligible and thus a conservative transport simulation was conducted.

### Table 1: Nitrate leaching per municipal district for pumping and nonpumping periods

<table>
<thead>
<tr>
<th>Municipal District</th>
<th>Nitrate load (kg/d)</th>
<th>Pumping period nitrate leaching (mg/l)</th>
<th>Non-pumping period nitrate leaching (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. Moudania</td>
<td>280.47</td>
<td>71.70</td>
<td>117.98</td>
</tr>
<tr>
<td>Dionisiou</td>
<td>169.82</td>
<td>64.10</td>
<td>108.73</td>
</tr>
<tr>
<td>Zografou</td>
<td>130.90</td>
<td>111.14</td>
<td>193.22</td>
</tr>
<tr>
<td>Portaria</td>
<td>330.99</td>
<td>47.69</td>
<td>103.12</td>
</tr>
<tr>
<td>Flogita</td>
<td>263.85</td>
<td>112.44</td>
<td>177.28</td>
</tr>
<tr>
<td>Ag. Panteleimon (flat area)</td>
<td>68.29</td>
<td>112.89</td>
<td>166.97</td>
</tr>
<tr>
<td>Ag. Panteleimon (hilly area)</td>
<td>15.69</td>
<td>72.19</td>
<td>87.03</td>
</tr>
<tr>
<td>Simantra (flat area)</td>
<td>170.95</td>
<td>88.88</td>
<td>148.28</td>
</tr>
<tr>
<td>Simantra (hilly area)</td>
<td>402.95</td>
<td>60.46</td>
<td>77.39</td>
</tr>
</tbody>
</table>

### 4. Results

#### 4.1. Basic simulation

The basic characteristics of this simulation regarding the various parameters of the transport model were presented in the previous chapter. Here, the results of the simulation for the study period (2001-2022) are displayed. Figure 2 illustrates the nitrate distribution at the end of the simulation period, indicating those areas that are affected the most. These are the municipal districts of Flogita, Zografou and Simantra. The greater values of nitrate concentrations are observed in the Flogita district. Figure 3 shows the nitrate concentrations at the various critical receptors (water-supply wells) in 2022. As it is obvious, nitrate concentrations in 23 wells located in Flogita, Simantra, Zografou, Dionisiou and N. Moudania exceed the 25 mg/l guide level set by the Nitrate Directive.

#### 4.2. Nitrate loading influence

In this simulation, the values of the various parameters of the transport model were kept the same apart from the nitrate loading which achieved a 50% reduction. Figure 4 illustrates the nitrate distribution at the end of the simulation period, indicating those areas that are affected the most. As before, these are the municipal districts of Flogita, Zografou and Simantra. But this time, nitrate concentrations are lower than before, since nitrate load was decreased. Figure 5 shows the nitrate concentrations at the various critical receptors (water-supply wells) in 2022. As it is obvious, nitrate concentrations only in 4 wells located in Flogita and Simantra exceed the 25 mg/l guide level. In most of the wells (17) nitrate concentrations are between 20 and 25 mg/l.
4.3. Denitrification influence

In this simulation, denitrification process was taken into consideration. As mentioned before, nitrate reduction by denitrification can be modeled by a first order irreversible rate reaction, taking into account the half-life of nitrates. For this simulation a value of 2.3 years was considered, which corresponds to a value of the first-order decay coefficient of 0.000825 d⁻¹. Results of this simulation show a remarkable decline of nitrate
concentrations at the end of the simulation period. The highest value at the critical receptors is approximately 3.75 mg/l, which is far from the values mentioned in recent investigations (Latinopoulos et al, 2003; Siarkos et al., 2012). So, denitrification may not take place in the study area or at least occur in slower rate, which can be attributed to the limited amount of available organic matter or pyrite. Moreover, the absence or at least the very low levels of nitrite in the water samples lead to this conclusion as well.

4.4. Dispersivity and porosity influence

In these simulations both longitudinal dispersivity and effective porosity were assumed to vary ±50% from their initial value in order to investigate the sensitivity of the simulated system. Regarding dispersivity the results showed that its variation has no effect at all on the nitrate concentrations. This can be attributed to the fact that for the nonpoint source contamination such as nitrate pollution for agriculture activities, the effects of longitudinal and transverse dispersion are of less importance since there is no transition zone between the contaminated and non-contaminated areas (Shamrukh et al., 2001). With regard to effective porosity, its variation results in remarkable variations of nitrate concentrations, especially in the case of decreasing its value. Figures 6 and 7 present the nitrate distribution in year 2022 for the various effective porosity values.

![Figure 6: Nitrates distribution in the study area (2022, +50% porosity)](image1)

![Figure 7: Nitrates distribution in the study area (2022, -50% porosity)](image2)

What is worth mentioning in the case of decreasing effective porosity value is not only the increased nitrate concentrations in the Flogita district which exceed the maximum allowable limit of 50 mg/l, but also the greater effect of the south boundary condition to the nitrate concentration field, since seawater intrusion occurs through this boundary. Moreover, Figure 8 shows the nitrate concentrations through the whole time simulation at a typical well for the various effective porosity values. The greater influence in the nitrate concentrations when effective porosity decreases is more than obvious.
5. CONCLUSIONS

In this paper, a transport model based on a calibrated transient flow model was developed in order to study the fate of nitrates in a rural area, as well as to assess the influence of the various transport parameters to the nitrate concentrations. To this task, several simulations were conducted in each of which a different parameter was examined. The results showed that, considering the basic simulation, nitrate concentrations are high enough (>25mg/l) in the most part of the critical receptors in the study area. The other simulations resulted that the model is more sensitive in certain parameters, such as effective porosity and denitrification rate, than others (e.g. nitrate load, dispersivity). With regard to denitrification the simulated nitrate concentrations demonstrate that this process may not occur in the study area, while as far as effective porosity is concerned, it has the strongest influence on the model, especially when its value decreases. Dispersivity has no influence over the results. For future research, an adequate calibration of the transport model should be performed, as well as a proper adjustment of the parameters of high uncertainty, through the calibration process.

REFERENCES