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Nitrate pollution from agricultural activities of a shallow aquifer in Chalkidiki Peninsula, Greece

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ABSTRACT

The south-western part of Chalkidiki Peninsula in Northern Greece is an area with intensive agricultural use. Uncontrollable application of fertilizers during the past years has lead to high nitrate concentrations in local ground waters. In order to assess the extent of contamination and to prevent further deterioration of the regional groundwater resources, a combined field and desk study of the area has been recently initiated. In the paper, results from the two approaches are presented. After the description of the geology and hydrogeology of the area, basic information on the agricultural land use is provided followed by the results of field investigations, which include water chemical analysis and a study of the nitrate concentrations frequency distribution and spatial variation. Finally, a numerical study refers to solute transport simulations along a representative vertical section of a local shallow phreatic aquifer, using a two-dimensional finite element model. The results of the whole study are expected to serve in the development of a long-term prognosis of the fate of the groundwater resources.

INTRODUCTION

The adverse effects to human health from exposure to water containing nitrate at high levels are mainly concerned with methemoglobinemia, an acute toxic response in sensitive populations, and especially in children. To eliminate this specific risk a drinking water standard has been imposed in most European countries which sets the maximum permissible nitrate concentration equal to 50 mg/l. On the other hand, there is no much evidence for adverse health effects, particularly carcinogenic, from chronic exposure to low levels of nitrate, so that the magnitude of this risk is still in debate [1].

The nitrate contamination of groundwater comes from natural as well as anthropogenic sources. With regard to agricultural activities, concentrations of nitrate greater than background levels are caused principally by the intensification of plant production which normally leads to high rates of nitrogen fertilization, but also by liquid manure production and by the conversion of large areas with grassland to arable land use. Today there is a clear evidence that, at least in Western Europe and the USA, nitrate contamination of groundwater can be considered as pandemic ([1], [2]).

As in most places in the world groundwater is a significant source of water for domestic and agricultural use, the issue of reducing nitrate contamination is nowadays of great importance. This explains the numerous research projects dealing with this subject worldwide. Despite the fact that in Western Europe field investigations related to nitrate contamination of groundwater have reached a rather satisfactory level ([2], [3]), the situation in Greece is yet not a promising one. Due to limited research activity, information on nitrate pollution in Greek aquifers is sparse and relevant publications are sporadic [4].

The present study concerns a combined field and desk analysis of an agricultural area in Northern Greece, of which the ground waters are nitrate-contaminated as a result of intensive fertilization. The purpose of the study is to present a first picture of the problem; it therefore comprises a brief presentation of all data available regarding geology, hydrogeology and water chemical analysis, followed by statistical and geostatistical analysis of nitrate concentrations. In addition, a numerical model suitable for groundwater flow and contaminant transport simulations in the vertical plane is employed in order to derive some basic conclusions concerning the nitrate distributions in the local aquifers.

DESCRIPTION OF THE STUDY AREA

The study area lies in the south-western part of Chalkidiki Peninsula in Northern Greece (Figure 1). Almost 85% of the area shown in Figure 1 is at present used as agricultural land; the rest, non-agricultural land use is mainly urban and touristic development. The coastal area under study is the lower half of a catchment, generally characterized by limited natural vegetation found only in its northern part, which is not shown in Figure 1. The hydrographic network is dense draining directly to the sea, while the most exploited part of the local groundwater resources is confined to three coastal phreatic aquifers (Figure 1).

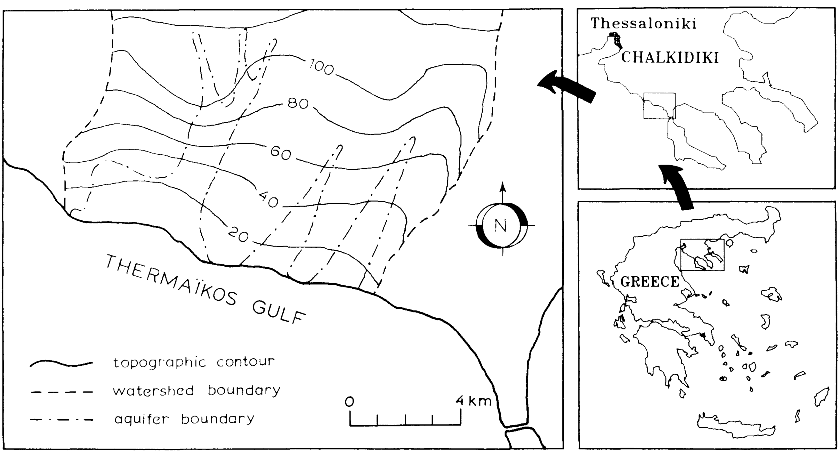

Figure 1. Location and simplified map of the study area.

Geology and hydrogeology

The three shallow phreatic aquifers present many similarities. In addition to their shape and average thickness, theses aquifers are very much alike regarding both geology and hydrogeology: they consist of quaternary alluvial deposits, predominantly comprised of superficial layers of sand and gravel with small pebbles in some parts; they are underlain by clayey formations that can be assumed impermeable; in the mass of clay a few lenses of sand, gravel and loam are found; groundwater flow is to the southwest, i.e. towards the coast. Moreover, these aquifers have been developed over the past 40 years for irrigation purposes by pumping through many shallow wells, usually at small abstraction rates. A limited number of boreholes, drilled in deeper formations, are used for domestic supplies by three small villages in the coastal area.

Figure 2 shows a representative section of the middle aquifer, as seen in Figure 1. Due to the above mentioned similarities, this aquifer was assumed to be a typical case and it was therefore adopted for a more detailed study. The hydrogeological survey was supported by geophysical prospecting methods - basically the apparent resistivity method - in order to estimate layers' thickness and consistency of the current geological deposits. Lithological data from various wells were also taken into account and they were related to the geophysical data.

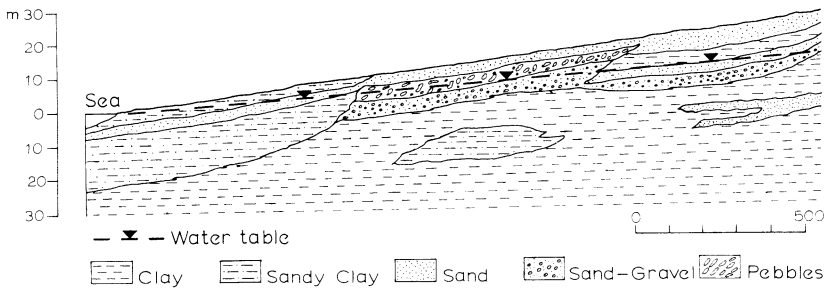

Figure 2. Representative section of the alluvial aquifer under study.

The water table shown in Figure 2 corresponds to recently recorded groundwater levels and has an average gradient value of the order of 0.006. Pumping tests performed in the central aquifer showed a variation of the hydraulic conductivity in the permeable strata of about 4 - 45 m/d.The average annual precipitation in the area is 410 mm. Recharge calculations for the period 1975 - 1992 using classical hydrological methods [5] lead to an annual average of 150 mm.

Agricultural land use

As mentioned in the introduction, the aquifer under study is situated in a region with intensive agricultural activities. During the last four decades, almost the total area has been used as agricultural land, with vegetables dominating among the common crops. Uncontrolled application of N fertilizers has lead to severe nitrate pollution of ground waters (see next paragraphs). The locally available information on fertilizer use gives an average value of 400 Kg N/ha/yr applied to crops.

Regarding the actual leaching of nitrate, the lack of in situ measurements is the major source of uncertainty of nitrate input into the groundwater. By adopting typical values for the relevant crops from the literature and applying standard methods, in which the average annual recharge is also taken into account ([2], [6]), the mean annual nitrate concentration of the groundwater recharge was estimated to be about 120 mg/l.

FIELD ANALYSIS

Water sampling and chemical analysis

In the field area 54 wells were established for sampling at different depths. About half of them are located within the three shallow phreatic aquifers shown in Figure 1. The rest lie in the broader area and are mostly deeper so that the whole range of well depths is 6 - 50 m. The sampling period was from August to November 1991. Sampling refers to pumped raw water which means that local variations can not be taken into account. Temperature, pH, and electrical conductivity were measured in the field while all common ions were analyzed in the laboratory using standard methods[7]. In particular, nitrate concentrations were determined with a nitrate ion selective electrode.

Excluding nitrate concentrations, the results of the chemical analysis were within normal ranges for most of the ions. Increased chloride concentrations, found in some deep wells located close to the coast, were more or less expected. However, high NO_3 concentrations were detected in most wells; therefore - and in concordance with the scope of this work - a detailed presentation of the NO_3 distribution in the area is given in the following paragraphs.

Frequency distribution and spatial variation of nitrate

A representative illustration of the location of the sampled wells and the distribution of nitrate concentrations is given in Figure 3. The set of 54 NO_3 concentrations was tested for normal and log-normal distribution, as it is common with this ion ([6], [8]), by means of the chi-square test. At a significance level a=5% the NO_3 concentrations showed to be log-normally distributed (Figure 4a). The basic statistical parameter values of this data set are (in mg/l): range = 10-123, arithmetic mean = 48.9, geometric mean = 41, median = 40.5, standard deviation = 29.8 and coefficient of variation = 0.6. This small variability could be explained by the fact that sampling was made in the same period of the year. A first conclusion drawn from this analysis is that, in order to reliably determine area-representative mean NO_3 concentrations, repeated sampling has to be done at different times([2], [6]).

A geostatistical analysis was next performed to investigate the spatial variation and correlation of NO_3.Results are shown in Figure 4b, where the experimental values of the normalized variogram function (i.e. the variogram function divided by the sample variance) are plotted against the lag distance between sampling points. A spherical theoretical model showing no nugget effect was fitted to the experimental data. The absence of a nugget effect and the apparent correlation of NO_3 concentrations with distance - up to 1750 m approximately - are rather questionable findings which may be due to the large area examined. In previous studies ([6], [8]), with lag distances less than 500 m, NO_3 concentrations were found spatially independent at lag distances greater than 10 m. From the above it can be inferred that a more dense sampling network would be more appropriate for future investigations.

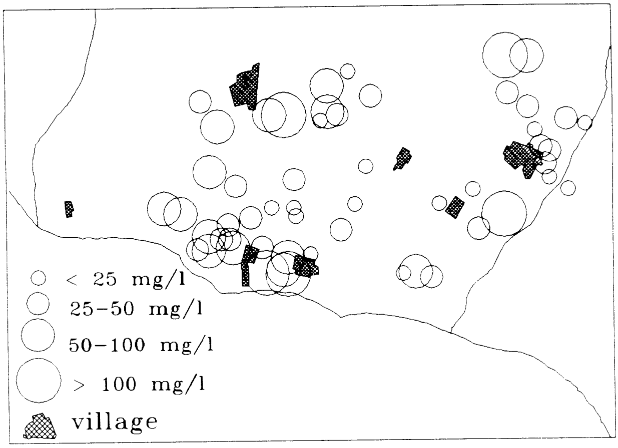

Figure 3. Field site, showing location of wells and nitrate concentrations.

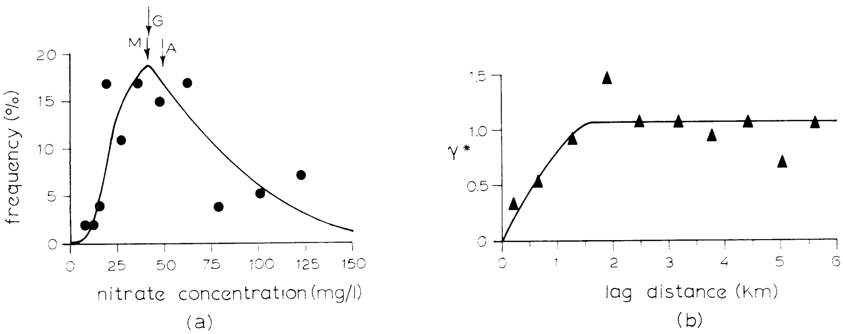

Figure 4. a. Frequency distribution of nitrate concentration (M=median: G=geometric mean: A=arithmetic mean) b. Normalized variogram of nitrate.

NUMERICAL SIMULATIONS

The groundwater flow and nitrate transport model

The numerical study refers to steady-state flow and transient transport simulations along the representative vertical cross section of the middle aquifer, shown in Figure 2. Vertically two-dimensional flow and transport models are very often used in non-point source pollution problems because the horizontal gradients of the contaminants, i.e. the nitrates in our case, are usually small [9]. Since the system of the three shallow aquifers in Figure 1 is characterized by an arealy distributed input of nitrate over their surfaces and by a similarly distributed well field with small abstraction rates, as mentioned above, the decision to make the analysis in the vertical plane is fully justified.

The large length-to-depth ratio of the cross section is the main reason to select the principal direction formulation for the solution of the flow problem. Thus, a well-proven model named FLONET is employed to solve the dual problem for potentials and stream functions [10]. Due to the small well abstraction rates, the flow domain is supposed to be not affected by the operation of nearby wells. Nitrate transport simulations are performed through an efficient finite element code based on a numerical scheme proposed by Leismann and Frind [11]. The flow net grid provided by the flow model is used to generate the finite element grid for transport simulations. The model solves the transport equation in the vertical plane, i.e.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_{xx}\frac{\partial c}{\partial x}\right) - \frac{\partial}{\partial z}\left(D_{zz}\frac{\partial c}{\partial z}\right) - u\frac{\partial c}{\partial x} - \lambda c \qquad (1)$$

where c is the nitrate concentration, D_{xx} and D_{zz} are the dispersion coefficients in the two principal directions, u is the velocity in the flow direction, and λ is the decay coefficient, assumed to represent denitrification as a first-order reaction ($\lambda = \ln 2/t^*$, where t^* is the half-life for denitrification). If the molecular diffusion is assumed to be negligible the dispersion coefficients are defined as

$$D_{xx} = \alpha_L u \quad \text{and} \quad D_{zz} = \alpha_T u \qquad (2)$$

where α_L and α_T are the longitudinal and transverse dispersivities, respectively.

Input data and model application

The limited site-specific data concerning the dynamics of nitrate transport does not allow for a reliable calibration of the transport model. On the contrary, the hydrogeologic data are sufficient to develop a very representative flow model for the area. The flow net shown in Figure 5 is generated by assuming two pricipal zones of different hydraulic conductivities, according to Figure 2, with mean values equal to 4.3 m/d for sandy clay and 43.2 m/d for sand and gravel layers. A ratio of anisotropy of 10:1 is also assumed for the hydraulic conductivities in the two principal directions x and z, respectively. A match of the observed water table position shown in Figure 2 is achieved by imposing an influx of 18.25 m/yr at the right boundary, in addition to the 0.15 m/yr recharge at the water table.

Since the parameters required in the transport equation (1) are not measured in the field, values taken from the literature for systems having similar physical characteristics and scale are adopted. The dispersivities chosen are α_L = 10m and α_T = 0.001m. Due to high uncertainty regarding nitrate reduction due to denitrification in the saturated zone, two different values of the decay coefficient, λ, are examined, i.e. for t^*=2 and t^*=0.5 years. Finally, a constant concentration influx of 120 mg NO_3/l is imposed at the water table.

In Figures 6 and 7 simulated distributions of nitrate concentrations for the two assumed denitrification processes are shown. Since the time period required to reach a steady-state situation is of a few years only, we accept that the distributions shown in these figures are representative of the present conditions. With this in mind, a straight comparison with measured raw water nitrate concentrations in the area favours the longer half-life scenario shown in Figure 6.

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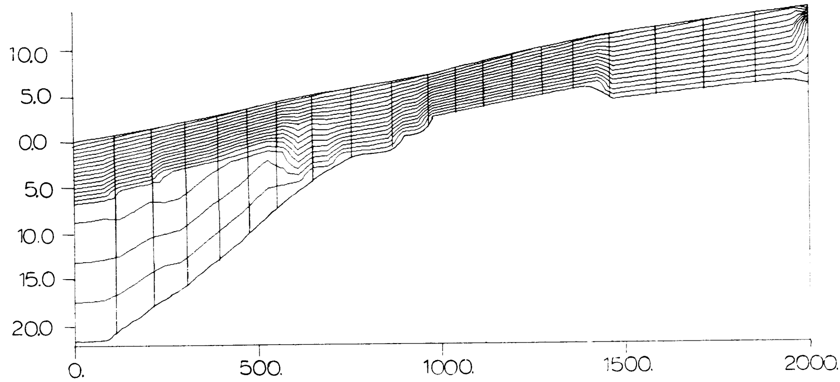

Figure 5. The cross sectional flow net.

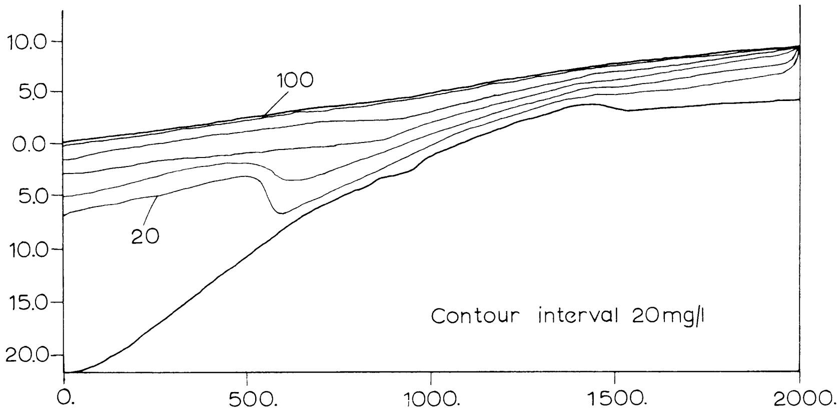

Figure 6. Simulated nitrate concentrations for t*=2 years.

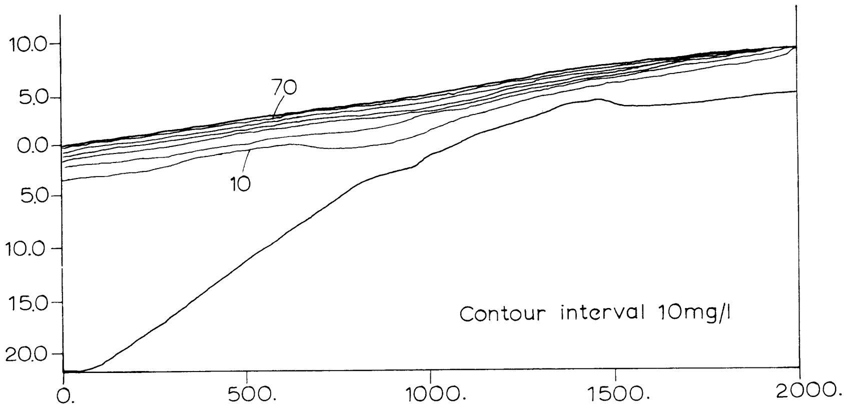

Figure 7. Simulated nitrate concentrations for t*=0.5 year.

CONCLUSIONS

The study of a typical shallow aquifer in Chalkidiki Peninsula presented in this work is, to our knowledge, the first integrated approach concerning agricultural nitrate pollution of groundwater in Greece. Yet, the lack of detailed in-situ investigations related to the dynamics of nitrate transport does not allow for reliable predictions for the quality of extracted groundwater. The results of statistical, geostatistical and numerical transport analyses are, nevertheless, elucidating the problem and can be used as guidelines for the continuation of investigations in the area.

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