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Groundwater Pollution from Agricultural Activities: an Integrated Approach

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1. Introduction

Non-point pollution is the most widely spread water contaminant on earth. Nitrate pollution is a serious problem in all European countries (Spalding and Exuer 1993, European Com. Report 1991, Anastasiadis 1994, Xefteris 2000). Nitrate contamination originates mainly from agriculture applications, particularly from the extensive use of nitrogen fertilizer and manure, which leads to nitrate leaching from large land areas in the soil and eventually into the groundwater. This-non point contamination cannot be delineated or controlled. The analysis and prediction of diffuse sources of groundwater pollution, as in case of nitrates, is a very difficult task, due to a variety of reasons such as a) the complex physical process of flow and transport, b) the large scale of the problem and c) the inherent difficulties of efficient sampling. All kinds of processes occur in both the unsaturated and saturated zones and it is, therefore practically infeasible to couple all individual models in order to understand the phenomenon as a whole.

Nitrate in soil and groundwater also derived from nature. Natural concentrations of nitrate in groundwater exist in many ecosystems, such as forest and grassland, which are nitrate conserving. This kind of concentration does not exceed 3 mg NO_3-N/l and is not available for leaching and transport to groundwater unless the ecosystems are disturbed by human activities (Bouchard et al., 1992). In European Union a slightly higher value of 11.3 mg NO_3-N/l is used, which is equivalent to 50 mg NO_3/l.

High nitrate contamination in drinking water has adverse effects on human health, mainly because they can cause a potentially fatal disease to infants called methemoglobinemia. Apart from that there is epidemiological evidence based mainly on correlation studies, that chronic exposure to nitrate can be related to hypertension, central nervous system defects and certain cancers (Dourson et al., 1991, NRC 1985, ECETOP 1988, Mirrish 1991).

As groundwater is the only source of potable water in many places on earth, assessing the health risks from chemicals and protecting humans are given priority in government decisions. For this purpose a complex procedure is required that integrates research and technical expertise from various scientific disciplines. An approach to face the nitrate problem would certainly include the study of the fate of nitrate in soil and groundwater, as affected by a variety of environmental and anthropogenic processes and the evaluation of existing and the development of new agricultural practices relating to quality control and management.

For Greece, a member state of European Union, agriculture is a very important sector for the economy and thus the cost of groundwater pollution is an inevitable consequence of its development. Agricultural activities in Greece employ 27% of active population when at the same time the average in European Union is 8%. (N. S. S., 1995). Additionally the 80-90% of total water consumption is used for agricultural activities.

2. The study area

The contaminant plume considered in this paper occurs in a coastal, shallow, phreatic aquifer which is located in the south-west part of Chalkidiki Peninsula in Northern Greece (Fig. 1). The aquifer under study is a part of a large watershed which drains to Thermaikos Gulf. A large part of the area is used as agricultural land. Intense agricultural activity during the last decades sustained by heavy nitrogen fertilization has caused severe nitrate contamination in groundwater removed from shallow irrigation wells and deeper boreholes.

The structure and hydrogeology of the system are typical of a coastal multiaquifer system in Greece. The upper part, which is the object of this study is characterized by alternating sands and gravels with small pebbles in some places. These formations are underlain by clayey layers at depths that vary from 5 to 25 meters. A geophysical prospecting method was used in connection with lithological data from various wells, in order to estimate the thickness of various layers and the consistency of the geological deposits. The groundwater flow direction is towards the coast and the average gradient of the water table has been found by resent groundwater level measurements to be an order of 0.006. A number of pumping tests performed in the aquifer lead to a range of hydraulic conductivity values between 4 and 45 m/d in the permeable strata. Recharge calculations using precipitation data of the last two decades gave result of an annual average of 150 mm.

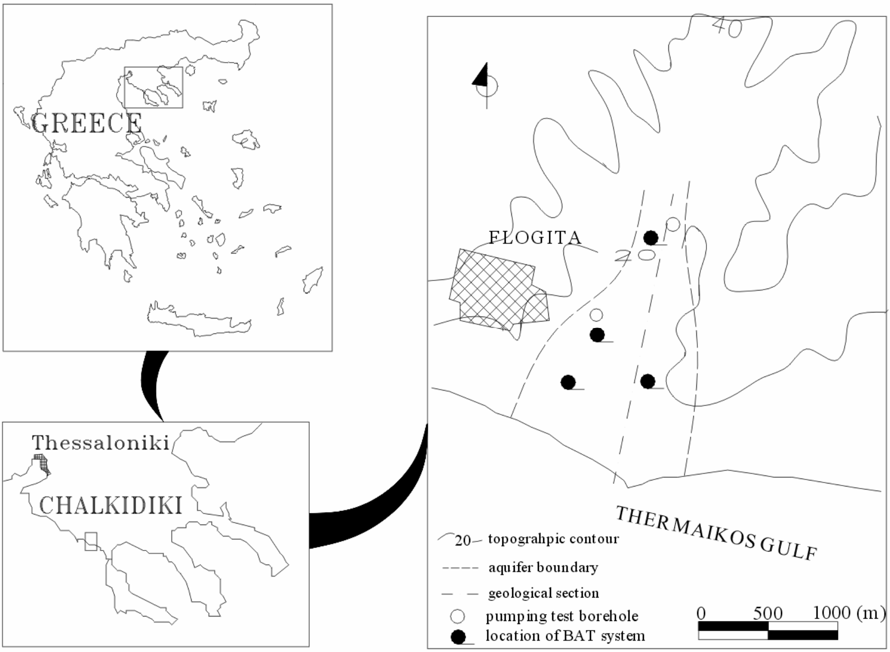
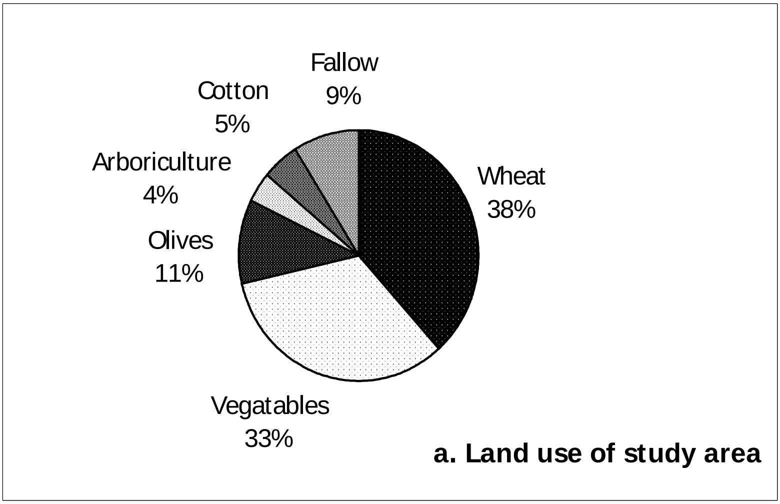


Fig. 1. Location of study area
Rys. 1. Położenie badanego terenu

Visual in-situ observations and land use data by a farmer interview survey were collected in the study area. The main observation was a definite rotation of crops throughout the year and that the cereals (mainly wheat) and vegetables dominate among other crops. The data was taken into account in the numerical simulations by applying the annual nitrate concentrations of groundwater recharge. Figure 2 presents land uses and the distribution of nitrogen fertilizer in various crops.

Finally, additional data, particularly from geology, hydrogeology and land use can be found in previous publications (Latinopoulos et al., 1994, Xefteris et. al., 1992)



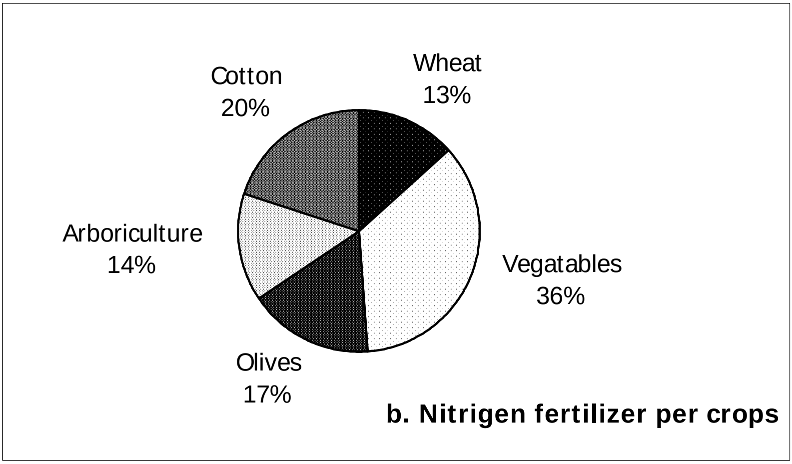


Fig. 2. a) Land uses, b) Annual distribution of nitrogen fertilizer for various crops
Rys. 2. a) sposób użytkowania terenu, b) roczne zużycie nawozów azotowych na różne uprawy

Groundwater samples collected during the period 1993-1996 from shallow wells. Samples have been collected from an innovative system for groundwater sampling and monitoring called "BAT system" (Fig. 1). This technique is well adapted to collect accurate and representative data without the necessity of pre-sampling, from different strata. This system guarantees a vertical sampling with no need of pumping from different depths, in contrast to traditional techniques of groundwater sampling that lead to vertically mixed samples by pumping from the existing standard wells. The major advantage of the BAT system is that only that small amount contained in the filter tip itself, must be purged from the system prior to sampling (Blegen et al., 1988, Latinopoulos et al., 1996).

3. Flow system simulation based

The field data indicate that the water level has been changing during the years. Figure 3 shows the water table contours for 1995. This map was produced by applying geostatistical methods. The flow system can therefore be assumed to be temporarily at steady state at some point within those periods. We assume that the hydraulic data for those periods represent steady-state conditions in the phreatic aquifer.

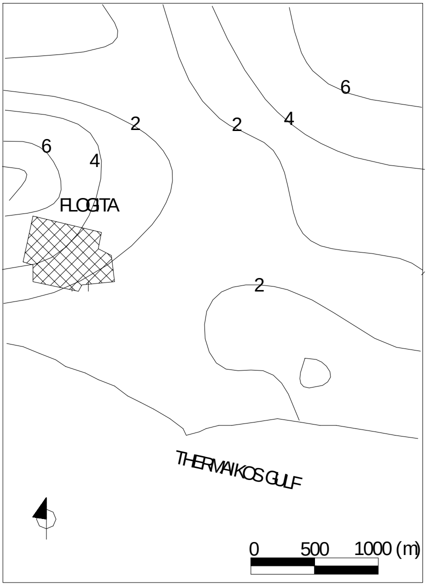


Fig. 3. Water table elevations (meters above sea level)
Rys. 3. Wysokość zwierciadła wody (metry nad poziomem morza)

The simulation domain (Fig. 4) is bounded by an impermeable base representing the top of a clay deposit and above by the water table. At the southern end is the sea and the potential is equal to the sea level. At the northern end of the geological section we assume an inflow boundary. The available hydrogeology data was used to prepare input data for the flow model which was solved for a representative section. We assumed two different homogeneous zones of hydraulic conductivities equal to 4.0 and 40.0 m/d for sand and gravel layers respectively, and the long-term precipitation leads to an estimation of annual uniform recharge of 100 mm. We also assumed a anisotropy ratio 10:1 in the two principal directions x and z.

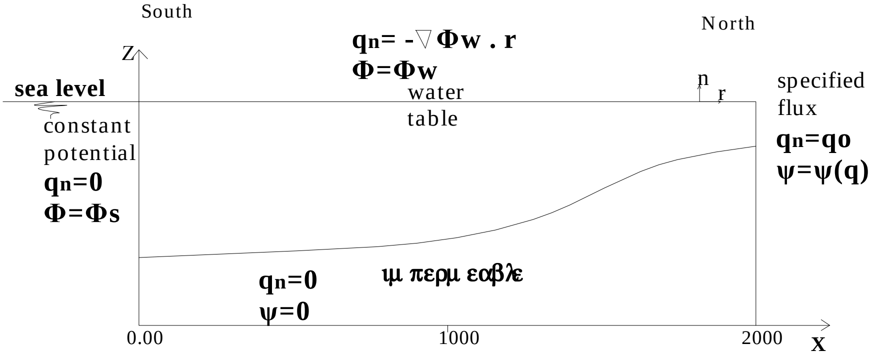


Fig. 4. Simulation domain with dual boundary conditions
Rys. 4. Domena symulacji z podwójnymi warunkami brzegowymi

A well-proven model named FLONET, which is based on the principal direction formulation for ground water flow was selected to solve the dual problem for potentials and stream functions (Frind and Matanga 1985, Leismann and Frind 1989, Frind et al., 1990). The large length-to-depth ratio of the aquifer dimensions favours the application of this model at a representative vertical section in the direction of the flow.

4. Statistical approach of nitrates

The nitrate pollution was first detected in 1991 by a systematic collection of water quality data (Latinopoulos et al., 1993). Within the period 1991-1996, which is reported herein, a lot of water samples were obtained by pumping from existing boreholes and without pumping with the BAT system, and routine chemical analyses were performed. Nitrate concentrations higher than 50 mg/l were found in about 40% of the sampled boreholes and for this the present analysis is restricted to the study of nitrate variation. It should be noted that the local scale of the detected problem does not allow for direct comparisons with the results of other large scale-studies (Kelly et al., 1991, Pedersen et al., 1991). Summary statistics for the nitrate data are given in figure 5. Inspection of seven boxplots in this figure rises some questions on central values, distributions and temporal variations, which are answered in the next paragraphs.

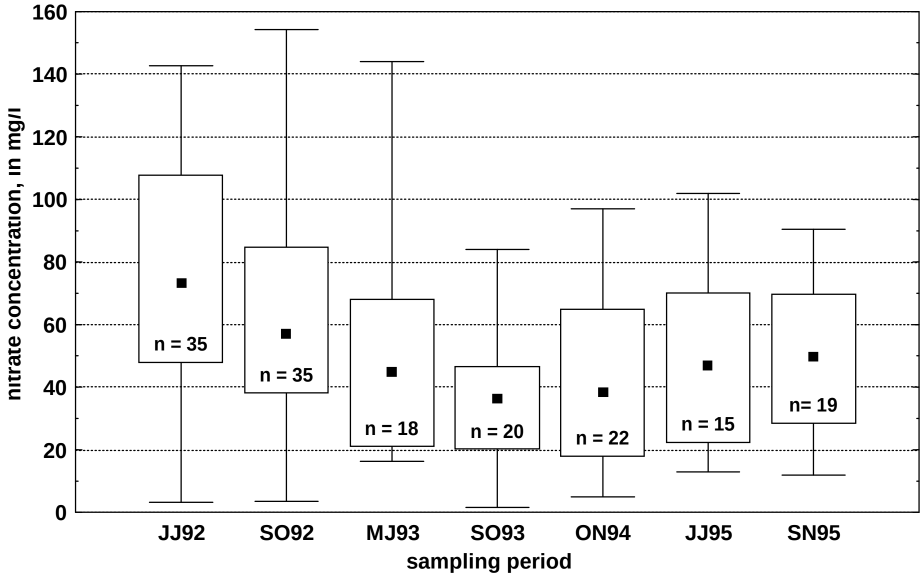


Fig. 5. Boxplots of nitrate concentrations
Rys. 5. Wykres skrzynkowy stężenia azotanów

The primary reason to test whether data follow a normal distribution is to determine if parametric test procedures may be employed. The null hypothesis for tests of normality is that the data are normally distributed. The most common test for normality is the Shapiro-Wilk test (Helsel and Hirsch 1992). Normality of all seven distributions is tested with the Shapiro-Wilk test and is rejected at a = 0.05 for the nitrate concentrations of the five campaigns in the period 1993-1995. In contrast to these five sets the calculated p-values for the two large sets of data are a little greater than 0.2 and thus the normality of their distributions can be accepted.

The distribution of nitrate concentrations is also examined to detect any significant temporal variation. A Kruskal-Wallis test on nitrates for the whole period shows that the seven groups are significantly different from each other. Application of the same test for five sampling campaigns in the period 1993-1995 shows no significant differences at 95% level. The Kruskal-Wallis test, like other non parametric tests, is computed by an exact method used for small sample sizes on a large sample ranks (Helsel and Hirsch 1992).

As far as the variation of nitrate with depth is concerned a nonparametric regression analysis shows that nitrate concentration does not correlate significantly with an increasing borehole depth to 50 m (Spearman p-value = 0.04). The spearman p-value correlation is based on ranks and measure of all monotonic relationships. It is also resistant to effects of outliers.

5. Solute transport model application

The flow net obtained from numerical solution of the dual problem was used to generate the grid for the transport problem. Solute transport simulations were performed with an efficient finite element code based on Galerkin finite element formulation (Pinder and Gray 1977, Pinder and Frind 1972) and was combined with a coordinate transformation which forms the common basis of the principal direction method (Frind and Germain 1986, Burnett and Frind 1987, Leismann and Frind 1989).

The model solves the transport equation in the vertical plan which reads

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

where:
C – the nitrate concentration,
Dxx and *Dzz* – the dispersion coefficients in the two principal directions,
V – the velocity in the flow direction,
λ – the decay coefficient (assumed to represent denitrification as a first-order reaction, λ = ln2/*t** where *t** is the half-life for denitrification).

The dispersion coefficients are expressed as:

$$Dxx = aL \cdot V \qquad Dzz = aT \cdot V \qquad (2)$$

where
aL and *aT* – the longitudinal and transverse dispersivities, respectively.

Using information taken from available literature for similar geologic formation and hydrogeologic conditions the dispersivities are given the values of *aL* = 10 m and *aT* = 0.001 m while the decay coefficient *λ* is calculated by *t** = 1.0 year. The applied fertilizers lead to an uniform influx nitrate concentration of 150 mg/l along the whole cross section of the aquifer.

Steady-state conditions of the transport phenomena are reached in about five to six years from the beginning of the simulation. This means that any change in the land use will be noticeable within this period and that recent solute influx concentrations can be safely used for short-term predictions. The results given in figure 6 concern the nitrate variation in the representative vertical section.

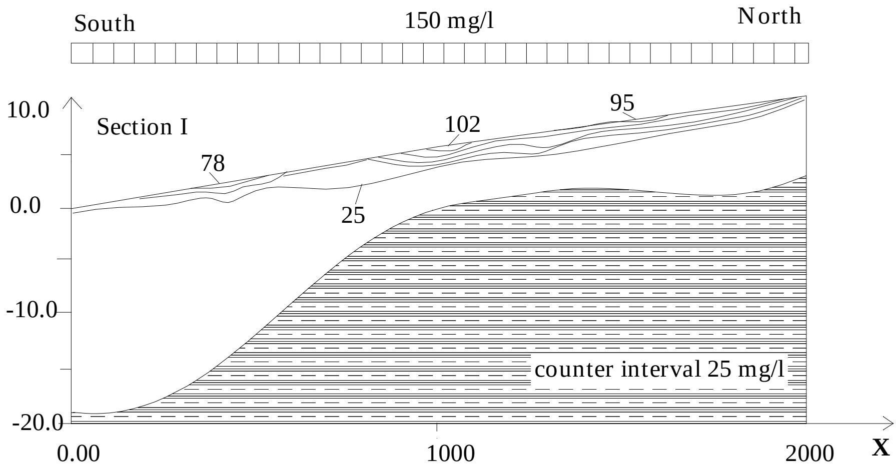


Fig. 6. Nitrate distribution in a vertical section
Rys. 6. Rozkład azotanów w przekroju pionowym

6. Conclusion

Groundwater nitrate contamination from agricultural activities will be a matter of concern for many years to come. In this work a wide range of models have been applied in a study case in Northern Greece. The value of each particular model relates directly to the amount of information and more generally of knowledge we have of every phenomenon, which means that even the more sophisticated models should be validated with reference to specific cases to which they are going to be applied. Due to the diffuse nature of non-point contamination field data are required that can describe to the highest possible level of accuracy the spatial and temporal variations of quite a number of parameters. Statistical and spatial models are very useful in obtaining average values and also in identifying the structure of parameters, variables and their relationships.

References

1. **Anastasiadis P.:** *Investigation of nitrate pollution of groundwater with application to a phreatic aquifer in Chalkidiki Peninsula.* Phd Thesis, Dep. Civil Engn. A.U.TH. (In Greek). 1994.
2. **Anastasiadis P.:** *Modeling techniques in the control of non-point sources pollution of groundwater.* 5th Conference on Environmental Science and Technology, (ed.T. Lekkas), Molyvos, Lesvos, Greece, pp.118÷125. 1997.
3. **Anastasiadis P., Latinopoulos P.:** *Prediction of nitrate contamination of an aquifer by numerical modeling.* 3th Conference on Environmental Science and Technology, (ed. T Lekkas), Molyvos, Lesvos, Greece, pp.97÷104. 1993.
4. **Anastasiadis P., Latinopoulos P.:** *Comparison between aquifer solute concentration and monitoring wells.* Annual Journal of Environmental Protection, vol.4, pp.207÷217. 2002.
5. **Anastasiadis P.:** *Relationship between aquifer nitrate concentration and monitoring boreholes.* Fresenius Environmental Bulletin, vol. 12, No 10, pp. 1246÷1251. 2003.
6. **Bear J.:** *Hydraulics of Groundwater.* McGraw-Hill, New York. 1979.
7. **Blegen R., Hess J., Denne J.:** *Field comparison of groundwater sampling devices.* NWWA Second Annual Outdoor Action Conference, Las Vegas USA 1988.
8. **Bouchard C.D., Willams M.K., Surampalli R.Y.:** *Nitrate contamination of groundwaters sources and potential health effects.* J. of AWWA, 82÷90. 1992.
9. **Burnett R., Frind O.E.:** *Simulation of contaminant transport in three dimension 2.Dimensionality effects.* Water Resour. Res., vol. 25(4), 695÷705. 1987.
10. **Daus A.D., Frind E.O.:** *An Alternating direction Galerkin technique for simulation of contaminant transport in complex groundwater systems.* Water Resour. Res., Vol. 21(5), 653-664. 1985.
11. **Dourson M., Stern B., Griffin S., Baily K.:** *Impact of risk-related concerns on U.S. Environmental Protection Agency programs.* Nitrate Contamination, NATO ASI Series vol., G30, eds. I. Bogardi and R.D. Kuzelka, Springer Vergal, Berlin Heidelberg, pp. 477÷487. 1991.
12. ECETOP, Nitrate and Drinking Water, European Chemical Industry, Ecology and Toxicology Center, Technical Report No 27, Brussels Belgium 1988.
13. European Economic Community. Council directive on the protection of waters from agricultural nitrate pollution, Official J. No. 91/676/EECL, 375, 1÷8. 1991.
14. **Frind E.O., Matanga G.B.:** *The dual formulation of flow for contaminant transport modeling: 1. Review of theory and accuracy aspects.* Water Resour. Res., 21(2), 159÷169. 1985.
15. **Frind, E.O., Matanga G.B., Cherry J.A.:** *The dual formulation of flow for contaminant transport modeling: 2. The Borden aquifer*. Water Resour. Res., 21(2), 170÷182. 1985.
16. **Frind, E.O.:** *The principal direction technique: A new approach to groundwater transport modeling, in Proceedings.* Fourth International Conference on Finite Elements in Water Resources, Technical University Hannover, Germany, June 1982.

17. **Frind, E.O. Pinder G.F.:** *The principal direction technique for solution of the advection-dispersion equation.* Scientific Computing, pp. 305÷313, North-Holland, Amsterdam. 1982.
18. **Frind E.O., Germain D.:** *Simulation of contaminant plumes with large dispersity contrast: Evaluation of alternating direction Galerkin models.* Water Resour. Res., 22(13), pp. 1857-1873. 1986.
19. **Helsel R.D., Hirsch R.M.:** *Statistical methods in water resources*. U.S. Geological Survey, Water Resources Division, 22092 USA, Elsevier. 1992.
20. **Kelly W.E., Curtis B. Adelman D.:** *Nitrate ground-water modeling for agricultural and other non-point sources.* In "Nitrate Contamination", NATO ASI Series, Vol. G 30, I. Bogardi and R.D. Kuzelka, Springer-Verlag, 97÷113. 1991.
21. **Kinzelbach W.K.H., Frind E.O.:** *Accuracy criteria for advection-dispersion models.* Proc. VI Inter. Conf. on Finite Elements in Water Resources, Lisbon, pp. 489÷501. 1986.
22. **Latinopoulos P., Anastasiadis P., Xefteris A.:** *Modeling of groundwater contamination from agricultural activities: A Greek experience.* In press: 5th International Conference, "Hydrosoft 94", 21÷23 September 1994, Porto Carras, Greece 1994.
23. **Latinopoulos P., Anastasiadis P., Xefteris A.:** *Nitrate pollution from agricultural activities of a shallow aquifer in Chalkidiki peninsula, Greece*. Proc. Second Inter. Confer. on Water Pollution, Milan, 631÷638, 1993.
24. **Leisman M.H., Frind E.O.:** *A symmetric-matrix time integration scheme for the efficient solution of advective-dispersion problems.* Water Resour. Res., vol. 25(6), 1133÷1139. 1989.
25. **Latinopoulos P., Xerteris A., Anastasiadis P.:** *Installation and operation system for groundwater sampling and monitoring.* Inter. Conference "Water Resources Management" Larisa Greece, pp. (In Greek). 1996.
26. **Mirvish S.S.:** *The significance for human health of nitrate, nitrate and N-nitroso compounds.* Nitrate Contamination, NATO ASI Series vol., G30, eds. I. Bogardi and R.D. Kuzelka, Springer Vergal, Berlin Heidelberg, pp. 253÷265. 1991.
27. **Spalding R.F., Exner M.E.:** *Occurrence of nitrate in groundwater – A review.* Journal of Environmental Quality, vol. 22, pp. 392÷402. 1993.
28. **Pedersen K.J., Bjerg P.L., Christensen T.H.:** *Correlation of nitrate profiles with groundwater and sediment characteristics in a shallow sandy aquifer.* Journal of Hydrology, vol. 124, 263÷277. 1991.
29. **Pinder F., Frind E.:** *Application of Galerkin's procedure to aquifer analysis.* Water Res. Res., 8(1), 108÷120. 1972.
30. **Pinder F., Gray W.:** *Finite element simulation in surface and subsurface hydrology.* Academic, Orlando, Flo. 1977.
31. National Statistical Services of Greece: *Distribution of Greek area by the land use, Inventory of agriculture and cattle-breeding.* G:71, Athens, 1995.
32. **Xefteris A., Darakas E. Latinopoulos P.:** *Fertilizers pollution on aquifer in Chalkidiki.* 5th Hel. Conference of Hellenic Hydr. Union, Larisa, Greece pp. 320÷327. (In Greek). 1992.

33. **Xefteris A.:** *Investigation of groundwater quality degradation in Kalamaria plain with emphasis to nitrate contamination*. Ph.D. Thesis, Dep. Civil Engn. A.U.TH Greece. (In Greek). 2000.

Zanieczyszczenie wód gruntowych w wyniku działalności rolniczej: podejście zintegrowane

Streszczenie

Ponieważ woda gruntowa jest jedynym źródłem wody do picia w wielu miejscach na ziemi, priorytetową sprawą w decyzjach rządów musi być oszacowywanie ryzyka zdrowotnego spowodowanego przez substancji chemicznych oraz ochrona ludzi. W tym celu potrzebna jest złożona procedura, która łączy badania i specjalistyczną wiedzę techniczną z różnych dyscyplin naukowych. Podejście, które pomoże rozwiązać problem azotanów na pewno powinno zawierać badanie zachowania azotanów w glebie i wodach gruntowych, które podlegają rozmaitym procesom środowiskowym i antropogenicznym a także ocena istniejących i rozwijających się nowych praktyk rolniczych, wiążąca się z kontrolą jakości i zarządzaniem.

Największe antropogeniczne źródło azotanów w wodach gruntowych to rolnictwo. Wysokie stężenia azotanów w wodzie, które często przekraczają normy dla wody pitnej, są głównie spowodowane intensywnego nawożeniem. Wysokie stężenia azotanów w wodzie pitnej mogą spowodować poważne problemy zdrowotne, szczególnie u niemowląt. Istnieje wiele sposobów modelowania i różnych typów metod, które są używane w wszystkich badań nad zanieczyszczeniem wód gruntowych azotanami. Stosowany jest szeroki zakres modeli, od prostych statystycznych do złożonych symulacyjnych i zarządzających. Będące w toku badania obejmują pomiary hydrogeologiczne in-situ, pobieranie próbek wody gruntowej jak również pracę teoretyczną rozszerzoną przez zastosowanie numerycznego modelowania zanieczyszczenia azotanami w płytkich formacjach wodonośnych; wciąż jest to jedno z niewielu zintegrowanych badań w Grecji. Wypracowanie modelu symulacyjnego równolegle z dostępną informacją z badań polowych ułatwia zarówno poprawę modeli oraz planowanie w przyszłości badań in-situ.

Rozpatrywana w tym referacie struga zanieczyszczeń pojawiła się w przybrzeżnej, płytkiej, nasyconej formacji wodonośna, która jest położona w południowo-zachodniej części Półwyspu Chalkidiki w północnej Grecji (rys. 1). Badana formacja wodonośna jest częścią dużego działu wodnego, który spływa do Zatoki Thermaikos. Duża część terenu jest używana jako ziemia rolnicza. Intensywna działalność rolnicza podczas ostatnich dekad wspomagana intensywnym nawożeniem spowodowała poważne zanieczyszczenie wód gruntowych azotanami.