Groundwater contamination by nitrates and seawater intrusion in Atalanti basin (Fthiotida, Greece)

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Abstract The aim of the present essay is to evaluate the groundwater quality in the coastal alluvial aquifer of the Atalanti basin (Fthiotida, Greece). For this reason, data from the physical and chemical analyses of groundwater samples for eight sampling periods were collected and nitrate pollution was studied thoroughly. The period of June 2005 is the most appropriate and representative as far as dispersion and number of samples are concerned. The most dominant water type is Mg-(Ca)-HCO_3, due to the presence of dolomite and ultrabasic rocks. Moreover, the Na-Cl hydrochemical type is recorded near the coast line, due to seawater intrusion. Furthermore, it can be concluded that a) the high nitrates concentration values are related with the intensified agricultural production, the applied fertilizers and the absence of sewage systems, b) higher Mg concentration and Mg/Ca ratio values are observed near the coastline due to high Mg concentration in sediments and seawater intrusion, c) high Cl and Ca concentration in the southern area are connected with the discharge of the karst, saline spring in Tragana and seawater intrusion, d) according to factor analysis there are three main factors that are related with the aquifer salinization, the dolomite/ultrabasic rocks dissolution and the nitrate pollution with intense use of fertilizers, e) according to the cluster analysis, there are two clusters of water samples in Atalanti: the ones near the coastline with increased hardness, that are affected by salts and the ones in the central basin with reduced hardness, due to the short residence time in the ground Finally, some recommendations are proposed in order to protect and improve the groundwater quality in the study area.

1 Introduction

The groundwater degradation of coastal aquifers, observed in the last few years, is associated with seawater intrusion, industrial urbanization and intensive agriculture that require thoughtless use of chemical fertilizers and irrigation water.

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The high values in NO_3^- are related with human activities, intensive agriculture, farms and uncontrolled urban waste disposal (due to septic cesspit). The agriculture constitutes the main source of nitrate pollution in surface and underground waters (Almasri 2007). Livestock production plays an important role in the aquifers' pollution by nitrates and phosphates. Increased nitrogen amounts are due to the high protein feed, which is greater than the animals' needs (Voudouris et al. 2004[a]).

The research program of 3rd Support Framework, which was successfully implemented by IGME, aims to monitor the qualitative and quantitative characteristics of aquifers across the country, including Atalanti basin. Part of the results of the above research program are presented in this essay and include an inventory of 650 sampling points, from which 100 were hydrogeologically selected for continuous monitoring of aquifers' qualitative and quantitative characteristics.

As found in the study area, the concentration of nitrates exceeded the thresholds that have been adopted by WHO (World Health Organization), ECE Directive 98/83 and Ministerial Decision Y2/2600/2001, according to which the maximum concentration is 50 mg/L for drinking purpose.

2 The Geomorphologic, geological and hydrogeological setting of the study area

The study area is located at Eastern Central Greece at Lokrida province of Fthiotida Prefecture. The complex geomorphology of Atalanti basin area (171 km^2 approximately) consists of areas with little or no slopes in valley where alluvial deposits are met and areas with very high and almost vertical slopes in rocky formations (Fig. 1).

The study area is open to the sea at Northeast and is surrounded by higher or lower mountains and hilly areas. Atalanti basin has a geomorphologic characteristic of diverged hydrographic network (streams, rivers), which has length of about several kilometers, converges to the east and reaches the sea. In any case there is no steady river flow but always seasonal, during winter and spring (Pavlidou 2010). The southern mountainous part of the above area has streams with very steep slopes and deep river bed, especially when passing through carbonate rocks.

One of the main causes for the geomorphologic setting of the study area is the water corrosion and its contribution to the weathering process. A very important factor in the above process is the intensive tectonic strain of rocks causing an extensive surface discontinuity, through which the erosion and weathering process begins (Palivos 2001).

The region's climate belongs to the Csa type (according to Koppen classification) which is representative of the Mediterranean climate with mild wet winters and mild hot and dry summers. The average annual precipitation is 555 mm. The

main features of climatic conditions in the region are the rotation period of a wet and cold season starting in October, according to precipitation and air temperatures and a dry and a hot one, starting in May. There is lack of uniformity in rainfall distribution between the lowlands and highlands with observed higher values in the mountains and lower ones in the valleys.

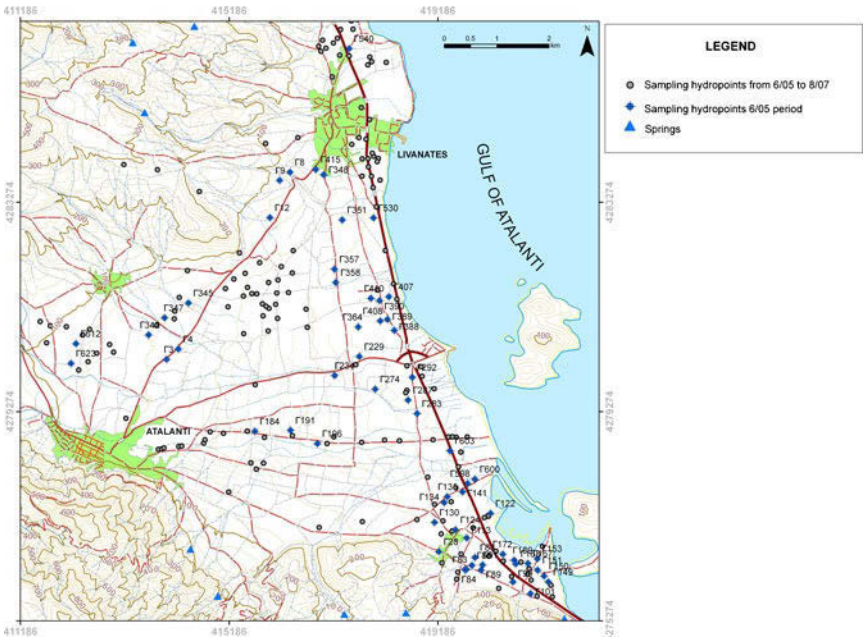

Fig. 1. The study's area topography with sampling points.

From a geological point of view, the study area belongs to the Subpelagonian geotectonic zone in a closed basin with post alpine deposits which has not been always communicating with the sea (Aggelidis 1992). The deposits have come from the surrounding mountain range rocks. Atalanti basin consists of formations which are as follows (Fig. 2):

- Paleozoic formations consisting of shales, sandstones and conglomerates. Triassic and Jurassic dolomites, limestones and ophiolitic rocks (gabbro, diabases, peridotites, serpentines), Creataceous limestones and flysch. Neogene sediments that were deposited after the closed basin formation consisting of marls, calcareous marls, marly limestones, clays, sandy loams, lignite and conglomerates.Quaternary formations have been deposited at the lower parts of the basin with materials derived from weathering of all previous formations, which come across at higher topographic positions. The main feature of the geological regime during Miocene is the large-scale faults in Atalanti basin which have created many faulting zones with West-Northwest and North-Northeast main directions.

The hydrogeological behaviour of geological formations depends on the lithological composition, degree of diagenesis and porosity. From the hydrogeological point of view, the study area is consisted of two main groups of rocks in which the groundwater flow mechanism and the storage capacity vary considerably. The first group consists of granular formations in which the hydraulic conductivity is based on the pores between the grains. The second group is composed by hard basement rocks which are limestones and igneous rocks, the hydraulic conductivity of which depends on fractures, cracks, karst pipes and other discontinuities that cross their mass. The main aquifer is developed in carbonate rocks; on the other hand aquifers of lower capacity are developed in the Quaternary-Neogene formations and igneous rocks. It is estimated that there is lateral communication between aquifers in carbonate rocks and the Neogene-Quaternary deposits, forming unconfined and semi-confined aquifers.

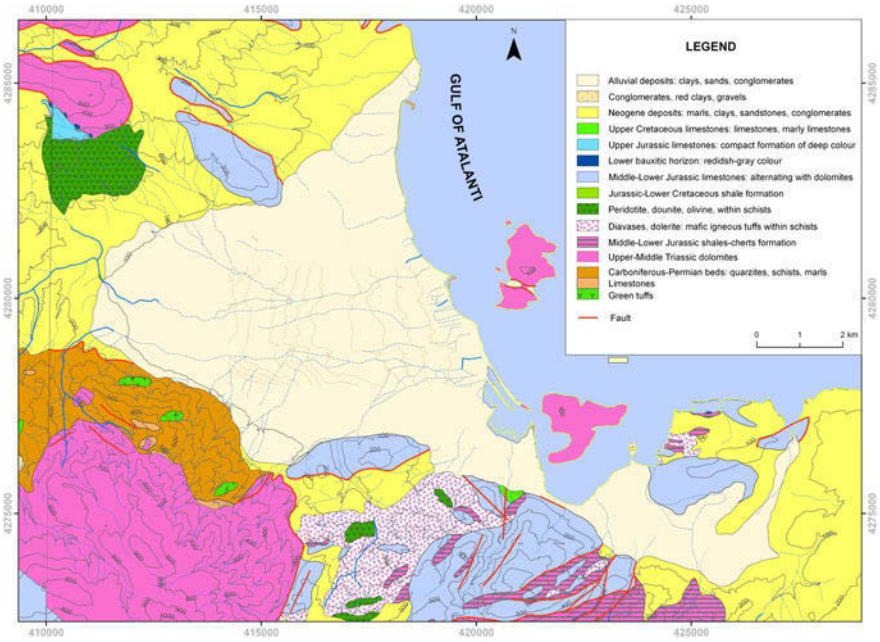

Fig. 2. The geological map of Atalanti area (Maratos 1965).

Unconfined aquifers are developed in carbonate rocks as well in granular formations with large effective porosity. On the other hand, the confined aquifers are developed within Neogene formations. The alluvial deposits due to their heterogeneity may be considered unconfined or semi-confined aquifers. The lowland aquifer, which is intensively exploited through boreholes (~ 650, mostly for irrigation use) is important for the economic development in the region. The depth to water table in the alluvial aquifer ranges from 1.5 to 86 m below surface ground or from 2.2 to 17.3 m above sea level. Groundwater flows are mainly from the West to-

ward East (Atalanti Gulf). This article is focused on the qualitative characteristics of the aquifer, which has already shown degradation problems.

3 Sampling data and evaluation of chemical analyses

Groundwater sampling took place along different periods so as to investigate the groundwater quality. During the period 2005-2007 and more specifically the months of June, July and August, 240 samples were taken. The results presented in this essay concern about 62 samples taken during the period June 2005.

Ca concentrations range from 30.5 to 179 mg/L, Mg from 1 to 149 mg/L and Na between 5.5 and 232.2 mg/L increasing linearly with salinity. Sulphate concentrations range from 6.2 to 195 mg/L and Cl between 3.5 to 691 mg/L (Fig. 3).

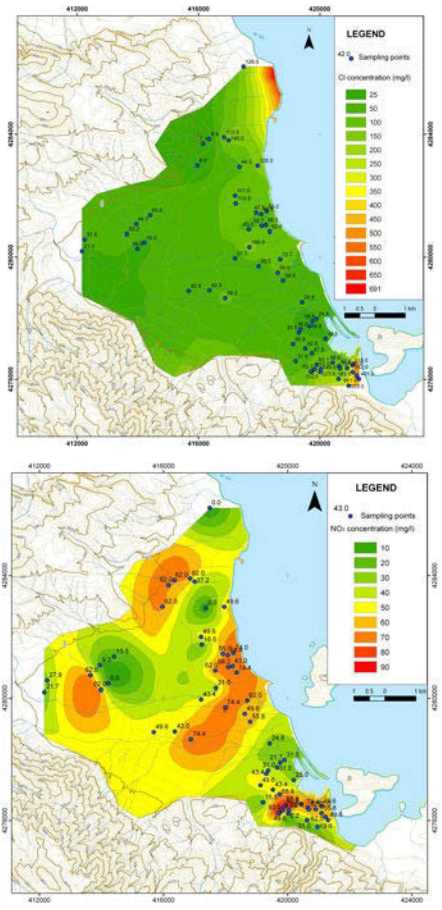

Fig. 3. Distribution map of a. Cl and b. NO_3 concentration in Atalanti basin.

Increase in electrical conductivity values is observed at the downstream area due to groundwater recharge with salts, but also because of seawater intrusion (Voudouris et al. 2004[b]). The highest values (2816 μS/cm) occur in the southern coastal part of the basin due to the aquifer's recharge with saline water from Tragana springs discharge. Furthermore, the over-exploitation of the coastal area's wells is observed which causes more rapid salinization. Finally, across Karagiozis stream, lower values of electrical conductivity and Cl concentration are met because of the upstream fresh water recharge (Pavlidou 2010).

According to Piper and Durov plots (Fig. 4) the majority of samples belong to Mg-HCO_3 water type (fresh water-recharge) associated with dolomitic limestones and ultrabasic rocks of bedrock, as well as sediments derived from erosion which have been deposited across the basin (Razack and Dazy 1990). Ca-HCO_3 water type is also met which indicates recharge waters from karst aquifers. Finally, Na-Cl water type is met at the coastal zone, where seawater intrusion takes place (Stamatis and Voudouris 2003).

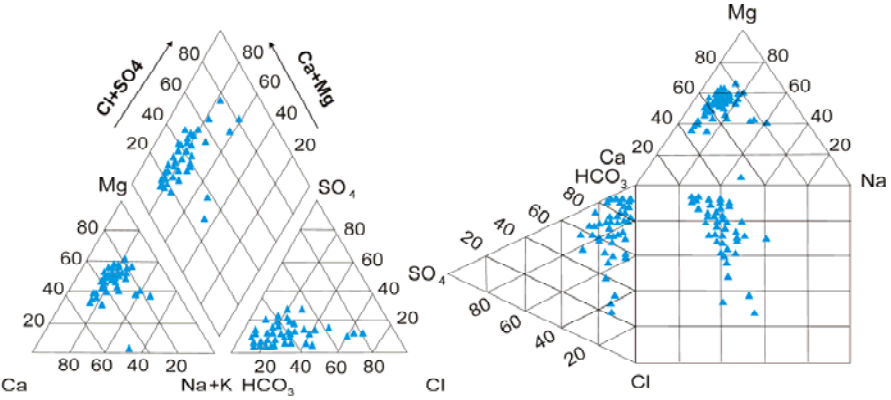

Fig. 4. a. Piper and **b.** Durov plots for Atalanti basin's groundwater.

Ion ratio of Mg/Ca from 0.5 to 0.7 is found at basin's margins where dolomitic limestones are met. Higher ion ratio at the coastal zone indicates Mg ions groundwater recharge because of the basin's sediments and seawater intrusion. Moreover, Na/K ion ratio points out that Karagiozis stream plays important role to groundwater movement. The Southwest basin's region is a recharge area due to the above stream control, on the contrary the central-north one is a discharge area. Finally, the low value of Na/Cl (0.3) during the period of June 2005 towards the coastal zone strongly indicates seawater intrusion (Hem 1985).

Nitrates concentration ranges from 0-93 mg/L with a mean value of 46.8 mg/L. Increased concentration of nitrates are generally presented in the plain and are attributed to agricultural sources of nitrate fertilizer (Antonakos and Lambrakis 2000, Tsioumas et al. 2008). Nitrate concentration is higher during dry periods and this is due to aquifer's infiltration of surface water rich in nitrates. In the western part of the area indicated high levels of nitrate concentration (over 70 mg/L)

are probably related to the existence of cemetery and livestock (Stigter et al. 1998). In the northern part, the high values (about 60 mg/L) are due to the existence of cropland and possibly of uncontrolled waste disposal. In the central coastal area nitrate pollution (60-75 mg/L) is associated with the wastewater disposal in septic tanks in settlements (Skala, Aghios Nikolaos). In the upstream area NO_3 concentration is also high due to intense agricultural activity. Finally, in the southern part values over 90 mg/L may be associated with industrial wastewater. It should be noted that the threshold of 50 mg/L set by the legislation has been exceeded by 27 samples (Fig. 3).

The applied multivariate statistical methods were conducted by means of SPSS. Factor analysis was applied to represent a large number of variables by a significant smaller number of variables, called "factors", each of which is a linear function of the original variables (R-factor analysis). The factor analysis is applied because of the limitations of trilinear diagramming (Piper), which utilizes relative percentages of ionic concentration rather than absolute values and further confining its analysis only to 6 variables (Voudouris et al. 1997, Razack and Dazy 1990, Briz-Kishore and Murali 1992, Antonakos and Lambrakis 2000). Factor analysis resulted in three main factors that interpret a great percentage of total variance: a) the aquifer salinization, b) the dolomite/ultrabasic rocks dissolution and c) the nitrate pollution due to the intense use of fertilizers.

Cluster analysis is a classification method of a large amount of data in groups with similar but distinctive characteristics (Ashley and Lloyd 1978). It resulted in two groups of samples: the first includes samples located in the coastal area rich in salts (hard water) and affected by salinization and the second contains samples belonging to the inner part of the study area with soft water due to the groundwater's short residence time.

4 Results – Conclusions – Proposals

The aim of this study was to determine the impacts of human activities on groundwater quality in alluvial aquifer of Atalanti basin. According to the results from hydrochemical investigation, using conventional methods and multivariate technique (factor and cluster analysis) two main groups of groundwater samples can be identified: Mg-(Ca)-HCO_3 (freshwater) and Na-Cl (water affected by seawater intrusion in coastal areas). Factor analysis resulted in 3 factors which are associated with: a) the aquifer salinization, b) the dolomite/ultrabasic rocks dissolution and c) the nitrate pollution due to the intense use of fertilizers.

The nitrate concentration in groundwater within Atalanti basin is increased with a maximum value of 93 mg/L. It should be pointed out that the majority of values is above the threshold of 50 ppm or very close to it. It is estimated that nitrate concentration will increase as intensive cultivation, use of fertilizers and uncontrolled sewage disposal continue, without protection measures and problem

awareness from the citizens and water users. Taking into account the chemical analyses, high nitrate concentrations are observed close to residential coastal areas. These cases are associated with the municipal wastewater disposal. In order to protect groundwater the following are proposed:

- Abide by the directives of the Ministry of Agriculture and agronomists to use the appropriate type and quantity of fertilizer per crop.
- Systematic monitoring of the evolution of nitrate pollution and seawater intrusion to ensure the future quality of groundwater.
- Direct application of project management of municipal wastewater and livestock so that they cannot enter to the hydrographical network or/and groundwater table by filtering. Thus, biological treatment for all settlements should be applied.
- Implementation of protection zones of water supply wells and springs to maintain the drinking water quality, taking into account the basin's hydrological and hydrogeological characteristics.
- Changes to the irrigation system (drops system, construction of irrigation network) and exploration of the possibility to use surface waters, artificial recharge using barriers along the streams in order to avoid overexploitation and seawater intrusion.

Finally, a monitoring program on groundwater quality should be established in selected sampling points, in order to improve the groundwater quality and avoid seawater intrusion phenomena and nitrate pollution on a large scale in the coastal aquifer system of Atalanti basin.

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References

Aggelidis C (1992) Engineering and geologic conditions of Atalanti area (Fthiotida prefecture, Greece). Unpublished Technical report, IGME, Athens

Almasri M (2007) Nitrate contamination of groundwater: A conceptual management framework, Environmental Impact Assessment Review, 27: 3, 220-242

Antonakos A, Lambrakis N (2000) Hydrodynamic characteristics and nitrate propagation in Sparta aquifer, Water Research, 34: 16, 3977- 3986

Ashley R, Lloyd J (1978) An example of the use of factor analysis and cluster analysis in groundwater chemistry interpretation, Journal of Hydrology, 39: 3-4, 355-364

Briz - Kishore B, Murali G (1992) Factor analysis for revealing hydrochemical characteristics of a watershed, Environmental Geology – Water Science, 19: 1, 3-9

Hem J (1985) Study and interpretation of the Chemical characteristics of Natural Water, 3rd edition, United States Geological Survey Water – Supply Paper 2254

Maratos G (1965) Geological map of Atalanti sheet, scale 1:50.000, Institute of Subsurface Geological Research

Palivos N (2001) Geomorphologic study of Atalanti area of Fthiotida prefecture. PhD, Department of Geology, School of Sciences, Athens

Pavlidou E (2010) Impacts of human activities on groundwater quality in Atalanti region. MSc Thesis, Hellenic Open University

Razack M. and Dazy J (1990) Hydrochemical characterization of groundwater mixing in sedimentary and metamorphic reservoirs with combined use of Piper's principle and factor analysis, Journal of Hydrology, 114: 3-4, 371-393

Stamatis G, Voudouris K (2003) Marine and human activity influences on the groundwater quality of southern Korinthos area (Greece). Hydrological processes, 17, 2327-2345

Stigter T, Van Ooijen S, Post V, Appelo C, Carvalho A (1998) A hydrogeological and hydrochemical explanation of the groundwater composition under irrigated land in a Mediterranean environment, Algarve, Portugal, Journal of Hydrology, 208: 3-4, 262-279

Tsioumas V, Zorapas V, Manakos A, Stamatis G, Gioxas G (2008) Groundwater deterioration by nitrates in Xynias basin (Greece), 8th International Hydrogeological Congress, Athens.

Voudouris K, Lambrakis N, Papatheodorou G, Daskalaki P (1997) An application of factor analysis for the study of the Hydrogeological conditions in Plio-Pleistocene aquifers of NW Achaia (NW Peloponnesus, Greece). Mathematical Geology, 29: 1, 43-59

Voudouris K, Nikas K, Antonakos A (2004[a]) Study of the evolution of salinization in coastal aquifers. Case study of coastal NW Achaia, Bulletin of Greek Geological Survey, Proc. of the 10th International Congress, Thessaloniki, XXXVI/4, 1952-1961

Voudouris K, Panagopoulos A, Koumantakis I (2004[b]) Nitrate pollution in the coastal aquifer system of the Korinthos (Greece). Global Nest: the International Journal, 6:1, 11-18