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Groundwater quality and location of productive activities in the region of Thessaly (Greece)

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Abstract

In the present study the involvement of human activities is assessed in the revalorization of groundwater quality. The groundwater quality was assessed on the basis of physical and chemical analysis (electric conductivity, pH, total dissolved solids (TDS), total hardness, NO_3^-, NO_2^-, SO_4^{-2}, Fe, Mn, Zn, Cu, B, residual sodium absorption (RSC) and sodium absorption ratio (SAR) for the period 2000–2004. From the analysis of results, it emerges that there are significant differences on the quality of water among the sample areas studied. The degradation of groundwater quality is mainly due to the pollution caused by the rural use of land, as well as its intensive exploitation. The salination and toxicity are potential problems of groundwater quality, especially in some areas, indicating that there is a need to take direct actions for the purpose of the optimum management of water resources in the Region of Thessaly.

Keywords: Groundwater quality; Groundwater pollution; Productive activities; Thessaly; Greece

1. Introduction

It is well documented that environmental pollution depends mainly on human activities (industry, agricultural cultivations, and domestic use) and to a lesser extent, to other natural phenomena, which contribute to this, like volcanoes, earthquakes [1].

The population density in big cities as well as industrial development and intensive land cultivation in which chemicals are involved, contribute to increased gathering of anions, heavy

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metals and toxic substances (pesticides and their metabolites) in both water and soil [2–7]. Moreover, groundwater pollution depends on insufficient management of urban, industrial and domestic wastes, organic compounds and pathogenic microorganisms, which are found in groundwater receivers. Additionally, excessive and uncontrolled uses of detergents, pesticides and fertilizers have a negative impact to quality of water receivers [8–11]. Especially, irrigation in hot and dry areas contributes in the transfer and deposition of inorganic compounds and salts in unsaturated soil's zone. Due to evaporation the concentration of salts is increased in superficial water and in case that it is transferred in deeper layers its concentration in salts increases by a factor of two or three than that of normal water. Boron constitutes also a problem in water irrigation due to its toxicity.

Over the past 20 years the intensification of agricultural and animal husbandry production, which is enforced by E.U. agricultural policy, creates serious environmental problems connected with the exhaustion of natural recourses [12]. It should be noticed that E.U. have proposed new Groundwater Directive, which is built on the requirements of Article 17 of the Water Framework Directive (2000/60/EC). In particular, it assesses the options for evaluating the chemical status of bodies of groundwater, and for identifying and reversing significant upward trends in the concentrations of pollutants. It also assesses measures to prevent and control groundwater from point and diffuse sources of pollution.

The aim of the current study is the assessment of groundwater quality in the region of Thessaly in central Greece, by determination of physical [electric conductivity (EC), pH, total dissolve solids (TDS) and total hardness (TH)] and chemical [Nitrate (NO_3^-), Nitrite (NO_2), Sulphate (SO_4^{-2}), Iron (Fe), Manganese (Mn), Zinc (Zn) and Copper (Cu)] parameters in urban-lowland, lowland, mountainous and coastal areas in this region. Additionally, for the lowland area, boron (B), residual sodium carbonate (RSC) and sodium absorption ratio (SAR) have been calculated too [13–15].

2. Materials and methods

Four representative areas (urban-lowland (ULL), lowland (LL), mountainous (M) and coastal (C)) were selected for the collection of water samples. From each area samples were collected twice per year, May and August, for a 5-year period (2000–2004). In May the water table is at high level due to the winter and early spring rainfalls, while at the end of the summer the level of the water table is as low as it can be due to the use of very large amounts of water for irrigation.

Nineteen sampling stations were selected and the samples were received from deep (80–100 m) wells. The sampling stations are shown in Fig. 1; ULL sample sites: cities of Larissa, Trikala, Karditsa and Farsala; LL sample sites: Giannouli and Falani (Prefecture of Larissa), Velestino (Prefecture of Magnessia), Megaloxori and Farkadona (Prefecture of Trikala), Sofades and Filo (Prefecture of Karditsa); M sample sites: Elassona, Rodia, Tsaritsani and Damasi (Prefecture of Larissa) and C sample sites: Stomio, Sotiritsa, Agiokampos and Messagala (Prefecture of Larissa). A total of 190 samples were collected and analyzed in the studied period.

Fourteen quality parameters were monitored within a period of five years (2000–2004) as follows: EC, pH, TDS, TH, RSC, SAR, NO_3^-, NO_2, SO_4^{-2}, Fe, Mn, Zn, Cu, and B. The analytical methods involved were standard procedures, as recommended by the European directive 98/83 [16]. Potentiometric methods were applied for EC and pH measurements; atomic absorption spectrometry was used for the determination of calcium, magnesium, potassium and sodium; chloride was measured by UV-spectroscopy, titrimetry was applied for bicarbonate monitoring and complexometry was applied for total hardness determination; trace elements were measured by

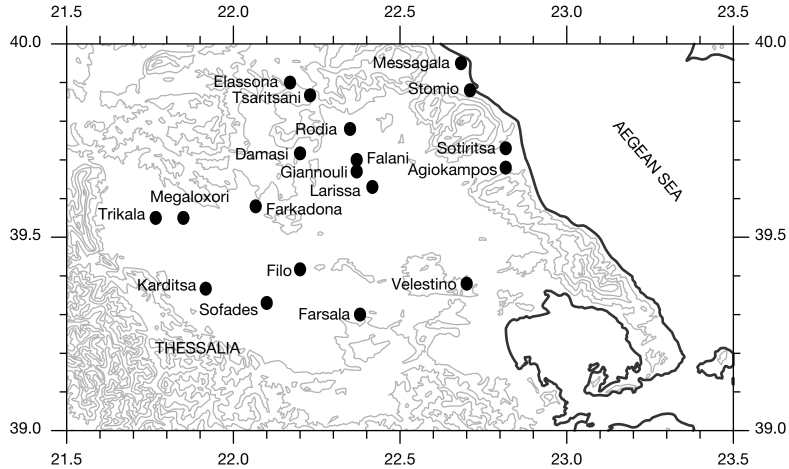

Fig. 1. Map of Thessaly (Greece), with sample sites.

a Varian 640-Z Graphite Furnace A.A.S. (Atomic Absorption Spectrophotometer) with background correction based on Zeeman Effect; finally, absorption spectrophotometry was the analytical method for nitrate analysis.

The operating parameters for working elements were set according to the recommendations of the manufacturers. The chemicals used for the analysis were of analytical reagent grade and all solutions were prepared using HPLC water.

The conditions for sampling, sample preparation, the calibration, the limits of detection and the procedure uncertainty are described in details elsewhere [16,17]. Water samples for trace elements analysis have been collected in high density polyethylene (HDPE) containers which have been filled with a 1:1 mixture of nitric acid p.a. 67% and HPLC water a week ago. The HDPE bottles minimize container pollution and favour sample preservation. After rinsing the bottles three times with sample water, they were filled and brought to 1% concentration with nitric acid and the water samples were transferred in a portable refrigerator to the laboratory. Continuously, the samples were filtered with pre-rinsed cellulose nitrate filters with 0.45 μm pore diameter, stored in the dark at 4°C to minimize sample deterioration prior to analysis. This sampling protocol provided representative samples for trace element analysis. Samples for nitrate and sulphate analysis were preserved with mercuricchloride; samples for cation and chloride analysis preserved with nitric acid.

The chemical parameters were measured in mg L^{-1}, EC in μS cm^{-1}, TDS in mg L^{-1} and TH in mg L^{-1} $CaCO_3$. The analytical measurements were performed in the Laboratory of Instrumental Analysis, Department of Medical Laboratories, Technological Education Institute (TEI) of Larissa.

The data quality was checked by parallel analytical determinations in two laboratories (in Larissa and Athens) and the results have indicated that the uncertainties in the analysis do not exceed 1–3% as relative standard deviation from the mean value for, at least, 25 parallel samples.

The information was recorder in an MS Excel database and processed using statistical software MedCalc version 6.15.000 and SPSS 12.0 for windows.

Table 1
Statistical characteristics of each physical parameter

Area	EC (μS cm^{-1})	pH	TDS (mg L^{-1})	TH (mg L^{-1} $CaCO_3$)
ULL	727.5 ± 249.1	7.85 ± 0.33	574 ± 129	292.3 ± 99.5
LL	732.5 ± 371.1	7.76 ± 0.48	553 ± 158	316.4 ± 103.5
M	659.8 ± 200.0	7.64 ± 0.44	442 ± 49	294.2 ± 85.9
C	890.3 ± 546.8	7.57 ± 0.29	346 ± 19	390.3 ± 167.7

Allowable limits: [EC (2500), pH (6.5–9.5), TDS (1500), TH (500)] [18].

3. Results

Physical and chemical parameter values determined during the study period are presented as mean ± standard deviation. Table 1 presents the statistical characteristics of all the examined physical parameters.

Electrical conductivity mean values are relatively low and progressively increase towards the coastal areas. The pH means are greater than 7, and their spatial progressive increase is C-M-LL-ULL, so the greatest mean of pH occurs in ULL areas. The means of total dissolved solids are relatively low and their appearance in order of size is C-M-LL-ULL. Finally, the means of total hardness are rather large and their spatial progressive increase is ULL-M-LL-C, so the greatest mean of total hardness occurs in costal areas.

Similarly, Table 2 shows the statistical characteristics of concentration (mg L^{-1}) levels of all the examined chemical parameters. The lowest mean nitrate concentration occurs in C areas and the maximum in LL areas. For the nitrite ions, the highest mean concentration occurs in ULL areas and the minimum in LL areas (M and C areas have been found nitrite free). The analysis of sulfate concentration mean values shows that the means of M, LL and ULL areas are lower than 250 (mg L^{-1}). Consequently, the sulfate concentrations mean value for C areas being higher than the corresponding allowable limit value [18]. This existence of violations indicates that the levels of sulfate concentration in coastal areas remain, for the whole part of the examined period, above the allowable limit values. Chloride mean values are relatively low

Table 2
Statistical characteristics of each chemical parameter

Chemical parameter	ULL	LL	M	C
NO_3^-	22.4 ± 19.9	74.2 ± 164.5	23.2 ± 12.3	13.5 ± 14.9
NO_2^-	0.08 ± 0.17	0.01 ± 0.03	0.00	0.00
SO_4^{2-}	150.6 ± 121.3	121.2 ± 98.4	26.2 ± 14.2	886.2 ± 345.9
Cl^-	66.2 ± 59.8	80.7 ± 106.5	35.4 ± 20.8	224.2 ± 197.7
Fe	0.52 ± 0.21	0.92 ± 1.05	0.10 ± 0.01	–
Mn	0.30 ± 0.37	0.21 ± 0.13	0.11 ± 0.01	–
Zn	0.21 ± 0.07	0.28 ± 0.25	0.08 ± 0.05	–
Cu	0.07 ± 0.05	0.13 ± 0.11	–	–

Allowable limits: [NO_3^- (50), NO_2^- (0.1), SO_4^{-2} (250), Fe (0.2), Mn (0.05), Zn (0.01), Cu (2.0), B (1.0)] (mg L^{-1}) [18].

Table 3
Results from the performed statistical analysis for the comparison of physical parameter averages among the considered areas

Areas	EC (µS cm^{-1})	pH	TDS (mg L^{-1})	TH (mg L^{-1} $CaCO_3$)
ULL vs LL	NS	NS	NS	NS
ULL vs M	NS	$P < 0.05$	$P < 0.05$	NS
ULL vs C	NS	$P < 0.001$	$P < 0.001$	$P < 0.05$
LL vs M	NS	NS	NS	NS
LL vs C	NS	$P < 0.001$	$P < 0.001$	$P < 0.05$
M vs C	NS	NS	$P < 0.001$	$P < 0.05$

and progressively increase towards the coastal areas. The mean values of trace elements are higher in ULL and LL areas than M areas. More especially, mean iron, zinc and copper concentrations were higher in LL areas than ULL areas (except for mean manganese concentration that was higher in ULL areas).

The values of physical parameters are normally distributed, according to the Kolmogorov–Smirnov criterion. Moreover, statistical analysis for the comparison of physical parameter averages among the considered areas was performed by the Student's *t*-test; $P < 0.05$ was considered statistically significant. The results of this analysis are presented in Table 3.

The concentration values of SO_4^{-2} and Zn are normally distributed, according to the Kolmogorov-Smirnov criterion. The statistical analysis for the comparison of these chemical parameter mean values, among the considered areas, was performed by the Student's *t*-test; $P < 0.05$ was considered statistically significant. For mean concentration values of the other chemical parameters (NO_3^-, NO_2^-, Cl^-, Fe, Mn and Cu) that did not follow normal distribution, the analysis was performed by the non-parametric Mann–Whitney test; $P < 0.05$ was considered statistically significant. The results of these analyses are presented in Table 4.

Additionally, for the lowland areas, the sodium absorption ratio was found 5.96 ± 10.8 and the concentration of residual sodium carbonate and boron were found 1.49 ± 2.32 meq L^{-1} and 0.58 ± 0.37 mg L^{-1}, respectively.

4. Discussion

The different land use served as a selection's criterion in the current study and the analysis of the samples revealed the following features.

Table 4
Results from the performed statistical analysis for the comparison of chemical parameter averages among the considered areas

Areas	NO_3^-	NO_2^-	SO_4^2	Cl^-	Fe	Mn	Zn	Cu
ULL vs LL	NS	NS	NS	NS	NS	NS	NS	$P < 0.05$
ULL vs M	NS	NS	$P < 0.001$	$P < 0.05$	$P < 0.001$	$P < 0.05$	$P < 0.001$	–
ULL vs C	NS	NS	$P < 0.001$	$P < 0.05$	–	–	–	–
LL vs M	$P < 0.05$	NS	$P < 0.001$	$P < 0.05$	$P < 0.001$	$P < 0.001$	$P < 0.001$	–
LL vs C	NS	NS	$P < 0.001$	$P < 0.05$	–	–	–	–
M vs C	$P < 0.001$	NS	$P < 0.001$	$P < 0.001$	–	–	–	–

The concentration values of the proposed physical and chemical parameters per year do not show significant differences ($P < 0.05$) during the 5-year study period. This reveals that human activities did not have a negative effect to groundwater quality during the study time period and the quality of groundwater remained stable in this time period. For this, contribute the actions that have been taken by industries (better water and wastes management) and in agricultural activities (using less quantity of fertilizers and using better methods for irrigation). It should be pointed out that implementation of these actions enforced by the Greek State and the E.U.

The data presented in Table 1 reveal that the different use of land does not affect significantly the values of physical parameters that were studied, which fluctuate in the allowable limits.

EC is low in freshwater recharge areas and progressively increases towards the coastline (Table 1). The high values of EC in C area can be attributed to the big amount of total dissolved salts in groundwater, and a reason for that is the phenomenon of seawater intrusion in some coastal aquifers.

The mean pH values are greater than 7 in all study areas, indicating the slight alkaline character of the groundwater. There are statistical differences of pH values among ULL-M, ULL-C, LL-C areas and this can be attributed to the different use of land.

Groundwater characterized soft in specific sites of ULL areas (TH values <100 mg L^{-1} $CaCO_3$) and there is not any problem for industrial use of groundwater (Table 1). In specific sites of C areas (TH values = 500–1000) groundwater hardness is big. Consequently, groundwater quality varies from soft to very hard in study areas.

The effect of high TDS values (>1200 mg L^{-1}) in groundwater is in its taste. Generally should be preferred water with TDS value smaller than 500 (mg L^{-1}). In our case TDS values exceed the desirable value of 500 (mg L^{-1}), in specific sites of ULL and LL areas, but this does not have any adverse effect on human health (Table 1).

The nitrate pollution in each area is very important and must be assessed. From the concentration level of nitrate ions (Table 2) it can be concluded that in areas where intensive agricultural activities take place groundwater is more degraded compared to other regions. In these areas the nitrate ions concentration level is increased and exceeds the allowable limits. A possible negative health effect of high nitrate concentrations is methemoglobulinemia, especially for infants. Nitrates are noticeable throughout the entire region rendering most of groundwater improper for human consumption. From Table 2, it can be seen that high concentration of nitrate (>50) occur in ULL, LL and M areas. These areas are characterized by intense industrial and agricultural activity and the high nitrate concentrations in groundwater are related to wastes and over-fertilization, respectively.

High nitrite concentrations are recorded in specific sites of ULL and LL areas and can be associated with human activities.

In ULL and LL areas concentration level of trace elements is increased comparing to mountainous areas. This may be attributed to human and industrial activities since in these areas there is an excessive use of detergents, pesticides and fertilizers and other chemical compounds resulting in groundwater pollution.

The concentration level of sulfates and chlorides in specific sites of a coastal area is very high and differs significantly from that found in other areas. This can be attributed to the fact that the vast majority of wastes are drained usually in particular sites in costal areas.

In LL areas SAR value is relatively low but in combination with EC values it can be concluded that in this area there is a potential risk of water salinity. Moreover, from the mean RSC value it can be concluded that there is a moderate danger of water salinity and a number of actions must be taken when these waters are used for irrigation (continuous monitoring the quality of irrigation water and the soils). Additionally, from the determined concentration of boron it is found that there is relatively danger of boron toxicity of irrigation water in this area. The quality of water for irrigation in LL area, taking into account the mean values of EC, SAR, B and RSC parameters, characterized as appropriate — moderate appropriate for irrigation and in some cases (depending in cultivations, quality of soils and conditions of irrigation) should take special actions in order to avoid the degradation of groundwater and soils.

Costs for groundwater protection arise for various factors: mainly agriculture, industry, transport, and private households. For agriculture, costs arise from reduced fertiliser and pesticide applications. They comprise diminished productivity through less intensive farming practices; information and learning cost for better fertiliser or pesticide management; changing to different crops, or to different combinations or rotations of crops; employing alternative, more costly weed eradication methods; and switching to alternative land uses, i.e. from tillage to pasture or forestry. Other costs for agriculture emerge through better storage of pesticides, and storage and treatment of wastewater and manure from farms. For industry, costs mainly emerge from protective measures that firms are obliged to install. These can be end-of-pipe measures to retain polluting substances, or more intergraded measures, i.e. by changing production processes to reduce the use of certain substances. Opportunity costs arise if polluting activities have to be ceased altogether to comply with environmental rules. In addition, substantial clean-up costs arise after accidental spills of hazardous substances, or to make up for insufficient protection in the past. For historical contamination, these costs are frequently not borne by the polluters, but by local or regional authorities. The sectors that are most affected by this are chemical industries and mining. In the transport sector, costs arise mainly from the installation of protective structures to prevent accidental spills of hazardous substances. Other cost factors are the substitution of methods used in the maintenance of roads and railways, such as road de-icing salts or pesticides used for weed eradication on railway tracks. For the larger part, private households are indirectly affected by the cost of groundwater protection. Since households in most parts of the Europe are connected to public sewerage systems, the cost for wastewater treatment is transmitted to them via water supply companies. Where there is no connection to the public wastewater system, cost arises for septic tanks, etc. Apart from this, households are also affected by restrictions on pesticide use in private gardens, or by protection requirements for private underground storage tanks [19–24].

The environmental problems met in the studied area may be considered as typical of many other areas in Greece. These environmental problems included: (i) pollution from the discharge of municipal sewage, industrial waste and agricultural runoff to the soils, (ii) uncontrolled disposal of municipal refuse, (iii) overuse of the water resources, (iv) uncontrolled use of pesticides and air spaying practices. The agricultural cultivations in this area are cereals, cotton, sugar lets, tobacco, vegetables, and tree plantations, etc. The average fertilization of soil by ($N\text{-}NO_3$ and $N\text{-}NH_4$) fertilizers reached 15 mg kg^{-1} of soil. Over the past 10 years the total quantity of N fertilizers is approximately 180,000 ton per year. The increased use of N- and P-fertilizers created unfavourable conditions for the environment. In some cases the NO_3^- concentrations increased significantly in groundwater because of leaching. During the last decade, a program that aims in decreasing nitrate concentrations in agricultural activities has been applied in the region of Thessaly. This program has been accepted and financed by the E.U. and National resources and up to the moment, the results of this program are positive.

5. Conclusions

It is well documented that anthropogenic activities affect negatively the quality of groundwater. Especially, intensive use of land associated with degradation of groundwater that is mainly caused by nitrate pollution.

The results of this study reveal that in the region of Thessaly, agricultural and animal husbandry activities are also important factors, contributing to nitrate pollution of groundwater. In industrial and agricultural areas, of the study region, there is increased possibility for groundwater pollution by trace elements but this is not at present significant environmental problem. The nitrite concentrations were also increased in these areas, probably due to fertilizer application and to the absence of septic tanks in some areas. In lowland area quality of groundwater for irrigation characterized as appropriate — moderate appropriate, so demanding continuous monitoring of the quality of irrigated soils and groundwater used for irrigation.

Taking into account the results of the present study it is obvious that in the areas studied of the region of Thessaly, it is essential the planning and implementation of a long-term program for the monitoring and improvement of groundwater quality.

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