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GROUNDWATER AND NITRATES IN GREECE - AN OVERVIEW

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A project has been carried out to evaluate nitrates in groundwater in Greece and to subsequently establish a continuous monitoring and data analysis program, according to directive 91/676 of the European Economic Community. Following detailed hydrogeological consideration and study, 165 sampling points were selected to cover all the hydrological departments and the main hydrologic basins of continental Greece and the island of Crete. The majority of the points selected are in alluvial or other porous media formations that are favorable for agricultural or industrial activities. The results show that current conditions appear to present few hazards, probably as a result of the choice of sampling times and the natural reduction of nitrates in the unsaturated zone. Better results are expected after continuous monitoring and data analysis.

INTRODUCTION

The main objective of this study was an initial investigation of nitrate presence (NO_3, NO_2, NH_4) in groundwater and the investigation of the distribution of groundwater vulnerability, according to the nature of the impacted aquifers and the origin of the contaminants. Furthermore, a data base has been established for the continuous monitoring of nitrates and data analysis.

The present study derives from a similar project at Athens University, under the direction of the author, on behalf of the Greek Ministry of Environment. The above project was designed in the framework of the Project of Regional Development and has been adapted to directive 91/676 of the European Economic Community for the protection of the groundwater against nitrate pollution having an agricultural origin.

In this framework, 165 sampling points have been selected (springs and shallow or deep wells) that are representative of the main aquifer systems and the corresponding areas presenting intensive agricultural, industrial or housing activity. A detailed hydrogeological, environmental and regional planning study has been carried out to ensure that the 165 sample points are representative.

Greece is divided into 13 major hydrological departments each of which is further divided in hydrologic basins. All the departments and the most important basins have been covered by the sampling program. Except for Crete, no other islands of the Aegean or Ionian sea have been investigated.

NITRATES AND GROUNDWATER

Dissolved nitrogen, usually in the form of NO_3, has wide potential as a contaminant in groundwater (Tebbutt, 1983). Less often, nitrogen can be present in the form of NH_4, NH_3, NO_2, N_2O and N_2 of organic or inorganic origin. The nitrogen sources are located on the ground surface as direct sources (wastes, fertilizers) or indirect sources which produce NO_3 from nitrogen of organic origin or from NH_4.

The procedures of NO_3 production are complicated, including ammonification and nitrification, which take place in the unsaturated or soil zone, where organic materials and oxygen are abundant (Vrba et al., 1994). Shallow water tables, formed in very permeable porous media or fissured media, can have a high concentration of NO_3, the latter being the stable form of nitrogen in an oxidation environment. Aquifers containing clay or silt sequences can cause reducing conditions, which are manifested by the partial transformation of NO_3 to NH_4, which is finally absorbed by the clay or silt. It is evident that reducing conditions, in the case of common alluvial unconfined aquifers which are characterized by a continuous heterogeneity, occur only locally.

The nitrogen of the soil is an essential nutrient for plants and natural concentrations of soil is rather low. In Greece this concentration, in cultivated soils without fertilizers, ranges from as 0.03-0.3 percent (300-3,000 ppm) (Stournaras et al., 1994). Some nitrogen compounds existing in the soil are volatile and are removed by the wind, or soluble in water and are washed away by surface water or groundwater. Nitrogen enters groundwater in the form of NH_4, NO_2 and NO_3 salts that include Na, K, and Ca.

Nitrogen in the soil has different origins. In areas that have a regular nitrogen distribution, the latter, in the form of soluble salts, results from the transformation of atmospheric nitrogen to NO_3 by atmospheric electric discharges. Some microorganisms transform atmospheric nitrogen by assimilation.

The heavy use of nitrogen fertilizers for soil improvement results in the contamination of surface water and groundwater and eutrophic phenomena in sea water. The quantities of fertilizers used in Greece differ according to the type of cultivation and official information about use is not confirmed by reality because of the excess quantities offered by private fertilizer services.

During rainfall, surface water carries away large quantities of nitrogen compounds. The concentration of these compounds is extremely high when the fertilization time coincides with rainfall. The relation between air-spraying or soil-spraying, and the impact on distant areas affected by these activities is not clear.

Additional point contaminant sources include some industrial installations, stockbreeding activities, cemeteries, domestic wastes and wastewaters.

SAMPLING DATA

The 165 samples that have been used within the framework of this research come from 13 hydrological departments and 80 hydrological basins. The sampling and the ground water chemical analyses were carried out in 1993.

Sampling was restricted exclusively to groundwater. Surface waters were tested in the framework of another project at the National Technical University.

Aquifers represent all porosity types and they have been grouped as follows:

- Porous media (alluvial deposits, plio-pleistocene, neogene formations and flysch sequences);
- Discontinuous media (peridotite, schist, conglomerate, ophiolite, non karstic limestone); and
- Karstic media (limestone, marble, travertine).

The majority of the samples (145) represent porous media aquifers, which is expected since the alluvial, plio-pleistocene and neogene formations provide the subsurface environment for agricultural (mainly), industrial and housing activities. Fewer samples were taken from karstic (14) or discontinuous media (6). Samples include 23 shallow wells, 134 deep wells and 8 springs. The high number of boreholes is expected since deep wells usually provide irrigation water for agriculture and eventually become contaminated by nitrates.

SAMPLING DETAILS AND RESULTS

Hydrologic department of West Peloponnese (01)

Of eight hydrologic basins, the most important of Alfios, Pamissos and Nedas were sampled. Significant potential contamination sources were not found. Contamination originates from diffuse and dispersed point sources, such as agriculture (mainly), industry and housing. The quantity of surface and groundwater is relatively high, hence dilution is usually achieved. High concentrations were found of NO_3 (two samples) and NO_2 (one sample). They were associated with alluvial and neogene deposits.

Hydrologic department of North Peloponnese (02)

Of fifteen hydrologic basins, these of Pinios, Pyrros, Selinountas, Vouraikos, Corinthos, Glafkos, Sythas, Krathis, Zapantis, Vergas, and Finikas were sampled. Agricultural or stockbreeding industries and sites of waste deposits are point contamination sources, while diffuse sources are connected to agricultural activities. The aquifer regime is characterized by local differentiation,

which globally reduces the capacity of each aquifer. High concentrations were found of NO_3 (two samples) and NO_2 (three samples). They were located in the major Corinth area in alluvial deposits.

Hydrologic department of East Peloponnese (03)

Of twelve important or less important hydrologic basins of the given department, the basins of Evrotas, Berbakas, Agios Andreas, Dafnonas and Inahos were sampled. A special characteristic in this department is the presence of big karstic springs in the Argolis area (Anavalos, Kefalari, Lerni, Goura etc.). These springs partially drain the karstic Arcadian plateau by means of sinkholes and karstic conduits. These karstic formations also transport pollutants and contaminants from agriculture and wastewaters. Agriculture, industry and housing activities are responsible for aquifer contamination by nitrates. The high volume of karstic aquifers helps to dilute pollutants. High concentrations were found of NO_3 (one sample) and NO_2 (one sample). Both samples were from alluvial deposits.

Hydrologic department of West Sterea Hellas (04)

This department presents three major rivers (Acheloos, Evinos, Mornos), some less important runoff systems and a number of natural or artificial lakes. These characteristics, coupled with high rainfall, favor dilution of pollutants by surface runoff. The essential aquifers are limited to the river deposits, which can only be affected by local contamination. Conventional point pollution sources exist, while the diffuse sources represent exclusively agricultural and stockbreeding activities. One sample from alluvial deposits had high NO_3.

Hydrologic department of Epirous (05)

In this department some special and apparently contradictory characteristics appear such as the highest rainfall in Greece, extended karstic areas and alluvial deposits, numerous karstic land forms, the closed basin of Ioannina, and important surface water features including the Louros, Arakhthos, Aoos, Kalamas and Aherontas rivers. Hydrological and hydrogeological conditions favor the dilution of contaminants, while agriculture, industry (including intensive stockbreeding) are the main pollution sources. Because of dilution, no samples with significant nitrates were found.

Hydrologic department of Attica (06)

This department has the highest number of housing, industrial, economic, transport or other activities in Greece. Almost half of the population of Greece (Athens, Piraeus and suburbs) is centralized within this area. Despite high urbanization, agriculture is still present. There are no extended, well distinguished or active hydrological basins because of the intensive human intervention in surface runoff systems. Besides agricultural activities, some regions (Megara, Aspropyrgos etc.) have a remarkable stockbreeding industry. High concentrations were found of NO_3 (three samples) and NO_2 (one sample). They were taken from both porous and discontinuous media.

Hydrologic department of East Sterea Hellas (07)

In this department, we included the somewhat typical island of Evia. Among the numerous hydrological basins, those of the rivers Viotikos Kifissos, Sperchios and Asopos are the most important. Compared to industrial activities, stockbreeding industries are less important, while other types of industries prevail in the Sterea Hellas area. In Evia (west coast), the opposite regime applies and agricultural activity is intensive. High concentrations were found of NO_3 (two samples), NO_2 (three samples) and NH_4 (two samples). All were from alluvial deposits.

Hydrologic department of Thessaly (08)

This department is one of the most agricultural areas of Greece and it is almost completely drained by the Pinios river. The closed basins of Karla (artificially drained), Xiniada and Kallipefki complete the configuration of this department. Extensive alluvial and karstic aquifers exist which are intensively exploited mainly for irrigation purposes. Industry and stockbreeding activities are also numerous. High concentrations were found of NO_3 (one sample), NO_2 (four samples) and NH_4 (four samples). They are from porous media and, in part, discontinuous media.

Hydrologic department of West Macedonia (09)

The main hydrologic basins in this department are these of Aliakmon river. A great number of small basins (usually tributaries to the previous basin), and some lakes (Vegoritis etc.) complete the configuration of the department. All kinds of potential contamination due to nitrates exist. Aliakmon receives most of the waste waters resulting from the agricultural and industrial activities. High concentrations were found of NO_3 (one sample), NO_2 (three samples) and NH_4 (one sample). All are from porous media.

Hydrologic department of Central Macedonia (10)

The Axios, Gallikos and Loudias rivers drain this department, which has many secondary basins. The city of Thessaloniki is in this department as well as intensive agricultural and industrial activity. Only one sample high in NH_4 was found in alluvial deposits.

Hydrologic department of East Macedonia (11)

This department is drained by the Strymonas river. The Nevrokopi basin is a closed one drained by sinkholes. It is about an intensive agricultural area, irrigated by both surface and groundwater. High concentrations were found of NO_3 (one sample) and NO_2 (one sample). All were found in porous media.

Hydrologic department of Thrace (12)

The rivers Nestos and Evros, originating in Bulgaria, drain this department. The remaining area is drained by minor basins, which are independent or tributaries to the main rivers. The region is characterized by intensive agricultural and industrial activities, while stockbreeding activity is still significant. High concentrations were found of NO_3 (two samples), NO_2 (four samples) and NH_4 (two samples). All are from porous media.

Hydrologic department of Crete (13)

There is no predominant river in Crete, and drainage is by 26 hydrologic basins. Agricultural and stockbreeding activities are the main contamination sources. High concentrations were found of NO_3 (two samples), NO_2 (one sample) and NH_4 (one sample).

DISCUSSION AND CONCLUSION

The essential problem of this study was the selection of 165 sampling points, covering practically the total active surface of continental Greece. These sampling points should represent the main geological formations, the main aquifer types and the main activities, especially agriculture. Areas without agricultural activities and confined aquifers were excluded. However, the resulting density of the sampling points cannot be considered as adequate.

The inadequacy of the sampling points results also from the fact that the sampling, from a practical standpoint, was not simultaneous in all the areas. Furthermore, the time of sampling did not always coincide to the use of nitrate fertilizers, since their use depends on the type of cultivation, the season within the hydrologic year, the local soil conditions, the local seasonal conditions, and the tendency of the local people.

In many cases it was very difficult to distinguish the nitrates resulting from fertilizers or other chemical source of an agriculture origin from other potential nitrate contamination sources, including stockbreeding or industrial activities, cesspools, and waste waters disposal sites.

Despite the above mentioned difficulties, and apart from the establishment of a data base and monitoring system , the initial results are of special interest.

The majority (145) of the sampling points are in alluvial deposits as well as plio-pleistocene or neogene formations, while the sampling points in karstic and discontinuous media are 14 and 9 respectively. This is expected since these geological formations offer the proper setting for intensive activities, especially agriculture. For the same reason the majority of the samples showing excessive values of nitrates are located in the same geological formations.

Although the majority of the contaminated points is normally concentrated in porous media aquifers, the density of these points is not high. This happens because within the porous media aquifers essential physical processes affect contaminant transport. These processes include advection, dispersion, retardation, filtration, and occurrence of different chemical processes in the unsaturated zone.

Most of the sampling took place during the dry season of the hydrologic year when the concentration of contaminants in the aquifer tends to be increased. The thickness of the unsaturated zone is simultaneously increased and thus the activation of processes that reduce contaminants is also increased. The mobility of nitrogen in the unsaturated zone is controlled by natural cyclic processes, anthropogenic influences and random events (Vrba, 1985). Factors affecting the presence of nitrogen are vegetation cover, soils behavior and the thickness and degree of heterogeneity of the unsaturated zone. During periods of deficient rainfall, as in the sampling period, the content of NO_3 is usually higher in the unsaturated zone than in the aquifer. The above regime, of course, can be modified during intensive irrigation periods.

The majority of the contaminated samples (72%) are found in deep wells, while less (23%) are found in shallow wells. Deep wells eventually become contaminated by nitrates, since they are usually drilled and operating in agriculture fields. Springs did not show contamination, except the Malia spring in Crete, which is a karstic aquifer transmitting groundwater in coastal alluvial deposits. The intensive activities near the spring cause groundwater contamination. For the rest of the springs, the absence of contamination was expected, since their hydrogeologic basin is usually extensive and their mountainous configuration restricts activities to stockbreeding.

Regarding the type of contamination source, the majority (68%) of the contaminated samples derive from point and diffused contamination sources. Contaminated samples from diffused contamination sources are about 26% of the samples, while only 6% are derived from point contamination .

The percentage of contaminants per aquifer media, sampling point, and contamination source are presented in Tables 1, 2, and 3, respectively.

Table 1. Distribution of Samples According to Aquifer Media

Media	Samples			
	Contaminated			Total
	NO_3	NO_2	NH_4	
Porous	14	19	9	145
Karstic	1	0	1	14
Discontinuous	2	1	0	6
Total	17	20	10	165

Table 2. Distribution of Samples According to Sampling Point

Points	Samples			
	Contaminated			Total
	NO_3	NO_2	NH_4	
Springs	1	0	1	8
Shallow wells	7	4	0	23
Deep wells	9	16	9	134
Total	17	20	10	165

Table 3. Distribution of Samples According to Contamination Sources

Sources	Samples			
	Contaminated			Total
	NO_3	NO_2	NH_4	
Point	2	0	1	12
Diffused	5	6	1	55
Point & Diffused	10	14	8	98
Total	17	20	10	165

Even if the density of the points cannot be considered as adequate, this detailed study of sampling point selection allows the results to be valid, at least in this initial stage. According to these results the nitrates situation in groundwater in Greece seems to be, generally speaking, under control. This is probably due to the sampling time related to local seasonal and agricultural conditions, and also to the role of the unsaturated zone and activation of natural contamination reduction processes. More valid results are expected after continuous monitoring and data analysis

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