

Assessment of Soil and groundwater Quality and Hydrogeological Profile of Drama's Prefecture, North Greece

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Abstract: One of the basic tools for the protection of environment and public health is the continuous monitoring of soil and groundwater quality. In the present study, it is reported the hydrogeological profile and the distribution of soil and groundwater physical and chemical parameters, in the Prefecture of Drama (Northern Greece). A total of 30 water samples and 750 soil samples were collected, and fifteen physical and chemical parameters for water and sixteen physical and chemical parameters for soils were determined and analyzed for the period 2004-2005. Water temperature, pH, electric conductivity, carbonate, calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride, nitrate, iron, manganese, total hardness and sand%, clay%, silt%, organic matter%, electric conductivity, SAR, pH, nitrate, phosphorous, potassium, magnesium, iron, manganese, zinc, copper and boron were the determined parameters for water and soil samples respectively. According to *Wilcox*, the majority of groundwater samples belongs to C2S1 category and can be used for irrigation with some precaution. The groundwater samples that came from the low part of the plain belong to C3S1 category, so they can be used for irrigation with the appropriate precautions, in soils without drain systems. Data analysis of the soil samples shows that there are not significant differences for every physical and chemical parameter (except for silt%, organic matter%, SAR, Mg and Mn) among the studied areas. The results of this study provide an overview of the hydrogeological and soil profile and hydrochemical functioning of water supply system for the studied area.

Keywords: Public health, Hydrogeological profile, groundwater quality, soil quality, irrigation water, Prefecture of Drama

1 Introduction

One of the basic tools for the protection of environment and public health is the continuous monitoring of soil and groundwater quality. Groundwater constitutes important natural resource functioning as a reservoir from which good quality water for human consumption as well as for other uses (agriculture, industry) can be drawn. Its contribution as a regulatory factor to the maintenance of wetlands and rivers during the periods of drought is also valuable [1].

Soil and groundwater pollution depends on insufficient management of urban, industrial and domestic wastes, organic compounds and pathogenic micro-organisms, which are found in groundwater receivers. Additionally, excessive and uncontrolled

uses of detergents, pesticides and fertilizers have a negative impact on the quality of soil and water receivers [2-15].

European Union, recognizing the importance of soil and groundwater quality, has issued a number of directives imposing rules and instructions for the assessment and the protection of soil and groundwater quality [16-23]. It should be noticed that E.U. has proposed a new Groundwater Directive, which is built on the requirements of Article 17 of the 2000/60/EC Directive (WFD). Main provisions of the proposed new groundwater directive are the definition of groundwater chemical status, the establishment of a "prevent" list, the identification and the reversal of trends, monitoring and reporting.

In the present work it is reported the hydrogeological profile and have been determined the quality of soil and groundwater of the prefecture of Drama.

2 Materials and Methods

2.1 Area of Study

The basin of Drama is surrounded by the mountains Falakro (2230 m) north, Lekani (1295 m) easterly, Menikion (1965 m) westwards, Paggeo (1955 m) and Symvolo (965 m) southerly. The total extent of the basin of Drama is 1875 Km². The mountainous and semi-mountainous area has an expansion of 1105 Km², while the semi-plain and plain areas occupy an expansion of 770 Km². The hydrologic basin of Drama is allocated in six areas whose expanse and distribution are given in table 1.

Table 1. Distribution of individual areas of basin of Drama

Areas	Surface (Km ²)	Surface (%)
Area of Falakro	547	29,17
Area of Lekani	276	14,70
Area of Menikio	140	7,46
Area of Symvolo	16	0,85
Area of Paggeo	126	6,72
Area of plain	770	41,10

The basin of Drama presents an asymmetrical hydrogeological network, as for the growth of central sectors and as for its expansion that is due to the new tectonic activities that have happened in the space of Southwest Rodopi.

The hydrogeological network of plain was created mainly by water from springs in the perimeter of the plain. In the wider region of plain the carstic basin of Nevrokopi (Vathitopos, Leukogia, and Kato Neurokopi) is also included, which is hydrogeological isolated concerning the basin of Drama.

Water of the carstic system of mountain Falakro and water that flows from swallow-holes that begin from the Ochiro and cover a way of 9 Km via an underground river, lead in the spring of Maara (122 m.) in the north-western area of the plain. These springs create the river Aggitis that follows the western side of the basin of Drama and accepts water from springs of Paggeo terms and western fringes of Menikion terms. Main contribution of the river Aggitis is the river of Drama that emanates from the homonym springs of city. The springs of Mylopotamos contribute more southerly with the river of Drama. In the southern utmost the plain the river of Drama contributes with water of drain channels of Philippos plain, with water of springs of Paggeo terms and water from drain channels of Eastern area of plain. Thus, in the plain of Drama, the river Aggitis becomes the final recipient of all spring's water that is released in the fringes of northern, eastern and south-western forehead of mountains Falakro, Lekani, Paggeo, Symvolo and Menikion. The exit of surface water of the plains is in the southern area, where the river Aggitis crosses the

valley Paggeo - Menikion and joins with the river Strimonas.

Analyzing the most important and most representative systems of springs, they can be categorized according to their areas of catering as follows:

- i) the springs of Drama, Mylopotamos (Kefalovryso), and Maara (Aggitis) in the northern area,
- ii) the springs of blue waters and Psathadika in the south-western area, and
- iii) the springs of Dikelitas – Krinides and Kefalari - Voirani in the eastern area.

2.1.1 Sampling

The hydrochemistry study of spring water and groundwater of the wider basin of Drama (Fig. 1) was based on the results of 30 water samples physical and chemical analyses. The samples of groundwater were taken mainly from the plain area of the Prefecture of Drama. August and September of 2004 and August and September of 2005 were the periods of sampling. The water samples correspond to 27 drillings (deep >100 m) and 3 springs (springs of Drama (Agia Varvara), Kefalari and Maara (Aggitis)).

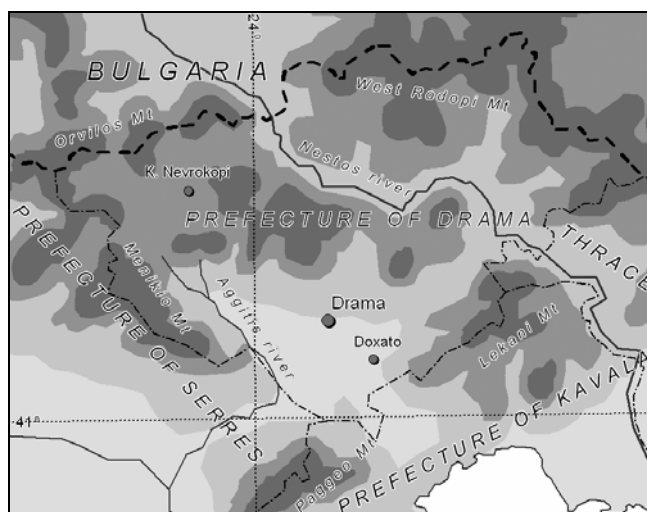


Figure 1. Map of Drama

A total of 750 soil samples were collected once per year, every September, from depth (0-30cm) and analyzed for the same studied period. The water samples were taken from drillings for irrigation in local municipal apartments as: Ftelia, Kalampaki, Nerofrakti, Agia Paraskevi, Mylopotamos, Argiroupoli, Aggitis, Choristi, Kokkinogia, Drama, Sitagri, Fotolivos, and Nikotsara. Three representative areas and 30 sample sites was selected for the collection of soil samples, LL area: lowland area (Drama, Kalifitos, Mavrolefki, Kalampaki, Kefalari, Doxato, Mikrokampos, Agios Athanasios, Nea Amisos, Kalamonas, Fotolivos and Mavrovatos), SM area: semi – mountainous area (Platanovrisi, Nikiforos, Peristeria, Agora, Kalithea, Exochi, Livadia, Ochiro, Lefkogia,

Pigadia and Perithori), and V area: the plain of Phillipos.

2.1.2 Methods

A. Groundwater: Fifteen quality parameters were determined and monitored within a period 2004-2005 as follows: Temperature (T), pH, electric conductivity (EC), carbonate (CO_3^{2-}), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), potassium (K^+), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), iron (Fe), manganese (Mn^{+2}) and total hardness (TH). The involved analytical methods were standard procedures, as recommended by the European directive 98/83 [16]. The determination of nitrate and nitrite ions in the water was carried out spectrophotometrically using the methods described in APHA [25]. The conditions for water sampling, sample preparation, the calibration, the limits of detection and the procedure uncertainty are described in details elsewhere [16, 24-28].

B. Soil: Sixteen quality parameters were determined and monitored within a period 2004-2005 as follows: sand%, clay%, silt%, organic matter%, electric conductivity, SAR, pH, nitrate, phosphorous, potassium, magnesium, iron, manganese, zinc, copper and boron. Soil samples were collected from each area according to Welch et al [26]. Physical and chemical parameters for soils were determined with the use of standard analytical techniques [25-28].

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

The chemical parameters of soil and groundwater were measured in mg.L^{-1} , electrical conductivity (EC) in $\mu\text{S.cm}^{-1}$, temperature (T) in $^\circ\text{C}$ and total hardness (TH) in $\text{mg.L}^{-1} \text{CaCO}_3$.

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

3 Results and Discussion

Physical and chemical parameter values of water samples determined during the study period are presented as mean, standard deviation (SD), min and max value. Table 2 presents the statistical characteristics of all the examined physical parameters. The temperature of studied water samples was within the reference temperature values concerning the sampling period. The mean values of pH are greater than 7.00 in all study areas (Table 1), indicating the slight alkaline character of groundwater. The pH of natural water usually varies in the region 6.50-8.50. The studied samples of water of drillings for irrigation

had pH values between 7.10 and 7.80. Thus the water is characterized neutral-basic and the lower values correspond to the samples taken from the lower area of the plain. The water of carstic springs presented values of pH between 7.53 and 7.69.

Table 2. Physical parameters of spring water and groundwater

Parameter	Mean	SD	Min	Max
T	18.07	3.30	12.70	25.50
pH	7.49	0.18	7.10	7.80
EC	704	285	211	1605
TH	282.2	81.6	166	554

EC is low ($400 \mu\text{S.cm}^{-1}$) in freshwater recharge areas (samples of the spring water system) and progressively increases towards the central area of the plain ($700 \mu\text{S.cm}^{-1}$) and becomes greater toward the low areas of the plain ($2000 \mu\text{S.cm}^{-1}$). The high values of EC in low areas of the plain ($2000 \mu\text{S.cm}^{-1}$) can be attributed to the large amount of total dissolved salts in groundwater. The majority of the values show that the water is renewed relatively fast contrary to the low area of the plain where the renewal of groundwater takes place slowly. The hardness of natural water is due to the geological constitution of rocks from which it passes through, and in our country because of the calcium carbonate constitution in many regions, water usually presents high values of hardness. Specific sites in the studied areas were characterized of medium and high hardness values and this is a problem concerning the use of groundwater in industrial activities. In addition, the mean values of total hardness in all areas did not exceed the acceptable limits. However in some cases the mean values exceeded the limit of $500 \text{mg.L}^{-1} \text{CaCO}_3$, which is the highest acceptable value. The comparison of mean values of TH among the studied areas shows that there is a significant difference between the studied areas. This can be attributed to geological differences among areas and to different uses of land.

Similarly, Table 3 shows the statistical characteristics of concentration (mg.L^{-1}) levels of all the examined chemical parameters.

Table 3. Chemical parameters of spring water and groundwater

Chemical Parameter	Mean	SD	Min	Max
Na^+	47.1	71.4	3.6	300.0
K^+	2.0	4.0	0.2	21.0
Ca^{+2}	73.6	35.4	32.0	187.0
Mg^{+2}	24.1	13.6	5.3	59.0
Fe	0.09	0.08	0.00	0.25
Mn	0.04	0.07	0.00	0.30
CO_3^{2-}	7.15	9.02	0.00	30.00
HCO_3^-	358.3	140.2	181.0	748.0
NO_3^-	9.5	13.1	0.0	64.8
Cl^-	36.6	36.8	8.9	186.2
SO_4^{2-}	35.1	52.2	0.0	282.0

The high concentrations of sodium (Na^+) depended on the period of time that the groundwater remained in the

soil and in the combined action of ionic exchange and dissolution of calcium carbonate, magnesium carbonate and aluminum salts. In the studied region the mean concentrations of sodium and potassium were found within the allowable limits. The concentrations of Ca^{+2} and Mg^{+2} in spring water and in groundwater depended on the natural origin of water and were due to the chemical constitution of rocks through which the water passes. Rocks rich in calcium and that enrich natural water are limestone and dolomites. In Greece, because of the calcium carbonate constitution of rocks, the water is rich in calcium. Consequently, the mean concentration values of Ca^{+2} and Mg^{+2} have been found within the allowable limits. The presence of iron (Fe) and manganese (Mn) in groundwater is attributed to the solution of various mining mainly oxides and sulphate salts, as well as carbonate and silica salts that contain these two metals. The concentration of Fe and Mn in groundwater usually did not exceed the values of 10.00 mg.L^{-1} and 2.00 mg.L^{-1} respectively. In the present study the concentrations were found between 0.00 and 0.25 mg.L^{-1} for Fe and between 0.00 and 0.30 mg.L^{-1} for Mn. Among the main anions prevails HCO_3^- with concentrations between 181 and 748 mg.L^{-1} . The high concentrations of bicarbonate are owed in the presence of dissolved CO_2 and in biochemical decomposition of organic materials in groundwater that produced bicarbonate. The nitrate pollution in each area is very important and must be assessed. A possible negative health effect of high nitrate concentrations is methemoglobinemia, especially for infants. From the concentration level of nitrate ions (Table 3) 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. 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. The chloride ions constitute one of the basic inorganic anions of water. In natural surface water and groundwater, the concentration of chloride differs and depends mainly on the chemical constitution of rocks that water passes through. In Greece in many regions high concentration of chloride has been observed in groundwater, mainly near coastal regions, because of the over pumping and the sea water intrusion. High concentrations of chloride degrade the organic characteristics of potable water, increase the rate of erosion of metal surfaces and have destructive consequences in the growth of most plants. The concentrations of chloride in the studied areas oscillate from 8.9 to 186.2 mg.L^{-1} and have been found in the maximum permissible limit (200 mg.L^{-1}) for drinking water. The presence of sulphate ions in spring water and groundwater can emanate from the geological constitution of rocks that water passes

through or from certain uses of water by humans. The control of sulphate salts in potable water is important, because it has been found that the sulphate salts of calcium and magnesium have purgative action in the human's health. The maximum permissible limit of sulphate ions in potable water is 250 mg.L^{-1} . The concentration of SO_4^{2-} in the samples that were studied begins from zero to 282 mg.L^{-1} . It is observed that in particular water samples the concentration of sulphate exceeds the allowable limit concerning drinking water.

The value of parameter $X = \text{Ca} + \text{Mg} / \text{Na} + \text{K}$ is a meter of continuous catering of groundwater. X that takes values much higher than 1 in the western and central area of the plain (5 until 23) declares the existence of continuous catering and renewal of groundwater. On the contrary, in the low areas of the plain (region Nerofrakti) the X that takes values smaller than 1 (0.47 until 0.67) declares that the hydrological horizon is characterized from the lack of continuous catering.

Physical and chemical parameter values of soil samples determined during the study period are presented as mean $\pm$ standard deviation (SD). Table 4 presents the statistical characteristics of all the examined physical parameters.

Table 4. Physical parameters of soil samples

Physical Parameter	LL area Mean $\pm$ SD	SM area Mean $\pm$ SD	V area Mean $\pm$ SD
Sand%	42.8 $\pm$ 13.7	44.9 $\pm$ 20.1	34.7 $\pm$ 23.0
Clay%	24.4 $\pm$ 9.2	29.3 $\pm$ 17.0	35.0 $\pm$ 22.1
Silt%	32.7 $\pm$ 7.6	25.8 $\pm$ 8.1	30.3 $\pm$ 7.8
Org. Mat.%	1.81 $\pm$ 0.31	2.76 $\pm$ 2.54	3.55 $\pm$ 3.68
EC	912 $\pm$ 899	845 $\pm$ 524	462 $\pm$ 38
SAR	0.32 $\pm$ 0.06	1.67 $\pm$ 3.03	0.50 $\pm$ 0.09
pH	7.16 $\pm$ 1.03	6.86 $\pm$ 1.22	7.82 $\pm$ 1.00

Similarly, Table 5 shows the statistical characteristics of concentration (mg.L^{-1}) levels of all the examined chemical parameters.

Table 5. Chemical parameters of soil samples

Chemical Parameter	LL area Mean $\pm$ SD	SM area Mean $\pm$ SD	V area Mean $\pm$ SD
NO_3^-	12.4 $\pm$ 18.8	22.2 $\pm$ 44.8	8.7 $\pm$ 4.5
P	132 $\pm$ 154	174 $\pm$ 203	97 $\pm$ 108
K	153 $\pm$ 91	208 $\pm$ 227	226 $\pm$ 168
Mg	308 $\pm$ 315	167 $\pm$ 156	325 $\pm$ 176
Fe	42.7 $\pm$ 52.8	46.4 $\pm$ 46.3	56.9 $\pm$ 56.0
Mn	21.1 $\pm$ 19.2	17.2 $\pm$ 16.5	8.6 $\pm$ 9.4
Zn	1.23 $\pm$ 1.79	0.70 $\pm$ 0.33	1.00 $\pm$ 0.55
Cu	2.12 $\pm$ 4.28	1.66 $\pm$ 2.27	1.39 $\pm$ 0.55
B	1.47 $\pm$ 0.72	2.16 $\pm$ 3.13	0.92 $\pm$ 0.38

The values of sand%, clay%, silt%, EC, Mg and Fe are normally distributed, according to the Kolmogorov-Smirnov criterion. Moreover, statistical analysis for the

comparison of the above parameter averages among the considered areas was performed by the Student's t-test; $P < 0.05$ was considered statistically significant. The analysis for concentration values of the other parameters that did not follow normal distribution, was performed by the non-parametric Mann-Whitney test; $P < 0.05$ was considered statistically significant. The results of this analysis are presented in Table 6 and Table 7.

Table 6. Results from the performed statistical analysis for the comparison of soil physical parameter averages between the areas

Parameter	LL vs SM	LL vs V	SM vs V
Sand%	NS	NS	NS
Clay%	NS	NS	NS
Silt%	$P < 0.05$	NS	NS
Org. Mat. %	$P < 0.05$	NS	NS
EC	NS	NS	NS
SAR	$P < 0.05$	NS	NS
pH	NS	$P < 0.05$	$P < 0.05$

Data analysis of the soil samples shows that there are not significant differences for every physical and chemical parameter (except for silt%, organic matter%, SAR, Mg and Mn) among the studied areas.

Table 7. Results from the performed statistical analysis for the comparison of soil chemical parameter averages between the areas

Parameter	LL vs SM	LL vs V	SM vs V
NO_3^-	NS	NS	NS
P	NS	NS	NS
K	NS	NS	NS
Mg	NS	NS	$P < 0.05$
Fe	NS	NS	NS
Mn	NS	$P < 0.05$	NS
Zn	NS	NS	NS
Cu	NS	NS	NS
B	NS	NS	NS

The statistically significant differences for the physical and chemical parameters between the different studied areas can be attributed to the origin constitution of soil and to the different use of the land. In SM area there are cultivations of trees (apple, cherry and grapes) in contrast to LL and V area where there are yearly cultivations (cotton and maize) and industrial activities.

The degradation of soil is bigger in SM area than the other two areas. The salinization is bigger in the same area, too. The mean value of pH in SM area is lower than 7. Nitrate and phosphate pollution of soil in LL and SM area is big and must be assessment. The concentration of trace elements and boron is high in many sample sites of all the studied areas. Inappropriate cultivations, wide use of fertilizers and pesticides and inefficient management of water resources are the main reasons for the pollution of soil

and groundwater of the studied areas. Moreover, reformation of cultivations is a necessary action to decrease the use of fertilizers and to improve the quality of soil and groundwater in these areas.

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5 Conclusions

Considered the concentrations of cations Ca^{+2} , Mg^{+2} , Na^+ , anions HCO_3^- , Cl^- , SO_4^{-2} , the value of X parameter, the value of electric conductivity and the value of total hardness the water can be categorized in two basic types. The first type of water represented the water samples of springs and groundwater in the higher topographic areas of the plain and their type was calcium-bicarbonate (Ca-HCO_3^- -type). On the contrary, the second type represented five water samples that were taken from the low areas of the plain (region Nerofrakti), and their type was sodium-bicarbonate (Na-HCO_3^- -type). The high concentrations of ions, the high values of EC, and the high values of TH are related with the layers of lignite in this area. The water of this type is not potable. The high concentrations of Fe that were observed in the lower areas of plain are connected with the high pressure of hydrological horizon and with the action of iron bacteria from the effect of lignite layers in a reductive environment.

According to Wilcox, the most groundwater samples belong to C2S1 category and can be used for irrigation with some percussion. The groundwater samples that came from the low part of the plain belong to C3S1 category, so they can be used for irrigation with the appropriate precautions, in soils without drain systems.

The nitrate and phosphate pollution of soil constitutes a big environmental problem and mainly due to the wide use of pesticides (NO_3^- , PO_4^{-3}). Fertilizers and pesticides also pollutes the groundwater so, some actions must be taken in local and central level. The protection of soil and groundwater quality is essential for the achievement of good quality of environment and public health. Moreover, the good quality of soil and groundwater affect positively to the agricultural production and this is extremely important for the local economy.

The right management of the water resources and agricultural activities are appropriate actions for the improvement of soil and groundwater quality.

Monitoring the quality of groundwater must be an ongoing process, so every change in pollutants should be recognized at an early stage. As a result, appropriate actions could be taken by official authorities to avoid

the expansion of pollution and protect public health [29].

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