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DETERMINATION OF HEAVY METALS CONCENTRATIONS IN WATER AND SOIL RESOURCES IN THE MESOGEIA VALLEY (ATHENS)

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Abstract:-

Nowadays, more than ever before, the intense agricultural activity, the increasing industrial development, the increasing urbanization, the overexploitation of the aquifers have led to the degradation of the quality of groundwater and soil resources. Heavy metals play a great role because they are not disintegrated, but remain in the upper soil layer with high absorption from the plants and humans causing major problems. This paper presents the heavy metal concentration values, the spatial distribution of them as well as the correlation among these elements with the aim of pointing out the water degradation and the soil deterioration in the Mesogeia Valley. For this reason, 86 water and 42 soil samples, taken from the study area, were tested by atomic absorption spectroscopy and the heavy metal values were determined. The results were statistically analyzed and groundwater and soil resources quality was described. The results of this study constitute a basis for the necessary protection steps that need to be taken to prevent any further degradation of the areas' natural resources.

1 INTRODUCTION

Water is an essential ingredient in human nutrition and holds a leading position not only to human health but also in social, cultural and economic development and environmental conservation. Both the quantity, but also the water quality are the keys to the survival of various organisms in the food chain and in various human activities. Although, water is abundant on our planet, covering 75% of the earth's surface, the largest percentage (97%) is allocated to the seas and oceans and only the 3% is fresh water located mainly on glaciers and ice poles (Kallergis, 2000; Soulios, 2004). The geographical distribution of water on the planet does not follow the corresponding distribution of the population. Increasing water demand and the gradual deterioration in its quality, makes water precious commodity.

On the other hand, soil is a complex dynamic system in which occur physical, chemical and biological processes. In agriculture it is of great significance, since not only it is a means of supporting plants but and nutrients warehouse for the plants. The concentrations of elements in soils is important for the quality of the environment and the balance of soil nutrients and depend on the geochemical nature of the parent rock from which emerged the soil, the degree of soil development and atmospheric depositions. Moreover they depend on external factors, such as land use, vegetation and sources of pollution (Martinez Cortizas et al., 2003, Zhang et al., 2002). Especially, the determination of heavy metals is of great importance because they are not disintergrated, remain in the same deposits and are accumulated in the upper soil layer with high absorption from the plants and the human. Thus, they cause many health problem to the human and animals and lead to the decrease of plants production.

In the present study, the water and soil quality assessment of heavy metals was analyzed in the Mesogeia valley. After constructing the International Airport of Athens "Eleftherios Venizelos" the motorway "Attiki Odos" and the "Suburban railway", a demographic blowup has turned up, which was sequent with the water need increase as well as the wastes quantities which end up to the environment, since all the towns of the area in issue are lacking of drainage system. The intense agriculture with excessive use of agrochemicals and fertilizers as well as the atmospheric deposition of exhaust gases from cars and airplanes contribute also to the contamination of soil and water resources. Although, quite studies (Mariolakos and Lekkas, 1974; Georgalas and Koumantakis, 1997; Alexakis and Kelepertsis, 1998; Stamatis et al., 2006; Bathrellos et al., 2008; Farmaki and Thomaidis, 2008; Champidi 2012) have been carried out in this area, the majority of them are concerned to the groundwater recharge of the aquifers and not the pollution. Within the framework of the present research, water and soil samples were taken by this valley and concentrations of heavy metals were calculated and presented. The purpose of this paper was to point out the water degradation and the soil deterioration of this area as far as the content of heavy metals are concerned.

2. Study area

The study area is located in the Eastern part of Attica county and lies between latitudes 37°55' and 37°95' and longitudes 23°55' and 24°10'. The investigated area is defined from the Penteli mountain at North, the Hymettus mountain at the western side, the watersheds of "Merenta" at South and the coastline Rafina-Artemis-Porto Rafti at East (Fig. 1). The relief is smooth at the central part, where the cultivated plain comes along and more intense at North and West where the mountains Penteli and Hymettus develop, with maximum heights 940 and 1026m respectively (Fig. 1).

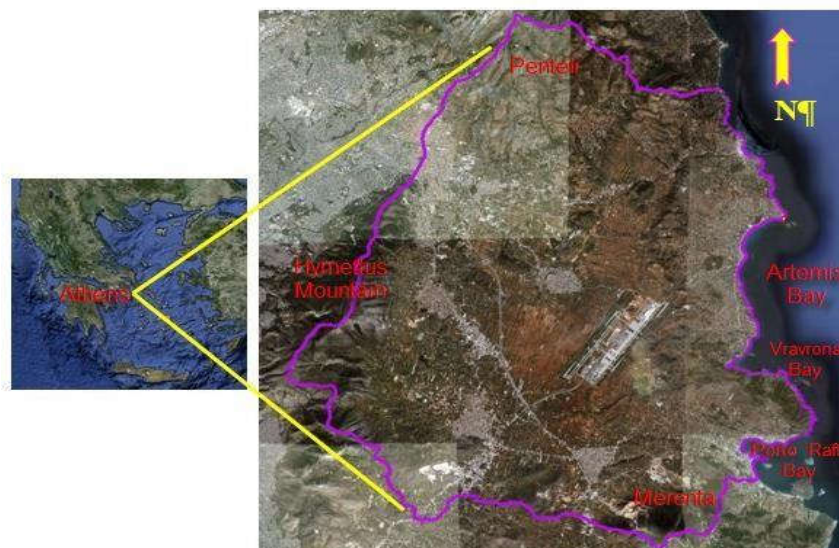


Figure 1: The Study area

The rousing development of the area gave rise to a demographic blowup and a conversion from the inveterate primary section to the tertiary section. The flora consists of *Pinus Halepensis* and bushy plants. The major lands in the area are sustained to agriculture with the olive and vine trees as the prevailing crops (Fig. 2).

The climate of the area is characterized by low precipitation and high temperatures during the summer, trending the dry-warming climate of the greater area. Precipitation is low even during the winter months, something that embounds the aquifer enhancement.

From geotectonic point of view, the area comprises a part of the Attico-Cycladic mass. The geological bedrock is structured by a big thickness of Mesozoic up to Mesoiocenic carbonate formations, limestone, dolomites and marbles, with intercalations of schist and marble layers of significant thickness (Fig. 3). The Late-Cretaceous limestone is developed over the ophiolitic bodies, intensively smashed and karsted.

In the biggest part of the area Neogene and Quaternary formations are developed. The Neogene formations consist of limestone, marls, sandstones and conglomerates while the Quaternaries consist of diluvial formations, talus cones, scree and alluvial deposits comprising of limestone, sandstones and marly materials, loams, clays, gravels and sands (Jacobshagen 1986; Katsikatos 1992). Generally, the geological formations of Attica are grouped in three major systems (Fig. 3):

a) the autochthonous system of Triassic and Jurassic schists and marbles that constitute the bedrock and the core of the Attica Mountains, b) the allochthonous system of Cretaceous limestones, schists and sandstones and c) the Tertiary and Quaternary deposits (Lepsius 1893).

The tectonic medium of the greater area is characterized by the anticline Hymettus-Parnitha-Marathonas development, whose axis has NE-SW direction. At the Eastern part of this anticline structure, the syncline of Mesogeia is developed, a part of which consists the area in issue. The Mesogeia syncline is parallel to the anticline of Hymettus with the same NE-SW direction. Only Mesogeia basin is found in terrestrial area. The Mesogeia syncline presents an intense faulting tectonic which is coming up with NE-SW and NW-SE faulting trends. The sequential origins of separation faults which took place during the Neogene brought out the exhumation of the metamorphosed rocks of Attica and the fulfillment of the basins with sediments. The separation fault of Mesogeia cuts the metamorphosed sediments of Penteli mountain off the Upper Miocene and After-Miocene sediments of Mesogeia basin. This fault was active after the Upper Miocene, contributing to the rapid formation of the relief and the erosion of the metamorphosed rocks of Penteli.

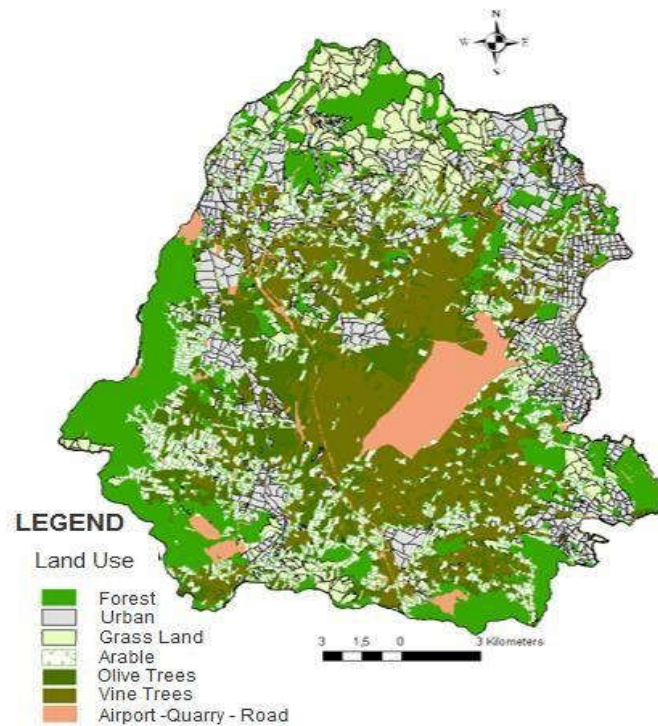


Figure 2: Land use map

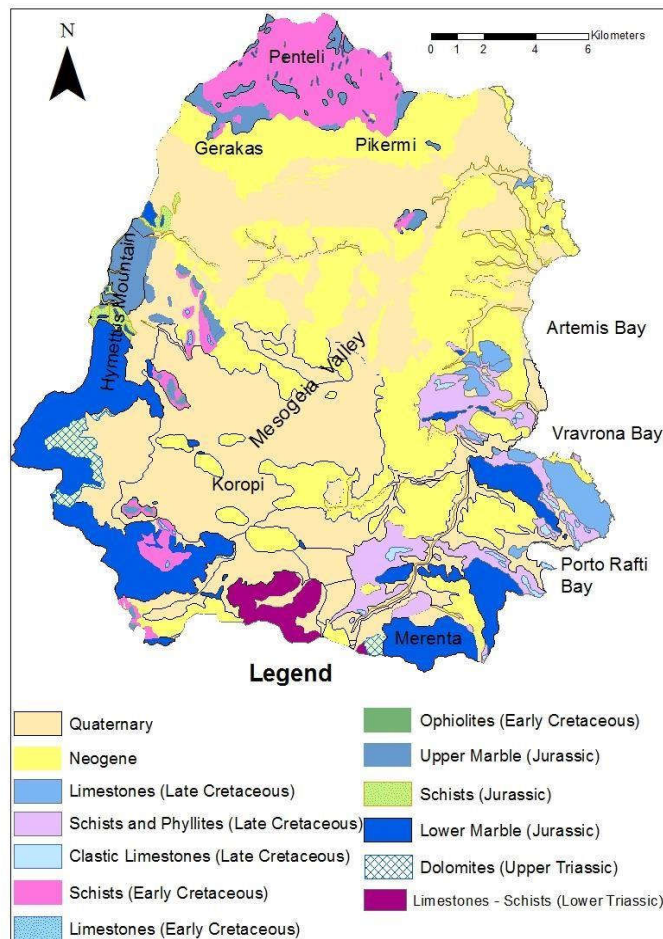


Figure 3: Geology of study area

4. Sampling and test procedures

In the frame of this study, groundwater samples from different aquifers was undertaken. Specimens were collected from 3 springs' outlets, which are fed from the Neogene aquifers, 65 wells and 18 deep boreholes, which are exploited the aquifers hosted in the Neogene and Quaternary formations, as well as the deep karst aquifer (Fig. 4). The parameters Fe, Zn, Mn, Cu, Cd, Pb, Ni, Cr, Co, were determined by atomic absorption spectroscopy (GBC/908AA). Furthermore, a total of 42 soil samples (Fig. 5) were taken with sufficient spatial dispersion so as to cover the entire basin, which has been filled with Neogene and Quaternary formations. For the determination of soil sampling points, the sampling points of groundwater were considered. Therefore, each soil sample was taken from near a water sampling point. The soil samples were collected from surface (depth of 0 to 30cm) and the determination of Fe, Zn, Mn, Cu, Cd, Pb, Ni, Cr, Co, were determined by atomic absorption spectroscopy (GBS/908AAS). All the analyses were conducted at the laboratory of Mineralogy-Geology, Agriculture University of Athens.

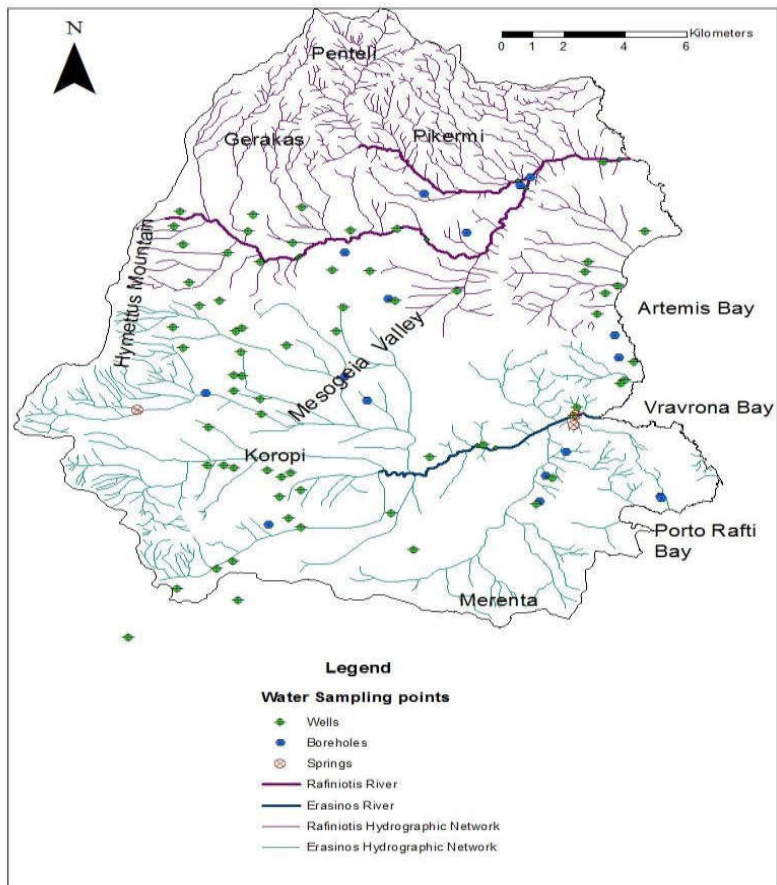


Figure 4: Groundwater Sampling points

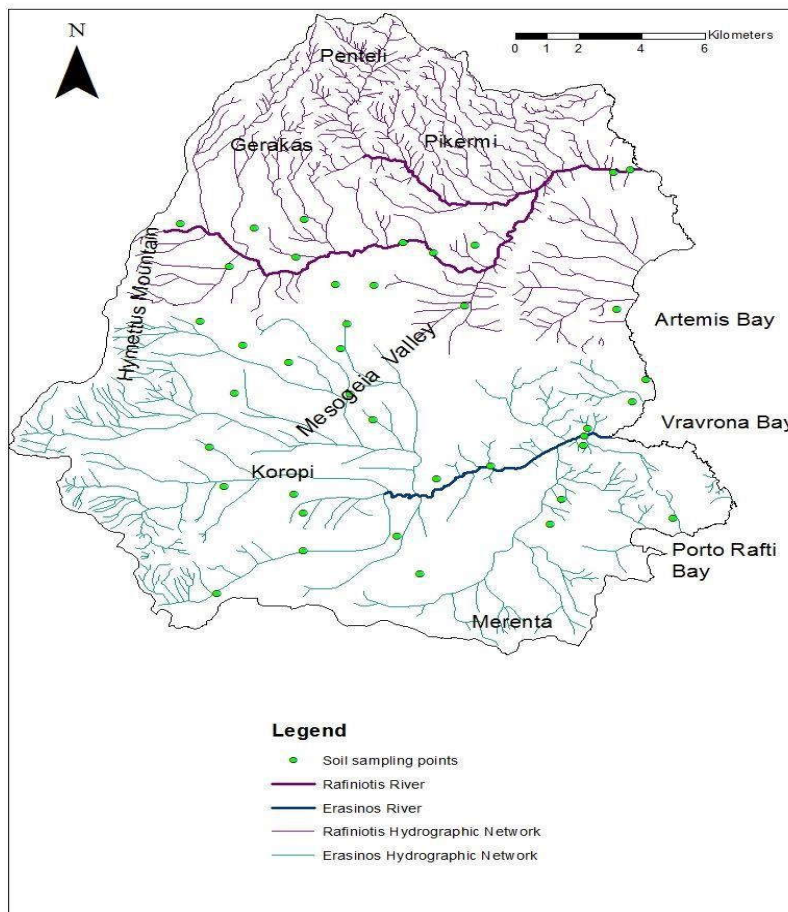


Figure 5: Soil sampling points

The content of heavy metals in soil and water, is very important because they are absorbed by plants and entered in the food chain, causing through bioaccumulation, a major problem in the diet of human and animals. Moreover, heavy metals affect the plants, decreasing the production. Most plants show deficiency when there is lack of some important elements like the above-mentioned and toxicity when there is overdose of them.

The presence of heavy metals in the soils and water can be either geogenous or anthropogenic origin. In the latter case the heavy metal can be derived from (Siegel, 2002):

- agricultural use and use of agrochemicals (Cd, Cr, Cu, Mn, Ni, Pb, Zn)
- metallurgical industries (Cd, Cr, Cu, Mn, Ni, Pb, Zn)
- Electronic (Cu)
- paint production (Cd, Cr, Cu, Mn, Ni, Pb, Zn, Co)
- production of plastic (Cd, Pb, Zn)
- waste deposition (Cd, Cr, Cu, Mn, Ni, Pb, Zn, Co, Fe)
- atmospheric deposition (Cd, Pb)

5. Statistical Analysis

First of all, the results of the tests were determined and presented. After statistical analysis, the range, the mean and the standard deviation value for each heavy metal were calculated. The interrelationships among the heavy metals of the groundwater are important, from a hydrochemical point of view. For this purpose, regression analysis was applied to express the relation among the elements. The correlation coefficient (r) is also determined. The simple correlation coefficient (Douglas and Leo, 1977; Ratha and Venkataraman, 1997) measures the strength of two parameters, when the dependent parameter is influenced only by independent parameter and vice versa. The statistical analysis technique, used to correlate the above-mentioned properties, was the EXCEL Analysis ToolPak program. The spatial distribution of heavy metals concentrations was plotted by the Surfer program, using the Kriging interpolation method.

6. Heavy Metals concentrations

6.1 Heavy metals in the groundwater

The maximum, the minimum, the average values and the standard deviation of the heavy metals in the groundwater are given in Table 1. The groundwater met in the Neogene formations presents the highest concentrations in most elements. The maximum values are met in the Zn (8.68ppm), while the Co presents the lowest values (0.001ppm).

Table 1: Statistical analysis of the heavy metal concentrations in the groundwater

Elements	Groundwater from Quaternary formations (ppm) (n:15)				Groundwater from Neogene formations (ppm) (n:50)				Groundwater from Carbonate formations (ppm) (n:21)			
	min	max	average	stdv	min	max	average	stdv	min	max	average	stdv
			e				e					
Fe	0.00 0	0.20 3	0.083	0.077	0.00 0	0.27 1	0.070	0.084	0.00 0	0.23 6	0.053	0.073
Mn	0.00 1	0.39 2	0.074	0.098	0.00 0	0.15 4	0.046	0.048	0.00 0	0.12 0	0.063	0.044
Cu	0.00 4	0.16 2	0.075	0.061	0.00 3	0.14 9	0.061	0.054	0.00 3	0.13 9	0.078	0.042
Zn	0.02 3	4.97 8	0.732	1.340	0.00 4	8.68 3	0.425	1.263	0.01 0	0.89 7	0.180	0.211
Cd	0.00 0	0.06 5	0.031	0.027	0.00 0	0.07 6	0.025	0.027	0.00 0	0.07 1	0.042	0.026
Pb	0.00 1	0.25 0	0.094	0.090	0.00 0	0.37 4	0.071	0.103	0.00 0	0.43 4	0.151	0.131
Ni	0.00 0	0.27 5	0.091	0.104	0.00 0	0.33 1	0.085	0.100	0.00 0	0.29 7	0.132	0.103
Co	0.00 0	0.00 2	0.0003	0.000	0.00 6	0.01 0	0.0005	0.001	0.00 0	0.00 1	0.0001	0.000
Cr	0.00 0	0.64 1	0.169	0.229	0.00 0	0.70 2	0.097	0.183	0.00 0	0.61 2	0.216	0.219

The presence of heavy metals in the groundwater, in this research, is related to both geogenic factors and human activities. In the western part of the region, ophiolitic masses, which are rich in chromium, are met. The mixed sulfide ores (Mixed Sulfides PBG) appearances, at the base of Cretaceous limestones, in the area next to Koropi, as well as the local appearances of schists are the main feeders in heavy metals.

Moreover, the organic material is the main cause for the supply of groundwater with heavy metals. The erosion of ophiolitic masses and the oxidation of sulphide minerals have contributed both in the charge of the formations and groundwater in heavy metals (Serelis et al., 2010, Alexakis et al., 1998).

In addition, another cause can be the use of phosphate fertilizers (Ross 1994, Kabata-Pendias and Mukherjee 2007) and pesticides (Stamatis et al., 2006). Finally, the uncontrolled disposal of the factories - industries, located at this area, contribute to the deterioration of the problem (Giannouloupolos and Gkintoni 2008, Kabata-Pendias and Pendias 1992).

In the Figure 6, the spatial distribution of heavy metals concentrations is presented. The southern and western areas are richer in heavy metals than the others confirming the abovementioned thoughts.

The correlation among the heavy metals are listed in Table 2. The strongest relations are between Cu and Cd ($r=0.89$, $p<0.05$) as well as Cd and Pb ($r=0.88$, $p<0.05$), while the lowest correlation coefficients are between Mn and Pb ($r=0.01$, $p<0.05$). The highest negative correlation is between Cu and Co ($r=-0.65$, $p<0.05$).

As far as groundwater quality, the trace element concentrations exceed the maximum acceptable levels, as these are determined by the Directives concerning waters of human consumption (98/83 E.U). The 96.50% of the water samples are considered as inadequate (Figure 7). The concentration of Zn is over the maximum limit of 100ppb (EEC/80.778, 1980; WHO, 2006), while the concentration of Cr exceeds 50ppb in the 50% of the water samples. Heavy metals such as Cd, Pb, Cu and Ni present also high concentrations.

6.2 Heavy metals in the soils

The concentrations of heavy metals in the soil samples were determined as it was afore-mentioned and the range, the average values and the standard deviation are given in Table 3. The total Fe presents the highest value (16420.50ppm), while the minimum values are met in the Cd (5.92ppm) and Co (8.08ppm). The next higher residual concentrations are these of Mn (499.30). The Fe, Mn values are attributed to Iron and Manganese oxides, which are affirmed by the red-brown soils of the area in issue. The Cu, Zn values range between 10.35 and 403.15ppm and between 1.95 and 295.70ppm respectively. The average values for Pb, Ni and Cr are 25.03, 12.32 and 25.59ppm respectively. The residual metals Zn, Pb and Cu are attributed to the schist and the mixed sulfide minerals which occur in the geological bedrock of the area. The residual metals Ni and Cr are attributed to ophiolitic bodies and their vitiation products. The mixed sulfide minerals which occur in the greater area, the schist and ophiolites are the major geogenic sources of the soils' heavy metals origin. In the Figure 8, the spatial distribution of heavy metals concentrations in the soils is presented. The southern and western areas mainly, are richer in heavy metals than the others. The relations among the heavy metals for the soils are presented in Table 4. High correlation ($r=0.75$, $p<0.05$) is observed between Cd and Zn, as well as Ni and Cr ($r=0.71$, $p<0.05$), while the lowest correlation coefficients are between Mn and Pb ($r=0.003$, $p<0.05$) as well as Cu and Cd ($r=-0.006$, $p<0.05$).

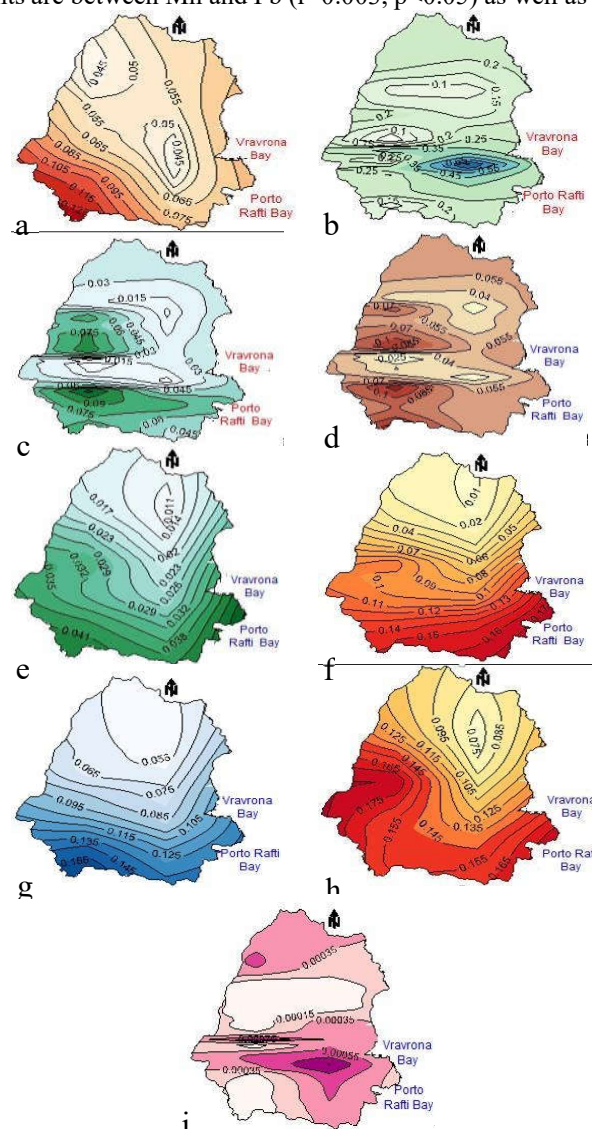


Figure 6: The spatial distribution of concentrations a) Fe, b) Zn, c) Mn, d) Cu, e) Cd, f) Pb, g) Ni, h) Cr, i) Co in the groundwater (mg/l)

Table 2: Correlations among the heavy metals for the groundwater

	<i>Fe</i>	<i>Mn</i>	<i>Cu</i>	<i>Zn</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Co</i>	<i>Cr</i>
<i>Fe</i>	1								
<i>Mn</i>	0.09486	1							
<i>Cu</i>	0.623941	0.043089	1						
<i>Zn</i>	-0.36954	0.204462	-0.42589	1					
<i>Cd</i>	0.551376	0.051488	0.893804	-0.45275	1				
<i>Pb</i>	0.442953	0.011026	0.731836	-0.41088	0.880179	1			
<i>Ni</i>	0.736417	0.054997	0.802676	-0.3919	0.813645	0.594651	1		
<i>Co</i>	-0.15916	0.498129	-0.65159	0.189758	-0.64185	-0.58976	-0.44764	1	
<i>Cr</i>	0.545103	-0.03724	0.718444	-0.33555	0.695574	0.489802	0.607249	0.42537	1

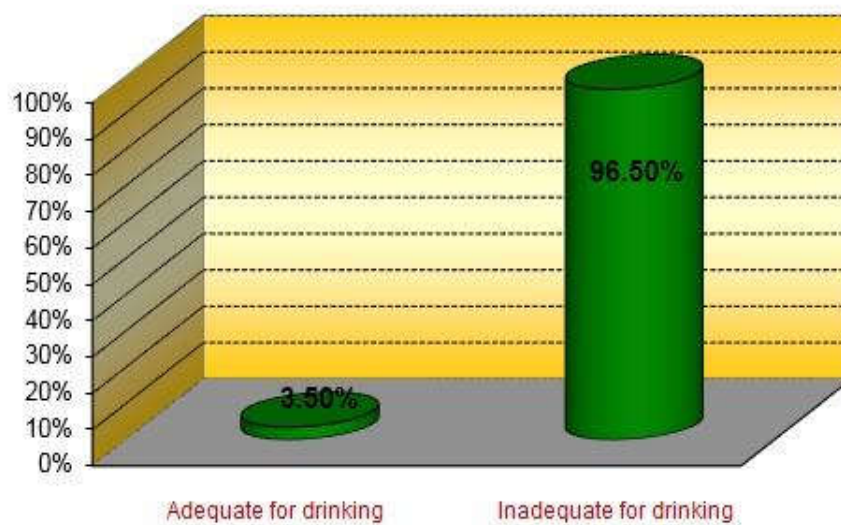


Figure 7: Groundwater quality based on heavy metals according to Directives 98/83 E.U

Table 3: Statistical analysis of the heavy metal total concentrations in the soils

Elements	Soil samples (ppm) (n:42)			
	max	min	average	stdv
Fe	16420.50	1236.25	7479.52	3545.91
Mn	499.30	78.15	255.33	99.02
Cu	403.15	10.35	26.85	60.19
Zn	295.70	1.95	37.77	54.94
Cd	5.92	1.25	1.96	0.78
Pb	81.80	6.60	25.03	15.25
Ni	79.05	0.05	12.32	16.45
Co	8.08	0.03	2.35	1.97
Cr	102.95	2.55	25.59	20.93

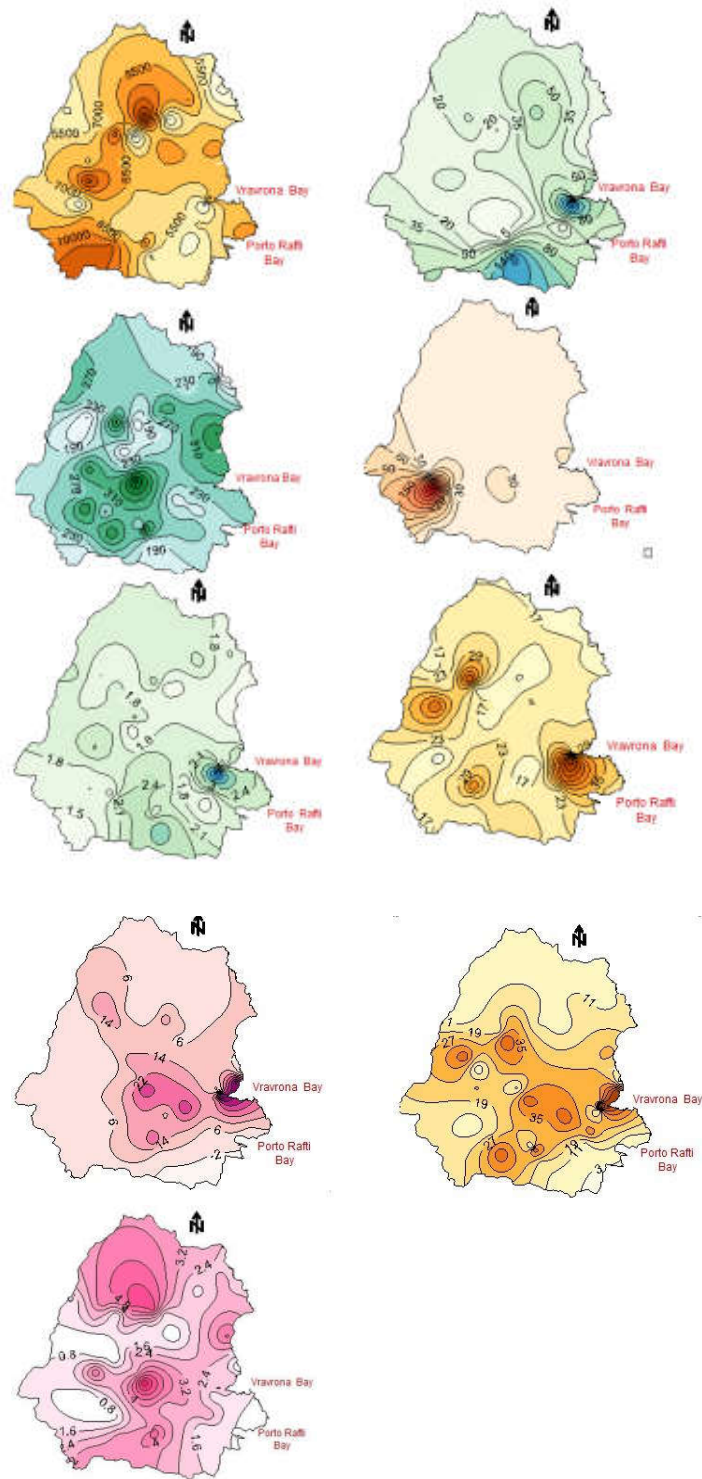


Figure 8: The spatial distribution of concentrations a) Fe, b) Zn, c) Mn, d) Cu, e) Cd, f) Pb, g) Ni, h) Cr, i) Co in the soils (ppm)

Table 4: Correlations among the heavy metals for the soils

	<i>Fe</i>	<i>Mn</i>	<i>Cu</i>	<i>Zn</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Co</i>	<i>Cr</i>
<i>Fe</i>	1								
<i>Mn</i>	0.269	1							
<i>Cu</i>	0.107	0.263	1						
<i>Zn</i>	-0.224	-0.035	-0.038	1					
<i>Cd</i>	-0.183	0.102	-0.006	0.751	1				
<i>Pb</i>	-0.101	0.003	-0.030	0.439	0.587	1			
<i>Ni</i>	0.053	0.161	-0.076	0.135	0.049	0.062	1		
<i>Co</i>	0.335	0.347	-0.179	-0.067	-0.081	-0.157	0.267	1	
<i>Cr</i>	0.340	0.158	-0.120	-0.114	-0.137	0.064	0.707	0.327	1

Finally, according to US Department of Agricultural Bureau Industry Soils and Agricultural Engineering, the soils in this research are mainly considered as sandy loam, sandy clay loam and loam (Figure 9).

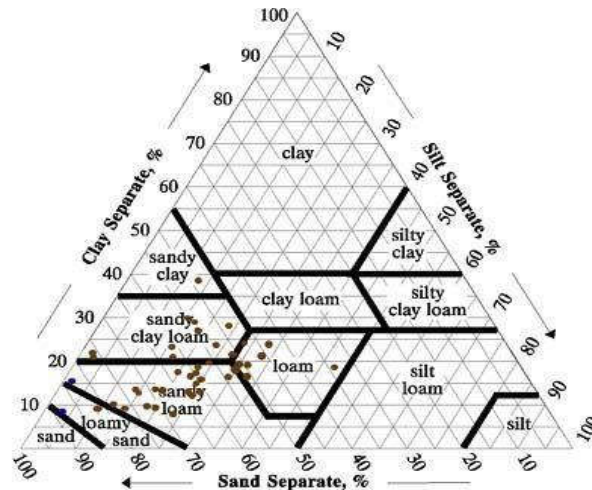


Figure 9: Soil Classification in accordance of US Department of Agricultural Bureau Industry Soils and Agricultural Engineering

7. Conclusions

Due to the fact that heavy metals is of great significance because they are not disintergrated, but remain in the upper soil layer with high absorption from the plants and the human, in this research, 86 water and 42 soil samples were taken by the Mesogeia valley (Athens) and concentrations of heavy metals were calculated and presented.

Mesogeia valley is structured from the crystalline rocks of the geological bedrock (schists, marbles, ophiolites), Neogene sediments (marly limestones, marls, clays, sandstones, conglomerates) and unconsolidated Quaternary deposits.

In the frame of this study, the analyses indicate that the groundwater is characterized by high concentrations of Zn (8.68ppm), while the lowest values are met in Co (0.001ppm). Generally, the presence of heavy metals in this area is attributed to geogenic influences by the mixed sulfide metals and ophiolitic complexes but also to anthropogenic activities such as the uses of pesticides, phosphate fertilizers and the disposal of sewages and industrial wastes. The lack of any biological processing of urban waste, are the main reasons for groundwater contamination. The statistical analysis of the laboratory test results indicates that there are very high relationships between Cu and Cd ($r=0.89$, $p<0.05$) as well as Cd and Pb ($r=0.88$, $p<0.05$), while the lowest correlation coefficients are between Mn and Pb ($r=0.01$, $p<0.05$). The most significant negative correlation is between Cu and Co ($r=-0.65$, $p<0.05$). As far as groundwater quality, the concentrations of heavy metals exceed the maximum acceptable levels, as these are determined by the Directives concerning waters of human consumption (98/83 E.U). Especially, the concentration of Zn is 8.68ppm exceeding the maximum limits of 100ppb (EEC/80.778, 1980; WHO, 2006), while the concentration of Cr exceeds 50ppb. Thus the groundwater of the study area is unsuitable for human use.

The research also demonstrates that in the soil samples, the concentrations of total Fe and Mn present the highest value (16420.50ppm and 499.30 respectively) due to consistence of Iron and Manganese oxides, which are affirmed by the red-brown soils of the area. The minimum values are met in the Cd (5.92ppm) and Co (8.08ppm). The Zn, Pb and Cu are attributed to the schist and the mixed sulfide minerals which occur in the geological bedrock of the area, while the ophiolitic bodies and their vitiation products are the causes for the presence of Ni and Cr in the area. Strong correlations exist between Cd and Zn ($r=0.75$, $p<0.05$) as well as Ni and Cr (0.71), while Mn and Pb are low correlated ($r=0.003$, $p<0.05$). The Cu and Cd present low negative relation ($r=-0.006$, $p<0.05$).

Finally, according to US Department of Agricultural Bureau Industry Soils and Agricultural Engineering, the soils in this research are mainly considered as sandy loam, sandy clay loam and loam.

To sum up, the intense agricultural activity, the increasing industrial activity, the construction of the Greek National Airport, the increasing urbanization, the overexploitation of the aquifers have leded in the degradation of the quality of groundwater and soil resources.

The results of this study constitute a basis for the necessary protection steps that need to be taken to prevent any further degradation of the areas' natural resources.

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