Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, τομ. XLVII , 2013
Πρακτικά 13[ου] Διεθνούς Συνεδρίου, Χανιά, Σεπτ. 2013

Bulletin of the Geological Society of Greece, vol. XLVII 2013
Proceedings of the 13[th] International Congress, Chania, Sept. 2013

ASSESSMENT OF GROUNDWATER POLLUTION IN RELATION TO HEAVY METALS OF THE ALLUVIAL AQUIFER OF THRIASION PLAIN (NW ATTICA)

Kyriazis D. [1], Zagana E. [2], Stamatis G. [1], Fillippidis F. [1] and Psomiadis E[1].

[1]Institute of Mineralogy-Geology, Agricultural University of Athens, Iera Odos 75, GR 11855 Athens, Greece, stamatis@aua.gr , dskiriazis@yahoo.com,, filippidis_fil@hotmail.com, mpsomiadis@aua.gr

[2]Institute of Hydrogeology, Department of Geology, University of Patras, GR 26110, Rio-Patras, Greece, e-mail: zagana@upatras.gr

Abstract

In this study the hydrogeological and hydrochemical characteristics of Thriasion Plain are presented focusing mainly on the presence of heavy metals in the alluvial aquifer. Two main aquifer systems exist in the study area: a) the karst aquifer hosted in the karstified carbonate formations, which structure the bedrock and the margins of the alluvial basin and b) the phreatic aquifer within the Quaternary deposits of the Thriasion Plain.

Coastal and submarine groundwater discharges show the direct connection of the aquifers with the sea causing intense salinization in both aquifers. The phreatic aquifer is characterized by high levels of TDS (483 – 13,067 mg/l) and correspondingly high degree of hardness (15.7 to 165.7 ^{o}dH). High concentrations of Na^+, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and PO_4^{3-} reflect the diverse anthropogenic influences on the aquifer. The strong presence of heavy metals, Cd, Cu, Fe, Mn, Ni, Pb, Sr and Zn has been determined in the most of the samples. Their origin is associated with geogenic factors, such as the occurrences of bauxites, oxides derived from the alteration of rocks, especially shischts, organic matter within the Plio-Pleistocene sediments of the region, as well as with intense pressures from anthropogenic activities. In some cases the groundwater is improper not only for human consumption but also for many other uses.

Key words: *Hydrochemistry, heavy metals, phreatic aquifer, Thriasion Plain.*

Περίληψη

Στην παρούσα εργασία παρουσιάζονται τα υδρογεωλογικά και υδροχημικά χαρακτηριστικά της περιοχής του Θριάσιου Πεδίου, εστιάζοντας κυρίως στην παρουσία των βαρέων μετάλλων στα υπόγεια νερά του προσχωματικού υδροφορέα. Στην περιοχή εντοπίζονται δυο ευδιάκριτες μεταξύ τους υδροφορίες, η καρστική υδροφορία που αναπτύσσεται εντός των καρστικοποιημένων ανθρακικών σχηματισμών, οι οποίοι δομούν τα περιθώρια και το υπόβαθρο της προσχωματικής λεκάνης και η φρεάτια υδροφορία που αναπτύσσεται εντός των Τεταρτογενών αποθέσεων. Η άμεση επικοινωνία των υδροφόρων με τη θάλασσα έχει ως αποτέλεσμα την έντονη υφαλμύρωση τους. Η υδροχημική έρευνα έδειξε, υψηλά επίπεδα αλατότητας και σκληρότητας, υψηλές συγκεντρώσεις στα κύρια στοιχεία Na^+, Cl^-,

SO_4^{2-}, NO_3^-, NH_4^+ και PO_4^{3-} και στα βαρέα μέταλλα Cd, Cu, Fe, Mn, Ni, Pb, Sr και Zn, τα οποία αντικατοπτρίζουν τις ποικίλες γεωγενείς και ανθρωπογενείς επιδράσεις που υφίσταται ο εκμεταλλευόμενος υδροφορέας. Η άναρχη ανθρωπογενής δραστηριότητα που συντελείται στο Θριάσιο Πεδίο, σε συνδυασμό με την θαλάσσια διείσδυση, έχουν συμβάλλει στη συνεχή υποβάθμιση της ποιότητας των υπόγειων νερών με αποτέλεσμα το περιορισμό της δυνατότητας εκμετάλλευσης τους, όχι μόνον για την ανθρώπινη κατανάλωση αλλά και για πολλές άλλες χρήσεις.
Λέξεις Κλειδιά: *Υδροχημεία, βαρέα μέταλλα, φρεάτια υδροφορία, Θριάσιο πεδίο.*

1. Introduction

Thriasion plain is an area characterized by several and intense human activities. Along the coastal zone and in the central part of the area intense building activity takes place, while in the north part the cultivation of vegetables prevails. The uncontrolled installation of various crafts and large industrial units, the operation of the military airport, the dense network of roads with the traffic of heavy vehicles are some features of the area. In recent decades the increased industrial activity has imposed significant environmental pressures in Thriasion Plain. These continual changes in land use, from cultivated land and pastures to industrial use, were not accompanied by the necessary infrastructures and implement measures (sewage treatment, biological waste water treatment, etc.) causing air, soil and groundwater pollution.

Soil studies, which have been conducted in the area of Thriasion plain, have recorded high loads of heavy metals in soil horizons resulting in surface- and groundwater pollution by mobilizing them (Massas *et al.,* 2013). Previous hydrogeological investigations in the study area have shown intense salinization of groundwater, in both coastal and inland region, where the front of seawater intrusion is detected in about 8.5 km away from the coast. At the same distance from the coast is also detected the high pollutant load that characterizes the alluvial aquifer due to various anthropogenic pressures (Kuna *et al.,* 1991; Karavitis *et al.,* 2001, Paraschoudis 2002; Lioni *et al.,* 2008, Iliopoulos *et al.,* 2011, Christides *et al*., 2011). In this paper the results of a hydrogeochemical study conducted in Thriasion plain are presented. The purposes of the study were the investigation of the general groundwater quality, the evolution of the degradation of the groundwater quality from human activities (urban waste, agriculture, livestock, industry, etc.), emphasizing in the presence of heavy metals, as well as the determination of the suitability of water for various uses.

2. Study Area

The study area is located in the northwestern part of Attica (Figure 1). The mountains in the eastern, northern and western part form the relief of the area. The Aigaleo Mt (453m) at the southeastern delimits Thriasion plain from Attica basin. Parnitha Mt. (700m) and Patera Mt (450m) defines Thriasion Plain to the east and north and to the west respectively, while in the south the study area is surrounding by Saronic Gulf. Low altitudes, from 0 to 100 m, dominate in the lowland area of Thriasion plain, which is a paleo-karstic depression older than Quaternary of age. It presents a semicircular shape. During Quaternary it has been filled with fluvial and lacustrine deposits with thickness up to 200m. Low limestone hills outcrop locally in this region. These could be defined as “residual hills” characteristic for the advanced stage of the kartsification of the area.

Geology: The study area belongs geotectonically to Pelagonian Zone and is built up by alpine and post – alpine formations. Alpine formations consist of Triassic-Jurassic dolomitic limestones and limestones of Cretaceous age. The dolomitic limestones consist of thick bedded up to imbedded often dolomitized limestones fragmented, fractured and intensely karstified with a variable thickness of approx 300-700 m. They occur in the eastern, northern and northwestern part of the region covering most of its surface. The low part of Cretaceous limestones are thin bedded, locally marly, with a thickness of approx. 100m and of Kenomanian age, while the middle part are thick bedded (Touronian age), with intense smell of bitumen and a thickness of approx 80m. Finally the upper part consists of thin bedded limestones that underlie the flysch formation with a thickness of 40m (Senonian age). They occur mainly at the northwestern of Thriasion Plain and at places in the northwestern part of the plain.

The post alpine deposits consist of semi-consolidated Neogene formations and unconsolidated Quaternary deposits. The Neogene formations in the eastern part of Thriasion plain consist at their low parts of alternating layers of lacustrine mainly marls, clays and sandstones, while the upper parts are continental deposits mainly conglomerates and red mud. The Quaternary deposits consist of old Pleistocene and Holocene alluvial deposits.

The Pleistocene sediments covering the northern part of Thriasion Field with a significant thickness of 100m are mostly torrential deposits, pebbles, gravel and sands of various origins. They usually occur with strong diagenesis as breccia-conglomerates including irregular intercalations of sand clays with calcareous debris. The Holocene sediments developed mainly in the coastal zone of Thriasion plain (Dounas *et al*., 1971; Katsikatsos *et al*., 1986) comprise clastic material, recent alluvial deposits and recent talus conus with a thickness of about 2 to 10m.

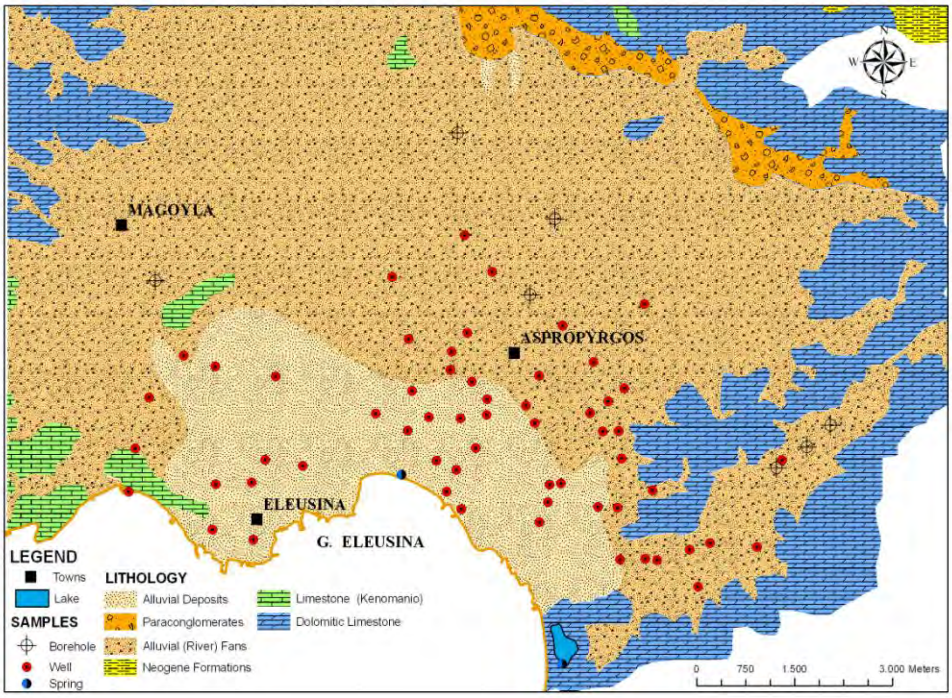

Figure 1 - Geological map of the study area (Digitized by IGME geological map 1:50 000, Sheet Athens to Eleusis (Katsikatsos et al. 1978)) and sampling points.

Hydrogeology: The climate of the study area is characterized as Mediterranean, semi-arid, with mild winters and hot summers. The average annual rainfall ranges between 300 and 400mm, with an average value of 390mm. The average annual temperature varies from 17^o C and 19^o C. The carbonate formations, which occur in great extent in Thriasion plain, are intensely fragmented and karstified, due to the tectonic activity of the area. Within these formations a highly productive karst aquifer is developed. The average hydraulic conductivity is estimated to be 10^{-3} m/s (Paraschoudis 2002). Paleozoic schist formations are the impermeable bedrock of the karst aquifer.

Coastal and submarine springs at lower topographic places drain the karst aquifer. A significant amount of karst water discharges in Koumoundourou Lake located at the SE part, while another amount of the karst water flows towards the Eleusinian Gulf in the SW part of the plain. Finally karst water flows and feeds lateral the alluvial aquifer. Within the Quaternary deposits a significant aquifer is developed. It undergoes intense exploitation through wells and boreholes for drinking and irrigation purposes. The discharge rate of the wells is over $20m^3/sec$, while the discharge rate of the boreholes ranges from 100 – 150 m^3/h (*Kounis et al., 1991, Parasxoudis 2001)*. The hydraulic conductivity ranges between 10^{-2} m/s and 10^{-4} m/s. The replenishment of the aquifer is realized by the infiltration of the rainwater, the infiltration of surface water, through the coarse sediment of its streambed as well as by the lateral feed of the karst system. In the coastal zone the aquifers adjoin the sea. Moreover the overexploitation of aquifer caused the decrease of the water level. Thus seawater intrusion phenomena occur resulting in the salinization of the groundwater.

3. Hydrochemistry

***Material and Methods**:* During the wet period (December 2006) 51 samples from wells and 14 samples from boreholes were collected. The physicochemical parameters, temperature (T), electrical conductivity (EC) and pH, were measured from untreated samples in-situ using the portable devices WTW/LF-330 for electrical conductivity and WTW/330i for pH.

The samples were collected in two different types of polyethylene bottles (100 ml and 1000ml volume). The first bottle type of 100 ml volume was filtered on site through 0.45μm pore size Millipore filters. It was then acidified to a pH about 2 with 65% ultra-pure HNO_3 for heavy metals determination, Cd, Cu, Fe, Mn, Ni, Pb, Sr and Zn (Table 1). The second non-acidified aliquot (1 L volume) was retained to determine major cation analyses and non-metal ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} NO_3^-, NH_4^+ and PO_4^{3-}) (Table 1). Total Hardness, Calcium Hardness, Temporal Hardness as well as Cl^- were determined with titration kits. The parameters SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and SiO_2 were determined by spectral photometry (HACH DR/3000) using the suitable HACH kits. The parameters Ca^{2+}, Mg^{2+}, Sr, Fe, Mn, Cu, Cr, Ni, Pb, Cd and Zn were determined by atomic absorption spectroscopy (GBC/908AA), while Na^+ και K^+ using Flamephotometer (INTECH/420). All the analyses were conducted at the laboratory of Mineralogy-Geology, Agriculture University of Athens.

Groundwater quality: The groundwater of the study area is characterized by a wide range of physicochemical parameters values. The water of the wells generally presents, except in certain cases, high concentrations of salts (TDS: 535-13,567 mg / l), high hardness (TH: 14.6-165.7 ^{0}dH), high salinization due to seawater intrusion (Na^+: 4.0-4045.9 mg/l, Cl^-: 17.7-7269.7 mg/l and SO_4^{2-}: 8.2-782 mg/l) and high concentrations of compounds of anthropogenic origin (NO_3^-:5.7- 293 mg/l, NH_4^+: 0.01-16.06 mg/l and PO_4^{3-}: 0.10-16 mg/l). The presence of all these elements and compounds reflects the geogenic and anthropogenic influences in the aquifer. The highest concentration is observed in the samples of the wells in the phreatic aquifer, which are located within the residential area, close to industrial units. In the most samples the concentrations exceed the upper allowable limits given by the Directive concerning the water quality for human use (EEC98/83 1998).

As is shown in Piper diagram (Figure 2) groundwater samples are classified mainly in three groups: i) In the first group belong the geo-alkaline waters with Ca-Mg-HCO_3 and Ca-Mg-Na-HCO_3-Cl-SO_4 hydrochemical types. ii) In the second group belong the brackish waters with Na-Cl-HCO_3 and Na-Cl hydrochemical types. They are mixed waters from sea water and karst water. iii) In the third group belong the water samples from wells and boreholes in the lowland of Thriasion plain, which present a geo-alkaline with high percentage of alkaline character. The hydrochemical types Ca-Mg-Na-HCO_3, Ca-Mg-Na-Cl-HCO_3 and Mg-Na-Cl-SO_4-HCO_3 prevail in this group, which exhibit seawater impacts. A small number of samples from boreholes present the hydrochemical types Ca-HCO_3 and Ca-Mg-HCO_3 revealing the recharge of the area with fresh karst water.

As it shown in Durov diagram (Figure 3) cation – exchange processes (Ca-HCO_3, Mg-HCO_3) and reverse cation - exchange processes (Na-Cl, Mg-Cl and Ca-Cl) take place in the area, while a significant number of the samples undergo mixing from sea water and fresh groundwater.

Table 1 - Results of hydrochemical analyses.

Samples	51 Samples of wells			14 Samples of boreholes		
	min	max	mean	min	Max	mean
Ta ^{0}C	11.5	20.2	16.2	13.5	19.4	17.4
EC μS/cm	674	23,100	3671	629	3780	1676
pH	7.0	8.27	7.4	7.12	7.9	7.43
Tot. Hardness ^{0}dH	14.6	165.7	53.4	15.7	85.9	38.2
Temp. Hardness ^{0}dH	11.7	41.3	24	15.4	31.1	20.6
Perm. Hardness ^{0}dH	0.0	154	29.7	0.0	68.0	18.8
Ca^{2+} mg/l	49.6	584.8	189.8	61.6	272.0	135.4
Mg^{2+} mg/l	10.6	421	115.7	26	286.3	85.4
Na^{+} mg/l	11.8	4045.9	412.5	29.6	540	129.4
K^{+} mg/l	0.3	166	17.5	1.9	18	6.9
HCO_3^{-} mg/l	256.2	899.7	523.9	335.5	677.1	440.3
Cl^{-} mg/l	39.0	7269.5	821.4	17.7	939.7	346.8
SO_4^{2-} mg/l	22.8	782	232.8	8.2	268.7	94.2
NO_3^{-} mg/l	5.7	293	91.3	12.8	239.3	93
NH_4^{+} mg/l	0.01	16.06	2.85	0.55	4.30	1.74
PO_4^{-} mg/l	0.1	1.14	0.35	0.12	1.05	0.3
SiO_2 mg/l	0.5	26.4	15.8	9.6	20.8	16.6
Cd ppm	0.027	0.064	0.046	0.028	0.072	0.049
Cu ppm	0.058	1.05	0.106	0.061	0.188	0.092
Fe ppm	0.001	0.636	0.154	0.001	0.279	0.138
Mn ppm	0.007	0.610	0.085	0.046	0.112	0.077
Ni ppm	0.001	0.282	0.111	0.001	0.300	0.125
Pb ppm	0.002	0.417	0.221	0.006	0.454	0.241
Sr ppm	0.613	4.016	2.281	0.689	2.370	1.925
Zn ppm	0.001	0.400	0.062	0.005	0.535	0.108
TDS mg/l	535	13567	2423	770	2714	1353

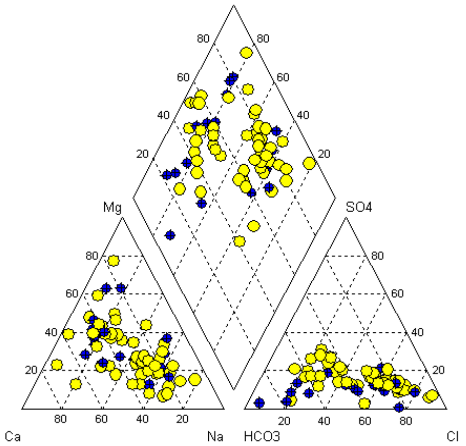

Figure 2 - Classification of groundwaters in the Piper diagram (○: wells. ✱: boreholes).

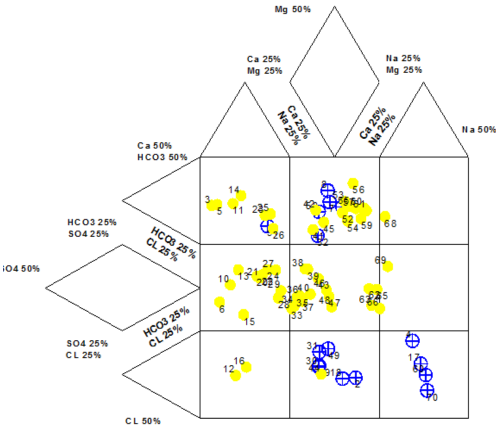

Figure 3 - Classification of groundwaters based on Durov diagram (○: wells. ✱: boreholes).

Heavy metals: The groundwaters of the study area present high concentrations of the heavy metals Cd, Cu, Fe, Mn, Ni, Pb, Sr and Zn. The concentration of Fe_{tot} ranges from 0.001 to 0.636ppm, while in 51% of the samples the concentration exceeds 0.2 ppm, the upper limit given by the Directive concerning the water quality for human use (EEC98/83 1998). Mn concentration varies between 0.007 and 0.610ppm, while in 74% of the samples the concentration exceeds 0.05ppm, the upper limit given by the Directive concerning the water quality for human consumption. Ni concentration varies between 0.001 and 0.29ppm, while in 59% of the samples the concentration exceeds 0.02ppm, the upper limit given by the European Directive. All the samples present Cd concentrations between 0.027-0.072ppm exceeding the upper limit of 0.005ppm. The concentration of Pb ranges from 0.002-0.454ppm, presenting in 95% of the samples values above the upper limit of 0.010ppm. The concentrations of Cu and Zn range from 0.058-1.050ppm and 0.001-0.535ppm respectively and do not exceed the upper limits of 2.0 ppm and 5.0ppm respectively (WHO 1993, EU-98/83 1998). The concentration of Sr is high and ranges from 0.613-4.016ppm. It could be attributed to the disillusion of the minerals selestine ($SrSO_4$) and strontianite ($SrCO_3$) included in the sediments and evaporates. The highest concentration of the heavy metals is associated with geogenic factors, such as the occurrences of bauxites, oxides derived from the alteration of rocks and the organic matter within the unconsolidated sediments of the region, which is characterized for its ability to bind the heavy metals. Intense pressures from anthropogenic activities, such as air pollutants from traffic and gas industrial plants, the function of Eleusis military airport, industrial and municipal waste, waste dumps and agricultural crops could also contribute to the significant presence of heavy metals in the groundwaters of the area.

The spatial distribution of heavy metals is shown in Figure 4. The presence of Fe prevails in the west part of the area, while Mn, Ni and Zn occur in the groundwaters in the east part of the area. This could be attributed to the presence of the landfill of Ano - Liosia located at the eastern margins of Thriasion plain. Cd, Cu, Pb and Sr present higher concentrations in the central and north part of the area. Their distribution is associated with both occurrences of bauxite in the north and west of Thriasion Field and the existence of distributed manufacturing units and the lack of waste water treatment facilities.

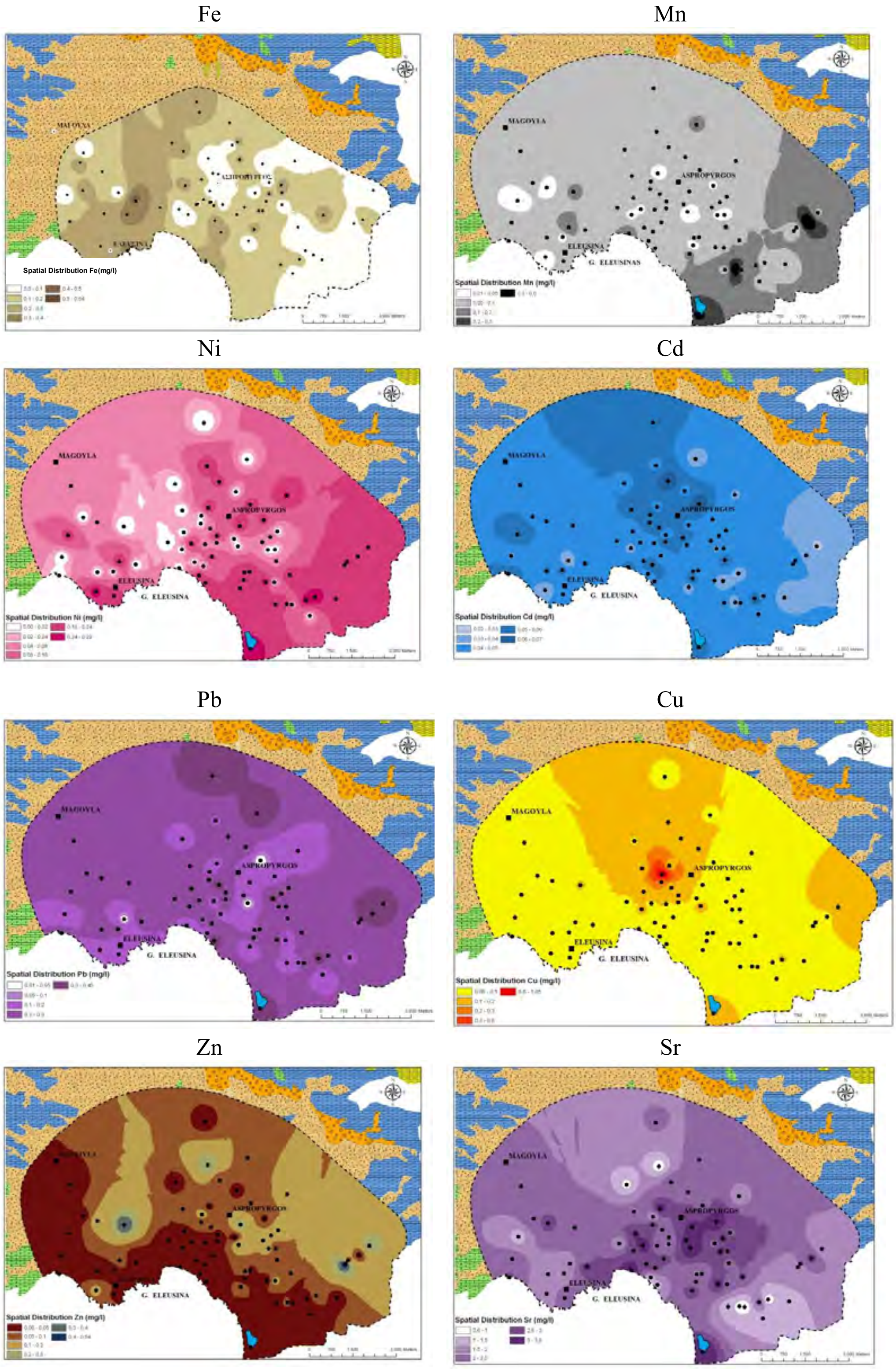

Figure 4 - Spatial distribution of heavy metals in groundwater at the Thriasio plain area. (Fe, Mn, Cd, Pb, Ni, Cu, Zn and Sr).

To detect relationships exist between the various elements and parameters, factor analysis is used with the statistical program SPSS. The method collects data into groups which are called factors. The load factors show how important is the participation of the respective variable factor (Davis 1986).

Table 2 - Results of factor analyses.

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Ca	.230	**.768**	-.123	-.129
Mg	**.724**	.299	-.276	-.110
Na	**.951**	.043	.010	.100
K	**.894**	-.222	.051	.120
Cl	**.953**	.140	-.072	-.003
SO_4	**.866**	.307	-.067	.068
NO_3	-.234	**.794**	-.271	.075
Pb	-.059	.039	.057	**.760**
Zn	-.139	-.002	.100	**-.691**
Ni	-.092	-.162	**.634**	-.049
Mn	.071	-.098	**.689**	.231
Sr	.355	**.731**	.060	.139
Cd	.151	-.035	**-.697**	.340
% of Variance	**32.2**	**15.7**	**12.0**	**10.1**

In Table 2 is shown that the first group, which accounts for 32.2% of the variance in the data matrix connecting the ions Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-}. It represents the brackish waters resulting from the seawater intrusion in the aquifers of the study area. The second group accounts for 15.7% of the total variance, connecting elements Ca^{2+}, Sr and NO_3^{-}. The coexistence of these shows the use of fertilizers. The relationship between nitrate and calcium could be explained as ion exchange relationship between the ion of ammonium resulting from the hydrolysis of ammonia fertilizer and calcium that is a component of carbonate minerals in the area. The coexistence of Ca^{2+} and Sr^{2+} is directly related to the chemical affinity of the two elements. The third and fourth groups accounts for 12% and 10.1% of the total variance, respectively. They connect the elements Ni, Mn, Cd, Pb and Zn that could be associated with the dissolution of bauxites and various oxides and obviously with different anthropogenic impacts.

4. Conclusions

Two systems developed in the study area, the karst system that structures the east, north and west margins of the basin and the greatly expanded in size clastic system of Quaternary age. In the coastal zone where the contact of carbonate rocks with the sea is immediate, intense salinization of karst waters takes place. The high concentrations of the main elements and heavy metals reveal the degradation of the alluvial aquifer, which could be attributed to both natural factors and anthropogenic impacts. These concentrations values exceed the upper limits for human consumption and the majority of groundwater samples are characterized as inappropriate. This is attributed to geogenic factors and other anthropogenic impacts, as Thriasion plain undergoes intense environmental pressure from various human activities.

4. References

Christides A., Mavrakis A. and Mitilineou A. 2011. A case of intense seawater intrusion to aquifer of the Thriasio Plain. Greece, *Proceedings of the 12th International Conference on Environmental Science and Technology (12th ICEST)*. Vol B:152-159.

Davis J.C. 1986. Statistics and data analysis in geology, Wiley, New York.

Dounas A. 1971. The geology between Megara and Erithres area. *PhD Thesis,* University of Athens.

EU Council directive 98/83 1998. Council Directive 98/83/EC of the European Parliament on the quality of water intended for human consumption, The European Parliament and the Council of the European Union, Off J L 330.

Iliopoulos V., Stamatis G. and Stournaras G. 2011. Marine and human activity effects on the groundwater quality of Thriasio Plain, Attica, Greece, *Advances in the Research of Aquatic Environment. Environmental Earth Sciences*. 3. 409-416. DOI: 10.1007/978-3-642-24076-8-48.

Karavitis C., Bosdogianni A. and Vlachos E. 2001. Environmental Management approaches and water resources in the stressed region of Thriassion, Greece, Global Nest: *the Int. J*. Vol 3. No 2. p. 131-144.

Katsikatsos G. et al 1986. Geological Map Athens-Eleusis 1:50.000. I.G.M.E.

Kounis G. and Siemos N. 1991. Spot hydrogeological investigation of the aquifers of Thriassio Plain for supply of Hellenic Petroleum Company, IGME.

Lioni A. Stournaras G. and Stamatis G. 2008. Degradation of Groundwater quality of Thriassio Plain through Natural Factors and human activity. *Proceedings* of the 8th Hydrogeological Congress of Greece. vol.2 p.577.

Massas I., Kalivas D., Ehaliotis C. and Gasparatos D. 2013. Total and available heavy metal concentrations in soils of the Thriassio Plain (Greece) and assessment of soil pollution indexes, *Environ Monit Assess*.

Paraschoudis B. 2002. Hydrogeological study of West Attica, *Unpublished report,* Ministry of Agriculture

WHO 1993. Guidelines for drinking water quality. vol.1. 2nd ed. World Health Organization. Geneva.