

Soil environmental study of Eastern Kopaida plain and risk assessment of potential hazards

E. Tziritis ⁽¹⁾, A. Vassilopoulos ⁽²⁾, N. Evelpidou ⁽¹⁾

⁽¹⁾ *University of Athens, Department of Geology & Geoenvironment*

⁽²⁾ *GeoCultural Park of Eastern Aegean*



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Study area and description

Lake Copais, Kopais, or Kopaida (ancient Greek Κωπαΐς, modern Κωπαΐδα) used to be in the centre of Boeotia, Greece, west of Thebes until the late 19th century. The area is still known as Kopaida (Fig.1). Homer and other ancient authors refer to Kopais as the "Kifisian Lake", after the name of Kifisos River. Strabo, however, argues that the poetic expression refers to the smaller Lake Yliki (Hylice), between Thebes and Anthedon. There was a legend that the lake came into being when the hero Heracles flooded the area by digging out a river, the Kifisos, which poured into the basin. Polyaeus explains that he did this because he was fighting the Minyans of Orchomenus: they were dangerous horseback fighters, and Heracles dug the lake in order to unhorse them. Another story has the lake overflow in the mythical time of Ogyges, resulting in the Ogygian deluge.



Fig. 1: Panoramic view of Kopaida plain

Towns of Aliartos (ancient Haliartus), Orchomenus, and Chaeronea were on Kopaida's shores. Rivers were running into the lake included the Kifisos, the Termessus, and the Triton. The lake is still surrounded by fertile land, but the lake increasingly encroached on the surrounding land because of inadequate drainage. In response to this, in 1867–1887 Scots and French engineers reclaimed the land for the British company Lake Kopais Ltd., by building channels to drain water from the lake to the Kifisos and from there to Lake Yliki (Fig. 2). In total about 200 km² were reclaimed. This land was returned to the Greek government in 1952. Nowadays, Kifisos is connected with Yliki with a new tunnel (Fig. 3) that was constructed in 1977.



Fig. 2: The old tunnel that connected Viotikos Kifisos River with Lake Yliki



Fig. 3: The new tunnel which connects nowadays Viotikos Kifisos River with Lake Yliki

Geographic location

The study area is located in Eastern Greece and more specifically in Viotia District, 110 km western of Athens. Kopaida plain originated from the drought of ex-Kopaida Lake, with total area coverage of about 215 km². The creation of ex-Kopaida Lake was a combinational outcome of tectonics and natural erosional processes. These processes are expressed through the extensive karstification of the prevailing geological formations (limestones), contributing in that way to the connection of the karstic Kopaida plain with the adjacent basins of Thiva and Yliki and even with Evoikos Gulf.

Kopaida plain is developed to an E-W direction (Fig. 4), with mean altitude of 95m above sea level. Its western boundaries are consisted of the extremities of mountain Elikonas, as well as from the mountainous regions of Akontio, Thourio and Ifantio. To the North, Kopaida is orientated from the extremities of Chlomon Mountain, to the East from the western side of mountains Ptoon, Finikio and Sfigkio, and lastly to the South from the NE part of mountain Elikonas.

Geological setting

The Alpine substrate of the area belongs to "Eastern Greek" and "Subpelagonian" Greek geotectonical units (Fig. 5). It consists in succession from bottom to top, Triassic dolostones and dolomitic limestones, a Jurassic tectono-volcanic complex (schists, sandstones and ultrabasic blocks), a Cretaceous sequence of pelagic limestones which hosts locally Fe-Ni rich ores and finally the typical Eocene flysch (Pagounis et al., 1994). The Post-Alpine sediments have great thickness and embrace in succession clays, breccias, sandstones, lacustrine marls of Plio-Pleistocene age, and a few lignitic intercalations among them. The upper sequence is consisted of Quaternary terrestrial and torrential phases with alluvial depositions (Allen, 1984; Pagounis et al., 1994). The thickness of post-alpine sediments is reasonable and therefore the conditions for soil formation are favorable.

The tectonic structure of the area is dominated by two individual phases of deformation, which contributed to the paleogeographic evolution. The first phase took place during Alpine formation and includes mainly tangential movements (overthrusts of external to internal Greek geotectonical units) and secondary as a sequel, deformations of the structured geologic environment, expressed through isoclinic folds and normal faults. The second phase reflects the neotectonic activity of the area, which includes tectonic episodes of fractural deformation, started at Miocene and continued till nowadays. Tectonism was significant through tensile tensions that formed faulting structures with prevailing directions of NE-SW and NW-SE (Pagounis et al., 1986, 1994; Mettos et al., 1997).

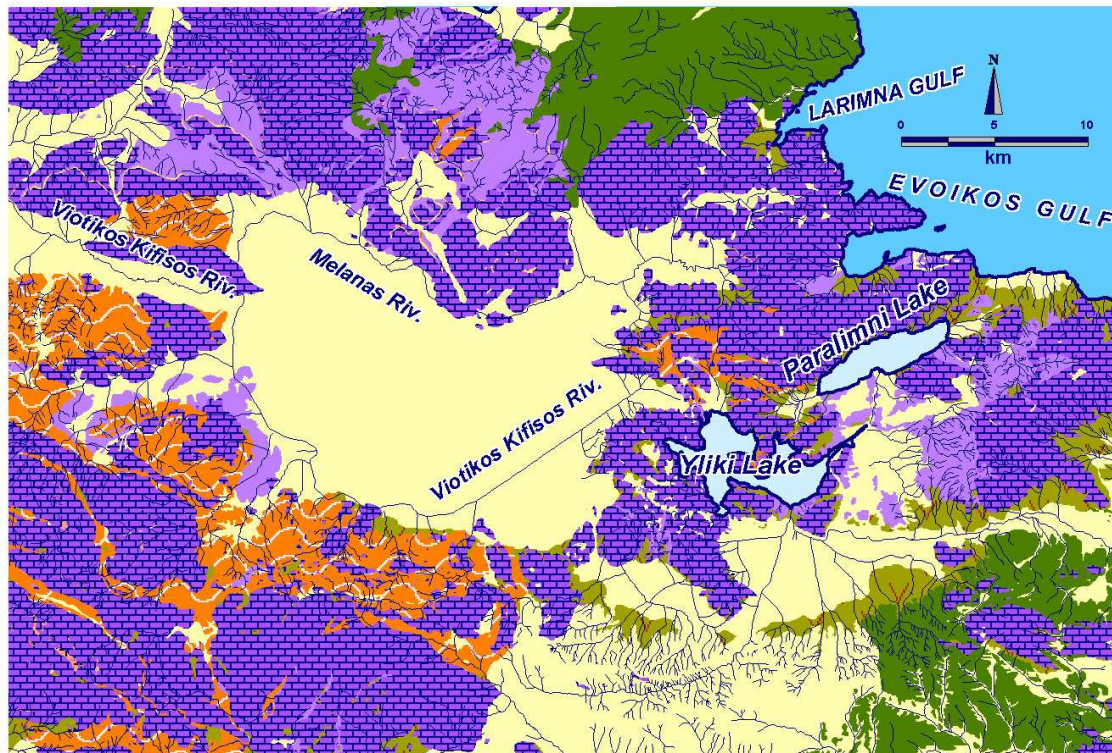


Fig. 5: Lithological map of the area

Finally, in the wider area of Kopaida have been reported and located from several researchers the existence of Fe-Ni-rich ores (Paraskevaidis, 1972; Koumantakis, 1975; Albantakis, 1984; Albantakis and Koundouros, 1984). The most well-known ore is the one of "Aghios Ioannis" which is located at the NE part of Kopaida. According to Albantakis and Koundouros (1984) the inclination of the nickeliferous layers is about 40° to South. The surficial existence of the aforementioned layer is located outside of the studied area (N and NE), but due to tectonic conditions it is underlying the Quaternary deposits of Kopaida plain, in depths that vary.

Geomorphological setting

Kopaida plain is an important geomorphological feature, since it consists a huge polje who has been influenced in a profound way by tectonism. In addition, an important geomorphological feature but in smaller scale, is the existence of numerous sinkholes (Fig. 6, 7, 8). Their majority has a surficial development, contributing in that way to the formation of area's specific conditions.



Fig. 6: Karstic caves developed along the Eastern part of Kopaida



Fig. 7: Karstic caves developed along the SE part of Kopaida

Most of them are located mainly in the Eastern part of Kopaida, with almost unstoppable development in a N-S direction. According to Papadopoulou (1990),

their majority is characterized as sub-horizontal karstic caves with high slopes. In general, they are created from the progressive development of tectonic discontinuities, mostly in places where the general direction of limestones is parallel with the direction of the shoreline or sometimes parallel to axes of isoclinal folds (Papadopoulou and Gournellos, 1993).



Fig. 8: The great sinkhole of Ag. Ioannis in the NE part of Kopaida

Slopes in the study area (Fig. 9) are mostly low, ranging between 0 and 0.3%. On the contrary, slopes in places where the substrate geological formations prevail are higher, reaching locally 97.2%.

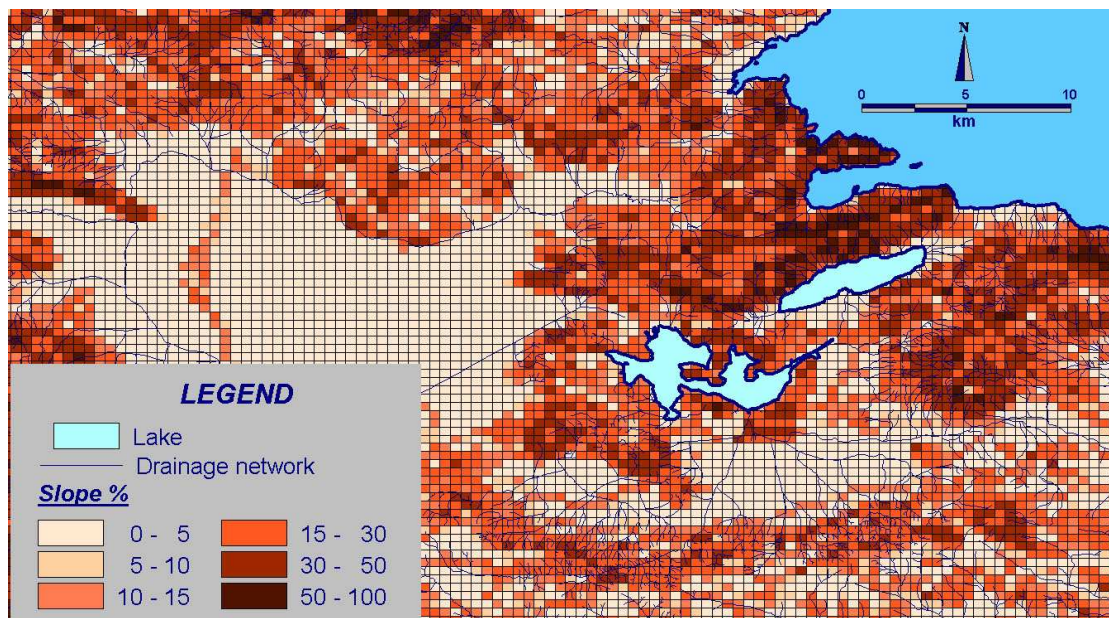


Fig. 9: Map of morphological slopes on the study area

Hydrological and Hydrogeological setting

Kopaida plain is characterized by the existence of both natural and artificial drainage pattern (Fig. 14). The major river of the area is Viotikos Kifisos (Fig.

10), whose hydrologic basin reaches 1950km² in total (Koutsogiannis, 2003). Kopaida plain is the latter of his basins in a row, with a total length of about 100km in E-W direction and an elevation difference of 900m between its starting and ending points (Tziritis, 2008). Viotikos Kifisos fountains from mountain Gkiona and outfalls through an aberrance of its flow via Karditsa tunnel (NE part of Kopaida plain) to Lake Yliki (Fig. 13). He is the final receptor of the water amounts carried by the natural and artificial drainage pattern (Fig. 11). In more details his supply is made by secondary rivers (Erkyna River), ephemeral creeks and major and minor irrigation channels. Moreover, he is connected through an artificial channel with Melanas River, which is the second major river of the area. Melanas River fountains from the homonymous springs (Fig. 12) which lie at the NW part of the area, and its route follows the northern borders of the plain. Its flow disappears into the great karstic cave of Aghios Ioannis (Fig. 8) at the NE part of Kopaida and is believed to be interconnected with Evoikos Gulf (Pagounis et al., 1994).



Fig. 10: Viotikos Kifisos River



Fig. 11: Central irrigation channel

The hydrogeological setting is mainly characterized by a quite well developed karstic network, which transfers great quantities of water. Spatially, the hydrogeological unit of Kopaida is the latter one of the three gradually elevated units of Viotikos Kifisos. The inflows of Kopaida karstic system are made mainly through the aforementioned units and through the hydraulic connection with mountain Elikonas, at the southern part of the area. The outflows are heading to three different directions, NE to the Gulf of Larymna, E to the Hydrological unit of Lake Yliki and SW to Vagia basin (Pagounis et al., 1994). Surficial inflows, despite their significance, don't seem to affect groundwater status, since there are no interconnections between surface and groundwater, due to the impermeable nature of the upper geological formations.



Fig. 12: Springs of River Melanas in the NW part of the area

The aquifers of the study area have been formed according to the specific geological and tectonic conditions. The stratigraphic contacts between formations of different permeability as well as the tectonic nappes and the various deformation episodes, have formed three individual aquifers. The upper one is developed inside Cretaceous limestones and is characterized by high permeability and karstic flow. The middle one is developed inside Jurassic limestones with elevated values of hydraulic conductivity, and the lower one is consisted of dolostones and dolomitic limestones and is differentiated from superincumbent aquifers due to the considerable decrease of permeability and karstic development. Finally, piezometric level is variable depending on local lithologic and tectonic conditions. According to Tziritis (2008) the level of saturated zone in some boreholes reaches ground surface, while in others is at 170 m depth. Discharges vary between 40 km³/h and 300 km³/h, depending on the type of the aquifer.



Fig. 13: Panoramic view of Lake Yliki

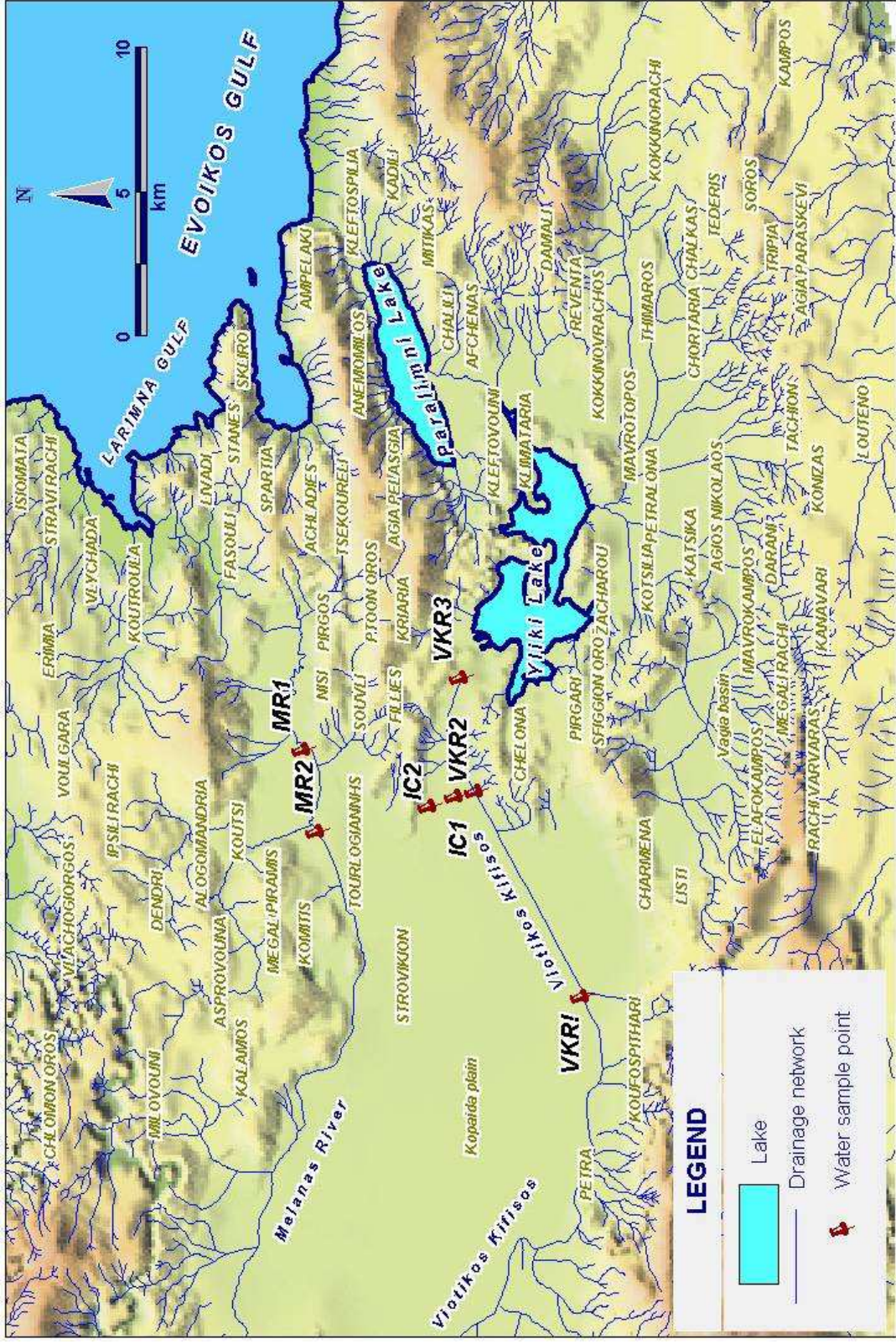


Fig. 14: Hydrological map of the study area

Pedology

Kopaida soils are characterised by red or brownish-red colour, with heavy texture and frequent presence of angulated breccias. According to Theocharopoulos et al. (1995), they are mainly consisted of non-evoluted calciferous lacustrine sediments and therefore are classified as "Typic Haplaquent" in most of the cases, while a minor part of them is classified as "Mollic Haplaquent". Presence of root systems is frequent as well, while the boundaries among the different horizons are abrupt and wavy. Soils' structure and cohesion are characterized as satisfactory about plants' growth and biological activity.

		Sample 1	Sample 2	Sample 3
Horizon		A	A	A
Depth (cm)		0-20	0-12	0-15
Clay (%)		24	26	44
Silt (%)		45	45	34
Sand (%)		31	29	22
pH		7.30	7.50	6.95
CaCO ₃ (%)		1.64	0.82	-
meq/100gr	Ca	25.5	22.0	20.5
	Mg	1.83	1.75	1.75
	K	1.22	1.10	1.50
	CEC	39	35	37
Organic matter (%)		5.76	4.69	6.84
Total N (%)		0.296	0.292	0.382
C/N		11	9	10
Phosphorus (ppm)	Total	500	600	1050
	OLSEN	5.4	6.6	7.6

Fig. 15: Pedological analysis of typical selected soil samples for Kopaida plain (after Anonymous, 2007)

As it is noted from Figure 5, soils' pH is ranging between 7.0 and 7.5, constituting nearly perfect conditions for the cultivation processes. Organic matter varies among 4.7%-6.9 %, with mean value 5.8%. The concentration of total Nitrogen at surface horizons ranges between 0.29%-0.39%, while the mean value of C/N ratio is convenient for plant growth. Total Phosphorus varies among 500ppm and 1050 ppm, while the concentration of exchangeable K⁺ ranges between 1.10meq/100gr and 1.50meq/100gr with an average value of 1.27meq/100gr. Additionally, the concentrations of exchangeable Ca²⁺ and Mg²⁺ ranging between 20.5meq/100gr-25.5meq/100gr and 1.75meq/100gr-1.83meq/100gr respectively.

Methods and materials

Sampling

A total of 20 soil samples were collected covering an area of 100 km² approximately (Fig. 16). Samples were taken with the use of an auger sampler from a depth of 30cm, while surficial debris, vegetation and A-soil horizon was before removed. After the proper preparation of samples they were digested with a mixture of HClO₄-HNO₃-HCl-HF and analyzed with an ICP-MS for the following

21 elements: Al, As, Ba, Be, Ca, Cd, Cu, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, V and Zn. Data quality was assured by introduction of internal reference samples and by analyzing the duplicates of 5 samples. The precision was calculated from these duplicates and it was found within the international standards. The results are shown in Figure 18.

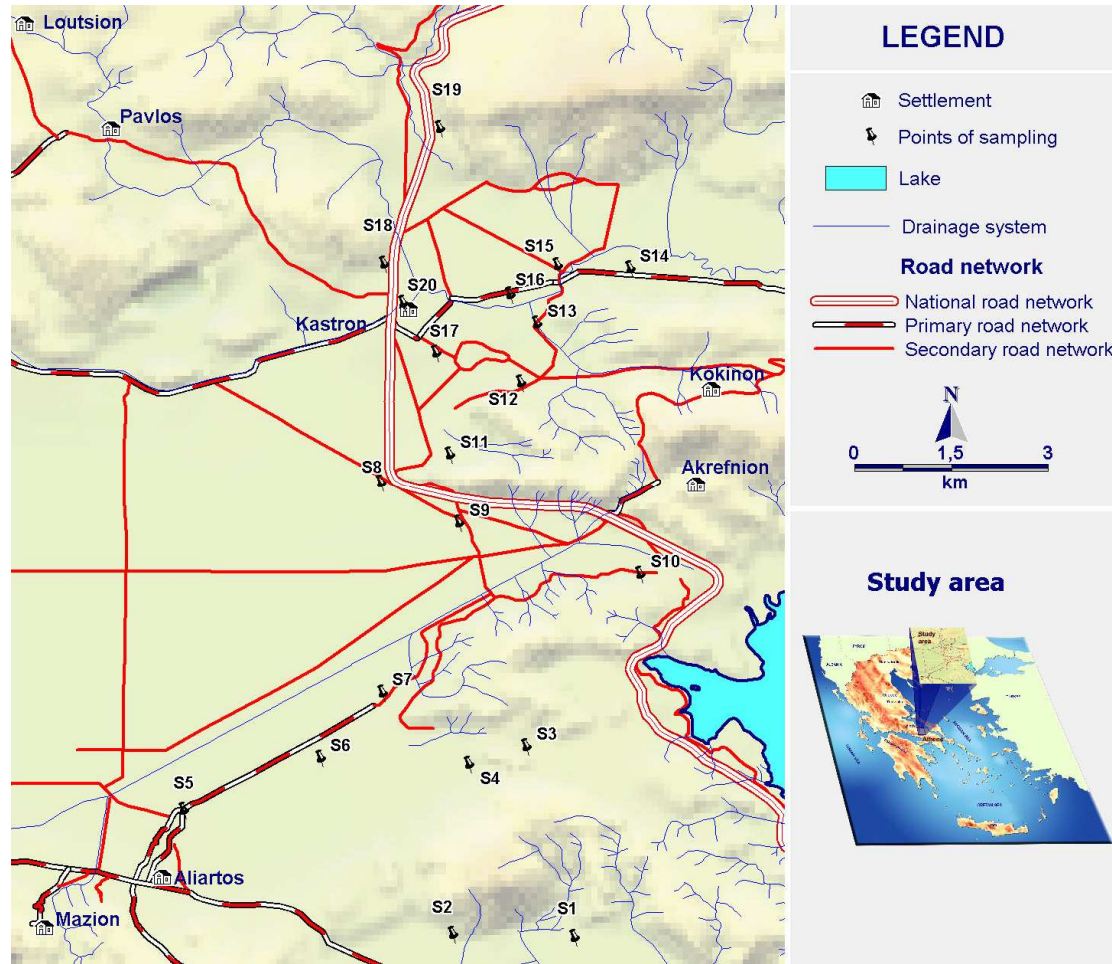


Fig. 16: Map of soil sampling sites

Apart from soils, water samples were collected as well from the major drainage pattern of the area. Sampling sites included major rivers (Viotikos Kifisos and Melanas) and major irrigation channels (Fig. 17). Surficial water samples were collected in polyethylene bottles and acidified to a final concentration of about 1% nitric acid. pH was measured in situ. Totally 15 parameters were determined with ICP-MS analytical method, including major ions (Ca, Mg, K, Na) and trace elements (As, Ba, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, Zn). Data quality was assured by introduction of internal reference samples and by analyzing the duplicates of 3 samples. The precision was calculated from these duplicates and it was found within the international standards. Finally, the results of chemical analysis were verified by electrical balance ratio (Appelo & Postma, 2005). Results are shown in Figure 19.

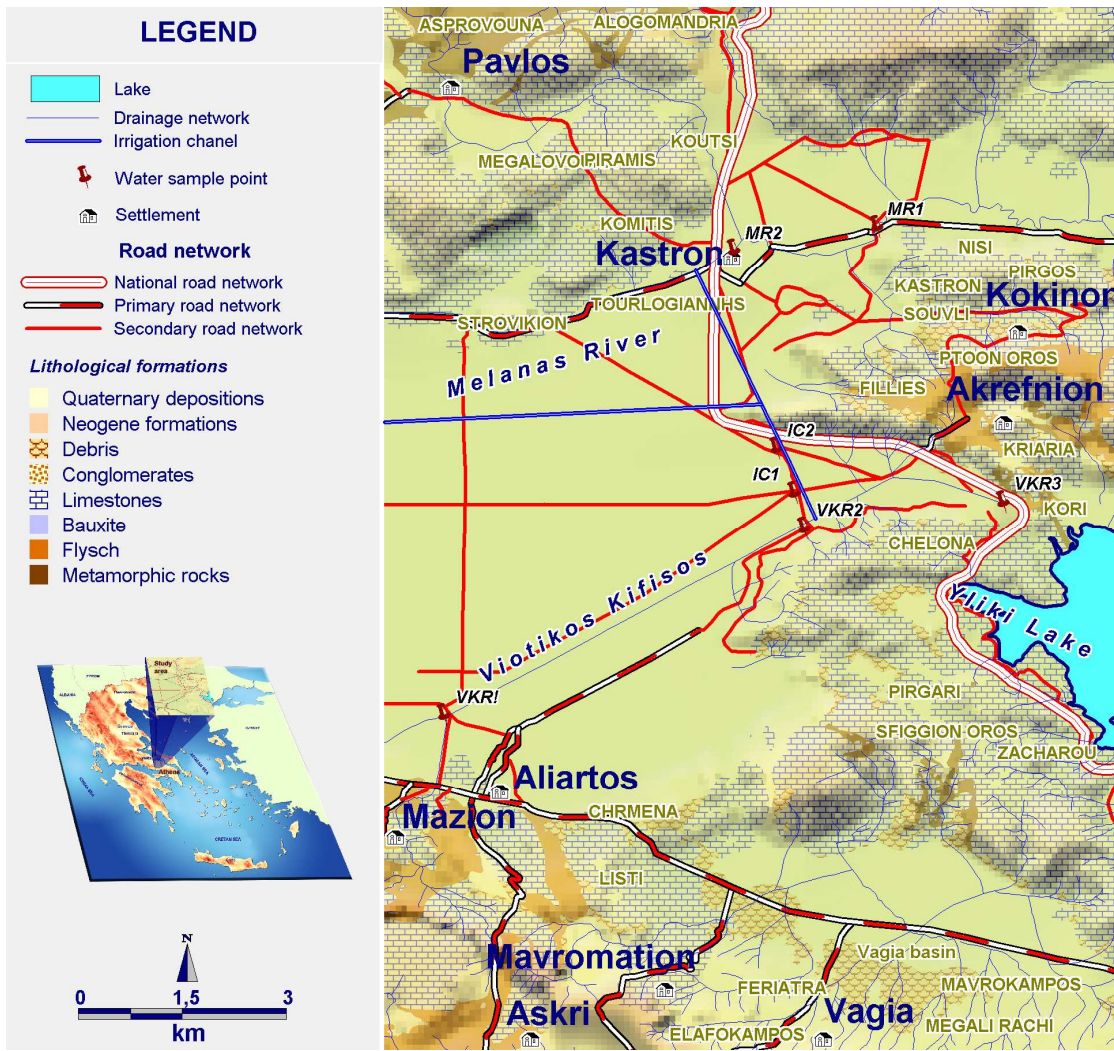


Fig. 17: Map of surface water sampling sites

Element	Al	As	Ba	Be	Ca	Cd	Cu	Co	Cr	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	Sn	V	Zn
Sample	%	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm
S1	3.7	4	238	1	14.7	0.2	32.7	31	399	3.8	0.7	2.0	814	0.3	0.2	400	11.8	0.3	0.9	80	69
S2	5.5	7	481	1	7.0	0.4	27.9	35	370	4.9	1.2	2.0	865	0.3	0.3	476	26.9	0.4	1.6	61	108
S3	2.6	5	231	2	3.2	0.4	38.8	12	486	1.7	0.6	0.5	260	0.5	0.7	124	10.4	0.7	1.7	103	38
S4	3.3	5	764	1	1.4	0.1	10.6	18	740	2.3	0.8	0.8	477	0.9	0.7	156	32.2	0.3	0.5	46	107
S5	4.0	4	302	1	7.2	0.5	25.4	25	422	3.3	1.1	1.5	705	0.8	0.8	267	14.8	0.6	0.8	59	66
S6	2.2	5	1294	1	21.2	0.2	27.9	11	135	1.8	0.5	1.1	554	0.5	0.3	125	54.4	0.4	1.2	82	106
S7	4.1	3	269	1	11.5	0.6	18.3	12	276	1.9	0.9	0.8	221	0.8	0.6	160	16.4	0.9	0.7	40	74
S8	1.4	5	979	1	26.5	0.3	26.4	6	69	1.1	0.3	0.9	391	0.7	0.2	74	55.4	0.4	1.2	66	114
S9	2.5	4	278	<1	20.6	0.8	15.4	10	129	1.4	0.6	0.9	258	0.6	0.3	112	21.4	1	0.5	19	48
S10	3.8	4	734	1	15.2	0.2	18.5	20	196	3.0	0.9	1.1	401	0.3	0.5	222	30.6	0.4	0.7	31	87
S11	5.2	2	315	1	8.6	0.4	19.3	13	248	2.9	1.1	1.8	186	0.3	0.4	168	20.6	0.7	1	48	94
S12	5.4	6	1665	1	10.5	0.4	20.1	22	236	3.6	1.1	1.3	601	0.6	0.4	217	65	0.6	1.1	68	157
S13	4.0	3	848	2	12.8	0.7	30.6	14	211	2.6	0.9	2.2	261	0.5	0.3	145	38.3	1.3	1.7	82	104
S14	0.9	2	1760	<1	31.0	0.6	10.2	4	42	0.6	0.2	0.6	263	0.2	0.1	53	63	0.8	0.4	8	110
S15	2.8	<1	199	1	22.5	0.3	13.2	13	163	1.9	0.5	1.1	278	0.2	0.1	179	9.7	0.3	0.9	35	39
S16	0.7	1	2733	<1	32.9	1.1	11.7	4	39	0.6	0.2	0.7	346	0.3	0.0	49	95.5	1.3	0.3	2	177
S17	0.7	3	344	<1	33.8	0.2	6.8	3	37	0.5	0.1	0.6	506	0.2	0.0	43	12.9	0.2	0.3	5	26
S18	3.5	8	320	1	13.7	0.4	23.1	40	587	3.8	0.7	2.2	600	0.3	0.3	547	20.3	0.6	1.2	52	73
S19	5.3	23	275	2	6.0	0.7	31.2	63	1458	6.6	1.1	2.9	1217	1	0.2	926	22.1	1.7	1.8	104	95
S20	2.3	3	684	1	24.7	0.4	14	14	153	1.8	0.4	1.2	353	0.3	0.1	197	27.4	0.5	0.8	30	70

Fig. 18: Results of chemical analyses for soil samples

	Ca	Mg	K	Na	As	Ba	Cd	Co	Cr	Fe	Mn	Ni	Pb	Zn	pH
	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	
IC1	72.9	28.1	1.7	17	1	25	3	bdl	4	70	4	1	0	19	8.2
IC2	50.6	23.2	1.3	12	1	22	4	bdl	2	75	2	2	1	26	8.2
MR1	79	21	0.9	10	3	27	0	bdl	2	5	1	bdl	bdl	2	8.2
MR2	51.5	32.1	2	28	1	46	1	bdl	7	15	46	3	bdl	11	8.3
VKR1	54.5	21.4	0.9	49	bdl	20	0	bdl	3	21	3	1	1	17	8.4
VKR2	47	24.9	1.6	47	2	25	4	bdl	1	5	1	1	1	30	8.4
VKR3	41.5	26.1	1.9	31	bdl	28	1	bdl	2	9	1	2	bdl	16	8.4

Fig. 19: Results of chemical analyses for water samples (IC: Irrigation channel, MR: Melas River, VKR: Viotikos Kifisos River)

Chemical analyses interpretation

Soils

As it can be seen from the analytical results (Fig. 18), the elevated values (S6, S8, S9, S14, S15, S16, S17 and S20) of Ca reflect the effects of the prevailing limestone formations. The ongoing process of karstification seems to be dominant, and the high amounts of calcite enrich soil horizons. As for Mg, its elevated values (S1, S2, S13, S18 and S19) seem to have dual origination. The main source stems from the Triassic Dolostones of the Alpine substrate but there is also a profound influence from the ultrabasic formations of the tectono-metamorphic melange.

On the other hand, elevated values of Cr (S1, S3, S4, S5, S18 and S19), Ni (S1, S2, S5, S10, S12, S18 and S19), Fe (S2 and S19) and Mn (S1, S2 and S19), seem to originate from the lateritic horizons which are hosted in Cretaceous limestones. Their presence is significant at the north-eastern part of Kopaida. An interesting assessment is made through the high values of Ba (S6, S8, S12, S14 and S16) who probably ought their elevated concentrations to a potential sulphide mineralization along with Pb and Zn. Values of As, Be, Cd, Co, Sb and Sn are low without any significant impact, while the presence of Cu and V is probably controlled by the ultrabasic formations of the area.

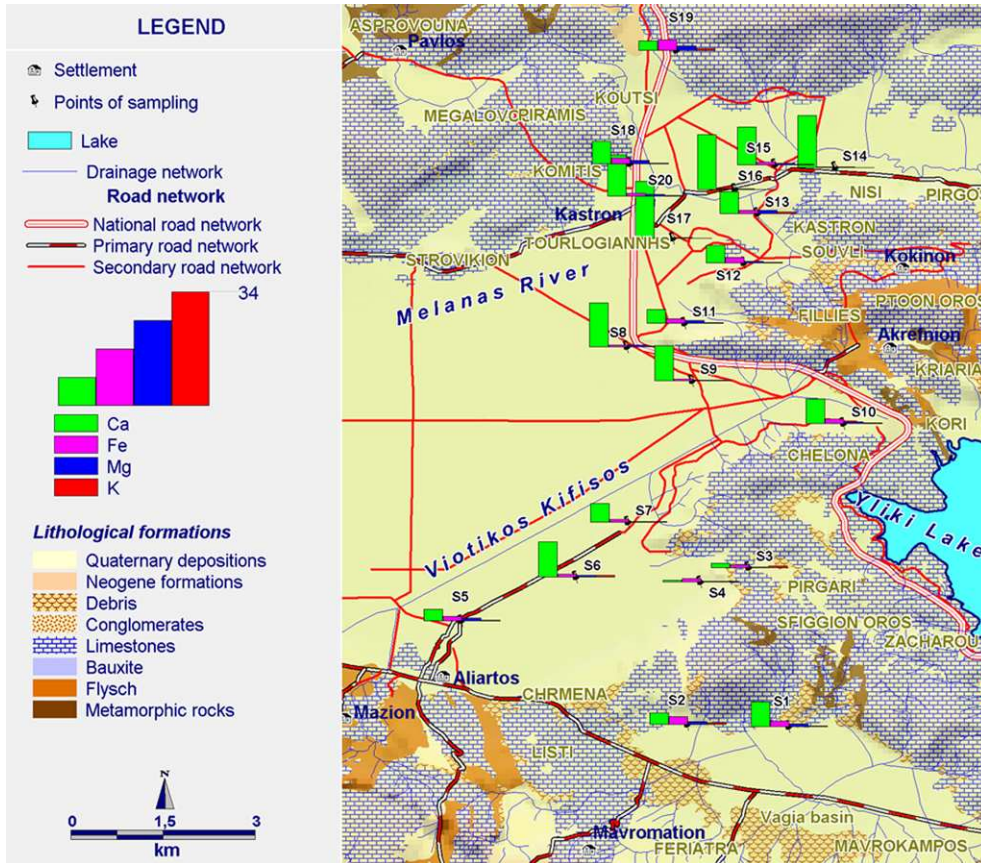


Fig. 20: Spatial distribution of Ca, Mg, K and Na (% p.w) in soil samples

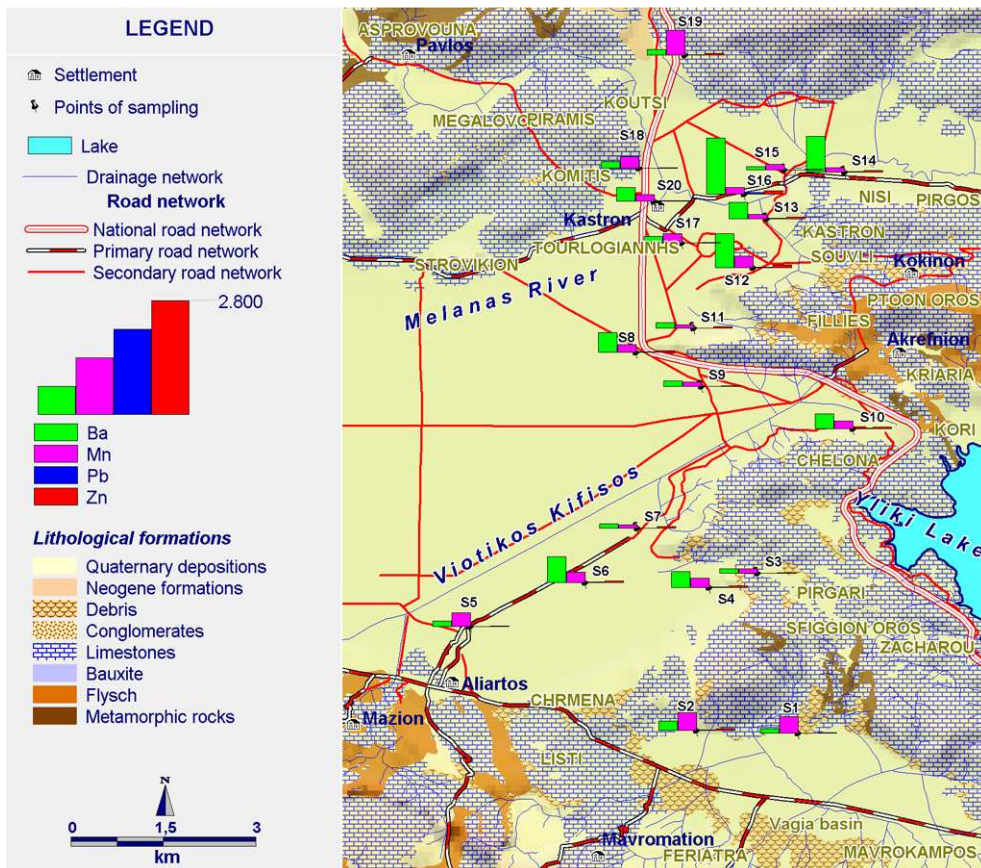


Fig. 21: Spatial distribution of Ba, Mn, Pb and Zn (ppm) in soil samples

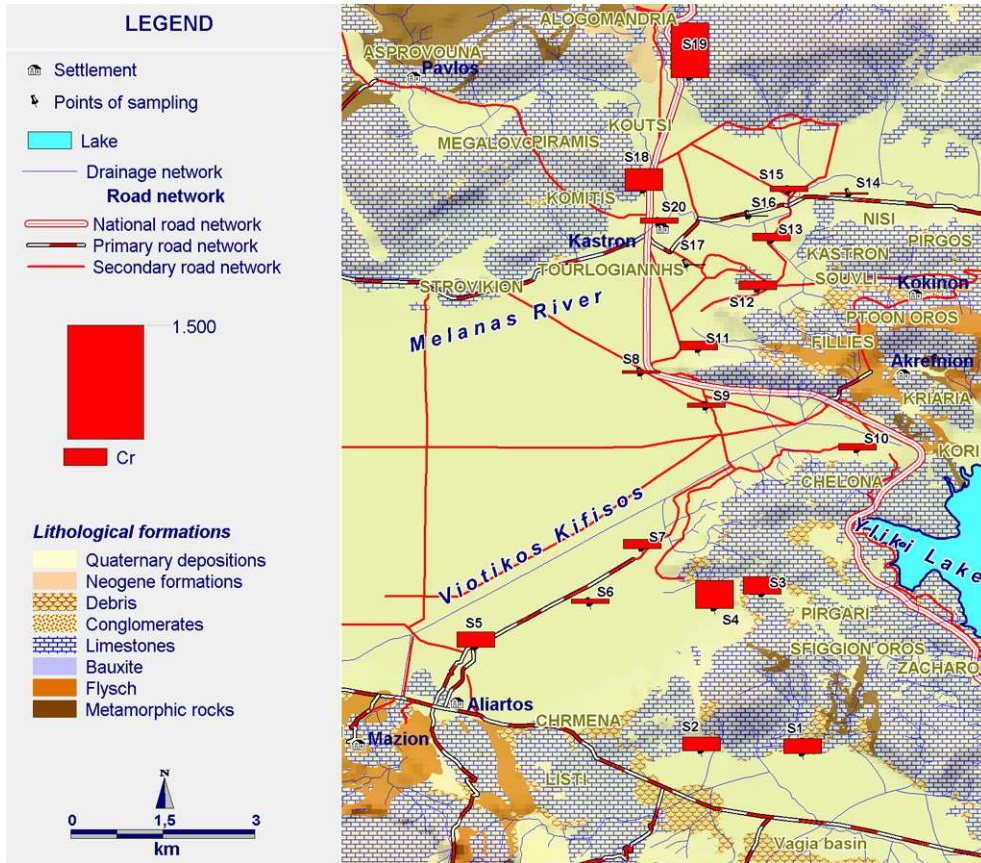


Fig. 22: Spatial distribution of Cr (ppm) in soil samples

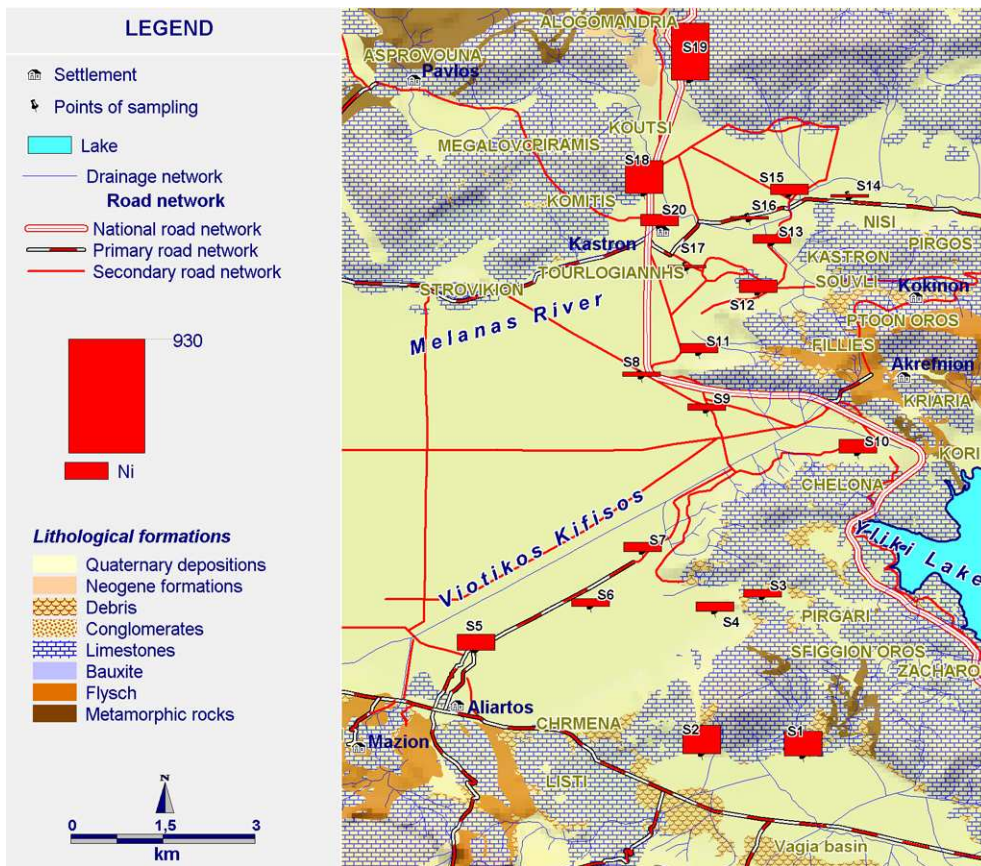


Fig. 23: Spatial distribution of Ni (ppm) in soil samples

Surface water

Chemical analyses of surface waters conclude to the fact that the dominant processes of karstification control the chemical variance of the majority of samples. Dolostone impact is negligible, since Mg concentrations are low. The concentrations of As, Ba, Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn are below the upper parametric values of 98/83 Directive. Despite this fact, concentrations of Cd in some samples (irrigation channels and VKR2) are close to this limit, reflecting in that way a potential environmental threat. These elevated values don't seem to have any correlation with the geological background or with the runoff which is influenced by soil's chemical status. On the contrary, agricultural activities and more specific the overuse of pesticides in the entire area is probably the major controlling process. In general, surface water chemistry is slightly affected by soils' status, since the elevated concentrations of Cr, Ni and Ba in soils are absent in water bodies, a fact which may also be depended on the elemental mobility in aqueous phase.

Estimation of major processes that affect geochemical status

The geochemical status of soils is directly related to the specific conditions of the wider area, in means of natural and anthropogenic impacts, such as the geological environment, hydrological conditions, land uses and various potential environmental pressures. In order to assess the major processes that affect soil's geochemistry as well as to establish the potential correlations between them, analytical results were elaborated through multivariate statistical techniques. In more details, R-mode factor analysis was performed for the specification of factors, few in number, which will explain the variation of variables and data. Each factor joined separated variables and finally correlated them directly or indirectly with a common process.

The analysis was performed only for those parameters that showed a reasonable variation to their concentrations, and therefore the parameters of As, Be, Cd, Cu, Co, Mo, Sb, Sn and V had to be excluded in order to avoid misinterpretations due to statistical errors. Before any calculation, parameters were first normalized. As an extraction technique, it was performed the Principal Components Analysis (Davis, 1984), as it explains in a better way the extracted results, even in cases of non-normal distribution of input data (Brown, 1998). Lastly, factor loadings were optimized with Varimax rotation method. As high factor loadings are considered those above 0.750, medium those which lie between 0.500 and 0.750 and finally weak those between 0.400 and 0.500 (Panda et al., 2006).

As it can be noted from Figure 24, the application of R-mode factor analysis concluded to the existence of four factors, which explain 95% of the total variance. The first factor with variance percentage of 34.1% has high positive factor loadings for the parameters Ni, Co, Mn, Cr and Fe, medium for Mg and weak for Cu, denoting the profound impact of lateritic horizons with Cr-Ni-Fe ores. The second factor explains 26% of total variance with high negative factor loadings for K, Cu and Al, medium negatives for Fe and Mg, and finally medium positive factor loading for Ca. The possible interpretation of this factor is correlated with the impact from ultrabasic formations that are hosted as blocks inside the Jurassic tectono-metamorphic sequence. The antithetic loading for Ca is probably due to limestone intercalations that occur in the same sequence. The third factor with 20.5% percentage of variance has high negative factor loadings for Zn, Pb and Ba, denoting the impact of a possible weak sulfide mineralization. Finally, the fourth and the last factor with 14.3% percentage of variance, includes with high negative factor loading the parameter of Na and with antithetic positive

loading Ca, probably reflecting the cation-exchange processes that occur between these elements at the soils of the area.

Variable	Factor1	Factor2	Factor3	Factor4	Communality
Ni	0.918	0.000	0.000	0.000	0.974
Co	0.899	0.000	0.000	0.000	0.982
Mn	0.893	0.000	0.000	0.000	0.836
Cr	0.865	0.000	0.000	0.000	0.927
Fe	0.765	-0.615	0.000	0.000	0.988
Mg	0.675	-0.622	0.000	0.000	0.893
Al	0.000	-0.864	0.000	0.000	0.972
K	0.000	-0.841	0.000	-0.432	0.982
Cu	0.432	-0.799	0.000	0.000	0.884
Zn	0.000	0.000	-0.968	0.000	0.985
Pb	0.000	0.000	-0.954	0.000	0.990
Ba	0.000	0.000	-0.930	0.000	0.978
Na	0.000	0.000	0.000	-0.923	0.943
Ca	0.000	0.534	0.000	0.729	0.954
Variance	4.7777	3.6362	2.8762	1.9973	13.2874
% Var	0.341	0.260	0.205	0.143	0.949

Fig. 24: Sorted factor loadings for the selected 14 parameters of soil samples Values below 0.400 are shown as zero

Apart from R-mode Factor Analysis, also cluster analysis integrated the statistical assessment of data. Cluster analysis has been performed on a hierarchical amalgamate technique based on the Euclidean distance, for the extraction of possible links between the chemical parameters (variables) of the 20 soil samples. Prior to statistical analysis data was standardized by means of: $K_{ij} = (X_{ij} - X) / S_{ic}$, where K_{ij} is the normalized value for X_{ij} , the i th variable for the j th sample, X is the mean value of i th variable and S_{ic} is its standard deviation (Hussein, 2003). This process gives equal weight to each parameter. As it is already mentioned, the measure of similarity (correlation) simply the distance as defined in Euclidean space (Eriksson, 1985). The distance between two samples (j, k) is given by:

$$d_{ij} = \left[\sum_{i=1}^N (K_{ij} - K_{ik})^2 \right]^{1/2}$$

Where K_{ik} the K th variable measured on object i , K_{jk} is the K th variable measured on object j . The data were classified in a relatively simple and direct manner with the results being presented as a dendrogram (Fig. 25). The resulted dendrogram interpreted to have classified 4 groups, confirming in that way the prior factor analysis.

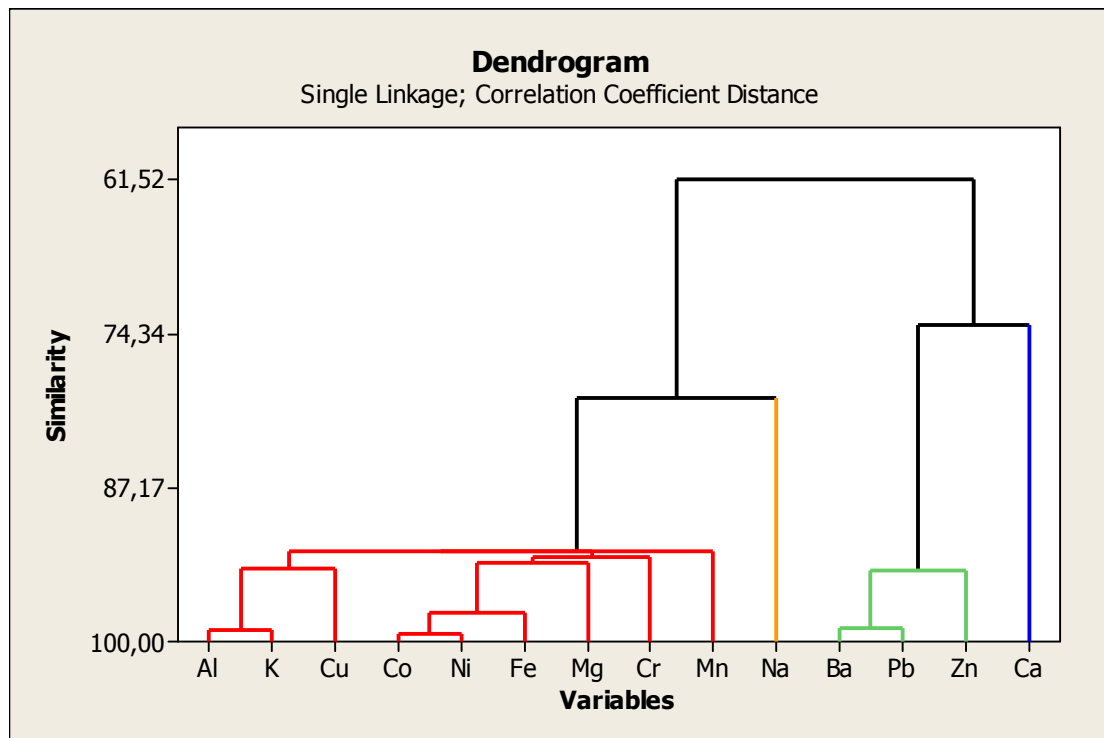


Fig. 25: Dendrogram for the 14 major parameters of soils, based on their Euclidean distance

The first group includes the variables of Al, K, Cu, Co, Fe, Ni, Mg, Cr and Mn denoting the correlation due to Cr-Ni-Fe ores, the second one includes the variables of Ba, Pb and Zn denoting the weak sulphide mineralization, and the last two groups (3rd and 4th) are consisted of an individual variable for each of them, denoting cation exchange between Na and Ca which originates in abundance from the calcareous geological environment (limestones).

Risk assessment

Greek legislation does not regard any parametric values for soil quality, either related to land use (domestic, industrial etc.) or to an absolute level of a significant parameter.

Likewise in European Union, the proposal for the relevant directive (Soil Directive, 2006), wasn't adopted by the state members, mainly due to the different soil quality characteristics of each country, and because of the deteriorations that would rise from the incorporation of a common Directive to the Environmental legislation of each country. Despite all, several state members have set soil quality standards (Fig. 26) for different land uses. Those standards differentiate from parameter to parameter, according to each country's specific characteristics (Fig. 26).

	AUT	BEL	CZE	FIN	ITA	LTU	NLD	POL	SVK	UK	DNK
As	50	110	70	50	20	10	55	22.5	50	20	20
Ba	-	-	1000	-	-	600	625	285	2000	-	-
Be	10	6	20	-	2	10	30	-	30	-	-
Cd	10	400	20	10	2	3	12	5.5	20	2	5
Co	-	15	300	100	20	30	240	45	300	-	-
Cr	250	700	500	200	150	100	380	170	800	130	1000
Cu	600	-	600	150	120	100	190	100	500	-	1000
Hg	10	470	10	2	1	1.5	10	4	10	8	3
Pb	500	-	300	200	100	100	530	150	600	450	400
Mo	-	-	100	-	-	5	200	25	200	-	-
Ni	140	-	250	100	100	75	210	75	500	-	30
Sb	5	-	40	10	10	10	15	-	-	-	-
Se	-	-	-	-	3	5	100	-	20	35	-
Sn	-	-	30	-	1	10	900	40	300	-	-
Te	-	-	-	-	-	-	600	-	-	-	-
Tl	10	-	450	-	1	-	15	-	-	-	-
V	-	1000	2500	150	90	250	250	-	500	-	-
Zn	-	-	-	250	150	720	720	325	30000	-	1000

Fig. 26: Maximum parametric levels (ppm) of soil quality for domestic use, according to EU members proposed standards (after Carlon et al., 2007)

	BelgiumWa	Czech Republic	Netherlands	Slovakia
As	12	30	29	29
Ba		600	160	500
Be		5	0.04	3
Cd	0.2	0.5	0.80	0.8
Co		25	0.38	20
Cr	34	130	100	130
Cr⁶⁺	2.5			
Cu	14	70	36	36
Hg	0.05	0.4	0.3	0.3
Pb	25	80	85	85
Mo		0.8	0.13	1
Ni	24	60	35	35
Sb			0.13	
V		180	42	120
Zn	67	150	140	140

Fig. 27: Screening values (ppm) for negligible risk have been derived in Belgium (Walloon region), the Czech Republic, the Netherlands and Slovakia (after Carlon et al., 2007)

For the purpose of the present study, all the estimations were made according to those proposed levels of maximum tolerated values of contaminants (Fig. 26), as well as to the screening values for negligible contaminant risk (Fig. 27).

As it can be noted from Figures 18 and 26:

- Values for As in Kopaida soils are below the proposed levels, except S19 (23ppm) which is above the proposed levels of 5 countries, proposing a potential environmental threat.
- Values for Ba are elevated almost in all samples. 14 of them exceed the proposed limit of one country (POL), 9 samples exceed the proposed limit of 3 countries, 3 samples exceed the proposed limit of 4 countries, and finally one sample (S16) is above the proposed levels of all 5 countries.

- Values for Be are below the proposed limits, except for S3 and S13 that have equal concentrations (2ppm) with the lower of all the proposed limits (ITA).
- Values for Cd are all below the lower (2ppm) of the proposed limits
- Values for Cu are all below the lower (100ppm) of the proposed limits
- Values of Co are slightly elevated according to the proposed standards. The concentrations of 8 samples are above the proposed limit of one country, 7 samples are above the proposed limits of two countries, 4 samples are above the proposed limits of three countries, and finally one sample (S19) exceeds the proposed limits of four countries out of 8.
- Values for Cr are quite elevated regarding the proposed limits. In more details, totally 16 samples are above the proposed limits of one country (LTU), 8 samples are above the proposed limits of 6 countries, 3 samples are above the proposed limits of 8 countries out of 11, and finally one sample (S19) exceeds the proposed limits for all countries, reflecting the imposed environmental threat
- Values for Mo are all below the lower (5ppm) of the proposed limits
- Values for Ni are elevated regarding the proposed limits. All of the samples exceed the lower of all the proposed limits (30ppm). 16 samples are above the proposed levels of three countries, 5 samples are above the proposed levels of 8 countries, and finally two of the samples (S18 and S19) exceed the proposed limits of all 9 countries, denoting Nickel as a direct environmental threat.
- Values for Pb are all below the lower (100ppm) of the proposed limits
- Values for Sb are all below the lower (5ppm) of the proposed limits
- Values for Sn are below the proposed levels, except 8 samples that exceed for short the lower of the proposed limits (1ppm). It has to be mentioned that the other proposed limits are quite higher, showing a wide variation to the estimation of the potential threat.
- Values for V are below the proposed levels, except 2 samples that exceed the lower of the proposed limits (90ppm).
- Values for Zn are below the proposed levels, except 2 samples that exceed the lower of the proposed limits (150ppm).

As it can be noted from Figures 18 and 27:

Concentrations of As do not exceed (except S19) the screening values for negligible risk, a fact which is not confirmed for Ba, since the concentrations of all samples exceed the relevant values. Concentrations of Be in their majority, exceed some of the screening values but not all, denoting minor conditions of environmental risk. The same note as the above can be made about Cd, Co, Cu, Pb, Mo, Sb, V and Zn. On the contrary, the elevated values of Cr and Ni, as it was confirmed by the previous notes that was made about Figures 18 and 26, propose a significant environmental. More specifically, none of the samples have concentrations below the screening values for negligible risk.

As it can be assumed by the aforementioned assessments, the dominant environmental threats for the soils of the area are Cr and Ni. The variation of their concentrations in the majority of the samples has a profound impact to the anthropogenic and natural environment, in terms of toxicity. Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Chromium III is much less toxic than chromium (VI). The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. According to

WHO (2008), shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure.

On the other hand Nickel occurs naturally in the environment at low levels. Nickel is an essential element in some animal species, and it has been suggested it may be essential for human nutrition. Nickel dermatitis, consisting of itching of the fingers, hands, and forearms, is the most common effect in humans from chronic (long-term) skin contact with nickel according to WHO (2008). Respiratory effects have also been reported in humans from inhalation exposure to nickel. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide. Animal studies of soluble nickel compounds (i.e., nickel carbonyl) have reported lung tumors. EPA has classified nickel refinery dust and nickel subsulfide as Group A, human carcinogens, and nickel carbonyl as a Group B2, probable human carcinogen.

Results

The creation of ex-Kopaida Lake, which was located to nowadays fertile parts of Kopaida plain, is a combinational outcome of tectonics and natural erosional processes. These processes are expressed through the extensive karstification of the prevailing geological formations (limestones), contributing in that way to the connection of the karstic Kopaida plain with the adjacent basins of Thiva and Yliki and even with Evoikos Gulf.

Kopaida's soils have a reasonable thickness and favourable conditions for cultivation. Their quality status depends on the geological environment, since none anthropogenic impact was recorded through the processing of the collected data. Totally 20 samples were collected and analyzed, in order to extract to potential environmental risk for 14 parameters. The collected water samples from the major drainage pattern, showed no impact towards them from soils, suggesting that their chemical status is more likely to be influenced by land uses and the erosional processes of the geological environment, rather than leaching of soils.

The major processes that affect soils geochemical status are correlated with the existence of the lateritic Fe-Ni-rich horizons, as well as from the karstification processes and a possible weak sulphide mineralization.

The environmental risk is obvious for Cr and Ni, since their values are elevated nearly in all the entire area, suggesting a profound environmental pressure for both anthropogenic and natural environment. The other analyzed parameters vary, but in general their environmental risk is negligible.

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