World Academy of Science, Engineering and Technology
International Journal of Geological and Environmental Engineering
Vol:18, No:7, 2024

Open Science Index, Geological and Environmental Engineering Vol:18, No:7, 2024 publications.waset.org/10013712.pdf

Geochemical and Mineralogical Characteristics of Soils in Areas Affected by the Fires on August 2021 at the Ilia Prefecture, Greece

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Abstract**—**This study delineates the geochemical, mineralogical and sedimentological characteristics of soils collected from woodland and forest areas affected by the fires of August 2021 at the Pelopio region, Ancient Olympia Municipality, Ilia prefecture, Greece. The mineralogical composition of the samples consists of quartz, calcite, feldspars (albite, oligoclase, anorthite) and clay minerals mostly smectite, kaolinite, and illite. Quartz ranges from 38% to 57% with an average of 48%, calcite ranges from 2% to 25% with an average of 14%, feldspars ranges from 7% to 26% with an average of 17% and clays ranges from 4% to 43% with an average of 21%. Sedimentological analyses classify most of the samples as loam to silt loam. Sand percentage ranges from 14.76% to 71.11% with an average of 35.01%, silt ranges from 21.68% to 62.34% with an average of 44.96%. Geochemical analyses of the soil samples applied for total organic carbon (TOC), total nitrogen (TN), total phosphorous (TP), Cu, Zn, Mn and Fe. TOC ranges from 0.28-0.83%, TN from 0.09-0.48 mg/g, TP from 0.02-0.26 mg/g, Cu from 10-21 ppm, Zn from 15-34 ppm, Mn from 612-1204 ppm, Fe from 9528-27500 ppm. The pH ranges from 7.5 to 9.07 with an average of 8.74, while the values of electrical conductivity (EC) range from 0.05-0.12 mS/cm, with an average of 0.07 mS/cm. Statistical analysis of the data shows a positive correlation between clays and Zn, Mn, Fe. TOC and TN show a strong positive correlation, while Fe shows a strong negative correlation with calcite.

Keywords**—**Soils, geochemistry, mineralogy, sedimentology, woodland, forest.

I. INTRODUCTION

FOREST fires have caused a great ecological and environmental disaster not only in Greece but also in Europe and worldwide. According to the European Copernicus service, 2021 was one of the worst years for catastrophic fires, with figures showing that this year more than twice as many large forest fires have been recorded in the European Union compared to the 2008-2020 average [1]. By early August 2021, the European forest fire information system had recorded 1,100 fires, 300 more than the annual average [2]. During August 2021, the area of Ancient Olympia at the prefecture of Ilia, Greece was affected by a wildfire that caused dramatic changes in the natural environment.

Forest fires impact the ecosystem and results in changes of the soil properties [3], [4]. During such events, tremendous amounts of thermal energy affect not only the aboveground and belowground biota, but also the physical, chemical and mineralogical characteristics of soils [4], [5]. Particle size distribution does not change, but the removal of the fine fraction through runoff and surface erosion lead to soil coarsening [6], [7].

Organic carbon consumption begins at about 200 ºC and total oxidation of organic matter occurring around 460 ºC [8]. Soil pH increases after fires because of the organic acids destruction, while EC is temporarily elevated from the release of ions after the combustion of the organic matter [9], [10]. Even if the mineralogical composition does not change in a great extent, there is evidence for mineral alteration with temperature, within the upper 1-8 cm of soil depth [9], [11]-[13].

In this study, we detect the environmental status of woodland and forest areas of the Pelopio region at the Ancient Olympia Municipality, part of the Ilia prefecture Western Peloponnese, Greece, affected by the fires of August 2021 in regard to the sedimentological, mineralogical and geochemical characteristics of selected soil samples.

II. MATERIALS AND METHODOLOGY

A. Study Area

The sampling was carried out at woodland and forest areas of the Pelopio region at the Ancient Olympia Municipality, part of the Ilia prefecture Western Peloponnese, Greece on July 2023. For the procedure, 18 sampling sites (samples 1-18) were chosen along the area of interest and one more sampling site as a reference material with coding Pel_R_23, sample code R (Fig. 1). All samples were extracted from the uppermost 10 cm of the soil horizon and well mixed and homogenized according to LUCAS topsoil survey methodology [14]. The coordinates of the sites were estimated using Maggelan Explorer XL G.P.S.

B. Soil Samples Analyses

During the extraction procedure all sampling sites were pictured with a scale index of 20 cm (Fig. 2 A). The amount of

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each soil sample was approximately 100 g. After the extraction, all samples were sealed in zipped polybags, transported to the lab, and dried in the oven for 1 hour at 72 °C (Fig. 2 B).

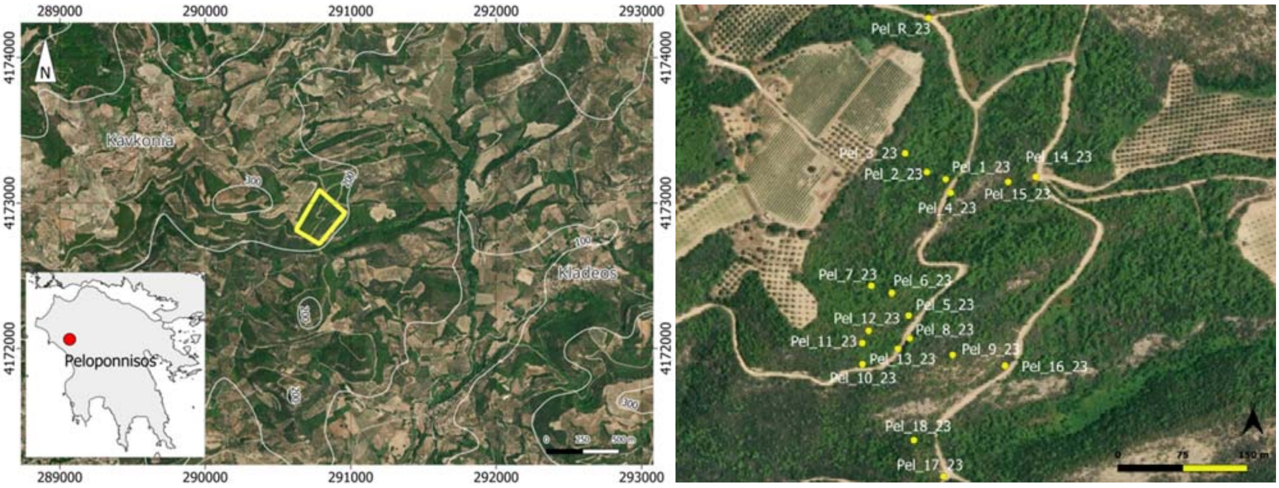

Fig. 1 Sampling sites at the Pelopio region at the Ancient Olympia Municipality, Western Peloponnese, Greece

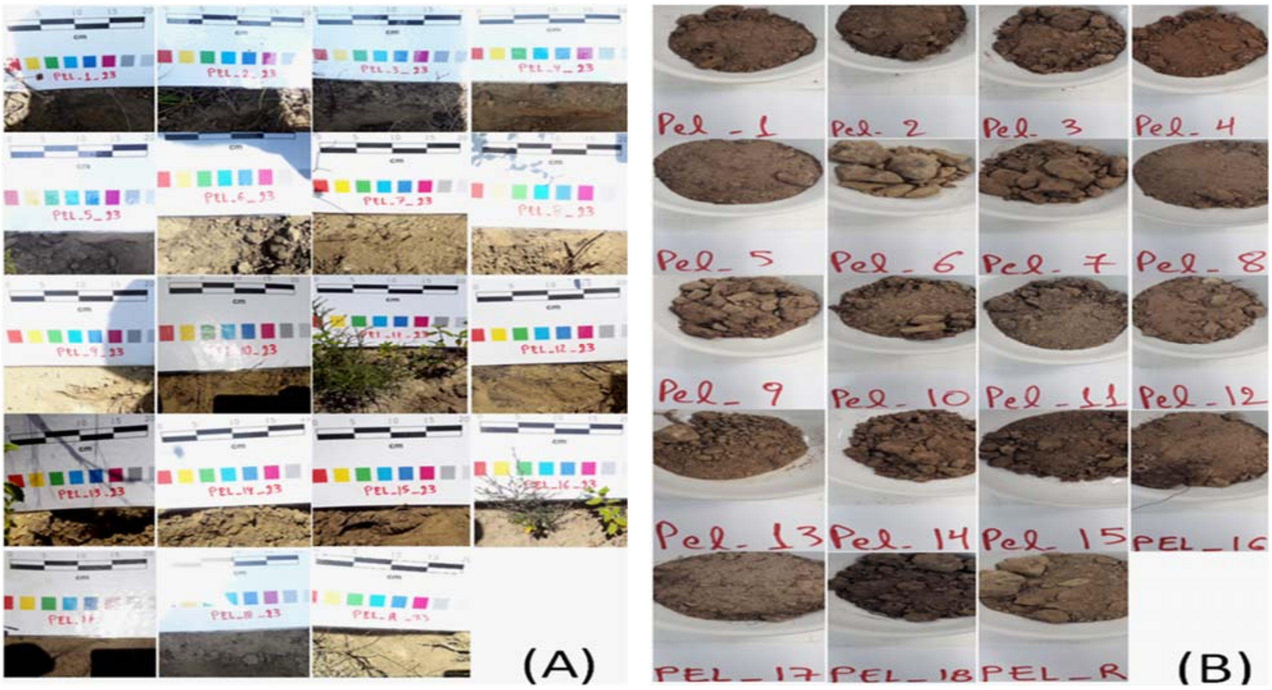

Fig. 2 Soil samples (A) after the extraction and (B) after the drying process

For the sediment classification of the soil samples, grain size analysis was carried out using Malvern Mastersizer 2000 Hydro. The percentage calculation of the sand, silt and clay fractions resulted in the statistical and lithological description of the samples, based on soil terminology. The results of the grain size analysis were plotted at ternary diagrams according to USGS and ASTM-D2487 standard. The statistical parameters of the soil samples were calculated using GRADISTAT V.4 software [15].

The values of EC and pH were estimated according to the standard methods of ISO 122565, 1997 and ISO 10390, 1997, respectively [16]. The solution for the analysis required 2 g of fine powdered soil samples diluted in a beaker with 50 ml of purified water. After 1 hour of resting time with periodical stirring, the solution was analysed using a portable multi-meter HACH HQ4300.

The geochemical analyses that were conducted in the soil samples included the determination of the TOC, total nitrogen (TN), total phosphorus (TP) and the X-ray Fluorescence analysis [17]. After the homogenization, the suspension is transferred to the elemental Shimadzu TOC analyser (TOC-VCSH) for measurement. A certain amount of the sample is inserted in a receptor full of the oxidative catalyst, Pt/Al_2O_3. Vaporization of water leads to the oxidation of the organic and inorganic carbon to H_2O and CO_2. The CO_2 moves to the analyser and is measured, calculating the concentration of TC. The acidification of the sample with HCl acid causes dissolution of carbonate salts, transformed finally into CO_2. In this way, IC is measured separately and from the difference between TC and IC, TOC concentration is inferred. For the determination of TN, a small amount of the sample is led into an inert purified air stream, through a quartz pyrolysis tube [17]. The total concentration of chemically bound nitrogen converts into NO. The NO encounters O_3, contained in the gas stream, resulting in the production of metastable nitrogen dioxide (NO_2*). The signal of the light emission, during the decay of NO_2*, is measured and is equivalent to the TN concentration.

The determination of total phosphorus values (TP) was performed according to Standard Methods APHA (2005) using a multi-meter HACH HQ4300.

Geochemical analysis of soil samples was carried out using an S1 Titan Bruker Handheld XRF Analyzer. An amount of 0.5-1 g of fine powdered soil sample was put under pressure to make pressed powder pellets. Afterwards, these pellets were measured at a range of 10-50 kV and 10-200 μA, using a Rhodium tube with 30 seconds exposure time.

For the mineralogical analyses, the bulk soil samples were placed in an oven for 1 hour at 50 ºC in order to remove any absorbed moisture, followed by subjected to sieving. Once powdered to a size less than 10 μm, the mineralogical analysis of the samples was conducted.

For the determination of each sample's mineralogical phase, X-Ray diffraction (XRD) was performed. For this purpose, a Bruker D8 Advance XRD diffractometer with CuKα radiation (λ = 1.54Å) and a nickel filter was used, at a scanning speed of 2º/min, while measurements were obtained between the angle range 2θ, 3-70º. The phase identification as well as the semi-quantitative analysis was determined using Topas v.3 software.

III. Results and Discussion

A. Sedimentological Characteristics

The results of the sedimentological analyses show that most of the soil samples are classified as loam and silt loam, while the rest of them are classified as sandy loam and silty clay loam. Sand, silt and clay fractions are plotted in a ternary diagram, according to USGS and ASTM-D2487 standard and display little variation of the grain size among the soil samples (Fig. 3).

Clay percentages range from 4.39% to 43.43% with an average of 20.63% with the higher concentrations existing at the northern section of the area. On the contrary, sand percentages range from 14.76% to 71.11% with an average of 35.01% and the higher values are recorded at the southern section of the region. The silt fraction concentrations range from 21.68% to 62.34% with an average of 44.96%, noting though a more normal distribution at the area.

Mineralogy of Soils

The presence of quartz, carbonates, feldspars, and clay minerals was observed in all studied samples in varying ratios. The spatial distribution and composition (%) of the studied samples based on the content in SiO_2, carbonates, feldspars, and clay minerals were illustrated in Fig. 4.

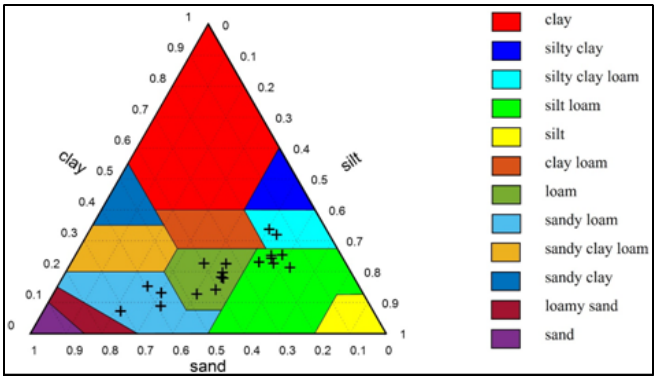

Fig. 3 Sediment classification of the soil samples

Quartz and carbonates are the main minerals, with values ranging between 38-57% and 2-25%, respectively. In detail, quartz is found abundantly in nature and has a high resistance to weathering and alternation subjected to rocks due to physicochemical parameters. Carbonates, and in this case calcite, are also known to have high resilience to temperatures up to 1000 ºC.

Among the feldspar group, the identified minerals are albite, and oligoclase, while anorthite was detected in a limited number of samples (4, 6, 7). Their presence in sedimentary rocks is frequently encountered in fine-grained rather than coarse-grained sandstones [18]. On the other hand, smectite, illite, and kaolinite appear to represent the secondary minerals, with montmorillonite (smectite) being the most common clay mineral. Kaolinite in particular is structurally damaged when the material is subjected to temperatures exceeding 550 ºC, where the dihydroxylation of kaolinite occurs [19]. As a result, the soil temperature in the sites, where samples 2, 3, 9, 12, 13, 14, and 18 were obtained, did not either reach a sufficiently high level in order to destroy kaolinite, or the duration of the fire was limited. Conversely, the lack of kaolinite in the remaining samples could be attributed to the locally elevated temperatures or the inherent absence of the mineral in each sample's composition.

C. Geochemistry of Soils

Geochemical analyses of the soil samples show that TOC range from 0.28-0.83%, with an average value of 0.60%. The TN ranges from 0.09-0.48 mg/g, with an average of 0.30 mg/g and TP from 0.02-0.26 mg/g with average value of 0.14 mg/g. The values of pH range from 7.5 to 9.07 with an average of 8.74, while the values of EC range from 0.05-0.12 mS/cm, with an average of 0.07 mS/cm. These values are consistent with the values reported by the Land Use/Land Cover Area Frame Survey (LUCAS) project for sampling and analyses of the main properties of topsoil in 23 Member States of the European Union [14].

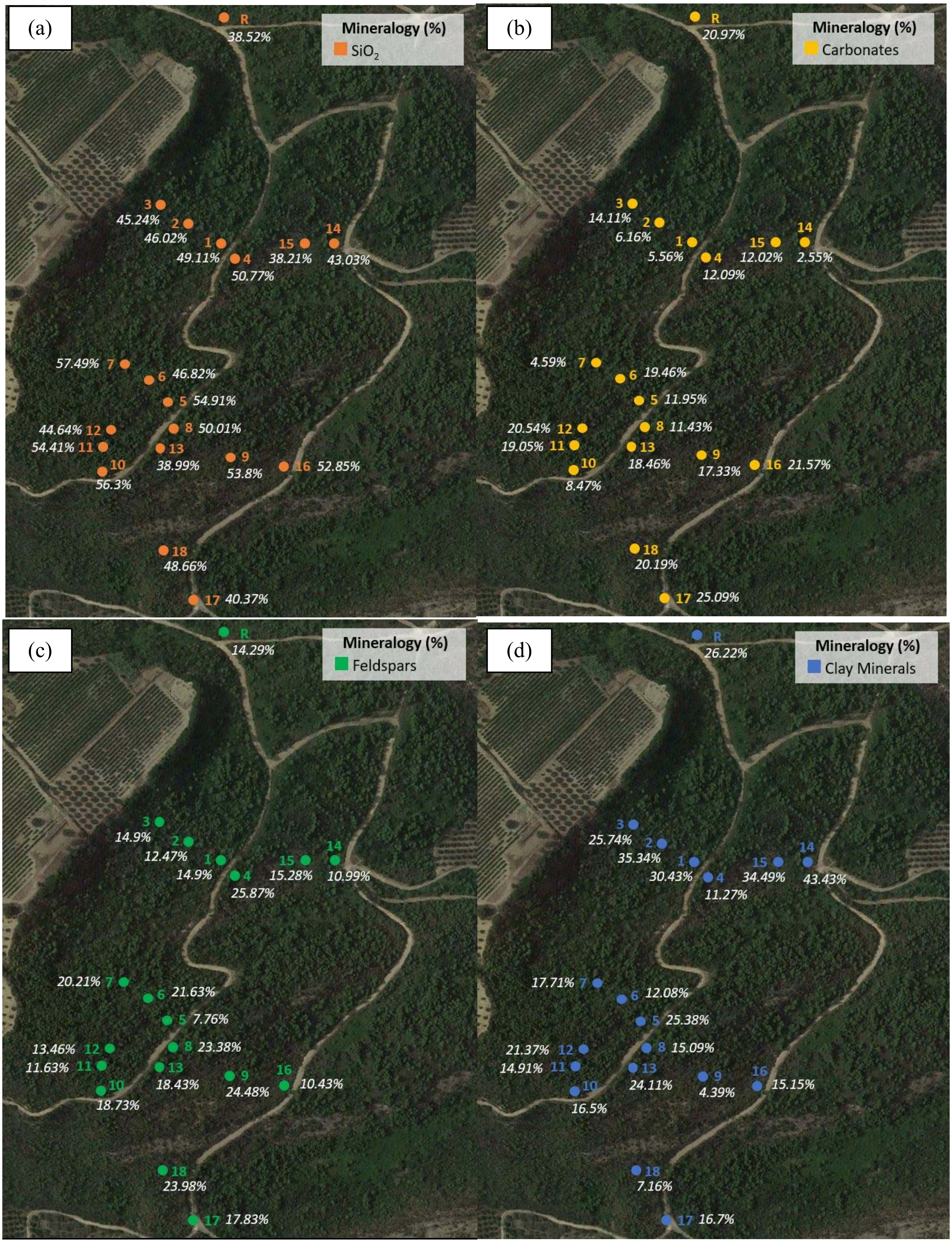

Fig. 4 Spatial distribution and composition (%) of the studied samples based on the content in (a) SiO$_2$, (b) carbonates, (c) feldspars, and (d) clay minerals

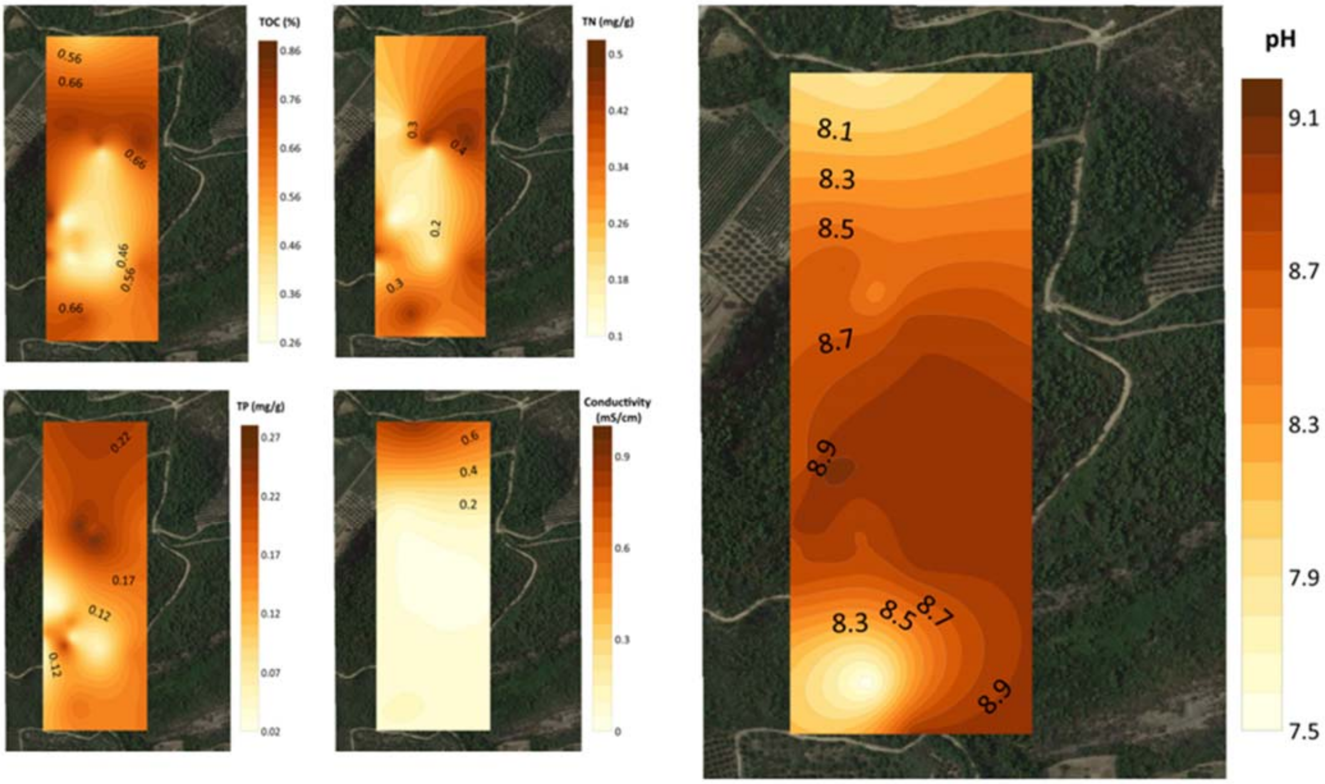

Fig. 5 Distribution in TOC, TN, TP, EC and pH of the studied soil samples

TOC concentrations appear to be lower in the central part of the study area with the highest being found in the northern and southern parts (Fig. 5). Similarly, the lowest concentrations of total nitrogen and total phosphorus are observed in the centre of the area, in contrast to the highest concentrations which are located respectively in the northeast and in the northern parts. The EC shows a clear increase towards the northern part of the region, in contrast to the pH values whose increase is observed from the northern and southern parts of the region towards its centre (Fig. 5).

In the soil samples of the studied area, Cu ranges from 10-21 ppm, Zn from 15-34 ppm, Mn from 612-1204 ppm, Fe from 9528-27500 ppm. The range for Cu values are well below the threshold value (100 ppm) for Cu in European soils [20]. In addition, Zn concentration in the study samples do not reach the lower guideline value of 250 ppm for zinc in European soils [20]. The values of Fe and Mn in the studied area show lower concentrations compared to the values reported for forest soils [21].

The results of the geochemical analyses for heavy metals show a similar distribution over the wider area. The lowest copper values are found in the central part of the region with an increasing trend in the northernmost, while the low zinc values are found even further south where their increase is found in the northeast (Fig. 6). The same variation is observed in the concentrations of manganese and iron, where from the south to the northeast, the increase in their respective values is recorded.

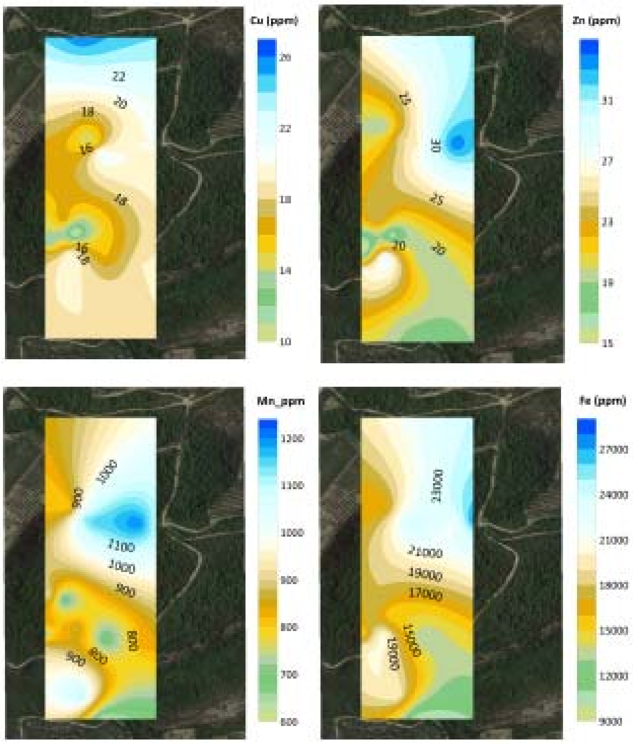

Fig. 6 Distribution in Cu, Zn, Mn and Fe of the studied soil samples

Correlation matrices (Pearson) of all examined geochemical and mineralogical parameters were calculated. The statistical analysis of the data shows a positive correlation between clays and Zn, Mn, Fe. TOC and TN show a strong positive correlation, while Fe shows a strong negative correlation with calcite and a strong positive correlation with Mn (Table I).

TABLE I
CORRELATION MATRIX (PEARSON) OF THE STUDIED SOIL SAMPLES

	TOC	TN	TP	Cu	Zn	Mn	Fe	Quartz	Calcite	Feldspars	Clays
TOC	1.000	0.701	0.072	-0.044	0.024	0.411	0.140	0.028	-0.330	-0.468	0.440
TN	*__0.701__	1.000	0.248	0.109	0.163	0.494	0.273	-0.200	-0.097	-0.434	0.404
TP	0.072	0.248	1.000	0.145	0.293	0.552	0.454	-0.557	-0.073	-0.241	0.492
Cu	-0.044	0.109	0.145	1.000	0.588	0.240	0.292	-0.359	0.125	0.417	-0.093
Zn	0.024	0.163	0.293	0.588	1.000	*__0.644__	0.775	-0.415	-0.540	0.142	0.510
Mn	0.411	0.494	0.552	0.240	0.644	1.000	0.835	-0.183	-0.618	-0.002	0.502
Fe	0.140	0.273	0.454	0.292	*__0.775__	*__0.835__	1.000	-0.251	-0.684	0.005	0.579
Quartz	0.028	-0.200	-0.557	-0.359	-0.415	-0.183	-0.251	1.000	-0.206	0.086	-0.486
Calcite	-0.330	-0.097	-0.073	0.125	-0.540	-0.618	*__-0.684__	-0.206	1.000	0.131	-0.591
Feldspars	-0.468	-0.434	-0.241	0.417	0.142	-0.002	0.005	0.086	0.131	1.000	-0.656
Clays	0.440	0.404	0.492	-0.093	0.510	0.502	0.579	-0.486	-0.591	-0.656	1.000

*Correlation is significant at the 0.05 level

The statistical analysis in Table I reveals that Fe, Mn and Zn concentrated in the same geochemical phase associated with clays and/or oxides/hydroxides, and not carbonates due to their negative correlation with calcite. By contrast, TN shows its affiliation with the organic fraction of the samples due to the strong positive correlation with TOC.

IV. CONCLUSIONS

The aim of this study is to identify the environmental status of soils collected from the Pelopio region at the Ancient Olympia Municipality, part of the Ilia prefecture Western Peloponnese, Greece. For this purpose, we detect the geochemical, mineralogical and sedimentological characteristics of topsoil samples from the studied area. Most of the soil samples are classified as loam and silt loam, while the rest of them are classified as sandy loam and silty clay loam. The silt fraction ranges from 21.68% to 62.34%, with an average of 44.96%. Clay fraction ranges from 4.39% to 43.43% with an average of 20.63% and the higher concentrations exists at the northern section of the area. Quartz, carbonates, feldspars, and clay minerals were observed in all studied samples in varying ratios. Quartz and carbonates are the main minerals, with values ranging between 38-57% and 2-25%, respectively. On the other hand, smectite, illite, and kaolinite appear to represent the secondary minerals, with montmorillonite (smectite) being the most common clay mineral in the area. TOC concentrations appear to be higher in the northern and southern parts compared to the central part. In the latest, the lowest concentrations of total nitrogen and total phosphorus are observed. The lowest copper values are found in the central part of the region with an increasing trend in the northernmost, while the low zinc values are found even further south where their increase is found in the northeast. On the basis of the statistical analysis Fe, Mn and Zn concentrated in the same geochemical phase associated with clays and/or oxides/hydroxides, and not carbonates due to their negative correlation with calcite. By contrast TN shows its affiliation with the organic fraction of the samples due to the strong positive correlation with TOC.

ACKNOWLEDGMENTS

The authors would like to thank the Green Fund of the Ministry of Environment and Energy, Greece for financial support. Green Fund decision number 222.3.2/2021.

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