PHYSICO-CHEMICAL AND GEOCHEMICAL FEATURES OF POST-ANTIQUE FALLOW LAND AT THE ARCHAEOLOGICAL COMPLEX OF THE EUROPEAN BOSPORUS

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ABSTRACT

The lack of field studies outcome on ancient wineries and land plots under vineyards in the Kerch Peninsula puts on agenda a higher demand for new data, which is essential for understanding viticulture development of the European Bosporus throughout 4th c. BC – 3rd c. AD. The geoarchaeological approach, with the involvement of the natural sciences resources (pedology, geochemistry, palaeobotany), was used to study the soil within the archaeological complex (10 km west of Pantikapaion (modern Kerch)) dated 4th – 3rd centuries BC and 1 c. BC – 1 c. AD. Climatic heterogeneity of economic activity conditions has been established by silicon microbiomorphs distribution according to post-antique fallow land profile, as evidenced by a comparison of modern phytocenosis and the composition of phytoliths at a depth of 16–27 cm produced because of turf ploughing. Physico-chemical parameters of soil types, structural state assessment, geochemical ratio and coefficients made it possible to establish a particular indicative range for post-antique fallow land and newly formed soil types. Using the results of cluster analysis as per concentrations of 22 chemical elements it was found that the geographical factor (soil location) serves as a determinant when grouping selective objects in multidimensional space. This proves the key role of parent rock biogeochemistry and soil types produced by rock in the context the concept of "terroir".

Keywords: soil geochemistry, antique vineyards, post-antique fallow land, agropedogenesis, Kerch Peninsula

INTRODUCTION

For grapes and for other plants, N, P, K, Ca, Mg, S and Fe are the main food elements, which are considered essential nutrients. The winemakers have encountered differences between vineyards constantly (over the decades), such as growth of vines and quality of the grapes and wine, even in vineyards close to each other [1]. The trace element, nutrients and other parameters in the soil layers, leaves and grapevines [2] content studies have shown that in addition to the main nutrients Na, Al, Si, Ba plays an important role in plant life, as well as trace elements – B, As, Mn, Cu, Zn, Co, etc. and

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even some of rare earth elements [3]. The Vineyard plant has great potential in forming a deep zone of rhizosphere and translocation of nutrients and trace elements from parent rock and soil to leaves and grapevines. It was previously shown [4] that the elements that could establish a reliable correspondence between the geolithological features of the vineyard soil and the chemical composition of grape berries are: Sr, Ba, Ca, Mg, Al, K, Zn, B, Ni, Co. Assessment of the critical concentration in micronutrients should be considered in order to explain and prevent symptoms of deficiency that could decrease the quantity and quality of wine grapes [5]. The viticulture experience [2; 6] has proven the positive role of incorporating many of trace elements (Co, Ni, Mn, B, Zn, etc.) into the soil. A priority list of chemical elements useful for plants (Ca, Zn, Mg, Ni, P, Mn) as monitoring indicators was substantiated [7]. The role of the contents of trace elements (Co, Ni, Mn, B, Zn, etc.) in the soil is just as important for growing high-quality grapes as is the content of the fundamental mineral elements (N, P, K, Ca, S, and Mg) [2; 8]. The purpose was to establish the possibility of using the pedoarchaeological approach in relation to the study of the two-period antique archaeological complex for palaeogeographic reconstruction of economic activity conditions and the use of pedomemory in the interpretation of archaeological data.

DATA AND METHODS

Description of the study area. Although there is a range of indirect data (palaeobotanical materials, scenes on coins, remnants of wineries) indicating the high level of viticulture in the European Bosporus, we know very little about this line of business. The 1962 archaeological excavations have confirmed that the lands of the Pantikapaion Chora in 4th – 3rd centuries BC had land plots which were fenced with stone walls and included fields for grain crops and vineyards [9]. 10 km northwest of Pantikapaion (modern Kerch) we have studied the soil near the Oktyabrskoe estate (4th – 3rd centuries BC and 1 c. BC – 1 c. AD). The climate of the area is warm but arid (precipitation is 400 (329÷438) mm yr^{-1}, average annual air temperature is 11 °C). Soils in this region are formed on eluvium of carbonate rocks. The archaeological complex included the territory of the estate, the boundary rampart (Figure, R) separating the upper terrace (under field crops, No 9) from the lower terrace (under perennial plantings, No 10) and the southern exposure slope suitable for viticulture (Figure, P2). The size of the land plot for field crops and perennial plantings was 4.5-5 ha [9]. The four sides of the plot were enclosed by stone double-paneled walls of 1-1.45 m thick made from large limestone blocks. The study objects were located on the upper terrace bounded by an earthen rampart located 10.5 m away from the southern steep-sloped fence, which also partially served as a retaining structure between the rampart and the wall. There, at a depth of 0.5 m, we have found some spots diameters from 0.3 to 0.45 m of soft soil, which probably filled holes for grape bushes [9]. Wine was prepared not for sale but only for the needs of the inhabitants of the estate. An assumption that the ancient farmers "separated the vineyard from the grain field with a stone wall" [9, p. 57] has determined it necessary to search for differences in soil fertility due to these types of land management (Figure, Plots (P1) with soil sections No. 9 and to the south of it No. 10). A new stage in the agricultural development of this region occurred at the turn of the era. Sizes of the vineyard in 1 c. BC – 1 c. AD, apparently, remained the same, but the area under crops was very increased [9].

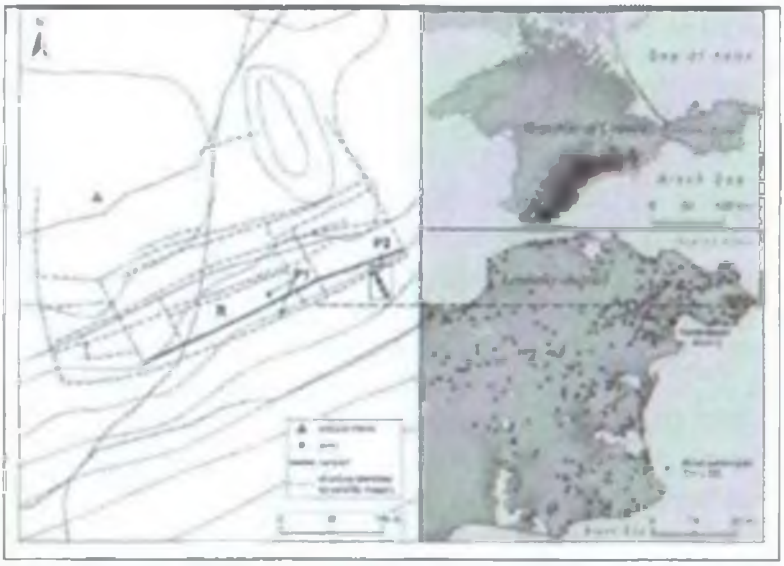

Figure. Archaeological complex near the village of Oktyabrskoe (10 km NW of Pantikapaion (modern Kerch))

METHODS

Soil colours (dry/moist) were described using the Munsell color Charts, 2000. The determination of Corg in the soil was performed by oxidation of the organic substance with a solution $K_2Cr_2O_7$ in sulfuric acid until the formation of carbon dioxide. The group and fractional analysis of humus (humic acid (HA) and fulvic acid (FA)) was fulfilled by Tyurin's method modified by Ponomareva and Plotnikova. Total nitrogen (N) was estimated by Kjeldahl's procedure. The pH values (H_2O) were determined by a potentiometric method (pH meter Sartorius Basic Meter PB–11) and CO_2 in carbonates by acidometry. Soil cation exchange (CEC) was estimated by Kappen-Gilkowitz procedure. A wavelength-dispersion X-ray fluorescence spectrometer (Spectroscan Max-GV) was used to determine the contents of chemical elements. The concentrations of macroelements and trace elements in soils (22 metals and oxides) were determined by measuring the fractions of metal mass and oxides in powdered samples. The eluviation coefficient (Ke) was determined by the formula: $Ke = SiO_2/(CaO+MnO+MgO+K_2O+Na_2O)$. Mobility factor was assessed using the formula: $Km = (Na_2O+K_2O+MgO+Zn)/SiO_2$. The sum of heavy metals covered a list of six elements: $\Sigma HM=\Sigma(As, Co, Cr, Cu, Pb, Zn)$. Soil quality (SQ) assessment was obtained by the formula: $SQ_i = (B_1 \cdot B_2 \cdot ...B_{10})^{1/10}$, where $B_1...B_{10}$ – (K, Mg, Ca); (Mn, Fe, Ni, Cu, Zn); (Si, Al). Dry sieving of the soil was carried out in a column of eight sieves with square cells (Fritsch GmbH). The water resistance of aggregates (dW) in fractions of 1-2, 2-3.15, 3.15-5 mm was determined according to the Andrianov method. The method is based on aggregates, which disintegrate in water over a certain period. The structural coefficient (Kstr) is calculated as the ratio of the mass of 1 to 7 mm aggregates to the mass of the total aggregates <1 and >7 m. The structural cloddiness (DEFL) has been determined by the content of aggregates of >1 mm. The content of silicon microbiomorphs and the distribution of nine diagnostic groups of the phytolith have been determined in the examined soils. Phytolith analysis results allow palaeoenvironmental reconstruction [10]. Grouping of the soils was conducted by the method of cluster analysis hierarchic classification (unification by Ward's method) based on the most informative indices normalized through mean-square deviation.

RESULTS AND DISCUSSION

At the time of the construction of the boundary rampart (4 c. BC) the climate was more humid than it is now. This is proven by a greater $C_{HA}:C_{FA}$ ratio value at the buried soil of the original accumulated rampart (2.25) than at the top of this rampart (1.99) as well as in the upper horizon of fallow soils (2.03-2.14). These $C_{HA}:C_{FA}$ values correspond to the range of parameters at the modern southern Chernozem. Therefore, the climate preceding the 4th century BC remained steppe but the annual precipitation was 20-40 mm higher than in the contemporary days, i.e. the potential soil bioproductivity was higher. Climate optimum for the northern Black Sea coast accounts for the period from 4th c. BC to mid 3rd c. BC with the subsequent transition to a heat-dry phase. It is no doubt that the first stage of viticulture development generally occurs on 4th – 3rd centuries BC when there are specialized wineries with vineyards being nearby, although it is possible, that the grape acclimatization period falls on the 6th – 5th centuries BC [11]. During the Roman times (up to the middle 3rd c. AD) the steppes of the northern Black Sea coast were characterized by a dry-out climate. Based on the number and types of wineries, the Bosporan viticulture began to flourish starting from the 1st century BC, and this business kept to be stable also later up to 3 c. AD [11].

Silicon microbiomorphes were presented in three layers of virgin soil and only in the lower layers of the object No 9 (17.5-26.5 cm) and 10 (5.5-18 cm). We have detected no phytoliths of five groups (cultivated cereals, reeds, arid grasses, needles of conifers and mosses). The composition of the microbiomorphic fraction on a post-antique deposit for grain crops (No 9) is only characterized by the presence of detritus and amorphous organic mass. It proves that the stubble was regularly burned and then ploughed. However, the 17.5-26.5 cm layer, which can reflect a typical deep-ploughed ancient turf layer, contains a phytolith complex of meadow grasses. The soil on the post-antique deposit under the vineyard (No 10) at a depth of 5.5-18 cm contains phytoliths of meadow grasses and shell amoeba, which is a diagnostic sign of soil overturning. It has been quite unexpected to have data for the soil, which we classified, as wild land (No 23) according to its morphological structure. Since a shell amoeba and pollen were found at a depth of 8.5-15.5 cm it has been determined that this layer used to be surface one. The same conclusion applies to the 15.5-22.8 cm layer since the number of phytoliths was the maximum for the soil profile No 23. The southern carbonate Chernozem was defined as a virgin soil based on the profile morphological structure. Ad, 0-8.5; A', 8.5-15.5; A'', 15.5-22.8; A1B, 23-47; Bca, 47-80; BC, 80-100 cm, powdery mealy neoplasms with a diameter of 5 mm from a depth of 100.5 cm. However, at a depth of 15.5-22.8 cm we have found the maximum number of phytoliths characterizing the meadow-steppe motley grasses, which is impossible in the current bio-climatic conditions of dry steppe it is safe to say that this area was probably subject to episodic ploughing with rotation of upper soil horizons. This event can be attributed to the late antique - early medieval period of using the fallow farming system. Mechanical cultivation on steep vineyard slopes can endanger soil fertility [12]. Therefore, it is justified to use terrace agriculture for perennial plantings on the southern slopes. The soil catena on the southern slope (Figure, P2) contain on average 28% CaO in the upper layer, which is close to the content of fallow land (24–29%). Compared to the virgin soil, horizon A in the post-antique fallow land has a higher content of carbonates and fewer mobile forms of P_2O_5 (Table 1). Based on the content of Corg and

N total the old fallow vineyard soil (No 10) was less transformed from ploughing than the soil under grain crops (No 9), which is probably due to the number of cultivations.

Table 1. Physico-chemical characteristics of soils on eluvium carbonate rocks

No	Depth, cm	Munsell color (dry): 10YR	pH (H_2O)	Corg	$CaCO_3$, %	P_2O_5, mg 100 g^{-1}	CEC, cmol(+) kg^{-1}	N total, %	C:N
Old fallow soil									
9-1	6-18	6/1.5	7.7	2.6	47.7	1.4	49.2	0.2	11
9-2	18-26	5/1.5	8.0	1.8	52.2	1.6	49.2	0.2	11
10-1	6-18	5/1.5	7.9	3.4	45.9	1.6	49.5	0.3	10
10-2	18-37	6/1.5	8.1	2.6	49.5	1.8	49.5	0.3	9
Virgin soil									
23-1	0-16	4/2.5	8.0	2.9	9.7	2.0	49.8	0.2	12
23-2	16-23	5/2.5	8.1	2.3	10.8	4.2	49.8	0.2	10

Soils forming on dense carbonate rocks have a dispersed structure and poor water resistance, so they are often subject to severe erosion [13]. Any differences in horizon A differentiation degree by water stability (AS criterion) in the upper and lower parts of the horizon (Table 2) tend to increase from the virgin soil towards grain crop soil (No 9) and vineyard soil (No 10). Moreover, vineyard soil has the greatest residual agrogenic degradation of water-stability structure in a more homogeneous horizon A (5.5-37 cm) as compared to the soil within any field crop plot. Vineyard fallow soil in the lower part of the horizon A (layer with some relict signs of agro-pedogenesis) is worse in water-stability structure than the soil in any grain crop plot, primarily due to the low water-resistant capacity of aggregates with a diameter of 1 to 2 mm.

Table 2. Indicators of the structural state of soils (numerator) and water resistance (denominator) of meso-aggregates with a diameter of 1 to 5 mm

No	Depth, cm	Structural units, mm			AS*
		5-3.15	3.15-2	2-1	
		%			
9-1	6-17.5	$\frac{10.7}{92.6}$	$\frac{22.2}{86.1}$	$\frac{28.0}{88.9}$	89.15
9-2	17.5-26.5	$\frac{9.4}{72.1}$	$\frac{17.8}{81.9}$	$\frac{23.6}{83.2}$	79.03
10-1	5.5-18	$\frac{6.5}{83.4}$	$\frac{19.1}{81.7}$	$\frac{28.7}{83.0}$	82.67
10-2	18-37	$\frac{13.0}{76.3}$	$\frac{24.5}{75.3}$	$\frac{23.2}{73.0}$	74.83
23-1	0-15.5	$\frac{12.5}{90.6}$	$\frac{11.7}{84.1}$	$\frac{13.9}{84.7}$	86.42
23-2	15.5-22.8	$\frac{11.2}{83.4}$	$\frac{10.0}{83.6}$	$\frac{13.0}{84.5}$	83.82

*AS is a criterion of water resistance (the ratio of the percentage of water-resistant aggregates to the share of structural units).

It was shown earlier [1] that a correct geopedological classification and mapping of both the parent rock and related soils are essential for supporting the territorial subdivision provided by the wine's product quality specification. The cluster analysis results have shown that the geographical factor (soil location) was crucial to group selected objects of multidimensional space into separate sets. In particular, we have established a fundamental difference in the concentrations of 22 chemical elements both between No 23 (wild land) and the residential zone, and between them and the other 11 objects of the archaeological complex, which reflect different zones of post-antique agricultural landscape. The centre of the land plot in 4th – 3rd centuries BC was occupied by a rural estate in the form of a small house with stonewalls and a tiled roof [9]. However, when using pedochronological dating method [14] and data on the capacity of newly formed soil in this estate (the thickness of horizon A was 190 mm, and that of humus (A + AB) – 318 mm) we have determined later time for end-of-life in this place – it is 1 c. AD. The soil on the top of the boundary rampart (Figure, R) had A horizon thickness of 230 mm, and that of humus (A+AB) 340 mm, which corresponds to the time of estate inactivation– 1 c. AD according to the pedochronological dating model [15]. A comparison of the averaged concentrations of chemical elements for three soil profile layers within the territory of the estate (soil that formed with 1 c. AD) and that of the wild land analogue has shown that several previous centuries were characterized by more xeromorphic conditions than it had been before. This is reflected in higher content of calcium and strontium (more than two times) as well as magnesium and sodium. This pattern is also confirmed when comparing data on 14 testing points at the archaeological complex as compared to horizon A (0-15.5 cm) of the virgin soil. In particular, this soil has a lower content of Sr, Ca, Mg, Na, as well as P, Mn, Zn, Ba than soils in the archaeological complex. And this is despite the fact that the sea proximity influence on pedogenesis could be more significant for the virgin soil (No 23) which is located 120 m away from the Sea of Azov than for post-antique fallow land near Oktyabrsky (7.8 km from the Kerch bay). The beginning of the first century AD was associated with changes in natural conditions due to the end of hot arid climate period, which existed in the previous 200 years [11]. The climate warming which was dated to the first centuries AD has contributed to viticulture development, which can be observed in some regions of the Northern Black Sea region where this business was underdeveloped before. The depth-comparable horizons of virgin and fallow soils are characterized by a higher content in soil No. 23 of such heavy metals as Co>Cr>Pb>Cu. However, the fallow soils being more carbonate than the wild land significantly exceed (6.5 times) strontium concentration. The values of various geochemical coefficients showing content or ratio of migrationally in-soil mobile and inert elements, and accordingly can diagnose eluviation processes, differ in fallow lands (on average according to Nos. 9 and 10) and virgin soil from 3.2 to 11 times (Table 3).

Table 3. The most informative geochemical relationships and coefficients

No. of objects	9-1	9-2	10-1	10-2	23-1	23-2
$(CaO+MgO+10*P_2O_5)/Al_2O_3$	4.48	4.9	4.31	5.24	0.78	0.89
Ke	0.54	0.59	0.61	0.58	6.93	5.86
$(CaO+MgO)/Al_2O_3$	4.17	4.57	3.9	4.82	0.6	0.71
Na_2O/Al_2O_3	0.37	0.44	0.36	0.43	0.11	0.13
$CaO+MgO+K_2O$	30.49	33.34	28.11	33.03	7.1	7.54
Km	3.59	2.99	3.53	3.17	1.07	1.01
$(FeO+Al_2O_3)/$	0.28	0.26	0.31	0.25	1.81	1.53
ΣHM	198.97	186.37	203.81	187.32	321.71	377.43
SQ	6.33	6.44	6.58	6.39	6.03	5.74

In this regard, the eluviation coefficient (Ke) is of particular importance. Judging by the coefficient values, the soil horizons which were turbocharged in ancient times to a depth of 26.5-37 cm have substantially higher Ca, K, Mn, Mg and Na to silica content than the virgin soil in horizon A. These particular features are integrally reflected in the fact that, according to SQ values, the fallow soils are 10% more enriched with elements, which are useful for plants than the virgin soil.

CONCLUSION

When using a natural science approach to the study of the archaeological complex which included post-antique fallow land (under field crops and perennial plantings) as well as newly formed soils on the cultural layer (antique mansion) and earth fills (rampart top), this makes it possible to create palaeogeographic context for the interpretation of archaeological data and to provide new knowledge about the natural and anthropogenic evolution of soils in the sub-Atlantic Holocene period. The confirmed climate optimum on the Kerch Peninsula in 4th c. BC was reflected in the phytolith complex of meadow grasses, which was found in the deep-ploughed turf layers of the post-antique fallow land both under grain crops and on vineyard plot. The studies of post-antique fallow land in different agricultural zones of the two-period mansion (4th – 3rd centuries BC and 1 c. BC – 1 c. AD) have shown that in comparison with the soil in the grain crops plot the vineyard soil retained greater agrogenic degradation of water-stability structure (primarily due to the low water-resistant capacity of aggregates with diameter from 1 to 2 mm). The topology-based geographical factor, that is, the location of the parent rock and related soils in this case, serves as the determinant for grouping the studied objects in a multidimensional space, which is consistent with the concept of "terroir". This was shown by the results of hierarchic classification soils by the concentration of macroelements (Ca, Si, Al, Fe, Ti, Mn, Mg, P, K, and Na) and trace elements (V, Cr, Ni, Co, Cu, Zn, As, Sr, Pb, Ba, Zr, and Rb) by the method of cluster analysis.

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