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Investigation of Soil Trace Elements Balance with a View to Ensuring Quality of Crop Products

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Abstract: Formation of microelement soil composition being developed in special bio-climatic conditions at the northern border of Mediterranean landscapes distribution are of great economic significance for viticulture evolution and growing up subtropical fruit and nut crops has been analysed by means of the concept of a soil chronofunction. The reserach objective consisted in determination of regularity in soil trace elements composition formation in a result of their concentration and dispersion under soil formation for rational organization of tillable lands monitoring and high quality assurance of crop products. Soil chronosequences were established in the course of studies at 20 archaeological sites dated from the ancient time to the first decades of the 20th century. Geochemical association of microelements which to the fullest extent reflects the results of biogeochemical accumulation during the calcaric cambisols soil formation was established. An offer was made with regard to the index of geochemical soil transformation or its individual genetic horizons which is based on the consideration of accumulation processes conserved components and removal of more migrationally movable ones of matrix soil. Specific lists of conservative and movable soil components depending on their carbonate content were ascertained allowing to determine the general change dependency of geochemical soil transformation index on time. Evaluation of geochemical soils transformation velocity has testified that this process proceeds in tree times more actively in leached soils than in carbonate ones. Slop lands with calcaric cambisols, being ploughed up by the plow ditcher under perennial plantings and under the influence of soil erosion are badly in need of fertilizer treatment for support of first of all, K, Mn, Co content in carbonate soil types and Zn, K, Mn, Mg in leached soil types.

Key words: Modelling, soil chronofunctions, soil quality, trace elements, Geochemistry, carbonate soil

INTRODUCTION

If estimates for conversion of the natural forest into developed areas in recent year are still relevant for some regions (Appianing *et al*., 2016), then for old-developed regions with a 1000 year history of land use change, they are more likely to reach the level of assessments in changing the quality of land resources.

The process of material composition transformation in a result of soil formation depends on specific soil-climatic conditions, it is characterized by slow rates, possesses poorly reverted nature and having modern land-use planning horizon it does not always fit the priorities when organizing soil-ecologic monitoring.

Early in the course of erosion and soil formation, the composition of microelements within the soil as a rule is inherited from the parent rock which in many ways determines the mineralogical content of soil. However, in due course microelement composition in the soils begins to differentiate under the action of dominating soil-forming processes (Kabata-Pendias and Pendias, 1984).

The soils contain mineral scattered particles appearing to be the source of nourishment accessible forms for the higher plants. This is due to the fact that particles possess a larger surface area per volume unit and contain a sufficient amount of adsorbed chemical elements.

The soils play an exclusively important and complex role in biogeochemical cycle of any element but in particular it concerns biophile macroelements (N, P, K, Ca, Mg, Si etc.,). However in case of long-term (hundreds of years) acrogenic loads in the arable Chernozem, the reduction of the microelements in the content is observed, namely Co, Ni, Mn, Cu, Zn, Pb as well as phosphorus and potassium (Lisetskii *et al*., 2015). Only four microelements (Cu, Zn, Co, Mn) and only sometismes Mg are observed on the arable land in the modern practice of agrochemical servicing of the Russian agricultural enterprises.

Investigation of natural correlation between macro and microelements within specific soils is of great significance for agricultural ecosystem's productivity promotion, where balance is disturbed in the soil between individual nourishment elements upon NPK-fertilizer application making negative impact on the growth and development of crop plants. The research objective lied in determination of peculiarities as to elements concentration and dispersion in a result of natural soil formation allowing defining priority indexes when organizing monitoring of arable lands in order to provide manufacture of high quality plant production.

MATERIALS AND METHODS

Study area: The Southern Coast of the Crimea (SCC) is a relatively narrow (width from 2-20 km) seaside line with low-mountain (up to 700-800 m a.s.l.) severe topography worked out in the clayey and sandy deposits of Middle Jurassic. Occupying 4% of Crimea's territory, the sub-Mediterranean landscapes of the Southern crimea stand out for their distinct soil-climatic conditions and record of human activity. The climate in SCC (up to 350-400 m high) is characterized by Mediterranean features: frost-free season -230-260 days, precipitation 350-650 mm per year, average temperatures in January +2.0, …, +4.0 °C, July; +23.0, …, 24.5°C. However, the climate is cooler in SCC that in areas as frosts occur up to -15 °C (Yalta), that limiting capacities of subtropical crops growth.

In terms of the soil types, the SCC constitutes the Crimean subtropical forest soil zone. Calcaric Cambisols (IUSS Working Group, 2014) or according to the nomenclature of Crimean soils, the cinnamonic forest soils, occur on the southern slope of the main ridge and in the foothills west and east of it. The parent materials are clayey schist, limestone and conglomerates. The most widespread are cinnamonic calcareous soils on eluvium and hillwash of parental rocks (66.6%) followed by similar but non-calcareous soils (29.3%) and finally by the salty cinnamonic mountain soils on hillwash of parental rocks (4.1%). The total area in the crimea occupied by calcaric Cambisols is 48,500 ha. The share of eroded cinnamonic soils is 69%. In Crimea the cinnamonic soils occupy the areas with maximum precipitation in Winter and the lowest incidence of frost and with presence of Mediterranean floristic elements (Cordova, 2015). These soils have formed under a cover of xeric forests (juniper and oak) and bushes alternated with areas of steppe vegetation.

Since, the end of the 18th century, both viticulture and horticulture were becoming the staple branches of farming in the Southern Crimea. Vineyards, fruit gardens, essential oil and other valuable crops within SCC are placed on the slopes with inclinations more than 10-12°. The soils in geochemical correlation are strongly transformed as affected by water erosion of soils and application of plow processing under perennial plantings.

Data used: As opposed to a small amount of antique monuments to the east of Herakleon Peninsula numerous medieval settlements and defenses (Isary) are located on the territory of SCC: early Byzantine fortresses, castles of high society feudal lords, reinforced abbeys and surrounded by walls settlements and shelters of village communities. Soils on the archaeological sites were studied in sections that revealed the entire soil profile formed after the end of residential occupation. The age of each site was determined archaeologically. Soil chronosequences were established in the course of studies at 20 archaeological sites situated within the SCC and dated from the ancient time (from the turn of the era to the 4th century AD), the Middle Ages (5-15th centuries AD) to the early 20th century AD. This dating technique is based on the concept of a soil Schronofunction (Jenny, 1980) which describes the mathematical relationship between time and certain irreversible genetic soil properties (e.g., thickness of soil horizons, biogeochemical indicators, etc.) (Lisetskii *et al.*, 2016).

Standard soil was necessary to compare mixed-age soils being selected on the territory of State Natural Reserve "Cape Martyan" (East of the city of Yalta). It is cinnamonic red deep clayey residual-carbonate poorly differentiated Earth on eluvium-deluvium of limestone rocks, being formed under relic vegetation of Mediterranean type (*Juniperus excelsa*, *Quercus pubescens*).

Concentration of macro and microelements within the soils were determined by technique of measuring metals mass fraction and oxides in powder samples using the method of X-ray fluorescence analysis on the X-ray spectrometer (Spectroscan Max-GV). The concentrations were calibrated by standard soil specimen (by means of state standards samples of the composition of the rocks and soils) and were compared in several iterations) in order to rise accuracy of obtained results. Colours were described using the Munsell-System (Macbeth, 2000). Chemical analyses of soils formed on the surface of each of the 20 sites included the following standard procedures: the organic Carbon (Corg) after Tyurin; CO_2 in carbonates by acidometry.

The classification of chemical elements (Bityutskii, 2011) was used in work on evaluation of the relations in the system soil-plant: sums of required macroelements for the plants (K+Mg+Ca), trace elements (Mn+ Fe+Ni+Cu+ Zn) and useful elements within the soils (Si+Al). The coefficient of elements accumulation proposed by Shaw (Shaw, 1964) was modified: relation calculation of dispersed elements (S_i/P_i) in the soil (S_i) and parental rock (P_i) was performed by adding element-biophils and not as arithmetic average (by Shaw) but by formula of average compound. Thus, the coefficient of microelements accumulation and biophile elements were determined by the equation:

$$K_s = (E_1 \cdot E_2 \cdot, ..., E_6)^{1/6} \quad (1)$$

where, E_i = S_i/P_i. i-Zn, Pb, Cu, Co, P, K. In the cluster analysis of soil data, we used Ward's method in which clustering procedures are based on the criterion of squared Euclidean distance.

RESULTS AND DISCUSSION

Geochemistry of parent rocks: Lithologic heterogeneity and diversity of mineralogical and consequently chemical composition of parent rock materials creates conversely a mixed character of soil cover chemical composition.

Under the conditions of sub-Mediterranean on SCC the peculiarities of parent rocks are determined by a prolonged process of various rocks erosion limestones, marls, clay slates, conglomerates, magmatic rocks) in the similar climatic conditions under the dry forests and brushwoods. With reference to the Earth crust, the soils are featured by enrichment (• 1-10) with the elements K, Na, Ca, Sr, Zn, Al, Ti, Si, Zr, Pb, Mn, As (Speidel and Agnew, 1982) which have been determined in our investigation. Calcaric Cambisols (on the Herakleian Peninsula) are characterized by the process of biochemical recovery of Fe, Mn, etc. in the one-metre thick layer. On Cape Martyan, on mount Ayu-Dag red-brown clays, which resemble tropical *terra rossa* are formed from products of weathering of the Upper-Jurassic limestone rocks. Soils on the products of limestones erosion obtain reddish shade (Table 1).

Since, in Table 1 the content of the most distinctive elements within individual parent rocks is represented under the principle a maximis and minima distinction (downward), thus, it is possible to conclude that eluvium of the upper-Jurassic limestone rocks (mount Sokol) and terra rossa are significantly different at least by 14 macro- and microelements. Carbonate weathering crust containing high level of calcium oxide and associated with it strontium is characterized by poor content of silica and sesquioxides. Relic character of red-colour rocks (mount Ayu-Dag and loam in fissures limestone rocks, Chersonesos) is well diagnosed as to strong degree of cations leaching, what is reflected in low values of proportion (Ca+K)/Ti.

Table 1: The most distinctive characteristics of the chemical composition of parental rocks of Crimean soils under the sub-Mediterranean conditions

Region	m. Sokol	Chersonesos	Chersonesos	m. Ayu-Dag
Rock [a]	WC	WC	L	CaG
Munsell	10YR	5YR	10YR	5YR
color (dry)	4/2	6/8	3/6	5/8
CaO (%)	30.7	27.5	0.7	0.4
P_2O_5 (%)	0.4	0.1	0.1	0.1
Fe (%)	1.9	2.6	9.4	5.8
Co (ppm)	1.9	10.0	13.1	32.3
MgO (%)	3.2	5.4	1.4	1.8
Ni (ppm)	35.0	54.5	120.5	47.0
Cu (ppm)	18.9	53.2	88.6	42.0
Sr (ppm)	170.3	208.7	70.4	59.0
Al_2O_3 (%)	8.2	7.8	19.7	15.9
Cr (ppm)	73.2	57.2	138.1	100.1
Zn (ppm)	107.8	65.4	163.6	117.6
SiO_2 (%)	19.5	27.1	44.5	48.0
MnO (ppm)	0.1	0.04	0.1	0.1
As (ppm)	9.2	6.0	6.0	8.1
SiO_2/R_2O_3	0.6	0.8	12.2	13.1
(Na+K)/Ti	74.1	86.9	3.9	1.7

Note: [a] Parent rocks: WC, Weathering Crust; CaG, Clay and Gravel; L, Loam. Ppm = mg/kg^{-1}

Characteristics of the chronosequences of cinnamonic soils: Pedopalynological studies (Cordova *et al*., 2011) in the western part of SCC (Herakleian Peninsula) have demonstrated that in comparison with the modern area, warmer and wetter climatic period fall within 2500-1200 cal years BP (with a peak of about 1650 years BP). In recent year a notable increase of annual precipitations is noticed in the general moisture regime of SCC territory and there is a significant reduction of precipitations in May, June and August on the background of high summer temperatures leading to growth in the number of thirsty phenomena (Korsakova, 2011). Soil-forming processes proceed with a sufficiently high speed under SCC conditions not stopping during the entire year (Table 2). Standard soil (on Cape Martyan) possesses a gross thickness of humus horizon (A+AB) equally 600 mm (2-11 in Table 2) in the course of the whole period of its formation.

The average annual rate of humus horizon formation (• H) decreases over time in the soils of chronosequences from 2-0.12 mm/year and the most steep decline in the rates is marked at the soil age of 400 years and more (Table 2).The accumulation processes rates of organic carbon accumulation and formation of A horizon thickness are featured on the whole by synchronism up to

Table 2: The major features of the cinnamonic soil chronosequences within the territory of the southern coast of the Crimea

No[a]	Soil age (years)	Parental rocks[b]	Horizon, depth (mm)	Munsell color (dry)	$CaCO_3$ (%)	pH H_2O	• H[c]
1-1	25	WC	AC, 0-29	10YR 5/3.5	4.62	7.9	1.17
2-1	37	CaG	AC, 0-77	10YR 5/3	26.24	8.2	2.05
1-2	42	L	AC, 0-25	10YR 5/3.5	–	7.3	0.60
2-10	87	CaG	A, 0-50	10YR 4/2	14.46	6.8	0.84
			AC, 50-73	10YR 4/2.5	14.77	7.5	
1-3	93	CaG	A, 0-40	10YR 5/3	22.49	8.4	0.79
			AB, 40-85	10YR 5/5	3.75	8.7	
1-4	100	L	A, 0-30	10YR 5/3	2.46	7.2	0.51
			AB, 30-50	10YR 5/3.5	2.15		
1-5	350	L	A, 0-66	10YR 5/4	3.38	6.3	0.41
			AB, 66-145	10YR 6/3	2.46	6.1	
1-6	350	L	A+AB, 0-83	10YR 6/2.5	1.54	4.8	0.30
			AB, 152-260	10YR 5/4	24.37	8.2	
			AB, 260-320	10YR 6/3	26.24	8.4	
2-7	560	WC	A, 0-64	10YR 4/2	2.77	5.9	0.33
			AB, 64-185	10YR 4/2.5	1.85	5.6	
2-2	600	CaG	A, 0-188	10YR 4/2	17.49	8.1	0.31
			B, 188-270	10YR 5/3	26.62	8.3	
2-5	700	CaG	A, 0-160	10YR 4/2	3.75	8.3	0.32
			B, 160-229	10YR 6/2	12.00	8.3	
2-8	700	CaG	A, 0-124	10YR 3/2	10.43	7.2	0.27
			AB, 124-190	10YR 4/3	18.77	8.2	
2-9	700	WC	A+AB, 0-180	10YR 4/2.5	19.08	8.0	0.25
2-3	700	WC	A, 0-60	10YR 3/3	6.77	8.0	0.26
			AB, 60-182	10YR 4/3	6.77	8.0	
2-4	700	WC	A, 0-135	10YR 3/3	6.46	7.9	0.28
			AB, 135-196	10YR 4/3	6.77	7.9	
1-7	700	CaG	A, 0-46	10YR 4/2	4.00	7.2	0.18
			AB, 46-103	10YR 4/2	4.62	7.6	
2-6	1700	WC	A, 0-130	5YR 3/2	4.25	7.8	0.11
			AB, 130-183	5YR 3/4	2.50	8.2	
1-9	1700	CaG	A, 0-152	10YR 5/3	23.62	8.2	0.12
1-8	1900	L + [A]	A, 0-25	10YR 4/1	3.69	6.3	0.13
			A, 25-120	10YR 5/1.5	2.77	7.0	
			AB, 120-254	10YR 5/1.5	3.08	7.5	
2-11	>10000	CaG	Ad, 0-60	5YR 3/1.5	4.75	8.0	0.06
			A, 60-200	5YR 4/4	2.50	7.4	

[a] Archaeological monument; [b] WC, Weathering Crust; CaG, Clay and Gravel; L, Loam. [c]AI, Average annua Lrate of Humus Horizon (A+ABS) formation, $(mm/year)^{-1}$.

2000 years, excluding the first 100 years, when humus accumulation (in case of annual reduction of attachment velocity Corg from 3.75 to 0.63%/year) advances the submersion process of humus agents deep into the profile. When increasing the soil age from 400- 2000 years, the attachment velocity Corg in the horizon A is gradually lowering from 0.14 to 0.02%/year.

Mixed-age soils in average contain particles <0.01 mm 18.8±1.0% and can be referred to sandy-loam. Source limestones with high content of initial and secondary minerals as well as the climate within SCC territory with interchange of dry and hot periods with wetter and warmer ones-these are two major conditions assisted in formation of terra rossa. Cinnamonic red-colour soils being younger than soil on Cape Martyan of A horizon colouring reddish brown (No. 2-11 in Table 2) are similar in colouration, they are brown (with a wide hue range) and only in the age of 1700 year, the limestone blocks of the Charax fortress (No 2-6 in Table 2) obtain a colouring dark reddish brown (5YR 3/2, 5YR 3/4).

soils in the upper horizon over time (t) required for the chemical elements of the plants (mg/kg): 1-useful elements within the soils (Si, Al); 2-sums of required macroelements for the plants (Ca, Mg, K) and 3 trace elements (Mn, Fe, Ni, Cu, Zn). If uniting all three groups necessary for elements plants, so a trend of sums variations of 10 specified elements within time in the course of 20th centuries are not perceptible in the newly formed soil. A week positive trend may be marked only for the microelements accumulation process. Thus, further on us focused on determination of the microelements ensemble, which mostly would reflect the results of biogeochemical accumulation in the course of soil formation (Fig. 1).

Evaluation of geochemical transformation of soils: Due to the colour, diversity of parent rocks it is possible to obtained more accurate evaluations than soils comparison on the content of chemical elements by means of correlation of their concentration in the upper accumulation horizon and parent rock in one soil profile.

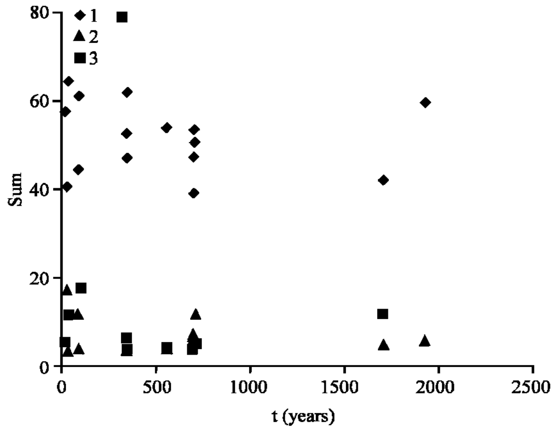

Fig. 1: Variations in the sums of accumulated cinnamonic

Concentration and dispersion of chemical elements are opposite phenomena determining one of significant geochemical approaches to the environment's study and their temporary states. Offered index of soil geochemical transformation or its individual genetic horizons (ST) reflects the balance of relative accumulation of soil material constitution conservative components in a result of carrying out more migrationally movable components. Using data about gross content, the index calculation of geochemical transformation of each soil member of chronosequence (ST_{tt}) at the point in time (t) is offered to be dome according to the equation:

$$ST_t = 100 \cdot \frac{(S_{C1} \mid P_{C1} \cdot S_{C2} \mid P_{C2} \cdot \ldots \cdot S_{Cn} \mid P_{Cn})^{1/n}}{(S_{L1} \mid P_{L1} \cdot S_{L2} \mid_{PL2} \cdot \ldots \cdot S_{Lm} \mid P_{Lm})^{1/m}} \quad (2)$$

Where:

C1, C2, ..., Cn	=	Stable components
L1, L2, ..., Lm	=	Mobile components of the real composition in the Soil (S) and in the Parent rock (P)

In due course by means of vertical migration, the upper soil horizon is characterized by reduction in concentration of movable soil components and increase of ST_t value. The analysis of averages values in chemical elements concentration proportion in the upper layer of mixed-ages Soils (Si) and Parent rock (Pi) demonstrated the accumulation of 11 chemical elements (Si/Pi>1) in the humus horizons which can be represented in the form of descending Pb>Ca>Zn>Mn>As>Sr> (K, Co)>P>(Fe, Ti) and 5 chemical elements are featured by carrying out to be represented in the ascending series: Na<Ni<(Si, Cu)<V.

It is essential to consider their paragenous association in the offered list of diagnostic elements as interaction between chemical elements may be antagonistic or synergistic, what influences upon the plant's capability to absorb selectively those or other elements. There is an increase in intensity of humus horizon and accumulation of Corg in it, where special interactions of organic-mineral complexes surrounding the plant roots take place. In time, there is a reduction in Cu, Mn, Zn antogonism with such elements as Al, Fe, Co, Ni due to leaching (decalcification) of soil upper horizons in case of calcium synergism with Cu.

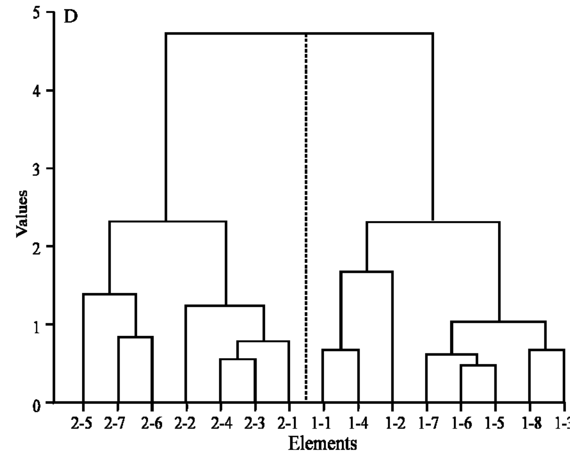

Fig. 2: Dendrogram of geochemical distinction in mixed-age soils by 16 chemical elements: t, year (along the X axis), D, threshold distance (along the Y axis). Genetic groups of soils: 1, Carbonate soils (right)) and 2, Leached soils (left)

Differences in geochemical transformation of carbonate and leached soils: The soils interlaid by compact bed rocks and having the entire soil formation to be concentrated within the erosion layer (No. 1-9, 2-8-2-10 in Table 2) possess special geochemical properties among 20 examined soils with different age. They are featured by high content of $CaCO_3$-in average 9.8% (over 17-26%). Then, the analysis of peculiarities was performed over 15 objects considered in the compositions of genetic soil types (Fig. 2).

However, these soils containing average amount of calcium carbonates within upper horizon 5.8% differ strongly on the $CaCO_3$ proportion in the soil and parent rock. The cinnamonic soils of dry forests and shrubberies on the eluvium and deluvium of bed rock occupy the SCC area of 46.5 ths. hectares, whereby correlation between carbonate and non-carbonate types is 69:31%.

According to soil development there will be changes in the thickness of soil profile and its separate horizons, degree of detrital material weathering, Fe release from the source minerals (growth of magnetic susceptibility), mineralogy of clay minerals. Thus, all morphological and material transformations can be represented as

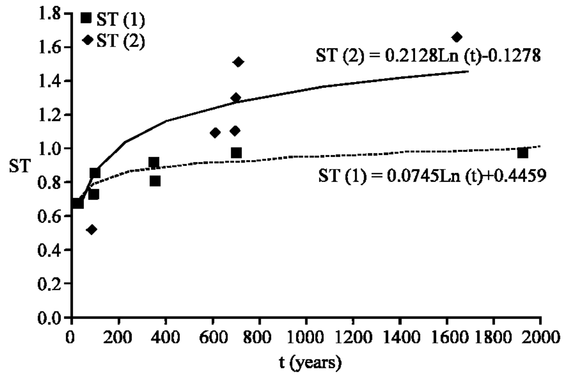

Fig. 3: Geochemical transformation index (ST) validation dependence in time (t, year): carbonate soils ST 1) and leached soils and ST 2)

a time function. Using elements grouping for stable and movable, the calculations by the index (ST_t) were performed according toEq. 2) for two genetic soil types (Fig. 3). The impact of alkaline geochemical barrier for the velocity of soil geochemical transformation reflects the differences in change rate of this process in due course of time (upon 100 year): the change rate of index ST(1) in average makes up 0.01/100 year and the change rate of index ST(2) 0.03/100 year (according to the equations on the Fig. 3). Thus, after the expiration 100 years the process of geochemical transformation passes in tree times more actively in the leached soils than in carbonate ones.

As to geochemical peculiarities, as it is shown on the dendrogram (Fig. 2), there are two groups selected differing by average Si/Pi value with regard to the calcium: in carbonate soils S/P = 2.2 and leached soils S/P = 0.8. Figure 3 demonstrated higher rates of even-aged soil transformation, if parent rocks were less carbonated, i.e. when their concentration correlation of calcium oxide within soil and rock would; S/P = 0.66±0.24.

Mixed-age soil objects presented in the Table 2 had that or those frequencies of higher or lower values of Si/Pi (with regard to a unit) in each of two groups. It allowed to determined its ensembles of stable (S/P>1) and movable (S/P<1) components in each of the group. Respectively, if calculating by the formula 2 as a stable component is referred to the carbonate soils Fe, Mn, Pb, Zn, Co, the movable component is Ti, K, Cu, Si, As, V, Ni, Sr, P and leached soils have its stable component to be Ti, Mn, Fe, Pb, Si, As, V, Zn, Sr, Co, P and movable is Ca, Na, K, Cu, Ni.

The group of carbonate soils under the average value of ST = 0.88 is the decreasing series of chemical elements (upon the correlation value Si/Pi >1): Ca>Zn>Mn>Pb>Fe>Na>Co. Wherein, calcium has values Si/Pi >2. Presentation about elements removal intensity from the upper soils horizon provides with a ranged increasing series of correlation values; S_i/P_i: Sr<V<Si<Cu = Ni<As<P<K<Ti. The group of leached soils under the average value of ST = 1.12 possesses a decreasing series of chemical elements (upon the correlation value S_i/P_i > 1): Pb>As>Mn>Zn>Ti>Co>Sr>Fe = V>Si. Wherein, the first four elements the correlation value is S_i/P_i >1.2. Presentation about elements removal intensity from the upper soils horizon provides with a ranged increasing series of correlation values; S_i/P_i: Ca<Na<P<Ni<Cu.

In general, P, Ni, Cu carrying out is peculiar for all Sub-Mediterranean soils and relative enrichment of upper soil horizons with Fe, Mn, Zn, Co, Pb. The relative mobility of trace elements in soils is of major importance with regard to their plant availability (Alloway, 1997) and translocation into food chains.

Evaluating negative impact of that or another chemical element, it is essential to consider the element finding in a specific geochemical situation. The soils investigated often possess faintly alkaline reaction of soil solution (pH = 7.3 (n = 33)), sometimes, average alkaline reaction (to pH(H_2O) = 8.2)) which may promote mobility in the soils of geochemical microelements associations: V, Zn, Co, Ni, Cu.

The peak values of geochemical soil transformation index are formed to the soil's age 400 years and relative decrease of values ST is marked to occur to 700 years, then there is a relative stabilization in the process of movable soil components from the upper horizons. It is notable that standard soils are characterized by the value of ST index being equal to 1.25-1.34 during the Holocene period.

As it was mentioned before in case more unfavourable bioclimatic situation as now, being created as 2500-1200 cal years BP (Cordova, 2011), the geochemical process within SCC soils should have been proceeding more actively. Thus, those soils (examined by us) being of the age more than 1700 year could save evidences of stronger geochemical transformation in the past. A comparative analysis of each of 15 S_i/P_i correlations with average values in its genetic soil groups has demonstrated that soils in the age 1700-10000 years differ by the most significant reduction in Ca, Sr, Na concentration of gross phosphorus.

Variation of microelements and biophile elements over time: Increase in soil formation duration determines the growth of total content of four microelements (Pb, Zn, Co, Cu) and such biophile elements as phosphorus and potassium. It is demonstrated by calculated values of microelements and biophile elements accumulation coefficient (K_S). The peak of this process falls at the soil's age of 6 years and then the accumulation process will stabilize. As it is shown for Chernozem carbonate soils (North-West Crimea) (Lisetskii *et al.*, 2011), dependency degree of horizon A geochemical maturity from the age demonstrates that the content of accumulated microelements, being diagnosed by soil formation, reach the peak when soil is 1400 year and then it decreases up to the period when soil reaches 2200-2400 years. It may be explained by the fact that after this time the process of intra profile redistribution of microelements proceeds more actively.

If comparing microelements accumulation intensity by two groups of soils (Fig. 2) the greatest degree of Pb concentration in leached soils is determined, Zn in both groups, they are notable conceded by Co (S/P = 1.1) and content of Cu varies from the soil age reaching the S/P = 1.28 peak in the standard soil (No. 2-11 in Table 2). It has been established before (Inrunak and Thorme, 1955) that minimal availability and solubility of Zn compounds correspond to pH 7.3-8.4 interval (these conditions completely correspond to the features of soils investigated by us (Table 2).

Copper is an elements of biogenic accumulation, its storing within humus horizons is caused by the fact that Cu absorption by organic substance is hardly washed away from the soil, and if pH increases the Cu concentration in the composition of organic-mineral complexes grows.

Some trace elements, including copper (Cu), zinc (Zn) are essential to plant growth in agroecosystems and some trace elements such as cobalt (Co) are not essential to plant growth but are required by animals and human beings (He *et al.,* 2005).

CONCLUSION

Yet, since antique times, wine growing had gained its development on the territory of the Crimean Peninsula and in the end of 18th-19th centuries from 30-40 grape varies already were grown here. Use of soil-climatic potential of the southern part of this region (the southern coast of the Crimea) is an especially valuable for growing sub-tropic fruit and nut-bearing crops: Fig, pomegranate, feijoa, persimmon, almond, etc. An informative analysis of pair bonding in microelements concentration and age of cinnamonic soils allowed determining the most stable accumulating elements: Pb, Zn, Co, Cu, as well as P and K. The investigation findings provide for forecasting the quickest loss of Si, K, Mn, Co in the arable Cambisols (in the carbonate types), Zn, K, Mn, Mg (in the leached soil types). Microelements carrying out with the harvest of agricultural crops are intensified when applying high doses of mineral fertilizers. Thus, application of microfertilizers is reasonable as it will promote in product quality improvement at the expense of balanced microelement composition and finally will positively influence upon the shortage control of those microelements in the food ration of animals and humans which participate in complex and physiological-biological processes and are unable to interchange. When growing up sub-tropic crops-the most valuable on the cinnamonic soils within the Sub-Mediterranean areas (fruit, nut-bearing, essential oil crops), apart from the list of five elements (Cu, Zn, Co, Mn, Mg) being applied in the practice of agrochemical servicing of arable lands, special attention in agro-ecological monitoring should be paid to control over the content of the quickest losing microelements; nickel and copper.

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