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# **Biogeochemical Features of Fallow Lands in the Steppe Zone**

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**Abstract**—Fallow lands in ancient agricultural areas of Northwestern Crimea which had experienced repeated phases of agricultural activity at different time periods (the Late Bronze Age, antiquity, and the last 150–200 years) have been studied. Differences in biogeochemical fluxes for virgin and fallow soils are analyzed from the chemical elements determining the composition of secondary clay minerals. The most informative and evolutionarily significant biogeochemical indicators of relict agricultural loads and duration of fallow periods are specified.

Keywords: secondary successions, fallow lands of different ages, agrogenic soils, old-arable lands, biogeochemical indicators

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### **INTRODUCTION**

Production process and pedogenesis are the main creative processes in the functioning of natural herbaceous ecosystems. In contrast to a separate investigation of these closely interrelated and interdependent processes, their conjugated study provides new information (Snakin et al., 2010). The soil is a provider (donor) and vegetation is a consumer (acceptor) of mineral elements, and their combination represents an integrated functioning system of ecosystem metabolism (Kerzhentsev, 2006). The quantitative assessment of ecology-soil relationships with consideration for the zonal-provincial and landscape features was substantiated (Dergacheva, 2009) as one of the most important and urgent problems of soil ecology. Based on analogies in biocenology, Vasenev and Shcherbakov (2001) distinguish evolutionary, successionary, and fluctuational changes and cataclysms.

The evolutionary approach to pedogenesis processes, which agrees with the new evolutionary view of vegetation changes, is supported in some recent studies of soil chronosequences (Huggett, 1998; Walker et al., 2010).

Soil features in diachronous series of postagrogenic (Lisetskii et al., 2015) and postresidential (Lisetskii, 2012; Lisetskii et al., 2013) landscapes and within ancient sacred sites (Lisetskii, 2012; Lisetskii et al., 2014) on the Crimea Peninsula were studied earlier under different soil-climatic conditions. In ecological terms, it is very important to reveal a correlation between the elementary soil processes and the factor conditions, which are controlled by both the periodicity of natural processes and the sequence of historical-geographical stages in the economic development of the area. In steppe ecosystems during the Holocene, the climatically controlled periods differed in the potential input of organic matter from leaf and root waste; in old-developed regions, they were repeatedly interrupted by agricultural stages with specific biogeochemical conditions developed in agrocenoses under some agrotechnological and reclamation practices.

The uniquely long history of agricultural development of the Crimean steppe opens up new opportunities for the joint study of the secondary succession of plants and soils (Whittaker, 1975; Mordkovich et al., 1985; Lisetskii, 1998; Vasenev and Shcherbakov, 2001; Wardle et al., 2009; Walker et al., 2010) in the series of agrogenic transformations, including their postagrogenic stages.

The aim of this work was to reveal biogeochemical features of fallow lands of different ages, including the uniquely long renaturation period in postantique agrolandscapes, with the substantiation of the most informative and stable geochemical indicators of soil memory.

# MATERIALS AND METHODS

Studies were conducted on two test areas— (1) Razdolnoe and (2) Saky—of the Tarkhankut Upland (Northwestern Crimea) (Fig. 1). In geobotanical and physicochemical terms, both areas belong to true steppes developed under insufficient moisture



Fig. 1. Region of study in Northwestern Crimea: (1) soil standard (virgin soil), (2) fallows of different ages (soil and root sampling sites), and (3) aboveground phytomass sampling sites.

conditions (the annual precipitation is 360–420 mm) and to one landscape: accumulation-denudation loamy loesslike upland with southern chernozems and soddy–calcareous soils under fescue–feathergrass vegetation with some petrophytic steppe zones.

Earlier geoarcheological studies substantiated the selection of representative plots for the study of fallow lands of different ages (20 to 2400 years old), including the prehistorical stages of the agricultural development of lands (Table 1). Of special interest are postantique fallow lands, which reliably were unplowed in the 18th–20th centuries; such lands are extremely rare in other antique colonization areas of the Northern Black Sea region.

During the antique period of land development in northwestern Crimea, Greek colonists in the 4th century BC saw not a virgin steppe but agrolandscapes already actively utilized by the settled aboriginal population. In 2007–2014, explorations in the catchments of the Donuzlav and Sasyk-Sivash lakes on the Tarkhankut Peninsula discovered more than 130 ancient settlements in the second half of the 4th century and 3rd century BC synchronous to Greek villas. Along with the largest antique center of Kalos Limen, no less than thirty antique Chersonese villas, including more than 20 villas near Kerkinitida, are known on the Tarkhankut Peninsula to date (Smekalova, 2010). In addition, 13 settlements of the Late Bronze Age and more than 5000 mounds are known in this region.

In the northern Black Sea region, a hot dry climate with strongly continental characteristics was established in the 3rd century BC after the relatively humid climatic period in the 6th–5th centuries BC (Vinokurov, 2004). In northwestern Crimea, the humid and moderate climate of the middle 4th century BC changed to a dry and hot climate at the end of this century. Several regular droughts occurred in the latter end of the 4th century BC and in the beginning of the 3rd century BC and probably resulted in the decline of agricultural settlements. This period was followed by a long period of dry and hot climate (310–280 BC).

An a priori reconstruction of the development history was proposed for each surveyed land plot on the basis of available archeological data and a historical-cartographic analysis (Table 1), and a hypothetical decreasing series of objects was formed in accor-

Object	Distance from the nearest	Current land	TPC,	Plant species	Historical reconstruction
Object	monument	Current land	%	per 1 m <sup>2</sup>	of development and fallowing
		Test area 1 (	Razdoln	oe)	
S4	At 147 m from a two-layer settlement (13th-19th centu- ries BC and the EIA) with double story yard	Postantique fallow in the massif of long fields (5 ha)	80	5	Plowland in the EIA, fallow of about 2300 years
\$3	At 216 m from S4	Fallow near a farm of the 20th century, cattle pasturage	95	4	Pasture in the LBA, plowland in the ancient times, pasture load in the middle 20th century
<b>S</b> 8	At 1.1 km from S4	Recent fallow	90	5	Plowland in the 19th-20th centu- ries, fallow of about 20 years
		Test area	2 (Saky)		
S19	At 305 m from the settlement of Tyumen' 2 (II century BC)	Intermound zone of 8 m in width (between mounds of the 4th century BC and the LBA)	90	4	Renaturation of scalped soil for a mound, about 2400 years and/or earlier
S17	At 373 m from the settlement of Tyumen' 2	Recent fallow	70	5	Virgin land plowed in the 1950s–1960s, fallow of more than 50 years
S15	At 12 m from the settlement of Tyumen' 3 (13th-12th centuries BC)	Old fallow, sheep pasturage	80	3	Yard agriculture and stock raising in the LBA (Sabatinovka culture), plowland in the 4th century BC, fal- low of about 2300 years

 Table 1. Characterization of the objects of study (2014)

(TPC) total projective cover; (EIA) Early Iron Age; (LBA) Late Bronze Age.

dance with the degree of their anthropogenic transformation: S15 < S4 < S8 < S3 < S19 < S17.

The aboveground grass layer was estimated during the period of its maximum development on record plots  $(1 \times 1 \text{ m})$ ; then, the samples were oven dried. The underground phytomass was determined by sampling soil monoliths of 1 dm<sup>3</sup> in the 0- to 10- and 10- to 20-cm layers in the end of the active vegetation of grasses. Plant roots were washed on a 0.25-mm sieve after repeated flotation; separated into rootstalks (>0.6 mm), active roots, and inactive roots; and weighed in the oven-dry state in accordance with the reported procedure (Utekhin and Hoang Tyung, 1976).

The concentrations of macro- and microelements in soils were determined on a Spectroscan Max-GVXray spectrometer according to the procedure developed for measuring the mass fractions of chemical elements. To improve the reliability of results, the data calibrated on the standard soil samples were compared in replicates. The determinations were performed for the upper (0- to 10-cm) and lower (10- to 20-cm on the average) parts of the A horizon, and the average weighted value was then calculated. From these data, the values of 37 geochemical ratios and coefficients were calculated (some of them are given in Table 2). The modification of coefficient  $K_s$  proposed by Shaw (1964) is related to calculating the product of the ratios of dispersed elements in the soil and the parent rock with the addition of biophilic elements using the formula for the geometric mean rather than the arithmetic mean.

Data on the A (0- to 36-cm) horizon of virgin soddy-calcareous soil from the northwestern Tarkhankut Peninsula ( $SQ_{st}$ ) were used as standard values of geochemically mature soil (Fig. 1). The profile was established on a plateaulike plot under a hairy feathergrass (*Stipa capillata*) community with the participation of herbs (no more than 10%).

A set of statistical methods was used to select the most informative biogeochemical indicators characterizing the effects of repeated and uniquely long stages of anthropogenic impacts and renaturation of soils and plants relative to virgin conditions. The relative dispersion measure of the *i*th attribute—coefficient of variation (V, %), which allows comparing sample groups from the general population—was used as the sensitivity criterion of geochemical relationships and parameters to agrogenic loads ( $K_i$ ). From statistical calculations for each  $K_i$  in the 0- to 10- and 10- to 20-cm layers of fallow soils of different ages (n = 12), low-sensitive attributes were preliminarily removed using the criterion value  $V \leq 10\%$  (low variation). The

Geochemical coefficient $(K_i)$	Coefficient calculation formula	Author, year
Potential soil fertility index	$FI = (CaO + MgO + 10P_2O_5)/SiO_2$	Taylor et al., 2008
Geochemical parameters of pedogenesis	Rb/Sr; Sr/Ba; Na/K; CaO/Al <sub>2</sub> O <sub>3</sub> ; Ti/Al; (K + Na)/Al	Eze and Meadows, 2014 (review)
Accumulation coefficient of microelements and biophilic elements (Si, P, K)	$K_a = (E_1 \cdot E_2 \cdot \ldots \cdot E_9)^{1/9}$ , where $E_i = S_i/P_i$ , and <i>i</i> denotes Ni, Zn, Mn, Pb, Cu, Co, Si, P, and K	Shaw, 1964 (authors' modifi- cation)
Coefficient of eluviation	$K_{\rm e} = \mathrm{Al}_2\mathrm{O}_3/(\mathrm{MnO} + \mathrm{CaO} + \mathrm{K}_2\mathrm{O} + \mathrm{MgO} + \mathrm{Na}_2\mathrm{O})$	Liu et al., 2009 (author's mod- ification)
Coefficient of mobility	$K_{\rm m} = \sum ({\rm Na}, {\rm K}, {\rm Mg}, {\rm Zn}) / {\rm SiO}_2$	Authors
Total heavy metals	HM = Co + Cr + Cu + Pb + Sr	_
Assessment of soil quality from the contents of essential macro- and microelements and useful elements in soils	$SQ_i = (B_1 \cdot B_2 \cdot \cdot B_{10})^{1/10}$ , where $B_1B_{10} - (K, Mg, Ca)$ ; (Mn, Fe, Ni, Cu, Zn); (Si, Al)	Authors Bityutskii, 2011
Soil bonitet	$B = 100 \cdot SQ_{\rm i}/SQ_{\rm st}$	Authors

Table 2. Main geochemical coefficients used for the diagnostics of agrogenic soil transformations

results were processed statistically using Microsoft Office Excel and STATISTICA software. Informative geochemical indicators of the agrogenic transformation of soils were selected by correlation, regression, and cluster analysis (Word method, Euclidean distance, values normalized by standard deviation).

#### RESULTS

#### Secondary Vegetation Successions

After the cessation of tillage, the adaptive transformation of the structure of restored steppe communities occurred syngenetically with the renaturation of soil. Comparisons with aboriginal communities (Lisetskii, 1998) revealed that the differences in the edificational structure of restored vegetation persist even after 16-35 centuries of self-development; therefore, long successions do not eliminate the differences in productivity caused by the ontogenetic maturity of soils. The formation of the series of agrogenic soil transformations should take into consideration that the periods of increased economic activities are chronologically related to the successions of natural vegetation and rotations of cultures, crops, and lands; therefore, the biogeochemical impact on the soil is variable at certain historical-geographical stages.

A study of recently abandoned agricultural lands in southern Ukraine (Bondarenko and Vasil'eva, 2008) showed that the flora of abandoned fields is supplemented with new, predominantly zonal anthropophilic species, by 20% when compared to that of plowlands, and the proportion of zonal steppe species on the abandoned fields increases 3 times: from 9 to 27%. In the region under study, the structure of the aboveground phytomass in the secondary successions on fallow lands of different ages differs from that of the aboriginal communities: the number of higher plant species on the fallow lands of different ages (Fig. 1, plots C2, C3) is 1.4 times lower than that on the virgin land (Fig. 1, plot C1), and the total aboveground phytomass dry matter is 1.6-2.0 times lower.

The highest proportion of steppe grasses, which pass from the rhizome-grass stage to the bunchgrass stage of demutation with the age of the fallow, is observed in the postantique fallow (*Stipa* sp., *Festuca* valesiaca Gaudin, *Bromopsis cappadocica* (Boiss. & Balansa) Holub) and recent fallow (*Stipa lessingiana* Trin. & Rupr., *Koeleria cristata* (L.) Pers.), while one dominant species (*Stipa capillata* L.) remains under virgin conditions.

As was shown earlier (Titlyanova and Sambuu, 2014), successions on all fallow lands relatively rapidly (for 17 years) result in communities whose species composition is similar to that of the original steppe phytocenoses; however, the structure of phytomass develops more slowly, especially in the underground zone.

The depositing of aboveground mortmass (R + SC) depends on the maximum reserve of green mass (F) and the decomposition rate of mortmass. The more active the production process (the relative measure of which is *F*) is and the lower the destruction rate is, the more the aboveground mortmass is accumulated. Under these conditions, the aboveground mortmass is maximal under virgin conditions (436 g/m<sup>2</sup>) and decreases on the fallow lands; its values on the recent fallows is 1.6 times lower than on the postantique fallow. The (R + SC)/F ratio reflects the relationship between the relative specific rates of the formation and destruction of plant material. Under virgin conditions, all structural components of the aboveground phytomass have the highest values. The postantique fallow is

		Aboveground	l phytomass	Under	ground phyt	omass in the layer,	cm
<b>O</b> bject <sup>a</sup>	<i>H</i> , cm	F + D	SC	0-10		0-2	0
		I' + K	50	living <sup>b</sup>	dead	living <sup>b</sup>	dead
		•	Test area	a 1 (Razdolnoe)			
S3	94	723.2	337.8	1273.7	1140.7	1556.3	1649.8
<b>S</b> 4	66	323.0	186.7	632.8	795.7	753.8	972.4
<b>S</b> 8	110	194.8	239.5	216.7(354.2)	529.3	328.5(415.7)	665.6
			Test a	area 2 (Saky)			
S19	40	134.4	68.0	1349.9(136.6)	1088.9	1508.2(136.6)	1355.8
S15	50	127.4	77.4	1956.2	959.2	2081.3	1196.9
S17	43	88.6	187.9 <sup>c</sup>	498.5(83.5)	786.6	709.1(83.5)	954.0

**Table 3.** Phytomass reserves  $(g/m^2)$  of higher plants under fallow conditions (October 2014)

(*H*) grass stand height, (*F*) green phytomass, (*R*) dead grass, and (*SC*) litter. <sup>a</sup> Plot locations are indicated in Fig. 1. <sup>b</sup> Mass of rootstocks (>0.6 mm in diameter) is given in parentheses. <sup>c</sup> Litter also includes sheep excrements ( $50.2 \text{ g/m}^2$ ).

characterized by the most active accumulation of aboveground mortmass at a smaller green mass. The destruction of plant material is most intensive in the recent fallow.

It was shown earlier (Snakin et al., 1991) that, although the primary production of two ecosystem types (absolutely protected steppe and scarcely exploited pasture) is significantly different (785 and  $389 \text{ g/m}^2$  annually, respectively), these ecosystems are very similar in content of decomposed plant material and the results of the annual cycle of humic substances. However, the time of the maximum input of plant carbon into the soil significantly differs in the intraannual dynamics: March on the virgin soil and October on the pasture.

For the petrophitic steppes of Crimea, a relationship was revealed between the peak on the flowering species curve and the interannual maximum of atmospheric precipitation (Golubev, 1978); therefore, it may be supposed that the maximum productivity of aboveground phytomass in Northwestern Crimea will be observed in late May-middle June. In fall (October), at the low pasturage of cattle on chernozemic soils, when Stipa capillata becomes predominant, the (F+R) mass is smaller than under virgin conditions by 55% (postantique fallow) and 73% (recent fallow) (Table 3). These differences obviously decrease under higher pasture load (sheep). An increase in the litter mass on the recent fallows compared to the postantique fallows is observed regardless the soil type and the pasture load. On chernozemic soils (plot 1), the mass of underground plant organs in the 0- to 20-cm layer of fallow soils makes up 54-44 wt % (depending on the fallow age) in the conventional aboriginal community (S3). On the soddy-calcareous soils (plot 2) under pasturage conditions, the mass of roots on the recent fallows is 42% smaller than in the quasi-climax ecosystem (S19).

# Biogeochemical Fluxes in the Soil-Plant System

The combination and contents of microelements largely affect many biochemical processes in the soil, including the accumulation, transformation, and transfer of organic substances in the ecosystem, because most microelements influence plants (Orlov et al., 2005).

The study of fallow ecosystems during the period of secondary successions in the dry-steppe zone (Egunova, 2011) showed that the aboveground phytomass and the mortmass that accumulated for 5-15 years contain 1.4–1.5 and 1.6–1.7 times more nitrogen and ash elements (Ca, Mg, P, K), respectively, than the roots. However, their amount is 3-16 times larger (Table 3) and the role of root waste in soil chemistry is more significant.

More favorable conditions in terms of NPK input into the soil develop in the fallow lands than in the virgin land (1.70 and 1.62 t/ha annually, respectively) due to the higher diversity of plant groups, despite the lower input of pant material.

It was found from the annual input of plant material with dominant species and the generalized data on their ash composition (Aidinyan, 1954; Bazilevich, 1962; Rodin and Bazilevich, 1965; Lisetskii, 1992) that the input of oxides determining the composition of secondary clay minerals (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO) decreases insignificantly under fallow conditions compared to the virgin land, although the inputs of  $Al_2O_3$  and MgO are higher and those of SiO<sub>2</sub> and  $Fe_2O_3$  are lower. Under virgin conditions, the biogeochemical activity of the dominant species (Stipa capil*lata*) expressed through the total input in the 0- to 20-cm layer with leaf and root waste (from the data in Table 3, the estimated transformation rates of plant material in long-term experiments (Lisetskii et al., 2011), and the averaged data on the ash composition) can be described as follows: Fe  $\leq$  Mg  $\leq$  Al  $\ll$  Si. For the fallow lands (Table 4), the biogeochemical features

	meters of fallow soils
•	e geochemical para
	Most informative
	Table 4.

0         0	1	S3			S4			Profi S8	ile and s	oil layer,	, cm S19			S15			S17	
0-10         10-20         0-10         10-20         0-20         0-10         10-20         0-20         0-10         10-20         10-20         0-10         10-20         0-10         10-20         0-10         10-20         0-10         10-20         0-10         10-20         10-20         10-20         10-20         10-20         10-20         10-20         10-20         10-20         10-20         10-20         10-10         10-10         10-10	2				2			2						2			2	
4.96         3.60         4.28         20.26         20.60         20.43         15.91         17.87         16.89         8.36         9.45         8.91         13.61         14.91         14.91         14.91           1         0.01         0.01         0.12         1.76         1.76         1.76         3.71         3.71         3.26         3.72         3.79         3.77           1         5.02         5.93         5.47         1.26         1.26         1.76         1.52         1.64         3.75         3.76         3.76         3.76         3.79         3.77           3.54         2.41         2.73         2.43         2.96         2.96         3.26         3.24         3.24         3.24         3.24         3.24         3.24         3.24         3.24         3.24         3.24         3.24	0 10-20 0-2	0-2	0	0-10	10-20	0-20	0 - 10	10-20	0-20	0-10	10-20	0-20	0-10	10-20	0-20	0-10	10-20	0-2
4         0.01         0.01         0.01         0.12         1.26         1.	4 11.38 10.	10	31	4.96	3.60	4.28	20.26	20.60	20.43	15.91	17.87	16.89	8.36	9.45	8.91	13.61	14.91	14.26
444         424         434         458         456         293         323         308         301         351         326         372         379         376           3         5.02         5.93         5.47         1.27         1.26         1.26         1.76         1.52         1.64         3.17         2.78         2.96         2.96         2.96         2.96           9         3.54         2.41         2.73         2.43         2.95         2.91         2.46         2.35         3.16         2.98         2.16         1.96         2.06           9         3.54         2.41         2.73         2.43         2.95         2.91         2.46         2.35         3.16         2.74         2.74         2.21           6         3.54         2.43         2.95         2.91         2.46         2.35         3.16         2.76         364         354         359           5         0.90         1.35         1.13         0.19         0.18         0.28         0.21         1.96         1.26         0.28         0.29         0.29         0.29         2.29         2.99         2.94         2.91           6         1.36 <td>3 0.04 0.0</td> <td>0.0</td> <td>4</td> <td>0.01</td> <td>0.01</td> <td>0.01</td> <td>0.12</td> <td>0.12</td> <td>0.12</td> <td>0.12</td> <td>0.13</td> <td>0.12</td> <td>0.04</td> <td>0.05</td> <td>0.04</td> <td>0.07</td> <td>0.08</td> <td>0.08</td>	3 0.04 0.0	0.0	4	0.01	0.01	0.01	0.12	0.12	0.12	0.12	0.13	0.12	0.04	0.05	0.04	0.07	0.08	0.08
35.025.935.471.271.261.261.761.521.643.172.782.982.161.962.0693.542.412.2132.932.932.912.942.353.162.963.593.542.412.2153.542.732.432.952.912.462.353.162.963.593.542.912.0153.1229830533334033634135034628027227636435950.901.351.130.190.180.190.280.240.260.580.510.500.260.2851.581.341.462.542.702.621.961.971.961.581.561.572.162.1941.161.251.200.800.790.791.020.971.911.961.931.0756.596.676.476.266.367.397.127.257.077.077.097.075959394918890104101102100100100100100100100100	9 491 475	475		444	424	434	458	455	456	293	323	308	301	351	326	372	379	376
3:54         2.41         2.73         2.43         2.95         2.91         2.46         2.35         3.16         2.96         3.29         3.54         2.41         2.21           312         298         305         333         340         336         341         350         346         280         272         276         364         359         359           312         298         305         333         340         336         341         350         346         280         272         276         364         359         359           0.90         1.35         1.13         0.19         0.18         0.28         0.24         0.26         0.58         0.21         2.70         276         364         354         359           1.58         1.34         1.46         2.54         2.70         2.62         1.96         1.96         1.58         1.56         1.57         2.16         2.23         2.19           1.16         1.25         1.20         0.80         0.79         1.96         1.96         1.56         1.57         2.16         2.23         2.19           1.16         1.25         1.20         1.96 <td>5 2.50 2.83</td> <td>2.83</td> <td></td> <td>5.02</td> <td>5.93</td> <td>5.47</td> <td>1.27</td> <td>1.26</td> <td>1.26</td> <td>1.76</td> <td>1.52</td> <td>1.64</td> <td>3.17</td> <td>2.78</td> <td>2.98</td> <td>2.16</td> <td>1.96</td> <td>2.06</td>	5 2.50 2.83	2.83		5.02	5.93	5.47	1.27	1.26	1.26	1.76	1.52	1.64	3.17	2.78	2.98	2.16	1.96	2.06
312         298         305         333         340         336         341         350         346         280         276         364         354         359           6         0.90         1.35         1.13         0.19         0.18         0.19         0.28         0.24         0.26         0.58         0.51         0.55         0.29         0.26         0.28           1         1.58         1.34         1.46         2.54         2.70         2.62         1.96         1.97         1.96         1.58         1.56         1.57         2.16         2.29         2.19           1         1.58         1.34         1.46         2.54         2.70         2.62         1.96         1.96         1.58         1.56         1.57         2.16         2.23         2.19           1         1.58         1.34         1.46         2.54         2.70         2.62         0.99         1.06         1.05	5 2.96 3.29	3.29		3.54	2.41	2.21	2.73	2.43	2.95	2.91	2.46	2.35	3.16	2.96	3.29	3.54	2.41	2.21
0.901.351.130.190.180.190.280.240.260.580.510.550.290.260.281.581.341.462.542.702.621.961.971.961.581.561.572.162.191.161.251.200.800.790.791.020.920.971.111.031.071.061.031.056.756.596.676.476.266.367.397.127.257.077.077.097.077.08959394918890104101102100100100100100100100100	3 289 301	301		312	298	305	333	340	336	341	350	346	280	272	276	364	354	359
1.58         1.34         1.46         2.54         2.70         2.62         1.96         1.96         1.58         1.56         1.57         2.16         2.33         2.19           1.16         1.25         1.20         0.80         0.79         0.79         1.02         0.92         0.97         1.11         1.03         1.06         1.03         1.05           6.75         6.59         6.67         6.47         6.36         7.39         7.12         7.25         7.07         7.07         7.09         7.07         7.08           95         93         94         91         88         90         104         101         102         100 <td< td=""><td>8 0.41 0.45</td><td>0.45</td><td></td><td>0.90</td><td>1.35</td><td>1.13</td><td>0.19</td><td>0.18</td><td>0.19</td><td>0.28</td><td>0.24</td><td>0.26</td><td>0.58</td><td>0.51</td><td>0.55</td><td>0.29</td><td>0.26</td><td>0.28</td></td<>	8 0.41 0.45	0.45		0.90	1.35	1.13	0.19	0.18	0.19	0.28	0.24	0.26	0.58	0.51	0.55	0.29	0.26	0.28
1.16         1.25         1.20         0.80         0.79         0.79         1.02         0.92         0.97         1.11         1.03         1.06         1.03         1.03         1.05           1         6.75         6.59         6.67         6.47         6.36         7.39         7.12         7.25         7.07         7.07         7.09         7.07         7.08           95         93         94         91         88         90         104         101         102         100	3 1.80 1.76	1.76		1.58	1.34	1.46	2.54	2.70	2.62	1.96	1.97	1.96	1.58	1.56	1.57	2.16	2.23	2.19
3         6.75         6.59         6.67         6.47         6.26         6.36         7.39         7.12         7.25         7.07         7.07         7.09         7.07         7.08           2         95         93         94         91         88         90         104         101         102         100 </td <td>0 1.08 1.1</td> <td>1.1</td> <td>4</td> <td>1.16</td> <td>1.25</td> <td>1.20</td> <td>0.80</td> <td>0.79</td> <td>0.79</td> <td>1.02</td> <td>0.92</td> <td>0.97</td> <td>1.11</td> <td>1.03</td> <td>1.07</td> <td>1.06</td> <td>1.03</td> <td>1.05</td>	0 1.08 1.1	1.1	4	1.16	1.25	1.20	0.80	0.79	0.79	1.02	0.92	0.97	1.11	1.03	1.07	1.06	1.03	1.05
2         93         94         91         88         90         104         101         102         100	2 7.23 7.2	7.2	3	6.75	6.59	6.67	6.47	6.26	6.36	7.39	7.12	7.25	7.07	7.07	7.07	7.09	7.07	7.08
	2 102 10	10	2	95	93	94	91	88	90	104	101	102	100	100	100	100	100	100

# BIOGEOCHEMICAL FEATURES OF FALLOW LANDS

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of oxides are slightly different: Fe < Mg = Al  $\ll$  Si, although the total inputs of these four elements into the soil are similar: 6.16 and 6.34 t/ha annually for the virgin and fallow land, respectively.

From the mineralogical composition in the A horizon of steppe soils (proportions of montmorillonite, vermiculite, and kaolinite with chlorite) and the contents of oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO) in each group of minerals, their relative fractions are calculated to be 46, 18, 12, and 24%, respectively. In the old-fallow soils, the corresponding values are 75, 17, 5, and 3% on the average for the 0- to 20-cm layer. In the postagrogenic fallow lands, the soil in the 0- to 20-cm layer is characterized by an increase in the proportion of silica and a decrease in the proportions of Al and Mg oxides compared to the virgin soil. These features are more manifested in the 10- to 20-cm layer compared to the 0- to 10-cm layer. Therefore, a dimensionless parameter such as the SiO<sub>2</sub>/ $\Sigma$ (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO) ratio is characterized by an increase in the postagrogenic fallow lands when compared to the renatured ecosystem (within the same test area, plots S3 and S19) of 0.3-0.4 for the 0- to 20-cm layer and 0.5 for the 10- to 20-cm layer.

Among the clay minerals, the highest content of  $SiO_2$  is in montmorillonite and the highest contents of  $Al_2O_3$  and MgO are in kaolinite and chlorite; therefore, it may be stated that this parameter is indicative of the active intrasoil weathering of the least stable minerals in the postagrogenic fallows. The degree of irreversible agrogenic transformation of the solid soil phase in the 10- to 20-cm layer is estimated at 17 (plot 1) to 21% (plot 2).

The dead plant material fulfills the role of a sorption, sedimentation, and mechanical barrier, where heavy metals are concentrated (Vedrova and Mukhortova, 2014). As for the soils, the anthropogenic input of pollutant metals can be due to the agriculture (under fertilizing conditions) and especially the impacts related to the vicinity of human settlements (combustion products etc.). The contents of heavy metals in the 0- to 20-cm layer (Table 4) are maximal in the recent plowland, where mineral fertilizers were applied (S8, the highest content of  $P_2O_5$ : 3.3 mg/100 g), and in the soils of plot 2, which is due to their high carbonate content. Increased contents of four heavy metals (except for Sr associated with Ca) in the 10- to 20-cm layer are found in the soils of the fallow lands occurring near the residential areas (S4 and S15) (Table 4).

# Biogeochemical Features of Fallow Lands of Different Ages

Ecological-genetic analysis can determine the capacity of postagrogenic soils to reflect, remember, and encode information on pedogenesis factors and processes in their properties, which is manifested in such soil characteristic as responsivity (Sokolov, 1985).

The comparison of old-fallow lands with their more mature analogues within each test area (S4 with S3 and S15 with S19) showed that, according to the accumulation coefficients ( $K_a$ ), all the fallows accumulate Ti, Fe, Si, K, Co, Cu, Pb, Zr, Rb, Cr, V, and Y and are depleted of Ca, P, Mg, Na, and Sr. The recently tilled soils differ in only one element, silicon, the content of which is 15–35% lower.

Kovda (1984) proposed the classification of the biogeochemical mobility of major pedogenesis products. In particular, nitrites and chlorites of alkalies and alkaline earths; Na, K, Mg, and Zn sulfates; and Ca and K carbonates were classified among the compounds of very high mobility. The last, fifth, group of mobility includes quartz and zircon, which are frequently considered marker compounds, against which the migratory abilities of other weathering and pedogenesis products are calculated. Using this classification, we developed a series of 15 coefficients, among which the mobility coefficient  $(K_m)$  optimal for the specific soil-climatic conditions was substantiated by comparison and substantial analysis (Table 2). If the  $K_{\rm m}$  value increases, this indicates the removal of compounds with the maximal biogeochemical mobility from the soil system. As was shown earlier (Lisetskii, 2008), this process accompanies the long-term agricultural load and persists in the soil memory for a long time. The main reasons for the agrogenically controlled formation features of soil morphology in the steppe zone are as follows: the water permeability of freshly tilled soil on the plowland is higher than that of a virgin soil, the wetting depth increases in spring; the period of soil water desuction is reduced, the more contrast drying results in a characteristic vertical fissuring of the humus horizon, water supply in fall becomes possible, the "dead" dry horizon disappears, a periodical percolative water regime is developed, and conditions are created for the rare (in extremely humid years) deep wetting of soils and sediments (Lisetskii, 2008).

The diagnostic potentialities of the mobility coefficient should also be manifested in its high values for objects with low removal rates (fallow lands renatured for a long time) if the impacts of the prehistorical stages, including the long-term agricultural loads, are ignored. An analysis of object groups on the test areas showed a steady regularity for most of the tested biogeochemical coefficients: the maximum removal of compounds with high biogeochemical mobility was noted for recent plowlands; durably renatured fallow lands are inferior, and the maximum proofs of agrogenesis persisted in the postantique fallows. It is noteworthy that the established coefficient  $K_{\rm m}$  is closely related to the CaO/ZrO<sub>2</sub> molar ratio (r = 0.81), which was recommended earlier (Gerrard, 1981) to be used as an indicator of chemical weathering, because cal-



Fig. 2. Dendrogram for the cluster analysis of fallow soils of different ages.

cium-containing protobase is more susceptible to weathering than zircon.

Under certain geographical differences between the test areas, the results of cluster analysis indicate the priority of such indices as the history and duration of anthropogenic transformations and fallow conditions in the classification of soil objects. It is important to note that the 0- to 10- and 10- to 20-cm soil layers of any object did not enter another cluster (Fig. 2). This fact reflects the genetic integrality of the upper part of humus-accumulative horizon and the paragenetic relation of its separate parts.

The old-fallow soils are in a peculiar class whose eight most informative geological parameters used in cluster analysis most strongly differ from the average values for the 0- to 20-cm layer. It should be emphasized that soils S3, S4, and S15, which could be subjected to preantique farming practices of the Sabatinovka-culture bearers in the 14th—9th centuries BC, developed under conditions of higher wetting and cooler climate.

According to the results of cluster analysis, the soils characterized by the lowest anthropogenic transformation expressed in their biogeochemical status (S19 and S17) are related on the low level of threshold distances. The interpretation of space images showed that object S17 is located at the periphery of the massif with traces of ancient land division. This massif characterizes plot S15, where low earth barriers (to 25 cm in height) of an ancient land-use system are still revealed under field conditions. The comparison of plots using the objective method of fallow dating based on the statistical processing of data on the volumes of stones sunk into the soil (Lisetskii et al., 2014) showed that the 50-year-old fallow (object S17) reliably (at P = 95%) differs from the old fallow (object S15), where stones are 16% deeper in the soil. However, only the integrated geochemical analysis proved the absence of preceding agricultural development of soil on object S17.

The arable soils without agricultural prehistory (S8) were more closely related to the low-transformed soils than to the old-fallow lands in biogeochemical terms. On the dendrogram, the typological group includes old-fallow soils if one (S4) or two (S15) stages of antique agriculture are objectively revealed for them or may be supposed with reason (S3), even when the objects are located on remote areas. The estimation of correlations from the eight geochemical parameters used in cluster analysis (Table 4) showed that the geochemical commonality of old-fallow soils is mainly determined by the Ti/(Al + Ca + Na + K), (Ca + Mg + K), and Ca/Zr ratios and the integral coefficients of eluviation ( $K_e$ ),

mobility ( $K_m$ ), and accumulation ( $K_a$ ). Thus, a higher accumulation of microelements and biophilic elements is observed in old-fallow soils than in other objects, which is confirmed by the lower biogeochemical mobility of the major pedogenesis products; however, the relict efficiency (due to agrarian loads) of the eluvial process persists: the values of  $K_e$  in the antique allotments exceed the mean level 2–3 times. In addition, the oldfallow soils are characterized by lower contents of essential macro- and microelements, useful elements, and the sum of five heavy metals; therefore, they are more leached of calcium carbonates (the CaO/ZrO<sub>2</sub> molar ratio is significantly lower) and some other elements of biological uptake.

The combinatory exclusion of each of the eight geochemical parameters proved the stability of the typological soil groups revealed by cluster analysis (Fig. 2). The fixation of evidences of geochemical transformation in soils due to agricultural loads of some duration results in the stable separation of soils into two large groups: objects retaining evidences of agrogenic evolution (S3, S4, S15) and objects with recent indices of agrogenesis (S8, S17) or without them (S19).

It was found using the parameters of the A horizon of virgin soil ( $SQ_{st}$ ) as a standard that the complete renaturation of the 0- to 20-m layer in geochemical terms occurred in the fallow soil (S3) and the soil abraded in ancient times (S19) (bonitet (B) = 102). The local diagnostics of residual anthropogenic transformation from the B values in the 10- to 20-cm layer showed the least completed renaturation of soil in objects S4 and especially S8.

## **CONCLUSIONS**

The reported estimates for the time of the complete restoration of plant communities during the virginization of fallows vary strongly, from 50 to 200 years. The quasi-climax state in the plant community is determined by the edaphotop (the ecosystem component with the longest characteristic time), which dictates the need for the diagnostics of the relict exhaustion of soils and renaturation processes using pedogeochemical indicators.

The biogeochemical features of the upper horizon of fallow soils are primarily determined by chemical elements such as Ca, Na, K, Al, Fe, Mg, Mn, and Zn, as well as the contents of accumulated microelements, biophilic elements, and some heavy metals. It is reasonable to include the above elements in the formulas for the calculation of geochemical relationships and the coefficients using stable elements in the diagnostics of elementary soil-forming processes.

The postagrogenic (completely unrestorable) transformation of the turbed soil horizons persists in the features of the soil solid phase for an unexpectedly long time and can be diagnosed using the set of complementary biogeochemical marker indicators. The analysis of geochemical parameters of the postagrogenic soil series in ancient agricultural regions of the steppe zone showed that the Ti/(Al + Ca + Na + K), SiO<sub>2</sub>/(Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + MgO), and Ca/Zr ratios; the sum (Ca + Mg + K) and that of five heavy metals; and the integral coefficients  $K_e$ ,  $K_m$ , and  $K_a$  are the most informative indicators of relict agricultural loads and fallow period duration. Thus, the old-fallow soils are characterized by an increased accumulation of micro-elements and biophilic elements because of the lower biogeochemical mobility of the main pedogenesis products, the retention of residual eluviation, and the higher degrees of leaching of calcium carbonates and some other elements of biological uptake.

The use of biogeochemical coefficients allows assessing the rate of agrogenically controlled transformations in the soil system, which are considered evolutionally significant impacts on the soil solid phase dependent on the duration of agricultural practices under the increase (decrease) of its effect by climatic periodicity.

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