Modeling of the Evolution of Steppe Chernozems and Development of the Method of Pedogenetic Chronology

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Abstract—Geoarchaeological methods were used to study chronosequences of surface soils in the steppe zone and to trace soil evolution during the Late Holocene in northwestern Crimea. It was found that the morphological and functional "maturity" of the humus horizons in steppe chernozems of the Late Holocene was reached in about 1600–1800 yrs. After this, their development decelerated irreversibly. The maximum concentration of trace elements accumulated in these horizons in the course of pedogenesis was reached in 1400 yrs. A new method of pedogenetic chronology based on the model chronofunction of the development of irreversible results of pedogenesis over time is suggested. Original pedochronological data and growth functions—the most suitable models for simulating pedogenesis over the past three thousand years—suggest that the development of morphological features of soil as an organomineral natural body follows growth patterns established for biological systems.

Keywords: geoarchaeology, chronofunctions, modeling, humus horizon, trace elements, steppe zone

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INTRODUCTION

Understanding the regularities of soil development over time is a fundamental challenge in pedology. Its practical application implies the possibility of controlling soil development, based on the principle of coevolution of the natural systems and human activity. The key problem is the development of reliable methods of soil dating. The creation of regional models of soil evolution with the prospect of their integration into universal models of pedogenesis is hampered by the scarcity of reliable pedochronological data. The significant potential of empirical data for dated soils buried in archaeological complexes, or formed on the surfaces of archaeological sites and features is still insufficiently used in soil science.

Soil studies are an important element of a new interdisciplinary science, geoarchaeology [62]. Depending on the particular research goals, such studies may be referred to as "pedoarchaeological studies" or as "studies in archaeological soil science" (or "archaeopedology"). Field studies by archaeologists in close contact with soil scientists have been performed in many regions. After the first general works published in the 20th century on the assessment of the rates of soil formation based on the historical method and on the radiocarbon dating of soil humus [1, 11, 12, 24, 34, 36, 39, 60], the number of pedoarchaeological studies has greatly increased; the pedoarchaeological method has become an efficient approach to studying soil evolution [7, 31, 33, 35, 40, 48].

In modern geoarchaeology, most attention is paid to the study of buried soils.[1] A combined study of buried soils and newly formed soils that have developed on the surface of archaeological sites contributes to our knowledge of the present and past; the retrospective approach allows us to reconstruct the conditions of soil formation in the past, until the point in time the soil was buried, whereas the modern state of the soils may be studied by the diachronic approach [9] via the examination of specific features of soil chronosequences. Twenty-five years ago, Gennadiev [5] noted that, in most cases, the study of surface soil chronosequences is limited to the qualitative information level. This statement remains true.

The aim of our work was to examine the course of pedogenesis over the past three thousand years using mathematical modeling based on a chronosequence of soils in northwestern Crimea dated by the historical and archaeological methods, duly accounting for previously obtained data on soil development in the steppe zone of the Crimean Peninsula.

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[1] It is worth noting that in the study specifically devoted to the application of pedoarchaeological methods [19], the soils that developed on the surface of archaeological sites are not mentioned at all.

OBJECTS AND METHODS

The Crimean Peninsula is an area with the centuries-old ethnocultural and economic history, making it possible to conduct geoarchaeological investigations in a broad chronological range. A large part of this region belongs to the Crimean steppe province, including the Tarkhankut Peninsula (Fig. 1) in the west and the Kerch Peninsula in the east. In the Greco-Roman period (6th century BC–4th century AD), the territories of these peninsulas were actively populated and developed by the Greeks.

This is the dry steppe region. The climate is moderately warm, with mild winters and droughty summers, and with an extended warm period (the duration of the frost-free period is 170–220 days, and the sum of active temperatures (>10°C) amounts to 3300–3500°C). Annual precipitation reaches 360–440 mm. In comparison with the central and eastern parts of the steppe zone, the Tarkhankut steppe is characterized by warmer winters, lower daily and annual temperature ranges, and more stable weather conditions because of its proximity to the sea and its remote position with respect to the Crimean Mountains [21].

According to the distribution map of energy expenditure for pedogenesis (calculated according to [4]), on the plains of the Crimean Peninsula, this varies from 800–900 MJ/m^2 per year in coastal regions to 1200 MJ/m^2 per year in the central region [16]. In Crimea, soils that developed on solid rocks and their colluvium occupy 33.7% of the territory. Calcareous chernozems and soddy calcareous (Rendzic) soils developed on the eluvium of calcareous rocks and chernozems that developed on loess sediments predominate. In calcareous chernozems, the CaO content of the humus horizon usually does not exceed 28%; in soddy calcareous soils, it reaches 30–37%. According to the first soil map of Ukraine compiled in agreement with the revised legend for the FAO soil map [32], Calcic Chernozems predominate in the Tarkhankut Peninsula, except for its western and southern parts, which show a predominance of Calcic Phaeozems. Stony steppes are widespread; about 63% of the territory is cultivated.

The studies of soil chronosequences were conducted during geoarchaeological fieldwork in 2011–2012 and were based on reliably dated (by archaeological methods) archaeological sites and on overgrown surfaces formed in the 14th–20th centuries AD (houses, trenches, etc.). The soils developed on the man-made earthen structures within archaeological sites were also examined.

For the purposes of our study, accurately dated and well-preserved soil chronosequences were important. Moreover, the soils of different ages had to be formed under similar conditions, that is occur on similar topographic elements (we studied the soils in autonomous positions), have similar parent materials, and developed under similar vegetation communities and mesoclimatic conditions. The study of archaeological sites of different ages made it possible to obtain sufficient pedoarchaeological data for statistical treatment. We used the same approach to describe the profiles of soils that developed on archaeological sites and features; in all, 24 geoarchaeological objects were investigated in northwestern Crimea. Our results were organized in a pedochronological database [3] that was used for modeling purposes. Data from other regions of the steppe zone of Crimea [14, 16] were used for comparison.

Fig. 1. Objects of geoarchaeological study on the Tarkhankut Peninsula: (*1*) soils on dated archaeological sites, (*2*) virgin soils, and (*3*) man-made earthen banks.

The statistical substantiation of the dependence of the thickness of the humus horizon of chernozems on the time of their formation (duration of pedogenesis) was based on the pedochronological study of soils in the anthropogenically disturbed landscapes with dated surfaces. The natural variability in the thickness of the humus horizon was assessed by the statistical method: for each object, the statistical sample was sufficiently large (as a rule, $n \geqslant 30$). The statistical samples were treated by the methods of descriptive statistics with calculation of the confidence interval at $P = 0.95$.

The soil color was determined in the dry state, using the Munsell color charts [49]. The chemical properties of the soils were analyzed by routine methods: the Corg content, by Tyurin's method; the fractional composition of humus, by Ponomareva–Plotnikova's method; the bulk nitrogen content, by Kjeldahl's method; the available P_2O_5 and K_2O, by Machigin's method. Standard methods were used to determine the content of exchangeable bases, the pH of water extracts, and the CO_2 of carbonates. An XRF spectrometer was used to determine the concentrations of trace elements. The coefficient of accumulation of trace elements (R_n) suggested by Shaw [54] was somewhat modified: we calculated the ratios between concentrations of trace elements in the parent soil (S_i) and in the parent material (P_i) with the use of the mean geometric values:

$$R_n = \sqrt[n]{\prod \frac{S_i}{P_i}}.$$

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

Substantiation of adequate models of soil development over time. For quantitative assessments and comparative analyses, prognostic models of soil development should include mathematical descriptions of soil characteristics (the dependence of the particular soil properties on the controlling factors) [23]. The state of a soil system may be described either via input–output signals (factors of soil formation–soil properties), or via macroparameters of the system (such as velocity and acceleration). The study of soil chronosequences with the development of the trend model of the formation of humus horizon makes it possible to calculate characteristic times and velocities of this process for separate stages of the evolution of soil profiles [15].

The pedoarchaeological method has certain advantages related to the accuracy of its estimates and the reliability of their interpretation, if we study chronosequences of surface and buried soils, rather than separate soils of different ages.

Dokuchaev's postulate about soil as a function of the five factors of soil formation was formulated in 1883; in 1927, Zakharov suggested its mathematical formalization [10]. As shown in [22], the well-known Jenny's equation [41] in the form suggested by Zakharov stands as follows:

$$S = f(cl, o, r, p, t, \ldots), \tag{1}$$

where S is the soil (or its properties), cl is climate, o denotes organisms, r is relief (topography), p is parent material, and t is time (age of the soil).

The concept of soil chronosequences was developed by Jenny [41], who formulated this as follows:

$$S = f\left(T_{cl,o,r,p,\ldots}\right), \tag{2}$$

where T is the time, during which the chronosequence of soils is formed.

The list of factors of soil formation may be further specified and complemented. Additional models [30] became more complex in terms of their evolutionary, landscape, and ecological aspects.

Jenny argues that the correct application of the concept of soil chronosequences is possible, if we study soil objects that differ in only one factor. In other words, the studied soils of different ages should be developed under more or less similar and stable conditions of pedogenesis. The independence of other factors from time, as suggested in Eq. (2), is relative. As suggested in [44], the group of spatially distributed factors of pedogenesis may be subdivided into factors subjected to ongoing changes over time (factors cl and o), and factors that specify the position of soils in space and remain relatively stable (p and r). Thus, according to the equation borrowed from [44] with some modification, the total transformation of a soil profile during the entire period of pedogenesis ($t = t_n - t_0$, where t_n is the present time and t_0 is the time of the beginning of pedogenesis) may be described in the following form:

$$S = \int_{t_0}^{t_n} f\left[cl(t), o(t), h(t)\right] dt \Big|_{p(t), r(t)}, \tag{3}$$

where $h(t)$ denotes human use of biological and land resources (vegetation burning, haymaking, pasturing loads, soil tillage, irrigation, application of fertilizers and ameliorants, etc.).

It has been justly noted [51] that, the major factors of soil formation are equally important, and their impact on pedogenesis may change over time, depending on soil age and the stage of soil development.

As shown in [56], Jenny distinguishes between the concepts of chronosequence (applicable when we discuss the relationships between soil properties and the relative age of the soils) and chronofunctions (when soil properties and the absolute ages of the soils may be quantified). The pedoarchaeological method makes it possible to apply chronofunctions to buried and surface soils of different ages, especially when we deal with soil objects formed in the second half of the Holocene.

Initially, soil chronofunctions were constructed as plots showing the character of changes in the soil properties over time; such plots were qualitative and rather hypothetical. Later, quantitative dependences of changes in the morphology and properties of the soils on soil age were found, based on empirical pedochronological data [26, 27, 29, 37, 38, 42, 52, 61, 63].

A review of a century-long experience in formalizing soil concepts through soil–factorial models [30] showed that qualitative models still predominate among the three typological groups of soil–factorial models (qualitative, quantitative empirical, and quantitative mechanistic models). In another review [44], more than 20 well-known models were subdivided into four groups, depending on the way in which they addressed the time factor. Most of these models are theoretical. Many of them are presented in the form of differential equations or integrals. Their practical application requires numerical solutions that use regional coefficients; they may be further specified on the basis of statistical treatment of empirical data.

The analysis of approaches to the development of chronofunctions of the processes of humus accumulation and the formation of humus horizons shows that various types of regression models may be applied to the analysis of statistical samples: linear, power, logarithmic, double logarithmic, second-order parabolic, third-order polynomial, exponential, and other functions have been tested. It is interesting that relatively simple approximation models are sufficient, if the analyzed pedochronological datasets are not large. However, the analysis of different types of equations [25, 28, 37, 47] for determining suitable chronofunctions indicates that nonlinear functions are best suited to long periods of pedogenesis associated with substantial empirical datasets.

It is interesting that as early as in 1883, Dokuchaev argued that "the rate of an increase in the thickness of chernozem cannot be proportional to time ... this increase does not proceed uniformly; it decelerates with time" [8, p. 390].

An important conclusion summing up different models was formulated in [37]: the development of soils over long periods follows the pattern characterized by the decrease in the rate of pedogenesis over time. Therefore, functions describing soil behavior over long periods should follow logarithmic or exponential patterns. The application of nonlinear functions may improve both the choice of adequate chronofunctions and our understanding of the real development of soil systems [53]. The formation of the humus horizon in the initial stages of pedogenesis may be described by the model that reflects a gradual increase in the rate of pedogenesis (proportional to the amount of organic matter entering the substrate in the course of the development of phytocenoses and an increase in soil biodiversity). Then, after reaching some maximum, the model should reflect a gradual deceleration of the rate of pedogenesis corresponding to the established equilibrium of the organic matter in the zone of the maximum concentration of soil biota in the substrate. Thus, we may conclude that the search for adequate chronofunctions is most promising among the group of S-shaped growth models. Such models have been developed to solve various problems of biology and ecology. Assuming that the regularities of soil formation are preserved at different stages of this process, the choice of a Gompertz function [35] seems appropriate for our purposes. The use of this equation makes it possible to outline key phases of the growth of the humus horizon in agreement with the following critical points on the curve: T1, the maximum acceleration of growth; T2, the maximum growth rate (the stage of mature soils), and T3, the minimum growth acceleration. The T1–T3 chronointerval corresponds to the characteristic time of growth processes.

Chronofunctions of changes in the thickness of the humus horizon of chernozems. Previous studies of pedogenesis on dated surfaces in Crimea [16] showed that the period of a sharp deceleration of the formation (growth) of the humus horizon and humus accumulation is observed after the soils reach the age of about 1100–1200 years. In general, the development of humus horizons (*h*) of Crimean soils is characterized by their relatively quickly reaching the state of quasiequilibrium with respect to the humus content. This is explained by the specific climatic conditions: the lengthy frost-free period favors the uptake of about 73–88% of annual precipitation by the soils; low evaporation and intense water infiltration through the soils increase the mobility of the newly formed soil organic matter.

A comparison of the average rates of the formation of soil humus horizons (Δh) in the Late Holocene for different soils [45] showed that southern chernozems and dark chestnut soils are grouped together with respect to this characteristic. According to Δh values, these soils head the list of zonal soils. They are followed by mountainous brown forest soils and by gravelly cinnamonic soils.

Data on the morphology and properties of soils formed on dated surfaces of archaeological sites and features are summarized in Table 1. On the basis of these data, we tried to develop chronofunctions for two soil parameters: the thickness of the humus horizon (A + AB) (*h*), that is a quantitative parameter that may be easily measured in the field, and the bulk elemental composition of the soil, which may be considered a qualitative parameter. The inclusion of both the humus horizon proper (A) and the transitional horizon (AB) in the quantitative parameter of the soil state being considered is explained by the fact that the A horizon forms much quicker, so that data on its thickness narrow the chronological range of the applicability of the pedochronological approach.

The pedochronological data shown in Fig. 2 makes it possible to obtain two types of chronofunctions showing the dependence of the thickness of the humus horizon (*h*, mm) on the time of soil formation (*t*, years) within the chronointerval $t = n \times 10^2 – n \times 10^3$ years:

(a) the exponential function

$$h = 800(1 - 0.913e^{-0.000234t}), \quad r = 0.98, \tag{4}$$

(b) the Gompertz function

$$h = 800e^{-e^{(0.785 - 0.000466t)}}, \quad r = 0.97. \tag{5}$$

Equations 4 and 5 describe the process when the impact of disturbing factors is minimal, that is when the surface of the developing soil is not subjected to erosion or alluviation.

Within confidence intervals, a group of curves reflecting intraregional differences may be defined. Thus, in the northwestern part of the Crimean steppes (on the Tarkhankut Peninsula), the soil formation process goes somewhat faster than in other steppe territories because of more favorable climatic conditions (Fig. 2). However, particular models will follow the same general pattern described by models 4 and 5.

The comparison of the specific calculated values for models 4 and 5, using the Kolmogorov–Smirnov

Table 1. Chemical properties of dated soils and their zonal analogues in the Tarkhankut Peninsula

No. (Fig. 1)	Archaeological site	Soil date (age)	Depth, cm	Munsell color	pH H_2O	Humus	$CaCO_3$	P_2O_5	K_2O	Exchangeable cations, cmol(+)/kg		
						%		mg/kg		Ca^{2+}	Mg^{2+}	Na^+
Virgin soddy-calcareous soil (Calcaric Phaeozem)												
S1	–	Holocene	0–36	10YR 5/3	8.4	4.2	36.1	5.2	170.7	18.50	2.68	0.28
			36–48	10YR 5/2	8.4	3.6	49.9	5.0	185.1	16.73	3.20	0.40
Virgin soddy-calcareous soil (Calcaric Phaeozem)												
S2	–	Holocene	0–24	10YR 7/3	8.3	3.4	59.5	11.7	458.4	10.20	2.20	0.80
			24–32	10YR 6/6	8.6	3.0	60.9	6.2	615.6	5.90	2.00	2.00
Recent soils												
S3	Earthen cover of a shed	47	0–11	10YR 6/5	8.3	8.2	39.1	31.2	706.5	13.90	1.55	0.60
S4	Trench	68	0–9.3	10YR 5/3	8.6	4.6	14.5	20.3	526.3	16.67	1.92	0.68
S5	Trench	68	0–12	10YR 7/3	8.7	3.7	70.4	8.3	411.6	9.51	1.46	0.60
Chernozemic soils developed on loose substrates												
S6	Necropolis	14th cent AD	0–20	10YR 5/3	8.0	6.9	7.0	5.5	849.6	23.10	5.40	0.55
S7	Excavation Kelsheikh 1	ca. 270 BC	0–18	10YR 4/2	8.2	7.5	12.8	13.6	402.6	21.55	1.70	0.60
			18–43	10YR 4/2	8.5	5.9	17.0	12.1	285.4	20.23	1.28	0.60
R1	Earthen bank, Kelsheikh 1	ca. 300 BC	0–24	10YR 5/3	8.1	5.7	5.8	0.9	258.0	24.15	5.20	0.60
			24–46	10YR 5/2	8.0	6.2	4.4	0.3	248.0	25.99	4.95	0.60
			[A + AB], 46–50	10YR 5/2	8.2	5.5	5.4	0	167.6	23.51	3.00	0.60
S8	Panskoe I	IV–270 BC	0–21	10YR 4/2	8.1	4.2	22.4	12.2	755.8	12.20	1.20	0.20
			21–34.5	10YR 4/2	8.1	3.4	19.2	12.8	568.4	12.80	1.60	0.30
S9	Settlement S11-029	ca. 270 BC	0–28	10YR 5/3	8.4	6.1	16.6	11.7	499.9	16.29	1.58	0.90
R3	Earthen bank over grain pit	ca. 270 BC	0–13	10YR 5/3	8.3	5.4	3.2	1.6	228.4	23.62	2.97	0.95
			13–33	10YR 5/2	8.4	5.0	0.7	0.8	184.5	25.18	2.83	0.95
			33–48	10YR 5/4	8.3	5.4	3.2	1.6	228.4	20.84	3.86	0.80
S10	Ak-Sarai	1st cent AD	0–14	10YR 5/2	8.0	7.7	10.0	62.3	1813.0	19.53	10.80	0.60
			14–34	10YR 5/2	8.1	6.1	12.1	64.7	1363.5	20.17	5.10	0.70

Table 1. (Contd.)

No. (Fig. 1)	Archaeological site	Soil date (age)	Depth, cm	Munsell color	pH H_2O	Humus	$CaCO_3$	P_2O_5	K_2O	Exchangeable cations, cmol(+)/kg		
						%		mg/kg		Ca^{2+}	Mg^{2+}	Na^{+}
S11	Dzhangul	4th cent BC	0–20	10YR 5/3	7.9	8.7	36.4	8.1	737.2	19.71	3.60	0.60
			20–38	10YR 5/3	8.0	6.0	43.9	1.8	473.6	18.47	2.55	0.50
Soddy-calcareous soils												
S12	Kalos Limen	3rd cent AD	0–22.5	10YR 6/2	8.8	7.1	45.6	167.6	1061.8	11.03	2.92	0.68
S13	Karadzha settlement	3rd cent AD	0–7	10YR 6/2	8.4	9.6	34.6	215.7	1119.5	14.91	1.40	0.60
			7–21	10YR 6/2	8.3	6.3	34.2	143.4	1213.0	14.18	1.49	0.70
R2	Land-division wall	270 BC	0–20.5	10YR 6/3.5	8.5	4.5	31.0	14.0	423.6	16.98	1.37	0.60
			20.5–51	10YR 5/3.5	8.6	3.8	27.0	6.6	299.1	16.46	1.70	0.60
S14	Kelsheikh 1, house H2	ca. 270 BC	0–25	10YR 3/2	8.3	9.0	6.3	8.9	615.9	24.74	3.06	1.00
			25–35	10YR 3/2	8.0	5.4	13.8	2.7	405.2	24.83	2.64	1.00
			35–47	10YR 5/2	8.0	4.8	16.5	1.3	355.2	24.09	3.39	1.00
S15	Settlement S11-029	270 BC	0–27	10YR 5/3	8.4	6.6	23.6	12.4	310.5	19.89	1.92	0.90
Soils on ashy deposits												
S16	Kalos Limen	1st cent AD	0–22	10YR 6/2	8.9	4.9	37.5	167.1	1015.3	9.62	2.97	1.30
S17	Kunan	2nd cent BC	0–19	10YR 5/2	7.9	9.1	34.7	225.6	2108.3	23.28	6.00	0.50
			19–38	10YR 5/1	8.1	7.1	18.9	278.4	1547.3	21.45	5.40	0.60
S18	Settlement S11-022 (Chernomorskoe)	15th–12th cent BC	0–18	10YR 5/2	8.2	8.4	9.1	103.9	455.2	24.35	2.50	0.45
			18–50	10YR 6/2	8.2	6.5	12.8	139.0	609.9	21.62	1.70	0.70
Intrazonal (salt-affected) soils												
S19	Yarylgach 2	7th–9th cent AD	0–15.2	10YR 5/3	9.0	3.0	27.7	4.7	1237.3	4.70	8.70	9.70
			0–21.8	10YR 5/3	9.3	1.6	38.1	2.3	1084.8	2.30	2.90	10.6
S20	Settlement on Cape Oirat	18th cent AD	0–17	10YR 6/2	8.9	3.3	35.8	7.3	1644.8	7.30	3.20	5.30

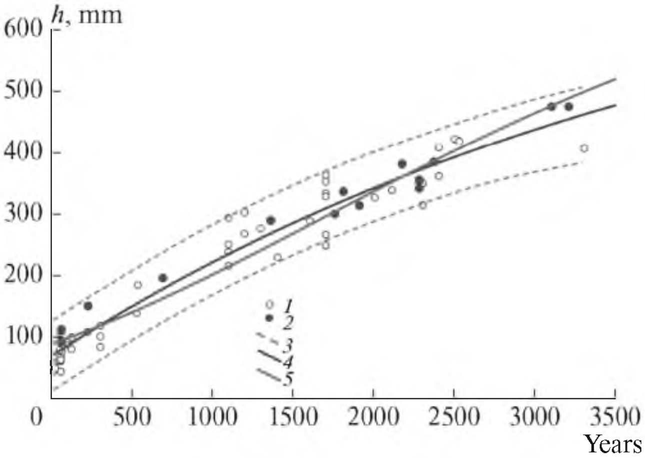

Fig. 2. Chronofunctions of changes in the thickness of the humus horizon of chernozems developed on loamy substrates over 3500 years. Empirical data were obtained by the authors in the course of geoarchaeological investigations of dated archaeological sites in (*1*) steppe Crimea and (*2*) the Tarkhankut Peninsula; (*3*) confidence interval ($P = 0.95$). Two types of equations modeling process $h = f(t)$: (*4*) Jenny's (exponential) function, and (*5*) Gompertz (double exponential) growth function.

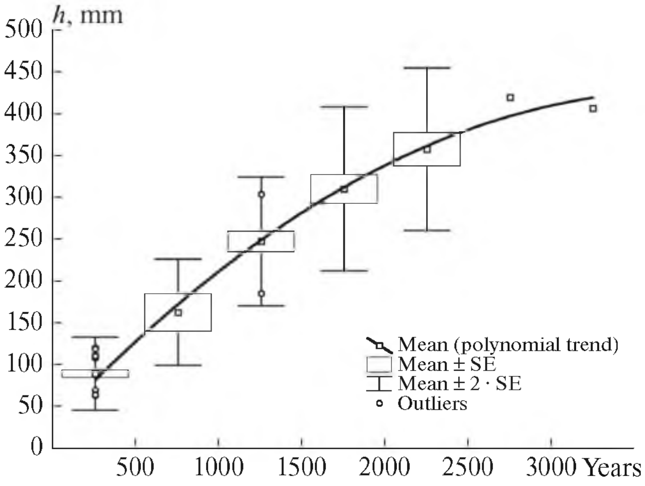

Fig. 3. Statistical characteristics of the chronosequence showing the dependence of the thickness of the humus horizon on soil age.

criterion [43], showed that the difference between these models (the Jenny and Gompertz models) is insignificant at $P = 0.95$.

The analysis of mathematical functions approximating the development of pedogenetic features makes it possible to identify diachronous regularities of pedogenesis. An analysis of the Gompertz function [35] offers valuable pedogenetic information. As noted above, this function is characterized by three "critical" points indicating radical changes in the dynamics of growth processes. The determination of these points is based on finding the first and second derivatives of the function, that is the velocity and acceleration of the growth.

Figure 3 presents variations in the dependence of the thickness of the humus horizon of Crimean chernozems on the time of soil formation. They illustrate different ranges of variability for separate chronointervals. The analysis of the curve approximated by a polynomial function and the analysis of average values for separate chronointervals attest to a gradual deceleration of the growth of the humus horizon over time.

The maximum growth rate is observed in the first decades of soil formation. It reaches 2–4 mm/year. During the next stage, whose final point is determined by the position of point T2 on the Gompertz function (1252 years), the soil reaches the mature state. After this stage, the rate of the growth of the humus horizon slows, provided that the conditions for soil formation (soil-forming potential of the environment) remain relatively stable or are subjected to minor fluctuations only. The position of point T3 specifies the time when the minimum growth acceleration is reached. For the analyzed curve, this time is equal to 3750 years; by that time, the thickness of the humus horizon reaches 546 mm. Thus, for chernozems of the Crimean steppe zone, the duration of the major stage of the increase in the thickness of the humus horizon is estimated at 3650–3700 years.

The dominant processes of the Subatlantic period (*cal* 2.8 ka) were soil leaching and humus accumulation [2]. The results of our modeling suggest that under the relatively stable climatic conditions of the Late Holocene, the morphofunctional maturity of the humus horizon of steppe soils was reached in about 1600–1800 years (taking into account model error). After this, the acceleration of growth processes becomes negative, as described by the Gompertz function.

The pedochronological method of soil dating. The problem underlying the study of soil development over time, based on archaeological information, was formulated by Ruprecht in 1866 [18]. He suggested that the archaeological dating of steppe kurgans could be used to determine the age of the soils. Later (in 1914), Gorodtsov used the method based on comparing the humus horizons of paleosols to date kurgans [6]. If geoarchaeological studies result in the development of reliable chronofunctions describing irreversible changes in the genetic properties over time, the problem of dating soils that developed on the surface of human-made structures will also be solved [59].

In a general form, based on chronofunction (4), an equation for the pedochronological dating of the surface of archaeological sites may be obtained:

$$t = -\frac{\ln(1 - h/h_{\lim}) + k}{\lambda}, \qquad (6)$$

where $h_{\lim}$ is the limiting thickness of humus horizon, k is the parameter characterizing the initial conditions of the growth of the thickness of the humus horizon h, and λ is an empirical coefficient of the nonlinear regression, whose dimension is inverse to time (1/year).

The real variability in the thickness of humus horizon h on archaeological sites makes it impossible to obtain reliable dates with an accuracy greater than ±52 years at $\alpha = 0.05$, ±68 years at $\alpha = 0.01$, and ±87 years at $\alpha = 0.001$. The use of the pedoarchaeological dating method based on Eq. (6) allows us to obtain relatively exact dates for archaeological objects in the range from the 7th century BC to the 15th century AD. When correctly used, this method may give even more accurate results than more costly analytical methods. This is related to the fact that soil morphology (in particular, the thickness of the humus horizon) deals with the features acquired by the soil in the course of pedogenesis, whereas many functional soil features, including the content and the age of the organic matter may be partly inherited from the parent material, especially if we deal with cultural layers. A specific feature of pedoarchaeological dating is that this method gives us information on when the human activity at particular sites stopped.

With regard to the area of our studies, Eq. (6) estimating the time elapsed since the beginning of pedogenesis atop the Iron-Age archaeological sites may be presented in a simpler form:

$$t = \frac{\ln(1 - h/800) + 0.156645}{-0.000190775} \tag{7}$$
$$= (-5241.777\ln(1 - 0.00125h) - 821.098) + \tau,$$

where τ is the expert-based estimate of the initial period of pedogenesis under the pioneer plant communities developing on the newly exposed substrate (in our case, this period lasts no more than 4 years).

Equation (6) ensures the most reliable results of soil dating for soils that are 200 to 2500 years old. This method was verified at two key sites in the area of ancient settlements of Panskoe I and Kelsheikh 1, which ceased to exist about 270 BC [57, 58].

According to the two statistical data samples for the thickness of the humus horizon at these sites ($n = 26$), the difference between humus horizons is insignificant: $H \pm t_{05}S_x = 358$ (355÷360) and 356 (352÷360) mm, respectively. The use of Eq. (7), based on the calibrated curve for the Tarkhankut Peninsula, gives us the age of corresponding soils that are about 2269–2293 years old, that is the soil formation on these sites began 260–280 BC, which is very close to the date established archaeologically.

We also studied structures that did not contain artifacts: an earthen bank at Kelsheikh 1 settlement (R1) and a system of land-division walls 14 km west of it (R2–R3). At present, earthen land-division walls have a width of 3.7 m; their relative height is about 16–17 cm. The first wall (R2) is found on a gentle slope of a ravine; its continuation (R3) was traced on the residual elevation between two erosional cuts that have reached the level of the hard limestone plate. Thus, such a wall could not have emerged during the recent stage of agricultural development of this territory (in the 18th–20th centuries). It is certainly more ancient. On wall R2, the newly formed soil is slightly thicker (by 1.4–2.1 cm) than the soils (soil humus horizons) formed on the cultural layers of ancient settlements. The humus horizon on wall R3 is 4 cm thinner than that of the soils developed on the cultural layers. Notably, wall 3 occurs in a position that is potentially subject to erosion.

According to Eq. (7), wall R1 was formed in the first half of the third century BC, and ridge R2 was formed in the second half of the fourth century BC. Taking into account the local environment, we may conclude that these walls were shaped no later than the very end of the fourth / the beginning of the third century BC.

While dating soils developed on the humified material of the land-division walls, one should keep in mind that such forms of microtopography may be subject to denudation. At the same time, the use of soil as construction material when the development of a new soil profile takes place within the thickness of the old soil profile without obliterating it leads to the formation of thicker humus horizons, compared to those that developed atop cultural layers of archaeological sites. This may be explained by the applicative soil profile inheriting the material already transformed by previous pedogenesis. Thus, the development of humus horizons proceeds somewhat faster. The processes denuding the surface and regenerating the soil profile work in opposition and can compensate for one another. However, this "autocompensation" proceeds differently, depending on the specific conditions.

In this context, the dating of soils developed on the humified material of the earthen structures requires certain corrections. We suggest that such corrections may be based on additional field studies and the results of chemical analyses. Data on soil morphology should be supplemented with data on soil chemistry. At the top of the studied wall, the total thickness of the humified layer (including the newly formed humus horizon and the buried humified material used in the construction) varies from 36 to 47.5 cm. In the field, it is difficult to separate the newly formed humus horizon from the buried humified material. The boundary between them may be found only through very thorough studies of the soil morphology, including variations in the color of the soil mass, soil structure, and orientation soil aggregates. In the dry state, the lower part of the newly formed humus horizon and the upper part of the underlying humified material differ in their colors by one or even a half level of lightness (value) and chroma. Usually, the lower layer of the newly

Table 2. Soil properties near the boundary between the newly formed soil and the buried soil (earthen bank at Kelsheikh settlement, early 3rd century BC)

Parameter	Horizon; sampling depth, cm	
	A, 34–37	[A + AB], 37–40
Munsell color	10YR 4/2	10YR 5/2
C org, %	2.22	1.66
N, %	0.27	0.19
C/N	8.3	8.9
C ha	19.14	10.79
C fa	40.54	34.17
C ha/C fa	0.5	0.3
Nonhydrolyzable residue	59.46	65.83
HA 2	5.85	0.55
FA 2	6.54	4.83
Type of humus	Humate–fulvate	Fulvate

formed soil is a half or one chroma more yellowish and one level lighter.

Three-centimeter-thick layers immediately above and below this boundary clearly differ in the contents of nitrogen and organic matter; they also differ in the qualitative composition of humus (Table 2). The calculation according to Eq. (6) allows us to estimate the age of this boundary, that is the age of the bank: it must have been constructed no later than the middle of the third century BC.

The soil buried in the body of the bank ([A + AB] horizons) differs from the newly formed soil (A + AB horizons) in a number of chemical properties (Table 3). Thus, the content of nonhydrolyzable residue (the humin fraction of humus) in the buried soil is 1.5 times higher; this soil is richer in CaO and in Sr (an element often associated with Ca). The levels of fulvic and humic acids are lower than those in the newly formed soil. The buried soil is characterized by the fulvate type of humus, and by the low C/N ratio (5.4). The content of the second (Ca-bound) fractions of the humus of buried soil is lower than that of the humus of the newly formed surface soil; the content of the third fraction of humic acids (the fraction that is presumably bound to sesquioxides) in the buried soil is also lower.

Specific features of the chemical and geochemical characteristics of newly formed soils in archaeological landscapes. Other soil characteristics than morphology also change over time. In order to improve the reliability of pedoarchaeological dating based on the thickness of soil humus horizons, other time-dependent soil properties may be explored.

The soils of the Early Iron Age that developed on the eluvium of calcareous rock are characterized by alkalinity (pH 8.5–8.8 compared to pH 8.3–8.4 in virgin soils); their Corg content is 2% higher than that of virgin zonal soils [46] and reaches 4.2%. The content of available P_2O_5 in these soils is relatively low (3–14 mg/kg), close to the range typical of virgin soils (5–12 mg/kg). The level of available phosphates in the plowed, soddy-calcareous soils of the Tarkhankut Peninsula is very low (4.0 ± 2.0 mg/kg) [17]. In contrast, the content of available K_2O in the newly formed soils is high 401 ± 122 mg/kg; in the background virgin soils, the content of available potassium is highly variable (171–458 mg/kg). In the plowed soddy-calcareous soils, the content of available potassium in the upper 30 cm is generally lower (156 mg/kg) [17].

The soils of the Early Iron Age that developed from loamy parent materials contain about 3.5% of Corg content in the humus horizon; the P_2O_5 content is 11.8 mg/kg, and the K_2O content is 577 mg/kg (in the full-Holocene soils, it is about 300–390 mg/kg).

In Crimea, a specific type of parent materials is represented by ash deposits that predominate the composition of cultural layers of Bronze and Early Iron age settlements. The chemical composition of the ash is closer to the chemical composition of loess than to the chemical composition of limestone eluvium. However, when compared to loesslike loam, this ash is richer in Sr (by 68 mg/kg), Zn, and Pb and contains smaller amounts of Mn, Cu, V, and Cr. The soils from archaeological sites that developed on ashy substrates have specific chemical properties: the Corg content in the A horizon reaches 4.6–5.2%; the levels of P_2O_5 and K_2O are 171 and 1162 mg/kg, respectively; among the exchangeable bases, the portion of Mg^{2+} is high.

A comparison of two dominant types of widely distributed parent materials in the Tarkhankut Peninsula—loess-like loams and calcareous rock eluvium—reveals that the loams (usually, silt loams and clay loams) differ from the limestone eluvium in their higher levels of Mn, Sr, Zn, Cu, Ni, Cr, Si, Pb, and Co

Table 3. Properties of the newly formed soil, and the soil buried under the bank the beginning of the 3rd century BC

Parameter	Horizon; sampling depth, cm		
	A, 0–24	AB, 24–46	[A + AB], 46–50
Munsell color	10YR 5/3	10YR 5/2	10YR 5/2.5
C org, %	0.92	1.76	1.26
C/N	5.1	13.2	5.4
C ha	21.52	19.38	4.21
C fa	30.54	25.23	18.49
C ha/C fa	0.7	0.8	0.2
Nonhydrolyzable residue	47.94	55.39	77.30
HA 2	7.94	3.98	0.08
HA 3	11.30	14.66	2.86
FA 2	9.35	8.24	0.71
Type of humus	Fulvate	Humate–fulvate	Fulvate
$CaCO_3$, %	5.8	4.4	5.4
SiO_2, %	49.66	46.97	43.47
CaO, %	5.23	5.16	8.03
Sr, mg/kg	125	139	144
pH	8.1	8.0	8.2
K_2O, mg/kg	258	248	168
P_2O_5, mg/kg	0.9	0.3	0

(the elements are listed in order of decreasing concentration). Calcareous rock eluvium is richer in Ca (by 10%).

The soils of the Early Iron Age that developed on these types of parent material in the areas of archaeological sites are also characterized by considerable differences in their bulk element composition. The R_n coefficient of the soils developed from the loamy cultural layer was calculated for the nine most informative elements (Mn, Zn, Cu, Pb, Ni, Si, Co, P, and K); in the soils developed on the calcareous rock eluvium, it was calculated for six elements (Mn, Zn, Pb, Ca, P, and K).

The cluster analysis of the data on the levels of elements typical of both types of parent materials (Ca, Zn, Pb, P, and K) showed that their initial grouping into clusters reflects either the territorial proximity of the studied objects, or their close ages. The type of parent material cannot be considered an unambiguous criterion for clustering. Clear separation of the clusters confirms the validity of coefficient R_n.

Relationships between the morphostructural and morphofunctional structures of soil systems. An increase in the thickness of the humus horizon is inevitable, if soils are developing in automorphic positions with minimal rates of denudation processes. If we consider soil properties that develop at different rates depending on the age of the soil, we may assume that the functional maturity of this soil (its chemical and mineralogical composition) is reached when its morphofunctional growth slows. By analogy with biological objects, we may apply the concept of ontogenesis [35]. This establishes the possibility of applying other biological categories in the study of soil age. Thus, we may distinguish among young, mature, and senile soils [50].

In soil ontogenesis, active accumulation of organic matter at the stage of fast growth is replaced by the extensive growth of the humus horizon, related to stabilizing organomineral soil complex upon its reaching the quasi-climax stage. The boundaries between these stages may be specified during the analysis of the sigmoid-type (Fig. 2) functions [35]. Two critical points corresponding to the maximum and minimum acceleration of the process should be found.

Various soil properties (e.g., the levels of organic matter, clay fraction, or $CaCO_3$) reach a maximum in their development; after this, the levels reached tend to drop. Such a lowering has an ontogenetic nature, that is it is unrelated to changes in the bioclimatic conditions. This was demonstrated by Jenny in his hypothetical soil chronosequence [41, p. 242]. Specifically, Jenny suggested that maximum humus accumulation would be reached in about 5000 years.

For steppe-zone chernozems, it has been established [14] that until they reach the age of 1700–1800 yrs the rate of humus accumulation (the rise in the humus content) is greater than the rate of the downward growth of the humus horizon. Chernozems of that age have a humus profile that is about 32–33 cm thick.

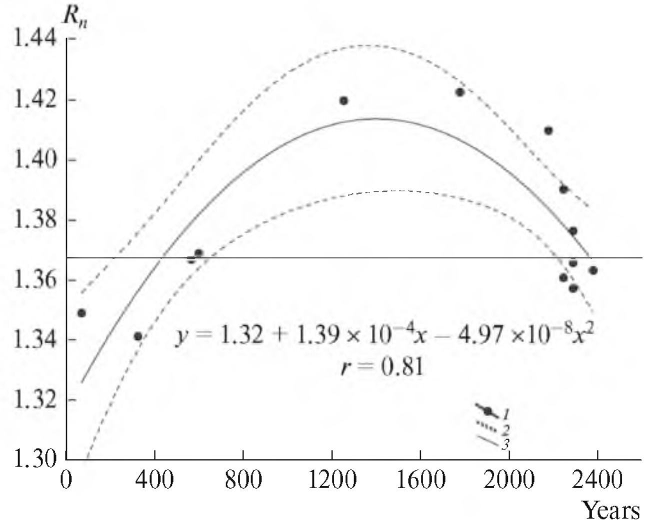

Fig. 4. The dependence of the geochemical maturity of soils as determined from the values of the coefficient R_n (according to the dates of archaeological sites on the Tarkhankut Peninsula). The straight line represents the mean zonal value of R_n (1.368 for full-Holocene soils).

This layer is most saturated by plant roots. Following this period, the morphostructural organization of the profile becomes more complicated, owing to the activation of other pedogenetic processes, such as leaching and migration of humification products.

In our study, we used the coefficient of accumulation of trace elements in the soils (R_n) to measure the geochemical maturity of soil profiles. We found that the values of this coefficient in the A horizon (Fig. 4) reach their maximum in about 1400 years. After this, they become lower, until the soil age reaches 2200–2400 years. This lowering may be explained by the activation of the processes of redistribution of trace elements in the soil profile.

According to the approximation model (a second-order polynomial, $y = c + bx + ax^2$ was used), it is possible to find the coordinates of the peak ($x = -b/2a$), which correspond to a soil age of about 1400 years. Thus, the accumulation of trace elements in the A horizon of soils is not permanent; as does the humus content, it reaches some maximum. After this, humic substances are renewed rather than accumulating further. The renewal of humic substances limits the applicability of the radiocarbon method for soil dating [13]. In our study, we considered stable and conservative properties of the soil system that reflect the integral result of the pedogenetic processes from the zero moment to the moment of observation. Such properties were referred to as "soil memory" (pedomemory, pedorecord) [20]. The soils from archaeological sites may be arranged in chronosequences. By modeling, we obtained a series of chronofunctions for separate, elementary pedogenetic processes. Such chronofunctions may become an important tool in multidisciplinary geoarchaeological studies of the objects of cultural heritage.

CONCLUSIONS

(1) The study we conducted aimed to develop a logical–mathematical model to determine the most suitable models of pedogenesis belonging to the class of S-shaped curves, which are applied as growth functions in biological and ecological investigations. The use of one of the functions from this class—a Gompertz function—proved feasible. This function allows us to reflect quantitative dynamic regularities of soil development at different stages. The critical points on the corresponding curves reflect the "turning points" of the pedogenesis. There are different views on the duration of the characteristic response time of soil processes, that is the time required to reach a state of quasi-equilibrium [1, 5]. The approach we suggest allows us to calculate this time based on a mathematical model. The results obtained attest to the effectiveness of this method for determining the characteristic response time for the formation of the humus horizon of chernozemic soils that develop on loose substrates. It is probable that the same approach may be used to assess other pedogenetic processes.

(2) Jenny illustrated his assumption about the stages of soil's functional ageing (its chemical and mineralogical composition) with a hypothetical soil chronosequence for the entire period of soil evolution. This assumption was confirmed by our study; we found that the stage of morphofunctional maturity of the humus horizon of steppe soils that develop for about 3.5 ka is reached in 1600–1800 years. After this, this process slows irreversibly. It may be accurately described by a Gompertz function. The maximum geochemical maturity of the humus horizon is reached in 1400 years.

(3) The suggested empirical models of pedogenesis on anthropogenically disturbed surfaces may be used for the pedochronological dating of archaeological sites and features based on a detailed study of humus accumulation in the corresponding soils. This method may be improved if we develop corresponding mathematical models for other pedogenetic processes, such as leaching, structuring, and geochemical transformation of the substrate.

(4) The pedochronological method of dating archaeological sites and features based on mathematical modeling of the dependence on the development of irreversible soil properties on time holds promise for an increased role of pedoarchaeology in the attribution and protection of cultural heritage. It may be helpful for archaeological purposes, especially when we deal with earthen structures (defense walls, field-dividing banks, hydraulic engineering constructions, etc.) that do not contain artifacts. The correct applica-

tion of this method implies that the soil-climatic conditions of the studied region are relatively homogeneous, and that the number of pedochronological data obtained is sufficient for statistical treatment. These data should be used to calibrate the chronofunctions of changes in soil properties over time, and to verify the soil dates for the equations applied.

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