THE 14C AGE OF HUMIC SUBSTANCES IN PALEOSOLS

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ABSTRACT. By comparing the radiocarbon age of the soils under burial mounds of known archaeological age with the surface-exposed (background) soils of the surrounding landscapes, we may evaluate the rates of humus renewal in these soils. In the cold climate of the mideastern areas of the Russian plains, the value of humus rejuvenation coefficient decreases. This shows that humus renewal is 5–10 times slower than in the warmer climate of the southern regions. Using the obtained data on the rejuvenation rate of humus substances, we can determine the age of paleosols and study the dynamics of the carbon exchange processes in the biosphere.

INTRODUCTION

Radiocarbon dating of paleosols (buried soils and relict soil horizons) is complicated by the fact that humic substances of such objects represent a partly open system for carbon exchange. As a result of processes such as accumulation, migration, and mineralization of humus, a considerable decrease in the ¹⁴C age of humic substances can occur.

Unlike surface soils, buried soils have a minimal rate of renewal of humic substances. Comparative dating of fossil horizons of buried soil and surface-exposed horizons permits age estimation and correction for the extent of humus rejuvenation in recent soils (Scharpenseel 1971). Our study of soil organic matter (SOM) turnover and the renewal processes of humic substances is based on the comparative ¹⁴C dating of the soils under independently dated burial mounds and surface-exposed ("background") modern soils. Previously, this study was performed for chernozems; a monogenetic model of soil development was assumed (Cherkinsky 1986).

The aim of this paper is to estimate the rate of organic matter turnover not only in monogenetic but also in polygenetic soils from some east European regions with different climates and vegetation, and to evaluate differences in the ¹⁴C ages of modern, relict and buried humus horizons as a function of depth from the surface.

The techniques we used consisted of comparative genetic and ¹⁴C studies of the soils that developed during the entire Holocene period (complete-Holocene soils) and the soils that started their development simultaneously with the soils of the first group, but were buried afterwards (incomplete-Holocene soils). We investigated paleosols beneath burial mounds and ramparts parallel to the surrounding surface-exposed (complete-Holocene) soils, which contain relics in most cases. For every pair of soil profiles studied (buried and background), we measured the ¹⁴C age of humic acids extracted from corresponding soil horizons (the upper, middle and lower part of burial and background soils, respectively). Based on ¹⁴C age difference within every horizon pair, the rejuvenation of humic acids was estimated. This method is similar to the one used by Scharpenseel (1971). The time of burial was established earlier by archaeological and ¹⁴C dating methods. This allows for a more accurate calculation of the humus rejuvenation rate. Also, sequences of multilayer soils buried under alluvial and colluvial deposits were studied. Humic acids extracted by the pyrophosphate method (Chichagova and Cherkinsky 1993) and charcoal were dated by ¹⁴C, using liquid scintillation counting (LSC).

The sites we studied have similar topography and sediments (Fig. 1). A complete description of the sites and methods can be found in Alexandrovskiy (1996) and Ivanov and Alexandrovskiy (1987). The watersheds, valleys and balkas (small flat-bottomed valleys) are covered by loess. However, the

climatic, vegetation, and soil characteristics of the studied sites are different. The Middle Volga basin (Vilovatovo site) is characterized by a cool climate with a mean annual temperature of -1°C; podzoluvisols are common under birch and deciduous broadleaf forests. The Ciscarpathian and northern Caucasus regions (Trayanov val and Novosvobodnaya sites, respectively) have warmer climates with mean annual temperatures of +8°C and +10°C, respectively. Gray and light-gray forest soils under oak and beech forests dominate here. The Tenginskaya site (northern Caucasus) is marked by the development of very deep chernozems at the boundary between the steppe and the forest-steppe zones. The climate here is relatively humid. The Chechkany (middle Volga basin) and, especially, Bogdanovka (southern Ukraine) sites have a dry climate. The Vilovatovo, Novosvobodnaya and Trayanov val sites represented the polygenetic model of soil development, whereas Tenginskaya, Chechkany and Bogdanovka represent the monogenetic model of soil development. The paleosols studied are well preserved beneath the thick loams and clays of burial mounds and ramparts.

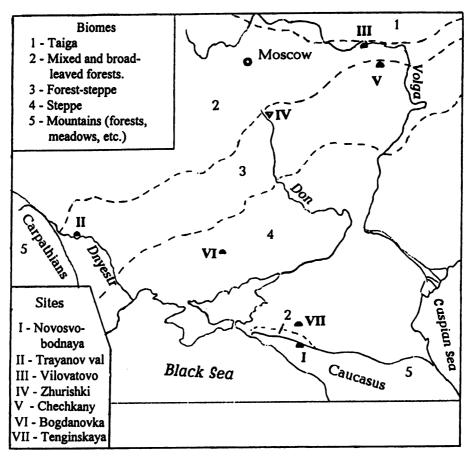


Fig. 1. Location of sites (I-VII) between Moscow and the Black Sea, where the paleosols were investigated

RESULTS AND DISCUSSION

Table 1 shows the ¹⁴C dates for humic acid extracted from the buried and adjacent surface-exposed (background) soils of the five sites (see also Fig. 1). Along with these data, we also used the previously obtained estimates of humus rejuvenation at the sites of Bogdanovka (Ivanov *et al.* 1994) and

Zhurishki (Alexandrovskiy 1996). Thus, a total of seven sites were used for correlation of ¹⁴C data for humic substances in the soils under burial mounds and ramparts of precisely determined age with data on background (i.e., nearby surface-exposed) soils and for calculation of the gradients and humus rejuvenation coefficients (Tables 2 and 3). Soils buried deeply are shown to be practically closed systems for carbon exchange. Background soils represent open systems, their lower horizons being only partly closed.

TABLE 1 14C	Dates of Humic A	cids in Buried at	nd Surface-F	xposed Soil for Ma	ain Sites Studied		
Lab code			Lab code		¹⁴ C age		
(IGAN)	depth (cm)	(yr BP)	(IGAN)	depth (cm)	(yr BP)		
1. Vilovato	vo. Burial mound:	$T_{obi} = 4000 BP$	L				
(a) Buried dark gray forest soil			(b) Background podzoluvisol				
Time of burial: 4000 BP			Time of additional exposure: 4000				
604	A1 0-8	5550 ± 150	608	A1 01-10	1190 ± 100		
603	A1E 8-15	7860 ± 100	606	E2h 18-22	5690 ± 70		
602	AEBth15-25	8190 ± 90	605	EBth 20-27			
2. Chechkany. Burial mound: $T_{obj} = 3500 \text{ BP}$							
(a) Buried chernozem			(b) Background chernozem				
Time of bu	rial: 3500 BP		1	Time of additional exposure: 3500			
675	A12 12-30	6290 ± 100	650	A12 35-45	5150 ± 180		
671	AB 30-50	8280 ± 170	646	AB 45-65	7330 ± 70		
3. Trayanov val. Rampart. ^{14}C : 2350 \pm 50 BP							
(a) Buried chernozem			(b) Background gray forest soil				
Time of burial: 2350 ± 50 BP			Time of additional exposure: 2350				
1060	A11 0-10	3420 ± 70	1067	A1E 01-3	308 ± 37		
1059		4210 ± 90	1066	E 15-23	1520 ± 90		
1058	AB 30-45	5870 ± 140	1065	EAh 30-40	2790 ± 110		
	50	6750	1064	BtAh 45-55	5030 ± 120		
1057	BA 60-75	7650 ± 120					
4. Novosvo	bodnaya. Burial m	$iound: T_{obj} = 550$	00 BP				
(a) Buried chernozem			(b) Background gray forest soil				
Time of burial: 5500 BP			Time of additional exposure: 5500				
1213	A11 0-15	6450 ± 100	1086	A1E 0-20	93 ± 9		
1156	A12 25-35	7100 ± 200					
1155	AB 55-65	8240 ± 330					
1154	BA 75-85	9780 ± 580	1084	BtAh 80-100	7130 ± 40		
5. Tenginsi	5. Tenginskaya. Burial mound: $T_{obj} = 5000 \text{ BP}$						
(a) Buried chernozem			(b) Background chernozem				
Time of burial: 5000 BP			Time of additional exposure: 5000				
1632	BA 105-120	9300 ± 1050	1650	BA 150-180	6065 ± 130		

^{*}Depths of buried soil horizons are given from the level of buried surfaces. Tobj is the time of construction of objects (mound, rampart), which is also the time of soil burial

From the decrease in the age of the background soils compared to buried soils (for comparable horizons), one can evaluate the rate of humus rejuvenation. For this purpose, we have calculated the following quantities: G_1 , the gradient characterizing the nonequilibrium state of humus (see Cherkinsky 1986); G_2 , the gradient of the age increase with depth (Ivanov, Chichagova and Cherkinsky 1993), and also, the coefficient of humus rejuvenation (CHR) calculated as $\binom{14}{\text{C}_{\text{bur}}} - \binom{14}{\text{C}_{\text{backgr}}} \times \text{depth (cm)}$

 T_{obj} (Tables 2 and 3). Here $^{14}C_{bur}$ is the ^{14}C age of buried soils horizons; $^{14}C_{backgr}$ is the ^{14}C age of background (surrounding surface-exposed) soil horizons; and T_{obj} is the age of the archaeological object and time of soil burial).

TABLE 2. ¹⁴C Dates of Humic Acids Extracted from Buried and Nearby Surface Soils and Some Calculated Indices and Gradients*

14C age 14C age Soil horizon (yr BP) G_2 Soil horizon (yr BP) G_2 D Vilovatovo-2. Burial mound: $T_{obj} = 4000$ (3800) BP Buried soil Background soil A1 1190 ± 100 -310 AEBth 8190 ± 90 2095 EBth 6440 ± 180 2680 Chechkany. Burial mound: $T_{obj} = 3500$ BP Buried soil Background soil A12 6290 ± 100 A12 5150 ± 180 AB 8280 ± 170 1195 AB 7330 ± 70 1330 Trayanov val. Rampart: ^{14}C : 2350 ± 50 BP Buried chernozem Background gray forest soil A11 3420 ± 70 A1E $308 \pm 37 \dagger$ -760 A12 4210 ± 90 E 1520 ± 90 -340 AB 5870 ± 140 EAh 2790 ± 110 -730 BA $(6750) \ddagger$ 840 840 840 840 840 840 840 840 840 840 840 840 84	$G_1 =$					
Buried soil	D/T_{obj}					
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AEBth 8190 ± 90 2095 EBth 6440 ± 180 2680 Chechkany. Burial mound: $Tobj = 3500 BP$ Buried soil Background soil A12 5150 ± 180 AB 8280 ± 170 1195 AB 7330 ± 70 1330 Trayanov val. Rampart: ^{14}C : $2350 \pm 50 BP$ Buried chernozem Background gray forest soil A11 3420 ± 70 A1E $308 \pm 37 \uparrow$ -760 A12 4210 ± 90 E 1520 ± 90 -340 AB 5870 ± 140 EAh 2790 ± 110 -730 BA (6750) \ddagger 840 BtAh 5030 ± 120 1000 630 Novosvobodnaya. Burial mound: $T_{obj} = 5500 BP$ Buried soil Background soil A11 6455 ± 100 A1E $93 \pm 9 \uparrow$ -850						
Chechkany. Burial mound: Tobj = 3500 BP Buried soil Background soil A12 6290 ± 100 A12 5150 ± 180 AB 8280 ± 170 1195 AB 7330 ± 70 1330 Trayanov val. Rampart: ^{14}C : 2350 ± 50 BP Buried chernozem Background gray forest soil A11 3420 ± 70 A1E $308 \pm 37 \dagger$ -760 A12 4210 ± 90 E 1520 ± 90 -340 AB 5870 ± 140 EAh 2790 ± 110 -730 BA $(6750) \ddagger$ 840 BtAh 5030 ± 120 1000 630 Novosvobodnaya. Burial mound: $T_{obj} = 5500$ BP Buried soil Background soil A11 6455 ± 100 A1E $93 \pm 9 \dagger$ -850	-0.08					
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A12 4210 ± 90 E 1520 ± 90 -340 AB 5870 ± 140 EAh 2790 ± 110 -730 BA $(6750) \ddagger 840$ BtAh 5030 ± 120 1000 630 Novosvobodnaya. Burial mound: $T_{obj} = 5500$ BP Buried soil Background soil A11 6455 ± 100 A1E $93 \pm 9 \dagger$ -850						
AB 5870 ± 140 EAh 2790 ± 110 -730 BA $(6750) \pm 840$ BtAh 5030 ± 120 1000 630 Novosvobodnaya. Burial mound: $T_{obj} = 5500$ BP Buried soil Background soil A11 6455 ± 100 A1E $93 \pm 9 \pm 90$ -850	-0.32					
BA (6750) ‡ 840 BtAh 5030 ± 120 1000 630 Novosvobodnaya. Burial mound: $T_{obj} = 5500 BP$ Buried soil Background soil A11 6455 ± 100 A1E 93 ± 9 † -850	-0.14					
Novosvobodnaya. Burial mound: $T_{obj} = 5500 \text{ BP}$ Buried soil Al1 6455 \pm 100 Background soil AlE 93 \pm 9 \dagger -850	-0.31					
Buried soil All Background soil AlE 93 \pm 9 \dagger -850	0.25					
Buried soil All Background soil AlE 93 \pm 9† -850						
	-0.15					
BA 9785 ± 580 535 BtAh 7130 ± 40 790 2850	0.50					
Tenginskaya. Burial mound: $T_{obj} = 5000 BP$						
Buried soil Background soil						
BA 9305 \pm 1050 400 BA 6065 \pm 130 350						

^{*} 14 C_{bur} = 14 C age of buried soils horizons; 14 C_{backgr} = 14 C age of background (surrounding surface-exposed) soil horizons. G₁ = the gradient of 14 C age; G₁ = 14 C_{backgr} - (14 C_{bur} - T_{obj})/T_{obj} (Cherkinsky 1986); G₂ = the rate of the increase in 14 C age with depth (years per 10-cm depth intervals; Ivanov *et al.* 1994). D= 14 C_{backgr}-(14 C_{bur}-T_{obj}).

Comparison of the ¹⁴C age of the buried and background soils showed that the buried soils (closed systems), isolated from modern influence, are generally older (Fig. 2). The change in ¹⁴C age and rejuvenation of humus substance took place in these soils before their burial. In fact, the Ciscarpathian paleo-chernozem (Trayanov val site), which developed as an open system for a longer period than the north-Caucasian one (Novosvobodnaya site), has a younger ¹⁴C age.

In the background soils, the ¹⁴C age is considerably younger. Even the relict humic horizons are 1.5–2.5 ka younger than the corresponding horizons of buried soils. In the upper part of the profile of background soils, the processes of humus renewal are very active because of the high biochemical activity.

¹⁴C dating of the pairs of buried and background soils make possible a calculation of ¹⁴C age gradients $[G_1]$: $G_1 = {}^{14}C_{backgr} - ({}^{14}C_{bur} - T_{obj})/T_{obj}$. $G_1=1$ is characteristic for humus in closed systems, and $G_1=0$ is indicative of the surface horizons (open system). The calculation of G_1 made for the mono-

[†]In the samples of soils that were affected by nuclear bomb ¹⁴C, the ¹⁴C age is determined according to the method of Cherkinski and Brovkin (1993).

[‡]Mean age value

genetic model (both background and buried soils are chernozems) revealed a regular increase of G₁ with depth from 0 at the surface to 0.7 at a depth of 50-60 cm (Cherkinsky 1986).

In the cases of the polygenetic model of soil formation, soil evolution is represented by transformation of the chernozemic type of humus into humus of Luvisols in the upper part of the profile. G_1 values drop to -0.3 due to instability of humus. In the lower layers, with inherited relict humus from horizon AC of initial Mid-Holocene chernozem (Fig. 2), values for G_1 are 0.25–0.5, thus indicating that the rejuvenation of humus is weaker there (Table 2). Humus renewal processes are very strong in the soils of the Trayanov val site up to a depth of 45 cm.

TABLE 3. Indices of Humus Rejuvenation and Environmental Conditions of Soil Formation of Seven Key Sites

Soil horizon;		Humus		
depth (cm)	14C _{bur} -14C _{backgr} *	rejuvenation (%)	CHR	Environment; mean annual temp
			CIIK	Environment, mean amuai temp
	riod of additional e			
A1 0-10	4360	100	5.5	Taiga/deciduous forests; (-1°C)
ABh 20-25	1750	44	9.9	
Chechkany. Pe	eriod of additional e	xposure: 3500 yr		
AB 40	1850	53	21.1	Steppe; (+1°C)
AB 50-60	950	27	14.8	
Zhurishki. Per	iod of additional exp	posure: 3500 vr		
A1 30-50	1500	43	20.0	Forest-steppe; (+3°C)
Bogdanovka. I	Period of additional	exposure: 4590 yr		
AB 40-70	1100-2300	23-50	20.0	Dry steppe; (+8°C)
Trayanov val.	Period of additional	exposure: 2350 yr		
A1 0-10	3110	100	6.6	Broadleaf forests; (+8°C)
AB 35	3080	100	46.0	,
BA 50	1770	75	37.5	
Novosvobodna	ya. Period of additi	onal exposure: 5500 y	r	
A1 0-20	6350	100	11.5	Broadleaf forests; (+10°C)
BA 80-100	2700	50	43.2	
Tenginskaya. F	Period of additional	exposure: 5000 yr		
AB 70-100	3785	75	75.0	Steppe/forest-steppe, (+10°C)
BA 150	3240	65	97.0	

^{*14}C_{bur}-14C_{backgr} is the difference between the ¹⁴C ages of genetic horizons, analogous to the buried and background soils.

Calculations have shown that the rate of humus rejuvenation depends on the depth of soil horizons and on climatic conditions during soil formation. In the south and southeast of Eastern Europe, within the forest-steppe regions with relatively warm and humid climates, active rejuvenation of humus substances is traced to a depth of 1.0 and even 1.8 m. Thus, for the Mid-Holocene relict-humus horizons at a depth of 40–100 cm, the rejuvenation of humus reaches 2.5 ka over the last 5 ka, i.e., 50% of humus substances have been rejuvenated. The maximum intensity of humus rejuvenation is in the very deep chernozems of the Tenginskaya site: 3.5 ka over the last 5 ka of additional soil exposure (65% of rejuvenation). In the drier conditions of the steppe zone, the rate of rejuvenation is considerably lower (2–3 times). To the north, in the colder climate at the center of Eastern Europe, the rate of humus rejuvenation substantially decreases, starting from a depth of 20–50 cm. It is 5–10 times lower than in the south of Eastern Europe and amounts to 1–2 ka over the last 3–4 ka of additional soil exposure (30–40%). Similar results (50% rejuvenation, but within a longer

period) were obtained in the soils of central Europe by Scharpenseel (1971). In the soils whose development follows the monogenetic pattern, the decrease in the rate of rejuvenation of humus with depth is gradual; in polygenetic soils, the rapid decrease in the upper part of soils gives way to a slower and more gradual decrease in the lower part of soil profiles.

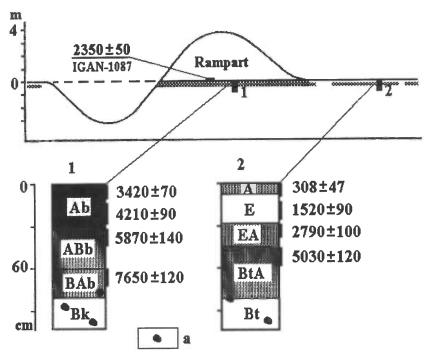


Fig. 2. Scheme of the Trayanov val. 1) buried chernozem; 2) surface-exposed (background) Luvisol with second humus horizon; a) Krotovinas of the chernozemic stage.

The data obtained also allow us to assess the renewal of humus in some paleosols. For example, the ¹⁴C age of the second humus horizons was estimated at 3.5–7.0 ka BP. By calculating the humus rejuvenation coefficient, the initial age of humus substances in these horizons may be assumed to be 2–3 ka older. The humus in the widespread buried paleocryogenic soils of the central Russian plain was rejuvenated by no more than 1 ka, thus dating their emergence to the Allerød stage (11–12 ka BP).

CONCLUSION

The comparison of ¹⁴C ages of the buried steppe soils and background forest soils enabled us to estimate the rate of humus rejuvenation in different soil and climatic conditions. The data on the key sites are introduced according to the geographical sequence. In the relatively cool climate of the mideastern areas of the Russian plain, the ¹⁴C age of the shallow (20 cm) second humus horizon in Podzoluvisols was rejuvenated by 1750–2500 yr over the last 4000 yr. In the warmer climate of the southern and southeastern parts of the Russian plain, the rate of rejuvenation of humus in gray forest soils (Luvisols) is considerably greater; at 50–80-cm depth, it equals 1700–2600 yr per 2350–5500-yr period. The zone of active renewal of humus in these soils (Novosvobodnaya and Tenginskaya sites) is 3–4 times thicker, and the humus rejuvenation is 5–10 times greater than those of the Podzoluvisols of the mideastern areas near the Taiga zone (the Vilovatovo site).

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