## THE <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C age of humic acids extracted from corresponding soil horizons (the upper, middle and lower part of burial and background soils, respectively). Based on <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C, 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

Proceedings of the 16th International <sup>14</sup>C Conference, edited by W. G. Mook and J. van der Plicht RADIOCARBON, Vol. 40, No. 2, 1998, P. 991–997 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  $-1^{\circ}$ 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  $+8^{\circ}$ C and  $+10^{\circ}$ 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 <sup>14</sup>C 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  $^{14}$ C 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.

Lab code	Soil horizon;*	<sup>14</sup> C age	Lab code	Soil horizon;	<sup>14</sup> C age			
(IGAN)	depth (cm)	(yr BP)	(IGAN)	depth (cm)	(yr BP)			
1. Vilovatovo. Burial mound: $T_{obi} = 4000 BP$								
(a) Buried	dark gray forest soi	1	(b) Background podzoluvisol					
Time of bu	rial: 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	6440 ± 180			
2. Chechkany. Burial mound: $T_{obj} = 3500 BP$								
(a) Buried	chernozem		(b) Background chernozem					
Time of burial: 3500 BP			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. <sup>14</sup> C: 2350 ± 50 BP								
(a) Buried	chernozem		(b) Background gray forest soil					
Time of bu	rial: 2350 ± 50 BP		Time of additional exposure: 2350					
1060	A11 0–10	3420 ± 70	1067	A1E 01-3	308 ± 37			
1059	A12 15-24	4210 ± 90	1066	E 15-23	$1520 \pm 90$			
1058	AB 30–45	5870 ± 140	1065	EAh 30-40	$2790 \pm 110$			
	50	6750	1064	BtAh 45-55	5030 ± 120			
1057	BA 60-75	7650 ± 120						
4. Novosvobodnaya. Burial mound: $T_{obi} = 5500 BP$								
(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	$7100 \pm 200$						
1155	AB 55-65	8240 ± 330						
1154	BA 75-85	9780 ± 580	1084	BtAh 80-100	7130 ± 40			
5. Tenginskaya. Burial mound: $T_{obi} = 5000 BP$								
(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			

TABLE 1. <sup>14</sup>C Dates of Humic Acids in Buried and Surface-Exposed Soil for Main Sites Studied

\*Depths of buried soil horizons are given from the level of buried surfaces. T<sub>obj</sub> 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  $({}^{14}C_{bur} - {}^{14}C_{backgr}) \times depth (cm)/$ 

 $T_{obj}$  (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).

	<sup>14</sup> C age	_		<sup>14</sup> C age	_		G <sub>1</sub> =
Soil horizon	(yr BP)	G <sub>2</sub>	Soil horizon	(yr BP)	G <sub>2</sub>	D	D/T <sub>obj</sub>
Vilovatovo-2.	Burial mound: 1	r <sub>obi</sub> = 4000 (	(3800) BP				
Buried soil		•	Background se	oil			
A1	5550 ± 150		A1	1190 ± 100		-310	-0.08
AEBth	8190 ± 90	2095	EBth	6440 ± 180	2680		
Chechkany. Bi	urial mound: To	bj = 3500 в	P				
Buried soil			Background se	oil			
A12	6290 ± 100		A12	5150 ± 180			
AB	8280 ± 170	1195	AB	7330 ± 70	1330		
Trayanov val.	Rampart: <sup>14</sup> C: 2	2350 ± 50 B	P				
Buried cherno	zem		Background g	ray forest soil			
A11	3420 ± 70		A1E	308 ± 37†		-760	-0.32
A12	4210 ± 90		E	1520 ± 90		-340	-0.14
AB	5870 ± 140		EAh	2790 ± 110		-730	-0.31
BA	(6750)‡	840	BtAh	5030 ± 120	1000	630	0.25
Novosvobodna	iya. Burial moui	nd: $T_{obi} = 55$	500 BP				
Buried soil		,	Background se	oil			
A11	6455 ± 100		A1E	93 ± 9†		-850	-0.15
BA	9785 ± 580	535	BtAh	7130 ± 40	790	2850	0.50
Tenginskaya. Burial mound: T <sub>obi</sub> = 5000 BP							
Buried soil		,	Background so	oil			
BA	9305 ± 1050	400	BA	$6065 \pm 130$	350		

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

 ${}^{*14}C_{bur} = {}^{14}C$  age of buried soils horizons;  ${}^{14}C_{backgr} = {}^{14}C$  age of background (surrounding surface-exposed) soil horizons. G<sub>1</sub> = the gradient of  ${}^{14}C$  age; G<sub>1</sub> =  ${}^{14}C_{backgr} - ({}^{14}C_{bur} - T_{obj})/T_{obj}$  (Cherkinsky 1986); G<sub>2</sub> = the rate of the increase in  ${}^{14}C$  age with depth (years per 10-cm depth intervals; Ivanov *et al.* 1994). D= ${}^{14}C_{backgr} - ({}^{14}C_{bur} - T_{obj})$ .

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

‡Mean age value

Comparison of the <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C age.

In the background soils, the <sup>14</sup>C 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.

<sup>14</sup>C dating of the pairs of buried and background soils make possible a calculation of <sup>14</sup>C age gradients [G<sub>1</sub>]:  $G_1 = {}^{14}C_{backgr} - ({}^{14}C_{bur} - T_{obj})/T_{obj}$ .  $G_1=1$  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-

genetic model (both background and buried soils are chernozems) revealed a regular increase of  $G_1$  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.

Soil horizon;		Humus						
depth (cm)	<sup>14</sup> C <sub>bur</sub> - <sup>14</sup> C <sub>backgr</sub> *	rejuvenation (%)	CHR	Environment; mean annual temp.				
Vilovatovo. Period of additional exposure: 4000 yr								
A1 0–10	4360	100	5.5	Taiga/deciduous forests; (-1°C)				
ABh 20-25	1750	44	9.9					
Chechkany. Period of additional exposure: 3500 yr								
AB 40	1850	53	21.1	Steppe; (+1°C)				
AB 50-60	950	27	14.8					
Zhurishki. Period of additional exposure: 3500 yr								
A1 30–50	1500	43	20.0	Forest-steppe; (+3°C)				
Bogdanovka. 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					
Novosvobodnaya. Period of additional exposure: 5500 yr								
A1 0-20	6350	100	11.5	Broadleaf forests; (+10°C)				
BA 80-100	2700	50	43.2					
Tenginskaya. Period of additional exposure: 5000 yr								
AB 70-100	3785	75	75.0	Steppe/forest-steppe, (+10°C)				
BA 150	3240	65	97.0					

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

 $^{*14}C_{bur}$ - $^{14}C_{backgr}$  is the difference between the  $^{14}C$  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 relicthumus 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

#### 996 A. L. Alexandrovskiy and O. A. Chichagova

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.





The data obtained also allow us to assess the renewal of humus in some paleosols. For example, the <sup>14</sup>C 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 <sup>14</sup>C 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 <sup>14</sup>C 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 2350–5500yr 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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