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# Dynamics of Carbonates in Soils under Different Land Use in Forest-Steppe Area of Russia Using Stable and Radiogenic Carbon Isotope Data

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Abstract: The work is aimed at the analysis of carbonate dynamics in soils under different land use. The studied area is located in the forest steppe - of the Central Russian Upland. Soils were sampled at four sites: a broadleaf forest, an adjacent 50-year continuously cropped field including plots under a corn monoculture, bare fallow, and a crop rotation area with a clean fallow every fourth year. The carbonates' morphology, their chemical composition, as well as their stable and radiogenic isotopes of carbon were studied. Clear-cut distinctions were found in the carbonate distribution throughout the profiles in the microstructure of carbonate pedofeatures, carbon isotopic composition, and radiocarbon age of carbonates between the pairs of the plots as follows: the bare fallow and the crop rotation on the one hand, and the corn monoculture and forest on the other. The distinctions are commonly assumed to result from repeating upward water fluxes, which are different in the bare soils and those with plant cover. A clear difference occurred in the hydrothermal regime for soils with and without plant cover, the carbonate migration upward occurs due to process of transpiration, whereas in soils devoid of plants, it occurs due to physical evaporation.

**Keywords:** pedogenic carbonates; forest-steppe soils; agricultural practices; stable and radiogenic carbon isotopes; upward water fluxes

# 1. Introduction

Pedogenic carbonates and humus status are the main properties that determine the taxa of soils in the steppe and forest-steppe zones of Russia according to the Russian and international systems of soil classification [1,2]. Previously, the investigations were only concerned with the humus status when studying changes of soil properties under different land uses in forest-steppe ecosystems [3–6]. Plowing is the most influential and common anthropogenic factor in relation to soils. In his work on the Russian Chernozem published more than 100 years ago, V.V. Dokuchaev [7] wrote about the humus content decrease in the upper layer of Chernozems under plowing. Pedogenic carbonates also undergo significant transformations in agricultural landscapes, but our knowledge of this subject in relation to the Russian forest-steppe ecotone remains insufficient.

It has been shown that the carbonate profile of forest-steppe soils on the Central Russian Upland is a "visible reflection" of their hydrothermal regime [8,9]. After a soil has been plowed, its hydrothermal regime changes significantly in comparison with virgin unplowed soils; so do the carbonates [10–12]. The soil hydrology on areas different in agricultural practices (bare fallow, monoculture of corn and winter wheat) and land uses (natural steppe and forest) has been studied extensively in the Kursk region (which neighbors the Voronezh region) for the last century [13–15]. The water from the soil



under the forest and crops comes to plant roots and is transpired through leaves. From the surface of the bare fallow, the soil water evaporates directly. It has been shown that the soil moisture deficit at the end of the vegetation season is much higher in the soil under crops than in the bare fallow soil. The clean fallow stage is usually practiced in the crop rotation system to store the soil water in agricultural soil for the next growing season.

Various agricultural practices or land uses produce an effect on carbonates in forest-steppe soils, which can bring a significant reorganization of their carbonate profile [16–19]. The carbonate profile of plowed soils is transformed (as compared with unplowed soils) to a new state [11,12,19–21], and the transformation may have negative effect on agriculture. For example, the appearance of carbonates within the formerly carbonate-free root-inhabited layer can affect the mechanism of crop nutrition and hence decrease crop yield and soil productivity [22,23]. Consequently, from the viewpoint of the sustainable development, it is of vital importance to gain an insight into the mechanism of the carbonate profile transformation under a changing hydrothermal regime in forest-steppe soils due to natural and anthropogenic factors.

There are two varieties of pedogenic carbon in soils: carbonate carbon and organic carbon [24]. The dynamics of pedogenic carbon content in soils in different types of land use is related to various aspects of the global carbon cycle [25–28] in changing environments.

Data on stable and radiogenic carbon isotopes in pedogenic carbonates are widely used for estimating parameters of (paleo) environments (temperature, precipitation, and atmospheric CO<sub>2</sub> concentration) at the time of the carbonate formation [29–34]. No studies of the isotopes for the purpose of better understanding the mechanism of the soil's carbonate status transformation due to different land use have been performed as of yet.

As has been recently shown, the carbonate profiles in arable and natural soils of the forest-steppe on the Central Russian Upland underwent evident morphological transformations in response to climatic changes in the last decades [8]. The meteorological instrumental observations revealed a distinct trend towards winter warming and precipitation increase in the central regions of Russia [35]. Hence, our knowledge about the carbonate profile and the predictability of its reaction to the climatic fluctuations are of particular importance. From our point of view, the investigation of carbon isotopes, stable and radiogenic, entering into the composition of pedogenic carbonates may be a clue to understanding the mechanisms of their development and transformation under conditions of different land use.

The aim of this work was to investigate the dynamics of pedogenic carbonates in arable soils of the forest-steppe area on the Central Russian Upland. We conducted studies of the soils affected by different agricultural practices (three variants) and of the virgin unplowed forest soil using an integrated approach including data on stable and radiogenic carbon isotopes.

# 2. Materials and Methods

# 2.1. Description of the Study Site

Soils were sampled at the Experimental Station of the Voronezh Institute of Corn (Voronezh Region of Russia), in the southern part of the forest-steppe area on the Central Russian Upland (Figure 1a). The studied site is located on the flat and uniform interfluve of the Don and Devitsa Rivers. Forests in this region are dominated by oak and linden growing on grey forest soils (according to the Russian soil classification [1]), or Haplic Luvic Greyzemic Phaeozems Loamic according to IUSS-WRB, 2014 [2]. According to archive materials (Provincial maps, county plans, maps, atlases, and town plans, 1785), the entire territory of the Experimental Station and its surroundings was forested 250–300 years ago. The existing plot of forest located near the station has not been disturbed for 250–300 years (Figure 1b). Agricultural soils have been affected by plowing for more than 250 years and are now classified as arable Chernozems (Haplic Luvic Chernozems Loamic). The problems of soil evolution and the change of soil types in tillage were discussed earlier [11,19] and are beyond the scope of this

paper. The studied soils are formed on a calcareous loess-like loam, well-drained, with groundwater level at the depths of 8–10 m. Loesses and loess-like loams on the East European (Russian) Plain are mostly aeolian in origin (partly reworked by wind), which were deposited in periglacial environments of the last (Valdai, Würm, Vistulian) glacial epoch correlated with marine isotope stage MIS 2 and is noteworthy for high rates of sedimentation [36].

The mineral composition of loesses is practically the same over the entire Central Russian Upland. They contain quartz (50–70%), K-Na feldspars (10–20%), calcium carbonates and—very seldom—magnesian carbonate (most often 5–20% of CO<sub>2</sub>) [37]. The carbonate CO<sub>2</sub> content of the loess-like rocks on the study site is 2–4%, and the content of clay fractions (particles < 0.002 mm) is 39–45% [38]. The volumetric correction factor of loess is 1. At the study site, the loess-like deposits are underlain by the Bryansk paleosol at a depth of 160–180 cm. The paleosol developed during the last mega-interstadial of the Late Pleistocene correlatable with MIS 3. The Bryansk paleosols on the Central Russian Upland typically have a high content of clay fraction (proportion of particles <0.001 mm is up to 38%, that of particles <0.002 mm—50%); carbonate CO<sub>2</sub> content amounts to 3.5–6.7%. The radiocarbon age of carbonates in these paleosols varies within 15.4–16.9 ka BP [39].



**Figure 1.** Location of the study site at the Central Russian Upland (**a**); location of the exploratory soil pits at the Experimental Station of the Voronezh Institute of Corn in the Voronezh Region of Russia (**b**,**c**): 1—soil pit on the plot under corn monoculture, 2—pit in the permanent bare fallow, 3—pit in the crop rotation field and 4—pit in the forest.

The mean annual air temperature in this area is 4-5 °C; the mean July and January temperatures are +22 °C and -11 °C, respectively. The annual precipitation is 480–550 mm, and the hygrothermal coefficient is 1.1–1.0. Precipitation is evenly distributed throughout a year; in growing season, short showers alternate with relatively long periods of soil drying. The weather conditions of the area are characterized by high time variability. For example, according to the "Voronezh, Agro" weather station data [40], the extreme values of air temperature in June were -2 °C (in 1967) and 38 °C (in 1924), the mean monthly value being 17.9 °C. With the mean monthly precipitation of 58 mm in

June, the extreme values of monthly precipitation recorded in June were 7 mm (in 1960) and 219 mm (in 1988); the extreme daily precipitation in June was 95 mm (in 1988).

The experiments on continuous practicing the corn monoculture, crop rotation and permanent bare fallow at the Voronezh Experimental Station began in 1966 [41]. There the soils were sampled from four different plots including a broadleaf forest and adjacent 50-year continuously cropped fields under corn monoculture (first plot,  $51^{\circ}36'27.0''$  N  $38^{\circ}58'13.6''$  E, h = 181.0 m), bare fallow (second plot,  $51^{\circ}36'26.8''$  N  $38^{\circ}58'13.8''$  E, h = 181.0 m) and crop rotation, which includes clean fallow every fourth year (third plot,  $551^{\circ}36'26.6''$  N  $38^{\circ}58'13.9''$  E, h = 181.0 m) (Figure 1b,c). All agricultural plots are located within the station area, and no fertilizer was applied to the sampled plots during the 50-year experiment. The distance between soil pits in the agricultural fields was 4.8-5 m (Figure 1c). The soil pit in the forest (fourth plot,  $51^{\circ}36'45.4''$  N,  $38^{\circ}58'55.4''$  E, h = 180.8 m) was approximately 500 m away from the agricultural field (Figure 1b). Before plowing, the agricultural plots and the plot within the forest belonged to the same landscape and ecosystem. All the soil pits were described and photographed in the field before sampling.

# 2.2. Soil Sampling and Analysis

Samples were taken from every pit described above. The depth of all the soil pits was 200 cm except for the pit at the crop rotation field dug to a depth of 140 cm (Figure 2). In the latter plot, the samples were taken from the depth of 160–200 cm using a hand auger. Samples (n = 3) were collected at 10-cm intervals from the upper 100 cm of each profile, and at 20-cm intervals—in the depth range 100 to 200 cm. They were air-dried in laboratory and disaggregated in ceramic mortar with a rubber pestle to a size less than 1 mm (so as to pass through a 1-mm sieve) for analyses. The carbonate  $CO_2$  content in the samples (n = 3) was determined using the samples treatment with a 10% HCl solution in sealed vessels with rubber stoppers. The  $CO_2$  content [42].



Figure 2. Morphological patterns of four studied profiles. Tape marked at every 10 cm.

Soil bulk density was determined at depths of 17, 40, 70, 130 and 170 cm (n = 3), which was equivalent to the average depths of occurrence of the identified soil horizons, using a  $100 \text{ cm}^3$  metal ring. For rough estimation of carbonate carbon stocks, values of bulk density were taken equal

in intervals 0–20, 20–40, 40–70, 70–130, 130–170 and 170–200 cm. Based on the distribution of the carbonate carbon over the profile and the bulk density values, carbonate carbon stocks within 0–50, 50–100, 100–150, 150–200, 0–100 and 0–200 cm layers were quantified for all pits. To obtain the stock value in any layer, a content of carbonate carbon in this layer was multiplied by a bulk density of this layer and by its thickness [43]. To get the units of stock to t/ha, the conversion factor is  $1\%/100\% \times 1$  g/cm<sup>3</sup> × 1 cm =  $1/10^{-2} \times 10^{-6}$  t/ $10^{-8}$  ha = 1 t/ha.

For stable isotope and radiocarbon analyses soil samples containing carbonates were collected from the upper part of the profile marked by the carbonate presence: 130–150 cm—in the pit on the plot under corn, 80–90 cm—in the pit under bare fallow, 85–95 cm—in the pit on the plot under crop rotation, and 135–145 cm—in the pit on forested plot. In addition, soil samples containing carbonates were collected for stable isotopes and radiocarbon analyses from the lowest horizon, 180 (190)–200 cm, in all studied pits.

Undisturbed soil samples with carbonate pedofeatures (CPs) collected from the upper horizons of all the profiles were used for micromorphological study. The thin sections were analyzed using a polarizing microscope (Carl Zeiss HBO 50, Carl Zeiss AG, Oberkochen, Germany) in the Chemical-Analytical Complex of the Institute of Physical, Chemical and Biological Problems in Soil Science, Russian Academy of Sciences, (Pushchino, Russia). The description of samples was given in accordance with Stoops [44] terminology.

The <sup>13</sup>C/<sup>12</sup>C ratio ( $\delta^{13}$ C) in samples (n = 3) was measured using a Thermo-Finnigan Delta V Plus continuous-flow mass spectrometer (Thermo Electron GmbH, Bremen, Germany), coupled with an elemental analyzer (Thermo Flash 1112, Thermo Electron, Waltham, MA, USA) at the Institute of Ecology and Evolution, the Russian Academy of Sciences. Samples were ground to pass through a 0.25-mm sieve; the quantity of the processed soil matter varied from 0.3 to 1.0 mg. The  $\delta^{13}$ C of carbonates in soil samples was determined after the sample ignition at 550 °C during 6 h to remove organic carbon. The CO<sub>2</sub> for analysis was obtained by treatment of the burnt samples with 100% H<sub>3</sub>PO<sub>4</sub> at 60–70 °C, and the subsequent freezing of the released CO<sub>2</sub> with liquid nitrogen; the mass spectrometer was used for the measurement. The mass spectrometer was calibrated relative to -31.47% standard. The isotopic composition of C was expressed in the  $\delta$ -notation relative to the international standard (VPDB):  $\delta^{13}$ C (‰) = [(Rsample/Rstandard) - 1] × 1000, where R is the ratio of <sup>13</sup>C/<sup>12</sup>C. Experimental analytical error for  $\delta^{13}$ C is 0.2‰ [45].

Radiocarbon dating of carbonates was conducted at the Kiev Radiocarbon Laboratory, NAS of Ukraine, using the scintillation method and a microreactor (Ki—laboratory index).

# 3. Results

#### 3.1. Carbonate Distribution, Content and Stocks

According to the field observation, in the pits under bare fallow and crop rotation carbonates are located about 60–80 cm higher (closer to the top of the profile) than in the pits under forest and corn. The CPs in the studied pits are present as soft powder cutans and hard nodules.

Clear differences in the carbonate carbon distribution in the profile are apparent when pairs of soil pits are compared as follows: first, pits in the corn monoculture field and in the forest; and, second, pits in the bare fallow and in the crop rotation field. The maximum content of carbonate carbon in the first pair of pits reaches 1.6–1.7% at a depth of 60–70 (80) cm, whereas in the second pair of pits—0.9–1.0% at 140–160 (180) cm depth (Figure 3a). In addition, the majority of visible CPs in the soil under bare fallow are located more closely to the day surface as compared with all the other pits.

There are two distinct patterns recognizable in the carbonate carbon stock values calculated to a depth of 200 cm. In the forest and corn monoculture plots these stocks vary from 50 to 60 t/ha, whereas in the bare fallow and the crop rotation plots they amounts to 240 and 200 t/ha, respectively (Figure 3b). It is noteworthy that the carbonate carbon stocks in the soils under forest and corn monoculture are close to zero within depth intervals of 50–100 cm and 100–150 cm, whereas in the soils under bare

fallow and crop rotation the carbon stock values in the two previously specified depth intervals are 50-60 t/ha and 100-116 t/ha, respectively. This confirms the patterns observed in the distribution of the carbonates throughout the profiles in the four variants of the studied experimental plots (in the forest, under monoculture of corn, crop rotation and bare fallow).



**Figure 3.** Distribution of carbonate carbon content (%) over the profiles (**a**) and carbonate stocks (t/ha) (**b**) in the studied soils at the Experimental Station of the Voronezh Institute of Corn.

## 3.2. Micromorphological Observations

Micromorphological observations in the upper part of the layer in which CPs are present in the studied forest profile show that iron-clay fine material is slightly impregnated with carbonates; no carbonate accumulations are found in the long channel voids (Figure 4a). Friable CPs are mostly located in comparatively large (more than 1 mm wide) pores and voids (Figure 4b) and are commonly interwoven with Fe oxide spots (thick arrow in the Figure 4b). The fragmentation of the margin of the carbonate feature in the void is clearly visible (thin arrows in the Figure 4b). This indicates a preferential dissolution and leaching of carbonates with periodical water stagnation [46] in the forest soil.

In the studied profiles of arable soils, the uppermost horizon containing CPs is noted for the groundmass being much heavier impregnated with carbonates as compared to the forest soil; i.e., the groundmass is calcareous. The packing voids of capillary size are filled with a cryptocrystalline mass of carbonate matter in the form of coatings and infillings (Figure 4c). Some specific voids arranged in the form of a circle are observed in the micro-areas of fine-dispersed material most heavily impregnated with carbonates, or inside the groundmass CPs, at the depth of 80–90 cm in the soil under a bare fallow field (Figure 4d). These voids are assumed to be desiccation fissures that appeared during the carbonate cementation, when the wet carbonate mass was drying out. It was previously supposed that such a phenomenon is characteristic of the colloidal carbonate matter [47,48].



**Figure 4.** Micromorphological pattern of the uppermost carbonate layers in the studied soil profiles: (a)—micro-areas of iron-clay fine material and a long channel void, both are practically free of carbonates, the soil pit in the forest; (b) friable carbonate feature in a comparatively large (more than 1-mm wide) pore interwoven with Fe spots (thick arrow), fragmentation of the margin of the carbonate feature (thin arrows), the soil pit in the forest; (c) intensive groundmass impregnation with carbonates, carbonate coatings and infillings are found inside packing voids, the pit in the corn field; (d) micro-area of fine-dispersed material heavily impregnated with carbonates, voids are arranged in the form of a circle inside this material, the pit in the bare fallow. All photos were taken under XPL.

# 3.3. Stable Isotope of Carbon in Carbonates

The  $\delta^{13}$ C determined for carbonates in the soil samples shows more negative values in the lower horizons compared with upper ones in all the studied soils, though in the most cases the differences is unreliable (Table 1). The absolute values of  $\delta^{13}$ C for carbonates in the pair of pits under bare fallow and crop rotation are less than those in the other pair of pits, under forest and corn. It is especially true for the soil under bare fallow.

Plot	Depth of Sampling, cm	$\delta^{13}C$ , $\%\pm$ Standard Deviation (n = 3)	<sup>14</sup> C-Date, Years BP	Laboratory Index
Corn	130–150 190–200	$\begin{array}{c} -9.06 \pm 0.20 \\ -9.74 \pm 0.30 \end{array}$	$\begin{array}{c} 11,\!100\pm100\\ 16,\!410\pm200\end{array}$	Ki-16054 Ki-16060
Bare fallow	80–90 190–200	$\begin{array}{c} -7.07 \pm 1.02 \\ -7.70 \pm 0.39 \end{array}$	$\begin{array}{c} 10,\!650\pm170\\ 14,\!670\pm200 \end{array}$	Ki-16049 Ki-16055
Forest	135–145 190–200	$\begin{array}{c} -8.07 \pm 0.23 \\ -11.15 \pm 0.64 \end{array}$	$\begin{array}{c} 4660\pm90\\ 7020\pm120\end{array}$	Ki-16045 Ki-16063
Crop rotation	85–95 190–200	$\begin{array}{c} -7.79 \pm 0.14 \\ -9.55 \pm 0.68 \end{array}$	$8020 \pm 100$ Not determined	Ki-16050

**Table 1.** Data of stable carbon isotopes in carbonates and radiocarbon dates of carbonates in the studied soils.

# 3.4. Radiocarbon Dating of Carbonates

While working with the radiocarbon age of carbonates, it should be kept in mind that the results of <sup>14</sup>C-determination (traditionally called "the age of carbonates") are in fact the activity of <sup>14</sup>C

proportional to the number of decaying atoms and expressed in the terms of age [49]. The actual age of carbonates when counted from the moment of their appearance in a horizon of the soil profile can be significantly older or younger than their measured <sup>14</sup>C-age. This may occur, first, due to the movement and deposition of ancient carbonate material with a low activity of <sup>14</sup>C (and therefore giving an ancient, or overestimated, radiocarbon age) in a soil profile and, second, due to dissolution and re-precipitation of carbonate material in situ adding the <sup>14</sup>C with high activity (i.e., the young—underestimated—radiocarbon age). Thus, radiocarbon activity measurements provide a peculiar geochemical marker that characterizes the processes of formation and transformation of carbonate material for them [49].

Radiocarbon dating of the soil samples at the Voronezh Experimental Station was performed on soil samples containing carbonates from the upper layers (if they are present in the studied profile) (Table 1) and on those from the lower layers, from a depth of 180 (190)–200 cm. The age of carbonates both in the upper and lower layers in the arable soils is 2 to 3 times greater than in the forest soil. We also recorded an older <sup>14</sup>C age obtained on carbonates in the arable soils as compared with the forest soils in other sites of the forest-steppe of the Central Russian Upland [50].

It is most important that carbonate samples taken from the soils under bare fallow, under crop rotation and under corn fields from the depth of 80–90 cm, 85–95 cm and 130–150 cm, respectively, yielded practically equal radiocarbon age (10,650  $\pm$  170 years BP, 8020  $\pm$  100 years BP, and 11,100  $\pm$  100 years BP).

#### 4. Discussion

Considerable differences are observed in the characteristics of the studied pairs of soils: between the soils under forest and corn, on the one hand, and those under the bare fallow and crop rotation, on the other hand. The soils differ in the carbonate distribution throughout the profiles, in micromorphology of CPs, in the composition of stable carbon isotopes in carbonates, and the <sup>14</sup>C-age of carbonates. The maximum content of carbonate carbon in the second pair of soils (under the bare fallow and crop rotation) reaches 1.6-1.7% at a depth of 60-70 (80) cm, whereas in the soils under forest and corn it was 0.9-1.0% at a depth of 140-160 (180) cm. The carbonate carbon stocks in soils under the forest and monoculture of corn in the 50–100 cm and 100–150 cm layers are about zero, while on plots under the bare fallow and crop rotation the stocks in the same layers are 50-60 t/ha and 100-116 t/ha. In general, carbonate carbon content and stocks are higher in the arable soils than in the soil under forest. Similar results were demonstrated for native and arable soils in the Kursk [51], and Belgorod [11] regions adjacent to the studied Voronezh Region; all the three regions belong to the forest-steppe zone.

As is seen from the analysis of the micromorphology, the groundmass in the upper layer of carbonate occurrence at the studied profiles is impregnated with carbonates to a greater degree in the arable soils than in the forest soil. This observation correlates well with the data on the carbonate carbon distribution and stocks in the studied profiles. In the pit under bare fallow the maximum degree of carbonate impregnation and accumulation is recorded in the layer closer to the day surface in comparison with the pit under corn.

The above-mentioned pairs of pits show distinct differences in the  $\delta^{13}$ C values of carbonates, the smallest negative values being recorded in the pit under bare fallow, both in the uppermost layer of the carbonate occurrence in the profile and in the lower one. In the pit under bare fallow the carbonates are evidently generated under processes of physical evaporation only due to absence of plant cover. Theoretically [52], evaporation should result in relatively enriched <sup>13</sup>C level in CaCO<sub>3</sub>, whereas soil CaCO<sub>3</sub> precipitated as a result of soil drying via transpirational water loss should be relatively depleted <sup>13</sup>C. In addition, carbon fractionation process in pedogenic carbonates is dependent on temperature and moisture [53]. According to experimental data in the forest-steppe area of Russia the mean annual temperature in bare soil in growing season is ~3 °C higher than in soil under plant cover till the 80 cm depth and ~1 °C higher—till the 120 cm depth [54]. The moisture in soil under bare

fallow is higher than in soil under crop during the whole growing season [15]. Hence, clear differences in the hydrothermal regime of the carbonate formation occur for soils with and without plant cover.

The <sup>14</sup>C-age of carbonates in the arable soils is 2 to 3 times greater than in the forest soil, both upper and lower horizons being dated. Practically equal values of the <sup>14</sup>C dates are obtained on the samples containing carbonates from the upper layer marked by the carbonate presence in the soils under bare fallow (sampled at a depth of 80–90 cm) and under corn (at a depth of 130–150 cm).

Before the beginning of the experiment, there existed a single arable field. We can assume that the differences in the carbonate profiles observed in the different variants of the experiment depend on the distinctions in agricultural practices on the plots within the formerly common field. In all arable soils, the content and stocks of carbonates are higher than in the forest soil. The increase of those values might be due to ascending water flow bringing "old" carbonates from the underlying rocks. In the case under consideration the source of the aged matter could be the Late Pleistocene Bryansk paleosols noted for a high content of carbonates and having comparatively "old" <sup>14</sup>C-age,  $\sim$ 16–17 ka BP [39]. The soil under corn differs insignificantly in the carbonate status from the soil under forest. In the soils under bare fallow and those under crop rotation (where clean fallow is being practiced every fourth year), the upward movement of carbonates is much more pronounced as compared with soil under corn. This result suggests the plant cover presence or absence can play a key role in the upward movement of carbonates in arable soils. This idea was previously tested by mathematical simulation of hydrological regime for the corn and bare fallow plots during the growing period. The modeling of hydrological regime of the soils using instrumental daily weather data provided supporting evidence for the conditions of the plot under bare fallow being much more favorable for ascending and accumulation of carbonates in the upper part of the profile than those under monoculture of corn [38].

Special mention should be made on the plot under crop rotation. The results obtained for the carbonate status are more expectable for the permanent bare soil than for the soil under crop rotation, which is underneath crops for three out of four years. We are forced to admit that when the crop rotation plot is under clean fallow, the conditions have more of an influence on its carbonate status than the other three years when this plot is under crops, due to more heating of the plot and more amount of soil moisture in this year during growing period.

As follows from the results obtained, the agricultural use of soils in the forest-steppe area, where a crop rotation system with clean fallow is practiced, leads to a change in its hydrological regime and, as a consequence, to the noticeable and comparatively fast ascending of carbonates in the middle part of the soil profile. An important point is that our results allow predicting the alteration of pedogenic carbonates under changing climatic conditions in the Central Russian Upland.

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**Author Contributions:** Olga Khokhlova performed the expedition with fieldwork and soil sampling, micromorphological analysis; Tatyana Myakshina analyzed the samples in laboratory; Olga Khokhlova wrote the paper.

Conflicts of Interest: The authors declare no conflicts of interest.

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