

The organic matter of the different ages fallow Luvisols

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Abstract. The study of the change in the humus state of the fallow Luvisols of different ages under the influence of weeds and meadow vegetation was carried out in dynamics (after 5 years). It is shown that both under weedy and meadow vegetation there is a statistically significant accumulation of organic matter in the upper part of the long-arable horizon. Based on the study of composition and spectral properties of soil organic matter in fallow soils of different ages concluded that the significant qualitative change of the humus state of fallow soils requires significant time, measured at least decades.

1. Introduction

The reduction of arable land is currently a worldwide trend which is most widespread on the territory of modern Russia [1, 2]. The formation of fallow soils there is characterized by the simple abandonment of arable land which is accompanied by spontaneous recovery of the original plant ecosystems. The formation of fallow vegetation in the forest-steppe zone begins with overgrowing of weeds (the pioneer stage of development of fallow soils) and then during a few years formation of the meadow phytocenosis. At the last stage of the development of fallow vegetation in the forest-steppe zone, under favorable conditions, occurs an introduction of woody plants and succession of wood communities [2]. Fallow phytocenosis at each stage of development should be considered as a modern dynamic state of vegetation which is characterized by a certain biodiversity, productivity, vertical, horizontal structure and mosaic. The stages of development of fallow vegetation will be reflected in the nature of the postagrogenic transformation of soils and, first of all, on the change in their humus state. The purpose of this research work is to study the changes in the humus state of the different-aged fallow Luvisols in dynamics under the influence of weeds and meadow vegetation.

2. Material and methods

Objects of research are the associated plots of different ages of fallow soils which are located in the Volga region of the Republic of Tatarstan (Russia). Fallow plots are confined to one relief element - slightly sloping slope of the south-eastern exposure. Samples were selected in 2010, when the young fallow soil was at the age of 2 years and was in the initial stage of overgrowth with weed vegetation, the old fallow soil of 70-75 years of age was represented by a stable herbage-cereal meadow phytocenosis. The fallow plot of 70-75 years of age is located on the territory of the local airfield (which ceased to exist in the early 90's) on the lands withdrawn from arable land in 1935-1940. This territory was subjected to intensive haymaking and has no signs of overgrowing by woody vegetation. Samples from the old plow horizon were selected layerwise (each 5 cm) on depth to 20 cm by the special drill from 7 sampling points dated for 7 clusters of the hexagonal systematic lattices put separately on each fallow plot. In 2015, repeated sampling was carried out according to the same



scheme with an indentation of 1-2 m in an arbitrary direction from the primary points when the fallow soils had the age of 7 and 75-80 years, respectively. Samples to characterize the horizontal spatial inhomogeneity were obtained by mixing of layered samples (0-5, 5-10, 10-15 and 15-20 cm) at sampling points. To characterize the vertical heterogeneity of the old plow horizon there were obtained 4 samples by mixing separately in layers 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm from the 7 sampling points. After careful selection of the roots, the soil was ground and passed through a 0.1 mm. In the mixed samples the total organic carbon content (C_{org}) and organic carbon soluble in sodium pyrophosphate was determined. For a qualitative characteristic of organic matter (OM) of long-arable horizons of fallow soils of different ages (2 years and 70-75 years) IR-Fourier spectrometry was used. The IR spectra of soil OM were obtained by the method of disturbed total internal reflection (DTIR) with the prefix PIKE MIRacle™ in the range 4000-660 cm^{-1} . For correction of soil minerals absorption bands as background used a mineral phase of samples which are selected on depth of 0-5cm, 5-10cm, 10-15cm, 15-20cm. The mineral phase was obtained by burning of soil OM with 30% H_2O_2 [3, 4]. Soil treatment with hydrogen peroxide allows to remove of OM from the surface of clay minerals by 85-95% [5, 6]. After drying, the soil sample without OM was ground and passed through a sieve of 0.1 mm diameter. This procedure allows to obtain IR spectra of OM of soil material with an automatic subtraction of its background mineral phase and provided an opportunity to interpret more informatively absorption bands associated with the OM. Interpretation of IR spectra was carried out on the basis of work Hyeong K., Capuano R.M. [7].

3. Results and discussion

In figure 1 the content of soluble and insoluble organic carbon in sodium pyrophosphate organic carbon in layerwise samples from old-plow horizons of different-aged fallow soils are presented. The total carbon content increases mainly in the upper part of the old plow horizon in accordance with the fallow age. According to the paired t-test, a statistically significant difference in the Corg content in the 0-20 cm layer of the old plow horizon is observed for the samples taken from the 7-point systematic lattices as between 2 and 7-year of fallow soils ($t = 3.72$ at $t_{st} = 2.45$), and between 70-75 and 75-80-year-old ($t = 4.56$ при $t_{st} = 2.45$). With increasing of the fallow soil age increases the horizontal variability of the Corg content in the old plow horizon. The coefficient of variation in humus content in the 0-20cm layer, according to the analysis of mixed samples, is 7.9% for the fallow soils of 2-year, 10.2% for the 7 years, 20.4% for the 70-75 years and 75-80 years is 21.5%. It can be concluded that, both at the pioneering stage of overgrowing and under meadow vegetation is observed the statistically significant accumulation of OM, which is characterized by a very high horizontal variability significantly exceeding the variability of the initial arable soils.

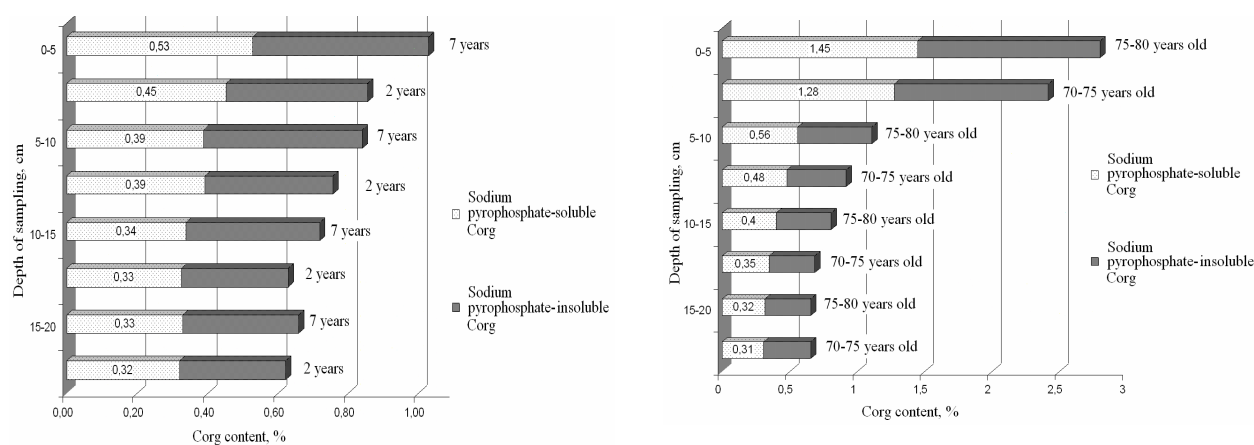


Figure 1. The content of soluble and insoluble in the sodium pyrophosphate of Corg in layered samples from old-arable horizons of uneven-aged fallow soils.

Also it can be concluded that the content of sodium pyrophosphate-soluble OM in the upper part of the old plow horizon increases. However, according to the paired t-test data the difference in the 0-20cm layer of the old-plow horizon of sodium pyrophosphate-soluble OM is statistically insignificant, both between the fallow soils of 2 and 7 years ($t = 2.43$ at $t_{st} = 2.45$), and between the fallow soils of 70-75 and 75-80 years ($t = 0.59$ at $t_{st} = 2.45$). A comparison of fallow plots with each other using the independent samples t-test shows the statistically significant difference in the content of sodium pyrophosphate-soluble Corg. The value of the two-sample t-test with the same variances for fallow soils of 2 and 70-75 years is 5.40 at $t_{st} = 2.18$, the value of the two-sample t-test with different variances for fallow soils of 7 and 75-80 years, respectively, 7.01 at $t_{st} = 2.20$. Thus, it can be concluded that the 5-year period is not sufficient for a significant accumulation of mobile soil OM, which would lead to a noticeable qualitative change of the humus state of postagrogenic soils. Probably, for a significant qualitative change of the humus substances composition the postagrogenic transformation is required for at least decades. Accumulation of OM in shorter intervals proceeds, most likely, due to the accumulation of detrital coarse humus [8]. Therefore, for the spectral estimation of the change of the OM qualitative composition of the old plow horizon of soils were used mixed layered samples from fallow soils which significantly different in age. The absorption frequencies of layered mixed samples from different ages of fallow soils (2 years and 70-75 years) are shown in table 1.

Table 1. Absorption frequencies of humus substances in fallow soils.

Depth of sampling, cm	Wave numbers, cm^{-1} (Group and π vibration)
Fallow soils 70-75 years old	
0 – 5	2960($\nu_{as}\text{CH}_3$), 2924($\nu_{as}\text{CH}_2$), 2874($\nu_s\text{CH}_3$), 2860($\nu_s\text{CH}_2$), 1732($\nu\text{C}=\text{O}$), 1451($\delta\text{CH}_2, \delta_{as}\text{CH}_3$), 1414($\delta_{as}\text{CH}_3$), 1339($\nu\text{C}-\text{N}$), 1262($\nu\text{C}(\text{O})-\text{O}$), 1160($\nu\text{O}-\text{C}-\text{C}$), 1081($\nu\text{Si}-\text{O}-\text{Si}$), 1020($\nu\text{Si}-\text{O}-\text{Si}$), 875($\nu\text{O}-\text{O}$), 840(trisubstituted), 731(trisubstituted), 703(ρCH_2)
5 – 10	2952($\nu_{as}\text{CH}_3$), 2924($\nu_{as}\text{CH}_2$), 2876($\nu_s\text{CH}_3$), 2853($\nu_s\text{CH}_2$), 1723($\nu\text{C}=\text{O}$), 1460($\delta\text{CH}_2, \delta_{as}\text{CH}_3$), 1378($\delta_s\text{CH}_3$), 1267($\nu\text{C}(\text{O})-\text{O}$), 1156($\nu\text{O}-\text{C}-\text{C}$), 1080($\nu\text{Si}-\text{O}-\text{Si}$), 1023($\nu\text{Si}-\text{O}-\text{Si}$), 889(fivesubstituted), 873($\nu\text{O}-\text{O}$), 730(ρCH_2)
10 – 15	2925($\nu_{as}\text{CH}_2$), 2855($\nu_s\text{CH}_2$), 1732($\nu\text{C}=\text{O}$), 1455(δCH_2), 1263($\nu\text{C}(\text{O})-\text{O}$), 1160($\nu\text{O}-\text{C}-\text{C}$), 1018($\nu\text{Si}-\text{O}-\text{Si}$), 777(disubstituted), 700(disubstituted)
15 - 20	1729($\nu\text{C}=\text{O}$), 1259($\nu\text{C}(\text{O})-\text{O}$), 1163($\nu\text{O}-\text{C}-\text{C}$), 1009($\nu\text{Si}-\text{O}-\text{Si}$)
Fallow soils 2 years old	
0 – 5	2927($\nu_{as}\text{CH}_2$), 2856($\nu_s\text{CH}_2$), 1731($\nu\text{C}=\text{O}$), 1450(δCH_2), 1263($\nu\text{C}(\text{O})-\text{O}$), 1177($\nu\text{O}-\text{C}-\text{C}$), 1076($\nu\text{Si}-\text{O}-\text{Si}$), 1020($\nu\text{Si}-\text{O}-\text{Si}$), 875($\nu\text{O}-\text{O}$), 733(ρCH_2), 683(monosubstituted)
5 – 10	2925($\nu_{as}\text{CH}_2$), 2854($\nu_s\text{CH}_2$), 1735($\nu\text{C}=\text{O}$), 1456(δCH_2), 1264($\nu\text{C}(\text{O})-\text{O}$), 1162($\nu\text{O}-\text{C}-\text{C}$), 1018($\nu\text{Si}-\text{O}-\text{Si}$), 913($\delta\text{CH}=\text{CH}_2$), 749(ρCH_2), 682(monosubstituted)
10 – 15	2926($\nu_{as}\text{CH}_2$), 2854($\nu_s\text{CH}_2$), 1732($\nu\text{C}=\text{O}$), 1441(δCH_2), 1264($\nu\text{C}(\text{O})-\text{O}$), 1160($\nu\text{O}-\text{C}-\text{C}$), 1072($\nu\text{Si}-\text{O}-\text{Si}$), 1009($\nu\text{Si}-\text{O}-\text{Si}$), 788(disubstituted), 760(ρCH_2), 684(disubstituted)
15 - 20	2924($\nu_{as}\text{CH}_2$), 2853($\nu_s\text{CH}_2$), 1732($\nu\text{C}=\text{O}$), 1457(δCH_2), 1264($\nu\text{C}(\text{O})-\text{O}$), 1160($\nu\text{O}-\text{C}-\text{C}$), 1013($\nu\text{Si}-\text{O}-\text{Si}$), 790(disubstituted), 766(ρCH_2), 691(disubstituted)

Application: ρ –wagging vibrations, ν –stretching vibrations, δ –bending vibrations.

In the 70-75-year-old fallow soils from the surface and up to the depth of 15 cm the increase in the absorption intensity in the region of about 3000 cm^{-1} corresponding to stretching vibrations of CH_2 and CH_3 groups is observed. The increase in their intensity with depth can be associated with an increase in chain length of saturated hydrocarbons. The frequencies values of the symmetric and asymmetric

stretching vibration of methyl ($\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{s}}\text{CH}_3$) and methylene groups ($\nu_{\text{as}}\text{CH}_2$ и $\nu_{\text{s}}\text{CH}_2$) remain constant to the depth of 10 cm. In the upper 10 cm layer of old-fallow soil the presence of the absorption band about 730 cm^{-1} (wagging vibrations δCH_2) indicates the presence of a number of directly related groups - CH_2 - with the amount of carbon atoms more than four. The combined absorption band due to the bending vibrations of the groups CH_2 (δCH_2) and CH_3 ($\delta_{\text{as}}\text{CH}_3$) in the region of $1460\text{--}1451\text{ cm}^{-1}$ and bending vibrations $\delta_{\text{s}}\text{CH}_3$ in the region of $1414\text{--}1378\text{ cm}^{-1}$ is also observed up to the depth of 10 cm. The change in the symmetrical vibration frequency of the CH_3 group to 1414 cm^{-1} in the 0-5 cm layer of the old-fallow soil is probably due to the addition of the methyl group to the nitrogen atom ($\text{CH}_3\text{-N}$), not to the carbon atom. In the underlying horizons (10-15 cm) only absorption bands of stretching and bending vibrations of methylene groups are observed. The frequency value of about 1339 cm^{-1} is observed only at the depth of 5 cm of old - fallow soils (70-75 years), which can be attributed to the stretching vibrations of C-N aromatic amines.

In the region of $875\text{--}873\text{ cm}^{-1}$ there are observed the stretching vibrations of the peroxide group (O-O) of aliphatic compounds that are found in the composition of humic substances. The peroxide group is found only in the upper 10 cm layer of 70-75 year old fallow soils and in the 5 cm layer of 2-year fallow soils, which may be due to the autooxidation of organic and organometallic compounds by air oxygen in the upper soil horizons.

In 2-year-old fallow soils the quantity of absorption bands decreases. From the surface and to the depth of 20cm in the region of about 3000 cm^{-1} only the absorption bands of methylene groups ($\nu_{\text{as}}\text{CH}_2$, $\nu_{\text{s}}\text{CH}_2$, δCH_2) are observed with relatively constant frequency. Absorption bands of methyl groups were not detected. The presence in the samples from a depth of 0-5 cm and 5-10 cm of the absorption band near 730 cm^{-1} (wagging vibrations of CH_2) is also indicated by the presence of a number of directly connected groups - CH_2 - with more than four carbon atoms. The absorption band of wagging vibrations of methylene groups in samples at depth of 10-20 cm shifts toward higher frequencies that may be due to a decrease in the number of bound methylene groups with each other.

The feature of all studied samples of uneven-aged fallow soils is the presence of common frequencies over the entire depth of the old plow horizon. The typical esters of the absorption band of the stretching vibrations of the carbonyl group (C=O) in the region $1310\text{--}1250\text{ cm}^{-1}$, which corresponds to the stretching vibrations $\text{C} (= \text{O}) - \text{O}$ and in the region of $1180\text{--}1130\text{ cm}^{-1}$, which corresponds to stretching vibrations of O-C-C group were found. Probably, these are esters of aliphatic acids, since absorption characteristic for aromatic compounds is absent. This indicates that these groups are the most stable and permanent structural units of humic substances of the studied soils that have not been mineralized as a result of agricultural use, before the transition of soils to a fallow state.

In the 2-year-old fallow soil inhomogeneous series of intense bands of silicic oxygen valence vibrations are identified, which by layerwise do not differ in intensity and wave numbers. It, probably, due to the fallow soil age in which the secondary accumulation of humus is not significant and changes in the soil OM spectra have to be very weak.

4. Conclusion

A general analysis of the results shows that the presence of Luvisols for 5 years both under fallow vegetation in the pioneer stage of overgrowing, and under developed meadow vegetation leads to the statistically significant quantitative accumulation of humus in the old plow horizon. However, the significant qualitative change in the humus state of fallow soils requires more time, measured at least for decades.

Acknowledgments

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