Studying Of The Layland Soils Organic Matter By Ir Fourier Spectroscopy Method

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Abstract- Organic matter uneven-age layland soils are investigated by method of IR-Fourier spectroscopy of the mixed exemplars. Exemplars of the arable horizon, selected on depths of 0-5cm, 5-10cm, 10-15cm, 15-20cm were investigated. For correction of quartz and clay minerals absorption bands in ranges of native exemplars as background we used the mineral phase received by combustion of organic matter of 30% H_2O_2 soils. Feature of the studied exemplars uneven-age layland soils is existence of reference absorption bands aliphatic acids ethers, which are the stablest and constant base units of organic matter. Use of this approach allowed to estimate specter absorption changes of the functional humic substances groups and fragments in fiber exemplars of uneven-age layland soils, bound to secondary accumulation of detritus (rough) humus in upper arable horizons under the influence of secondary vegetation.

Keywords: soil organic matter, humus, acid-base extraction, IR spectrums.

Introduction

The Soil Organic Matter (SOM) represents composite system which can be defined as a set of the high-molecular compounds differing on molecular masses and chemical inhomogeneity [1]. Difficulties of its studying are bound to presence of organic matter (OM) in the free form, as well as bound to mineral part of the soil. Traditional approaches to SOM research are based on destruction of these connections with the help of various chemical extraction [2,3] methods and studying of the received preparations with application of the methods developed for natural and simulated organic compounds analysis. Along with labor input and procedure duration an essential flaw of chemical methods is change of the initial nature of the humic substances (HS) [3,4]. In the existing literature various approaches to the soft selection of humic substances are offered. Among them the most widespread are the soft basic hydrolysis of OM copper oxide in the nitric environment [5], selection by means of soft "cation exchanger - alkaline" serial extractions procedures [6], extraction by dimethylsulfoxide [7], dipolar aprotic solvents, etc. Common fault of the offered soft extraction methods is

considerably smaller completeness of HS extraction in comparison with rigid extraction that cannot but influence qualitative structure of the received preparations. Complexity of SOM research demands a combination along with the methods based on HS preparations studying of the non-destructive methods application focused on studying of native HS as a part of soil material.

The method of IR-Fourier spectroscopy is one of the most informative and fast methods of natural objects qualitative and quantitative structure study. The majority of soil works, bound to research, as methods of IR-Fourier spectrometry are devoted to sharing method of diffuse reflection infrared spectroscopy and method of least squares, models, necessary for construction, and the quantitative determination of various soil properties [8-16]. However at all advantages of IR-Fourier spectrometry, its application to soils has an essential shortcoming - imposing of potent absorption bands of mineral part on rather soft strips of HS functional groups that considerably reduces method informational content.

The work purpose is the structure analysis of HS layland soils by means of native exemplars IR-spectroscopy, using as background mineral soil material after removal of OM rigid processing by hydrogen dioxide.

1. Objects and methods

Objects of research - the conjugate sites of uneven-age deposits (2 years and 70-75 years) located in Predvolzhye of the Republic of Tatarstan (Russia). Layland sites are dated to one relief element - to low-sloping slope of southeast exposition. Soils - light gray forest (Luvisols).

The young deposit is in incipient state of overgrowing by weed vegetation. The deposit of 70-75-year age is presented by a stable mixed-herbs-cereal meadow phytocenosis. Exemplars from the old arable horizon were selected layerwise (each 5cm) on depth to 20cm by the express drill from 7 tapping points dated for 7 clusters of the hexagonal systematic lattices put separately on each layland site. For the soils OM characteristic we defined the content of organic carbon and common nitrogen [17].

For IR-Fourier spectrometry we used the mixed fiber exemplars from the old arable horizons prepared for two types of deposits separately. Exemplars after screening of roots were pounded and passed through a bolter of 0,1 mm.

IR spectrums of HS were received by method of the broken total internal reflection on Perkin-Elmer spectrometer with PIKE MIRacleTM prefix in the range 4000-660 cm^{-1}.

For correction of quartz and clay minerals absorption bands as background we used a mineral phase of the exemplars which are selected on depths of 0-5cm, 5-10cm, 10-15cm, 15-20cm, which was received by combustion of OM soils of 30% H_2O_2 according to the technique [18,19]. This technique allows to delete organic components from a surface of clay minerals for 85-95% [20-22]. After oxidation decomposition of SOM for removal of the hydrogen peroxide rest, the soil was washed out by the 3rd multiply distilled water at centrifugation. The soil shot without OM, after an exsiccation was pounded and passed through bolter of 0,1mm diameter. This procedure allowed to receive HS IR

spectrums with an automatic deduction of its background mineral phase. Interpretation of IR-ranges was carried out on the basis of works [23].

2. Results and discussion

The characteristic of OM of the old arable layland soil horizons investigated is presented in table 1.

Table 1. The content of organic carbon, common nitrogen and relation C/N in exemplars of the layland soils

Depth of sampling, cm	Deposit of 70-75 years			Deposit of 2 years		
	Total C, %	Total N, %	C/N	Total C, %	Total N, %	C/N
0-5	2.42	0.26	9.5	0.86	0.14	6.1
5-10	0.92	0.17	5.3	0.75	0.11	6.6
10-15	0.69	0.16	4.3	0.63	0.12	5.1
15-20	0.66	0.16	4.1	0.58	0.10	5.6

In high layers the content of organic carbon and common nitrogen is higher, than in lower, especially it is characteristic for deposit of 70-75 years age. Relation C/N in high layers is also significantly higher. For the 75th year old deposit relation C/N in a layer of 0-5cm is 2,3 times higher, than in a layer of 15-20cm; that it is possible to connect with accumulation of detritus (rough) humus fraction. Results show that in the top 0-20 cm layer of earth under secondary vegetation there is a considerable, but nonuniform on depth, accumulation of humus which differs on the qualitative structure.

In figure 1 IR spectrums of native HS of the studied soil exemplars are presented.

Frequencies of absorption are presented in table 2. On IR spectrums of the studied soil exemplars two absorption bands - wide in the field of stretching vibrations OM groups -(~3400cm^{-1}) and narrow (1620±20см$^{-1}$) are observed. Existence of these absorption frequencies can be bound to the water adsorbed on surface of clay minerals. Presence of water-absorbing combined water does not allow to identify some areas of fluctuation common to NH, OH, C=C connection groups, and also stretching vibrations of benzene ring.
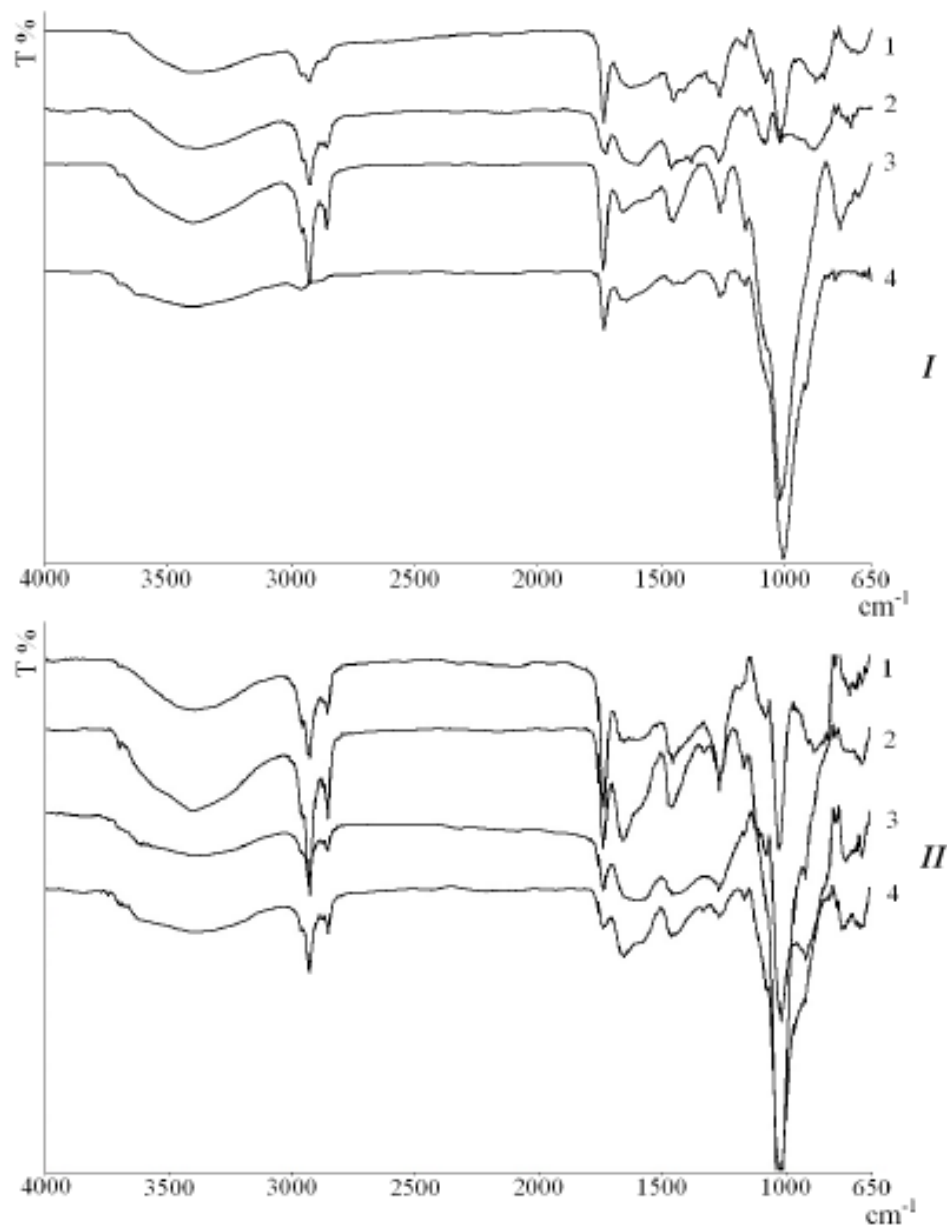
Fig. 1 IR spectrums on depths (1 – 0-5cm, 2 – 5-10 cm, 3 - 10-15 cm, 4 – 15-20 cm) the layland soils (I – 70-75 years, II – 2 years).

In the layland soil (70-75 years) from surface and up to depth of 15cm the increase in absorption intensity in area near $3000cm^{-1}$ corresponding to stretching vibrations of CH_2 and CH_3 of groups is observed. The increase in their intensity with depth can be bound to increase in chain length of saturated hydrocarbons. Values of frequencies, the reference for symmetric and asymmetric stretching vibration of methyl groups ($v_{as}CH_3$, v_sCH_3) and methylene groups ($v_{as}CH_2$ and v_sCH_2) up to the depth of 10cm remain rather constant. In top 10cm layer of old laysoils existence of an absorption band close to $730cm^{-1}$ (wagging vibrations δCH_2) signifies the existence of directly related number of groups- CH_2 - with amount of carbon atoms more than four.

The combined absorption band caused by bending vibrations of groups CH_2 (δCH_2) and CH_3 ($\delta_{as}CH_3$) in area of 1460-$1451cm^{-1}$ and

bending vibrations $\delta_s CH_3$ IN THE RANGES 1414-1378cm^{-1} is also observed up to the depth of 10cm. Change of symmetric vibrations CH_3 groups frequency to 1414cm^{-1} in a layer of 0-5cm of layland soil is possibly connected with accession of methyl group to atom of nitrogen (CH_3-N) rather than to carbon atom. In the underlying horizons of layland soils (10-15cm) only absorption bands of stretching and bending vibrations of the methylene groups are observed.

Table 2. Frequencies of HS layland soils absorption

Depth, cm	Wave numbers, cm^{-1} (Group and fluctuations)
Soils deposits of 70-75 years old	
0 – 5	2960($v_{as}CH_3$), 2924($v_{as}CH_2$), 2874(v_sCH_3), 2860(v_sCH_2), 1732($vC=O$), 1451($\delta CH_2,\delta_{as}CH_3$), 1414($\delta_{as}CH_3$), 1339($vC$-N), 1262($vC(=O)$-O), 1160($vO$-C-C), 1081($vSi$-O-Si), 1020($vSi$-O-Si), 875($vO$-O), 840(trisubstituted), 731(trisubstituted), 703(ρCH_2)
5 – 10	2952($v_{as}CH_3$), 2924($v_{as}CH_2$), 2876(v_sCH_3), 2853(v_sCH_2), 1723($vC=O$), 1460($\delta CH_2,\delta_{as}CH_3$), 1378($\delta_sCH_3$), 1267($vC(=O)$-O), 1156($vO$-C-C), 1080($vSi$-O-Si), 1023($vSi$-O-Si), 889(five-substituted), 873(vO-O), 730(ρCH_2)
10 – 15	2925($v_{as}CH_2$), 2855(v_sCH_2), 1732($vC=O$), 1455(δCH_2), 1263($vC(=O)$-O), 1160(vO-C-C), 1018(vSi-O-Si), 777(disubstituted), 700(disubstituted)
15 - 20	1729($vC=O$), 1259($vC(=O)$-O), 1163(vO-C-C), 1009(vSi-O-Si)
Soils deposits of 2 years age	
0 – 5	2927($v_{as}CH_2$), 2856(v_sCH_2), 1731($vC=O$), 1450(δCH_2), 1263($vC(=O)$-O), 1177(vO-C-C), 1076(vSi-O-Si), 1020(vSi-O-Si), 875(vO-O), 733(ρCH_2), 683(monosubstituted)
5 – 10	2925($v_{as}CH_2$), 2854(v_sCH_2), 1735($vC=O$), 1456(δCH_2), 1264($vC(=O)$-O), 1162(vO-C-C), 1018(vSi-O-Si), 913($\delta CH=CH_2$), 749(ρCH_2), 682(monosubstituted)
10 – 15	2926($v_{as}CH_2$), 2854(v_sCH_2), 1732($vC=O$), 1441(δCH_2), 1264($vC(=O)$-O), 1160(vO-C-C), 1072(vSi-O-Si), 1009(vSi-O-Si), 788(disubstituted), 760(ρCH_2), 684(disubstituted)
15 - 20	2924($v_{as}CH_2$), 2853(v_sCH_2), 1732($vC=O$), 1457(δCH_2), 1264($vC(=O)$-O), 1160(vO-C-C), 1013(vSi-O-Si), 790(disubstituted), 766(ρCH_2), 691(disubstituted)

Note: ρ – wagging vibrations, v – stretching vibrations, δ – bending vibrations.

Value of frequencies about 1339 cm^{-1} is observed only at a depth 5cm under the layland soils (70-75 years) that it is possible due to stretching vibrations of C – N arylamines.

In area the 875-873cm^{-1} stretching vibrations of peroxide group (O-O) of aliphatic compounds in structure of HS are observed. The peroxidne group is found only in top 10cm of a 70-75 year old deposits layer and in 5cm of a 2-year deposit layer that can be connected with spontaneous oxidation of organic and organometallic air oxygen compounds in the top horizons of soils.

In 2-year-old layland soils quantity of absorption bands decreases. From the surface and up to the depth of 20cm in area near 3000cm^{-1} only absorption bands of the methylene groups are observed ($v_{as}CH_2$, v_sCH_2, δCH_2) with rather constant frequencies. Absorption bands the metyl groups were not revealed. Existence in exemplars from depth of 0-5cm and 5-10cm of absorption bands close to 730cm^{-1} (wagging vibrations of CH_2) also signifies about existence of a number of

directly related groups - CN_2-with amount of carbon atoms more than four. In exemplars at depth of 10-20cm the absorption band of wagging vibrations of the methylene groups is displaced towards larger frequencies that can be bound to decrease of related methylene groups number with each other.

Feature of all studied exemplars of uneven-age layland soils is presence of the common frequencies on any depth. The reference are found for absorption band of carbonyl group (C=O) stretching vibrations in area of 1310-1250cm^{-1} that corresponds to stretching vibrations C (= O) - O in area of 1180-1130cm^{-1} corresponding to stretching vibrations of O-C-C group. Probably it is ether aliphatic acids as absorption reference for aromatic compounds are absent. It confirms that these groups are the stablest and constant base units of the studied soils HS, which mineralization resulting from agricultural use is not exposed.

In uneven-age layland soils frequencies in areas of 1100-1000cm^{-1} which can be carried to stretching vibrations are observed Si-O-Si. However in the top horizons absorption bands are narrow and also differ in form and intensity from absorption bands of clay minerals. Possibly, their existence is bound to stretching vibrations of Si-O-Si in the form of a cycle-$(R_2SiO)_4$ (~1080cm^{-1}) and cyclo-$(R_2SiO)_3$ (~1020cm^{-1}), where R is aliphatic group. In underlying thickness of 1018cm^{-1} and 1009cm^{-1} frequencies are caused by stretching vibrations of clay minerals silicium oxigen groups. Frequencies emergence of the reference to clay minerals is possibly bound to

decrease in maintenance of OM in the underlying horizons.

In the 2-year layland soil of intensive strips nonuniform series of the silicium oxigen stretching vibrations in area of 1100-1000cm^{-1}, which layerwise do not differ on intensity and wave numbers come to light. It probably is connected with layland soil horizon age at which secondary accumulation of humus is not considerable, and changes in SOM ranges have to be shown very poorly.

Summary

The layland soils of 2 years and 70-75 years age are feature of the studied exemplar absorption bands existence for the reference ether aliphatic acids which are the stablest and constant base units of SOM.

The peroxidne group is found only in top 10cm of a 70-75 year old deposits layer and in 5cm of a 2-year deposit layer that can be connected with spontaneous oxidation of organic and organometallic air oxygen compounds in the top horizons of soils.

In the 2-year layland soil of intensive strips nonuniform series of the silicium oxigen stretching vibrations, which layerwise do not differ on intensity and wave numbers come to light. It probably is connected with layland soil horizon age at which secondary accumulation of humus is not considerable, and changes in SOM ranges have to be shown very poorly.

Conclusion

The conducted researches show that studying of OM layland soils by means of IR-

Fourier native exemplars spectroscopy, using as background the mineral soil material received after deep removal of SOM by processing with 30% hydrogen peroxide is more informative, than traditional methods. Use of this approach allowed to see changes of the functional groups and fragments of HS absorption spectrum, bound to secondary accumulation of detritus (rough) humus in an upper horizons under the influence of secondary vegetation.

Acknowledgments

References

1. Shinkarev AA, Giniyatullin KG, Latypov MK, Gnevashev SG. Methodological aspects of fractionation of humus substances. Euras. Soil Sci. 2004. 37(5): 479-485.

2. Artemyeva AP. The soil organic matter and the soil granulometric system. Moscow: GEOS, 2010.

3. Bohn HL, McNeal BL, O'Connor GA. Soil Chemistry. New York: Wiley&Sons; 2001.

4. Kononova MM. Soil organic matter. Its nature, properties and methods of study. Moscow: SA USSR; 1963.

5. Kovaleva NO, Kovalev IV. The aromatic structure of lignin in the organic matter of gray forest soils. Moscow University Soil Sciences Bulletin. 2002. 2: 23-29.

6. Shirshova LT, Ghabbour EA, Davies G. Spectroscopic characterization of humus acids fractions isolated from soil using different extraction procedures. Geoderma. 2006. 133(3-4): 204-216.

7. Law IA, Hayes MHB, Tuck JJ. Extraction of humic substances from soil using acidified dimethyl sulphoxide. Int. humic substances soc. 2nd int. conf.; Birmingham; 1985. P.18-21.

8. Aslan-Sungur G, Evrendilek F, Karakaya N, Gungor K, Kilic S. Integrating ATR-TIR and data-driven models to predict total soil carbon and nitrogen towards sustainable watershed management. Research Journal of Chemistry and Environment. 2013. 17(6): 5-11.

9. Hladký J, Pospíšilová L, Liptaj T. Spectroscopic characterization of natural humic substances. 2013. 80(1): 8-14.

10. Janik LJ, Skjemstad JO. Characterization and analysis of soils using mid-infrared partial least-squares. II. Correlations with some laboratory data. Australian Journal of Soil Research. 1995a. 33(4): 637-650.

11. Janik LJ, Skjemstand JO, Raven MD. Characterization and analysis of soils using mid-infrared partial least squares. I. Correlations with XRF-determined major element composition. Australian Journal of Soil Research. 1995b. 33(4): 621-636.

12. Leifeld J. Application of diffuse reflectance FT-IR spectroscopy and partial least squares regression to predict NMR properties of soil organic matter. European Journal of Soil Science. 2006. 57: 846-857.

13. Mimmo T, Reeves JB, McCarty GW, Galletti G. Determination of biological measures by mid-infrared diffuse reflectance spectroscopy in soils within a landscape. Soil Science. 2002. 167(4): 281-287.

14. Reeves JB, McCarty GW, Reeves VB. Mid-infrared Diffuse Reflectance Spectroscopy for the Quantitative Analysis of Agricultural soils. Journal of Agricultural and Food Chemistry. 2001. 49(2): 766-772.

15. Viscarra-Rossel RA, McGlynn RN, McBratney AB. Determining the composition of mineral-organic mixes using UV–vis–NIR diffuse reflectance spectroscopy. Geoderma. 2006a. 137(1-2): 70-82.

16. Viscarra-Rossel RA, Walvoort DJJ, McBratney AB, Janik LJ, Skjemstad JO. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma. 2006. 131(1-2):59–75.

17. Vorobeva LA. Theory and practice of soil chemical analysis. Moscow: GEOS; 2006.

18. ISO 11277:1998. Soil quality – Determination of practicle size distribution in mineral soil material – Method by sieving and sedimentation. Switzerland: Int.Organ.Stand; 1998.

19. Pansu M, Gautheyrou J. Handbook of soil analysis. Mineralogical, organic and inorganic methods. Berlin, Heidelberg: Springer-Verlag; 2006.

20. Eusterhues K, Rumpel C, Kögel-Knabner I. Stabilization of soil organic matter isolated via oxidative degradation. Org. Geochem. 2005. 36(11): 1567-1575.

21. Hyeong K., Capuano RM. The effect of organic matter and the H_2O_2 organic-matter-removal method on the δD of smectite-rich samples. Geochim. Cosmochim. Acta. 2000. 64(22): 3827-3829.

22. Giniyatullin KG, Shinkarev AA (Jr.), Shinkarev AA, Krinari GA, Lygina TZ, Gubaidullina AM, Kornilova AG, Melnikov LV. Irreversible fixation of organic components in labile inter-spaces as a mechanism for the chemical stabilization of clay-organic structures. Eurasian Soil Science. 2012. 45(11): 1068-1080.

23. Smith AL. Applied Infrared Spectroscopy. London: John Wiley and Sons; 1982.