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Soils response to the land use and soil climatic gradients at ecosystem scale: Mineralogical and geochemical data

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ABSTRACT

Ecosystem in responses to land use change create feedbacks in soils and ecological processes in Critical Zone (CZ). The identification and quantification of such changes is needed as a part of understanding the relationship between climate, CO_2 emission, humidity, biological activity, soil carbon, surface redox, and plant nutrient cycling and lithology, mineralogy, biogeochemistry of bedrocks. The CZ observation as complex investigation of three Luvic Phaezoem soils under secondary deciduous forest, grassland and cropland from Moscow region, Russia, was fulfilled with the main goal to study weathering processes in soils along global gradients of environmental change. Detailed study of mineralogy and chemistry (XRD, XRF), surface area, porosity, organic matter, carbon/microbial biomass, moisture content, monitoring of total soil respiration was performed. Ecosystem in responses to land use change the parameters of CZ (CO_2 emission, humidity, biological activity). Land use change result in climate parameter on a local scale (soil climatic gradients) and formed feedback in weathering intensity and basic soil properties-organic matter, acidity, bulk density, WHC, surface properties and porosity, mineralogy and geochemical changes. The decreasing of smectites in the upper parts of the profile and the increasing of illite and vermiculite content was observed. Montmorillonite into vermiculite transformation, which took place only under the forest, which caused the decreasing of pH, soil vermiculite may also derive from muscovite. The intensity of the given process increases as the following: forest soil < grassland < cropland. The given tendency was explained by both the mineral transformations and redistribution of mineral components within the soil profile. The redistribution of chemical elements between the different sub-fractions of silt and clay is in relationship to the land use. As a general trend, we can conclude that clay fractions in a comparison with bulk soil samples are enriched in both OC and N. Mineralogical and chemical changes influenced the surface properties and porosity. The 50–150 years of different land use resulted in these feedbacks with maximum in aboveground zone and soils as main point of surface of a given CZ.

1. Introduction

The beginning of 21th century outlined a new interdisciplinary study, a science of Earth's 'Critical Zone', as the integrated and life-supporting system of Earth's surficial terrestrial processes. "Critical Zone" (CZ) is defined as the, "heterogeneous, near-surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine the availability of life-sustaining resources" (National Research Council (NRC, 2001)). The theoretical base of CZ is growing from the concept of the 'Biosphere' (Vernadsky, 1929, 1998). Biosphere includes the hydrosphere, troposphere, and the upper part of the Earth's crust and the constant exchange of matter and energy between the living and inorganic matter supports the existence of the biosphere. The CZ, in particular Earth's surface and soil, is a product of multiple environmental factors that have varied over time (Richter and Yaalon, 2012). CZ responds to climatic and anthropogenic forcings, and quantifying and modeling the paleo and modern CZ is a central challenge for achieving a sustainable environment (Brantley et al., 2007). Soil is at the central junction of the CZ, representing a geomembrane across which water, energy, gases, solids, and organisms are actively exchanged with the atmosphere, biosphere, hydrosphere, and lithosphere, thereby creating a life-sustaining environment (Amundson et al., 2007; Brantley et al., 2007; Chorover et al., 2007; Lin, 2010). In contrast to the other spheres of the Earth system, the pedosphere is a unique, relatively immobile sphere that is easily impacted by human activities. Each soil is relatively immovable and formed in situ as a natural body, which records environmental changes by transformations according to the interactions of

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climatic, biotic, and anthropogenic factors, as conditioned by geologic and topographic settings, over geological and biological time scales. We have taken in to account since the soils can be transformed or to be lost by the anthropogenic action, as land use and other. Because of the uncertainty in how soil ecosystems will change under altered climate scenarios, and the potential for large-scale disruption of important soil processes resulting from altered precipitation, temperature and elevated CO_2, research is needed to evaluate the potential for dramatic shifts. Climate change has the potential to alter soil ecosystem structure and function in non-linear ways, particularly in high-latitude ecosystems. Land use change can result in the emissions of greenhouse gases that may result in a positive feedback loop to climate change by increasing flux of CO_2 to the atmosphere. Climate change also affects the productivity of land, which in turn leads to further land-use change. Soil can also influence climate on a smaller scale (soil climatic gradients), soils that are wetter or denser hold heat and stabilize the surroundings from temperature changes more so than drier, looser soils. This makes the monitoring of soil change an excellent environmental assessment, because every block of soil is a timed “memory” of the past and present biosphere-geosphere dynamics (Arnold et al., 1990). A growing world-wide international network of CZ Observatories (CZOs) enables experiments across global, regional, and local environmental gradients, providing the scientific base for the understanding of the CZ processes with response to the land use and climate change (Banwart et al., 2011).

In this paper, we emphasize the importance of CZ at ecosystem scale, as local environmental gradients, and focus on their effect on mineralogical and geochemical changes in soils profiles. The complex investigation of three Luvic Phaezoem soils under secondary deciduous forest, grassland and cropland from Moscow region, Russia, were fulfilled with the main goal to study the state of solid phases of soils along global gradients of environmental change: land use and climate. This study was a part of the ISTC Project No. 4028 “Quantification of carbon stocks and pollution loads in northern latitude soils: assessment of potential release resulting from climate change” (2010–2012).

2. Materials and methods

The experimental plots are located in the territory of the Experimental station of the Institute of Physico-chemical and Biological Problems in Soil Science, Russian Academy of Sciences (54°50′N, 37o34′E, ~100 km to the south of Moscow) on a clay grey forest soil, Luvic Phaezoem (loamy). Some physico-chemical characteristics of the surface A1 horizon of the three soils are given in Table 1.

The catchment area is 0.5 km^2, on a watershed with a mean elevation of 230 m above sea level (Fig.1). The climate is humid continental; average annual temperature varies from +3.5 to +5.5 °C and average annual rainfall is within 450–650 mm. The investigations were conducted in situ over three years (2010–2012) in soils under secondary mixed forest (age 150–200 years), grassland (last 45 years; cereal herbs) and cropland (~50 last years, cereal-fallow rotation). The weekly monitoring of CO_2 emission, soil and air temperatures, soil moisture was carried out in all three ecosystems. The total soil respiration (root respiration + heterotrophic soil respiration) without the above ground plant respiration was determined by a close chamber method (Kurganova et al., 2011). The data for total soil respiration were taken between 9 and 11 a.m. because soil respiration at this time of the day corresponds to an average daily rate. On average, 5–10 replicates were taken during the growing season and 3 in winter. The measurements of soil moisture and temperature in the upper 0–5 cm soil layer as well as meteorological data (air temperature and humidity, wind speed, precipitation, etc.) were registered each time.

The soil samples were taken from each profile in 3 replicates in 10 cm increments (layer 0–50 cm) and in 25 cm increments (layer 50–100 cm) and from the genetic horizons of soils for mineralogical and geochemical investigations. The most part of analysis were made for soil samples taken at the soil depth, particle size analysis was done for samples taken in each genetic horizon for comparison with mineralogical and geochemical data including analysis of fractions content. The laboratory study of soils included basic soil properties (particle size, bulk density, water holding capacity (WHC) and pH-values in KCl extracts was determined using the standard procedures for soil analysis (Van Reeuwijk, 2002).

Organic carbon and nitrogen were determined by means of CHNS analyzer Elementar (Vario EL III). In fresh samples of Phaeozems the respiratory activity and biomass of soil microorganisms (substrate induced respiration method) were determined.

Autopore IV 9500 (Micrometrics INC, USA) mercury porosimeter was used to determine the pore size distribution. The undisturbed soil samples were oven-dried at 105 °C and degassed in a vacuum under pressure of 6.67 Pa at the temperature of 20 °C before intruding mercury in step-wise pressure increments in the range from 0.0036 to 400 MPa. The measurements were done in three replicates

The mineralogical composition was determined by X-ray diffractometry using CuKα radiation and a Bruker–D2 Phaser diffractometer (0.02° step scan and a count time of 1 s per step) was used to identify bulk and clay (< 2 μm) mineralogy. Bulk mineralogy was studied using the randomly oriented specimens. Specimens were prepared on the glass slides from the ethanol suspension with 10% of ZnO addition as the inner standard. The clay fraction was separated by

Table 1
General characteristic of Luvic Phaeozems soils, (mean values from three replication).

Land use/ Ecosystem Depth, cm	Forest (DF1)	Grassland (DF2)	Cropland (DF3)
Bulk density of soils, g/cm^3			
0–5	1.01	1.24	1.34
5–10	1.06	1.48	1.36
15–20	1.29	1.46	1.31
35–40	1.34	1.44	1.50
55–60	1.46	1.54	1.55
75–80	1.54	1.48	1.53
95–100	1.53	1.56	1.49
Water content in air dried soil samples %			
0–5	2.38	1.01	0.45
5–10	2.40	0.34	0.38
15–20	2.85	0.19	0.19
35–40	3.32	0.11	0.18
55–60	3.78	0.10	0.20
75–80	4.01	0.14	0.50
95–100	4.02	1.77	4.99
Water holding capacity of soil samples, % (gravimetric)			
0–5	57.5	47.1	41.0
5–10	43.1	39.9	41.5
15–20	41.7	39.4	39.8
35–40	39.3	39.9	37.7
55–60	40.2	40.0	38.5
75–80	38.8	39.5	40.2
95–100	39.4	38.8	40.9
Content of total carbon in soil samples, g C/kg of soil			
0–10	30.03	20.92	10.51
10–20	11.54	10.82	11.03
20–30	6.11	7.32	7.42
30–40	4.68	3.98	4.67
40–50	4.49	3.33	3.37
50–75	1.36	1.19	2.33
75–100	1.42	0.72	1.26
Content of total nitrogen in soil samples, g N/kg of soil			
0–10	2.35	2.03	1.10
10–20	1.08	1.25	1.11
20–30	0.60	0.85	0.80
30–40	0.50	0.55	0.55
40–50	0.48	0.49	0.46
50–75	0.00	0.00	0.00
75–100	0.00	0.00	0.00

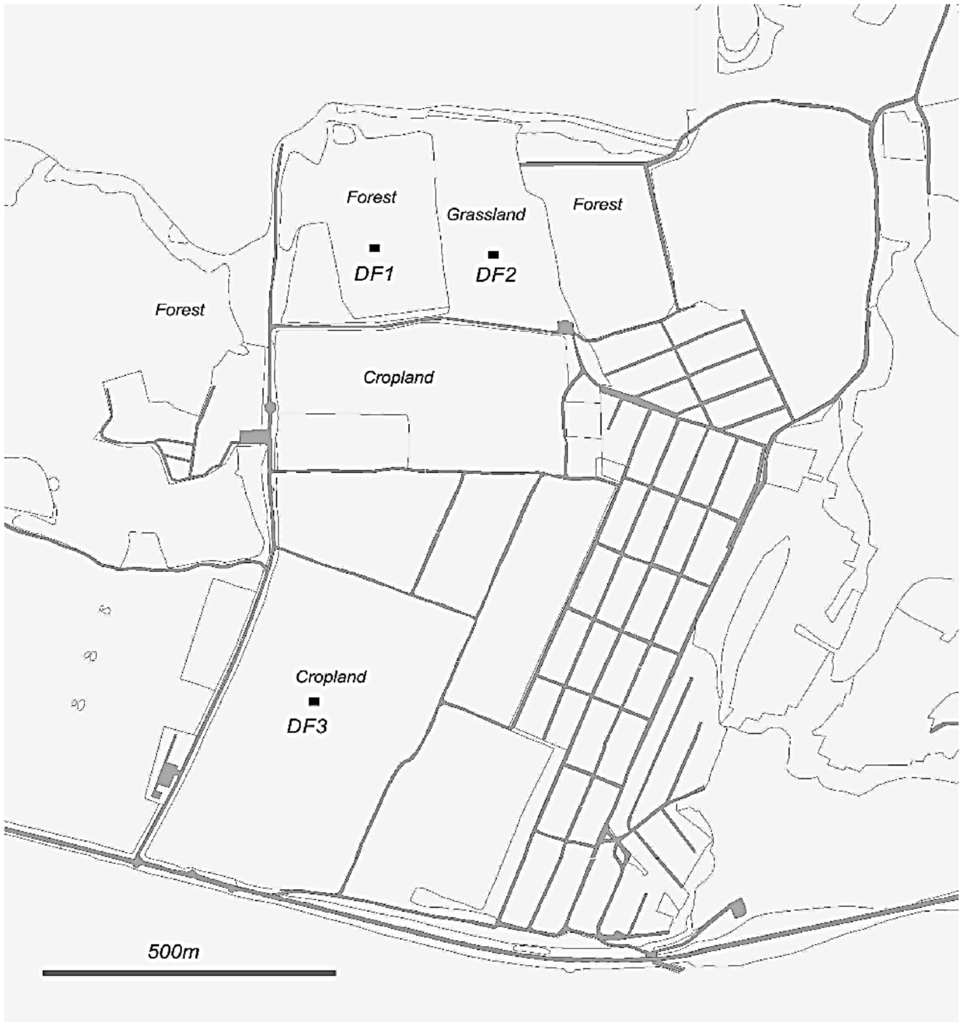

Fig. 1. Map of the catchment area with soil profiles' location.

sedimentation. Parallel oriented specimens of clay fractions were prepared by the sedimentation of a water suspension with standard concentration on a glass slide of standard size 15 × 15 mm. The set of tests was applied for the identification of clay minerals : (1) Mg^{+2} saturation at room temperature; (2) Mg^{+2} saturation and ethylene glycol solvation for 24 h at room temperature; (3) Mg^{+2} saturation and heating at 350 °C for 2 h; (4) Mg^{+2} saturation and heating at 550 °C for 2 h; (4) K-saturation at room temperature, for vermiculite recognition, followed by heating of the K-saturated samples at 110 °C, 335 °C and 550 °C, for HIV/HIS and chlorite recognition ; (5) Li + saturation, heating at 250 °C for 24 h and ethylene glycol solvation for 24 h. Quantitative estimation of the main clay mineral groups was performed on the basis of the peaks area based on the Biscaye method (Biscaye, 1965) and using «QUANTA» (ChevronTexaco) program. The identification of clay minerals was done in agreement with Srodon (2006). Geochemical data were obtained with the desktop WD-XRF crystal diffraction scanning spectrometer 'SPECTROSCAN MAKC-GV' (Russia). The preparation included drying and grinding of the soil samples to the particle size of about 50μm and pressing into pellets for measurement. The quantitative analysis was based upon 24 standard rock and soil calibration samples. All statistical analyses were performed using Statistica 6 software and Excel to carry out the multiple stepwise regression analysis to examine the correlation between soil properties and land use.

3. Results

3.1. Basic soil properties and ecosystem gradients

Phaeozem soils were developed from loam. The main granulometric fractions of parent material of soils are coarse silt (10–50 μm) 31–35%, clay (< 1 μm) 29–32% and fine sand (50–250 μm) 24–30%. Profiles are visibly differentiated: upper 40–60 cm of profiles have a lighter composition, the content of clay here is lower, whereas the increasing of coarse silt fraction occurred. Such tendency took place in DF-1 and DF-2. Profile under the cropland (DF-3) has visibly less content of fine sand and the granulometry of this profile is coarser. Eluvial-illuvial redistribution of clay is the most visible process in the profile under the forest, where the concentration of clay in the top horizon is 12% in comparison with 18% in DF-2 and 20% in DF-3 profile. Additionally, we separated and investigated the different sub-fractions of silt. Clay and silt profile distributions are given in Table 2. For all three profiles the predominant fraction is the coarse silt (10–100 μm) – up to 65%. Topsoils of all three profiles are enriched in this fraction. Top horizons of DF-1 and DF-2 additionally are enriched in sand (> 100 μm).

The content of organic matter (OC) and organic N in bulk soil samples varied in soil profiles under the different ecosystems. The higher OC concentration was obtained for the top layer of the forest soil– 3.63%, under the grassland its content was 2.60%, and under the cropland –1.16%. For N, its content in top layer falls down from 0.3% in DF-1 to 0.25% in DF-2 and 0.12% in the DF3. For all three profiles only

Table 2
Content of clay and silt fractions in Luvic Phaezoem (μm), %.

Profile	horizon	Depth, cm	< 2	2–5	5–10	10–100	> 100	error
DF- 1	A1	0–12	9.99	1.33	9.27	62.71	11.01	5.69
	A2B	12–42	9.81	4.57	8.90	62.29	5.96	8.46
	B1	45–77	20.85	4.37	9.57	55.55	5.79	3.87
	B2	77–115	20.80	3.90	10.58	56.45	3.71	4.56
	BC	115–150	17.84	4.67	8.81	62.20	2.94	3.54
DF-2	Ad	0–6	9.27	2.82	9.43	64.17	9.24	5.07
	A1	6–23	18.03	1.99	7.99	64.78	5.70	1.51
	A2B	26–53	21.12	5.44	6.99	57.51	4.71	4.23
	B1	53–80	23.49	5.13	8.39	53.27	5.27	4.45
DF-3	Ap	0–22	17.41	6.97	11.30	59.64	2.53	2.15
	A1	22–34	24.03	5.57	9.12	53.93	1.45	5.89
	A2B	34–72	34.27	5.08	8.57	47.05	1.67	3.35
	B1	72–90	36.57	5.27	9.34	45.17	1.44	2.20
	B2	90–130	35.35	5.17	7.97	48.16	0.94	2.41

upper 30–40 cm are relatively rich in organic matter. Below this depth OC content is visibly lower, becomes constant with depth and is similar for all 3 profiles (0.2–0.3%). For organic N the values are between 0.04–0.05%.

Similarly, to the particle size composition and organic matter content, we observed the following variations in bulk density in the upper 0–10 cm layer: DF-1 –1.05 g/cm^3, DF2- 1.3 g/cm^3 and DF3-1.35 g/cm^3. Below 50–60 cm the bulk density became constant with depth and is similar in all 3 profiles -1.5 g/cm^3 (Table 1)

Phaeozem profiles slightly differ in acidity. High acidity was observed in soil under the forest; below 25 cm to the depth of 1.5 m it decreased to pH -4.0–4.2. Under the grassland and cropland soils, in the same range of depth, the values were 4.4–4.6 and 4.6–4.7 respectively. The opposite distribution of pH in topsoil's (0–20 cm): DF1-5.4, DF2-4.9 and DF3-5.2

The water holding capacity (WHC) ranged from 41.0 to 57.5%. The uniformity was observed in all soils below 25 cm where it reached 40%. The main variations were found among the top soil horizons (0–10) cm: DF1-57.5%, DF2-47.1% and DF3-41.0%. The water holding capacity was found to be positive and significantly correlated with organic carbon ((squared multiple correlation, $r^2 = 0.62$), a weak or non-existent relationship ($r^2 \sim 0.3$) for clay, and porosity ($r^2 = 0.57$). However, a negative relationship (R^2) of WHC was also observed with pH (-0.2), sand (-0.3), silt -0.29), bulk density (-0.28).

The climatic parameters variation for the period of observation is given in Fig. 2. The main gradients were found for the soil moisture variability and CO_2 emission rate. During winter season 2011–2012, the average CO2 emission from forest soils constituted 0.69–0.71 g C/m^2/day and it was slightly higher in comparison with grassland soils (0.53–0.59 g C/m^2/day). In the other periods of the year the values of emission are higher in the grassland soil and are particularly higher in the summer period. In the cropland soil CO_2 emission is always lower than the other two soils, with the exception of the last period March-May 2012 where all the soils exhibited the same values. The lowest soil CO_2 flux was observed in the cropland soil. The biological activity of soils (soil microbial biomass and respiratory activity of soil microorganisms) significantly differed at the ecosystem level and reached a maximum in the surface soil horizon under forest. Below the surface horizon, soil microbial biomass showed always the highest values in the cropland soil, while it was often equivalent in the forest and grassland soils (Fig. 3).

3.2. Differential pore size distributions

Pore size distribution measurements are important characteristic of soil structure, because they affect many important water transmission and storage functions of soil and root growth, and reflect agricultural management effects and evolution of soil. Fig. 4a indicates that the differential curves are multi-modal. The peaks in the cropland soil at equivalent pore radius at approximately 0.6 μm, 5 μm and 94 μm was much similar in the two surface soil horizons and of smaller magnitude 0.15–0.23 cm^3 g^{-1}. Upper horizons of forest and grassland soils were characterized by the new peak at equivalent pore radius at approximately 1.47 μm with larger magnitude 0.25–0.30 cm^3 g^{-1} and increasing of magnitude of the peak at 94 μm. The existence of the multi modal pore size distribution indicates a more heterogeneous pore system in these soils. The bimodal curve is characteristic for the forest soil horizon A2B (12–42 cm) with pore radii at 0.44 and 110 μm and magnitudes of 0.16 and 0.24 cm^3 g^{-1}, respectively. The maximum of porosity were registered in the top horizon of profiles DF-1 and DF-2 (Fig. 4b), with values of 55% in forest soil and 48% in cropland soil.

3.3. Mineralogical composition of bulk samples and clay fractions

In bulk soil samples of all three studied soils the main minerals were: quartz (30–40%), 2 kinds of feldspars : K-feldspar 20–33% and plagioclase (15%), 2:1 layer silicates (smectites and mica) (20-30%), kaolinite (5-12%). The concentration of 2:1 aluminosilicates is lower in the upper 50 cm of soil profiles where the contents of quartz and feldspars increase. Profile distributions of minerals are given in Fig. 5.

The obtained XRD spectra for < 2 μm clay fraction are presented in Fig. 6 and in Supplementary material 1. All three profiles are developed from a parent material with a similar clay mineralogical composition where the main mineral is smectite (51–56%). Results of K- and Li-tests, and the position of (060) peak of smectite based on the XRD - spectra of non-oriented specimens ($d_{060} = 1.501$ A) show that smectite is present as the low-charged dioctahedral phase – montmorillonite. The second mineral phase is dioctahedral mica with the similar position of (060) diffraction peak (28–32%). Additionally clay fractions contain kaolinite and vermiculite. The clay fraction for all studied soils are enriched by fine dispersed quartz. In the upper 1 m of the studied soil profiles, smectite concentration decreases and reaches 22–31 % in topsoils being the largest in DF-1 and the smallest in DF-3 (Fig. 7). In this part of the profile, smectite is the component of the irregularly-interstratified mica-smectite phase. Simultaneously with the decreasing of smectites in the upper parts of profiles, the increasing of mica content takes place and it reaches 49–53 % in A-horizons. The intensity of the given process is increasing as the following: DF-1 < DF-2 < DF-3. The main difference between studied profiles is, however, the behavior of a vermiculite phase. The considerable enrichment of it within upper 80 cm of DF1 profile was observed. Whereas DF2 has the traces of vermiculite, and DF3 does not contain it, as well as the clay fraction of parent material.

3.4. Elemental analysis

On the base of XRF data (profile distribution of TiO_2/Al_2O_3) we confirmed the uniformity of deposits under all ecosystems. The profile distribution of the Chemical Index of Alteration (CIA) using the whole rock geochemical data of major element oxides (Nesbitt and Young, 1982) also demonstrated the uniformity of profiles starting from 50 to 60 cm depth downwards. This index is essentially based on the monitoring of the hydrolysis of feldspar and the respective changes in the content of the major cations offers the best quantitative measure of chemical weathering. Kaolinite has a CIA value of 100 and represents the highest degree of weathering. For illite the values are between 75 and 90, muscovite -75, feldspars -50. ((Nesbitt et al., 1997). Soil profile DF1 is less weathered in comparison with the grassland soil: CIAs for top horizons of these two soils are 58 and 68 respectively. The line of profile distribution of CIA within the upper 50 cm is shifted to the high values for DF -2 in comparison with DF-1 for 5 units. This result is confirmed by the profiles distribution of the ratio Quartz/F-spars, with values of ~ 2 for DF-2 and of 1.5 for DF1, respectively

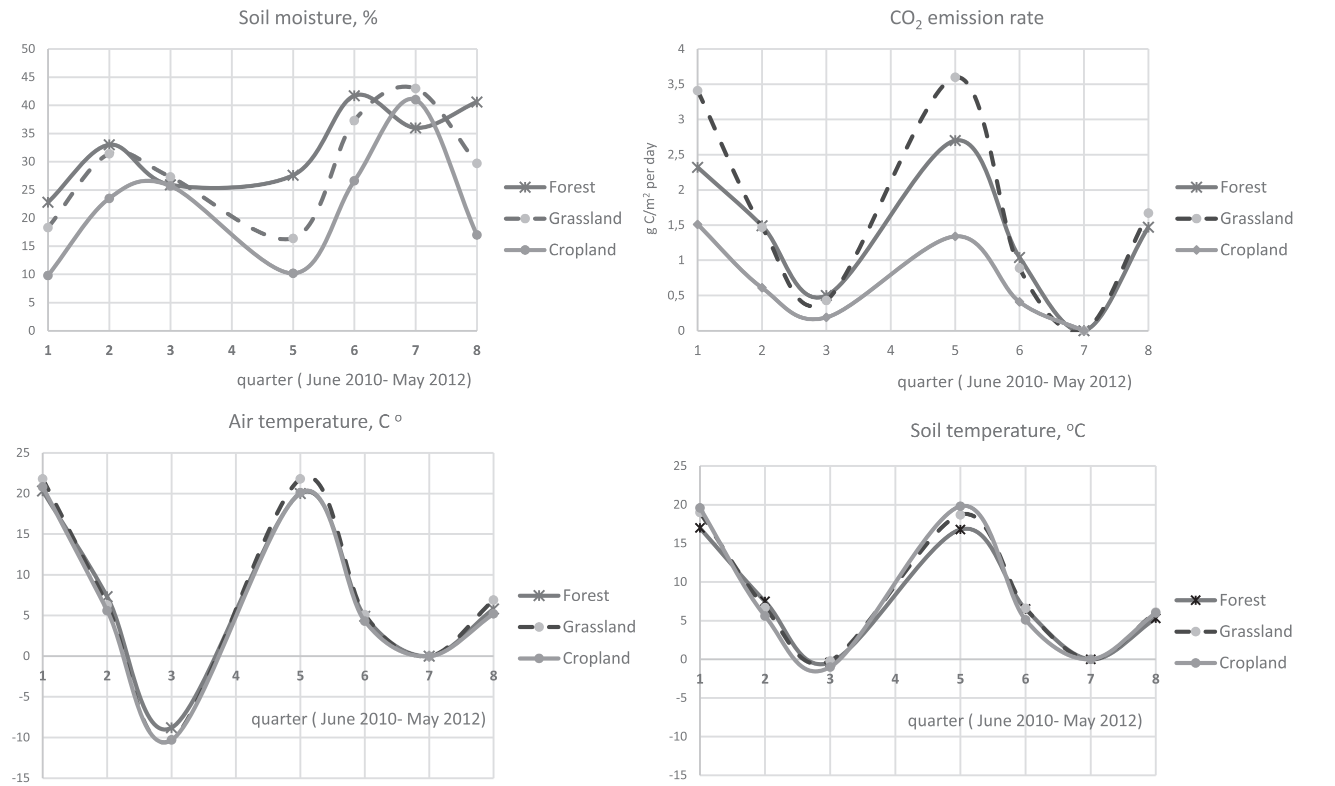

Fig. 2. The local ecosystem gradients for the observation period (2010–2012, average for each quarter) relative to soil moisture (mass base), air temperature, soil temperature and CO_2 emission rate.

(Fig. 8).

In addition to particle size analysis, we separated and investigated the different sub-fractions of silt (Table 2). The profile distribution of chemical elements such as Si, Al, Fe, K, for bulk sample looks very similar (Supplementary material). On the contrary, in the case of the analysis of element concentration in different sub-fractions of silt and clay we observed the redistribution with a connection to the ecosystem. Fig. 8, 9C, presents an exam ple for Fe_2O_3 distribution in the studied soil profiles. The main part of iron is linked to the clay ($r^2 = 0.83$) and 10–100 µm fractions ($r^2 = 0.33$). In all three soil profiles the process of illuviation was observed, the maximum intensity of the redistribution of iron towards the clay fraction was observed in the cropland soil profile. A similar tendency of redistribution among the granulometric fractions was observed for SiO_2, Al_2O_3, K_2O, MnO (data in supplementary material). The maximum intensity of weathering and as results the redistribution of elements from silt fractions (> 100 µm and 10– µm) to the clay fraction is characteristic of cropland soil profile.

Based on the comparative data of the content of OC and N in different granulometric fractions from A horizons of the studied soils we can conclude that clay fractions in a comparison with bulk soils samples are enriched in both OC and N. Minimal OC and N is observed in 10–100 µm fraction. Fraction > 100 µm is characterized by the very

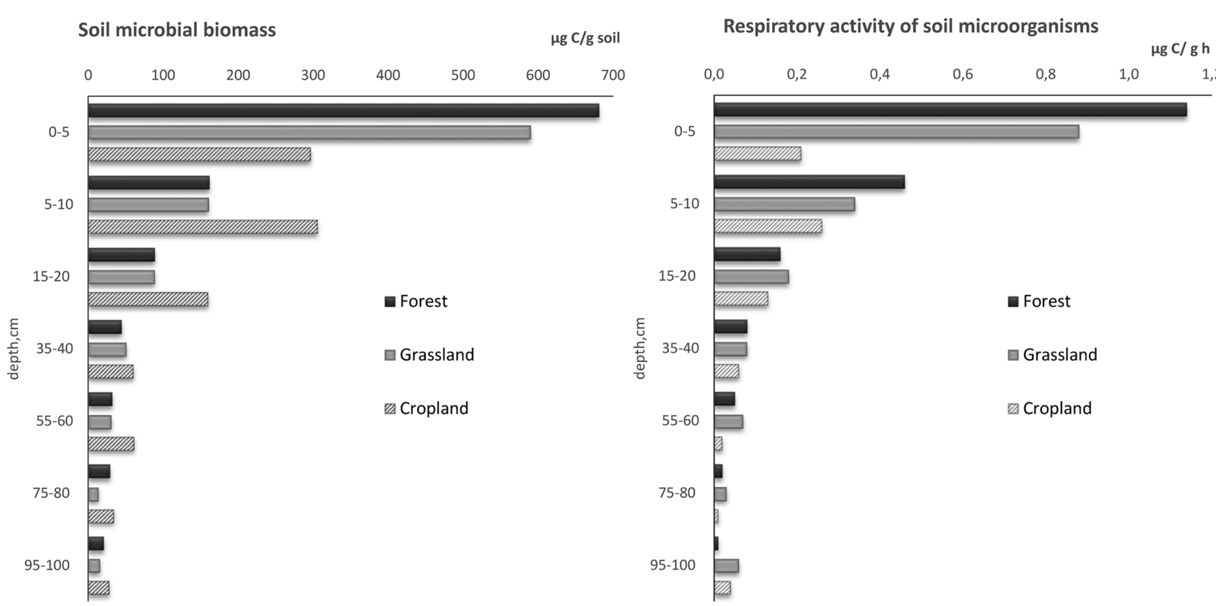

Fig. 3. The biological activity of soils as evinced by soil microbial biomass and respiratory activity of soil microorganisms.

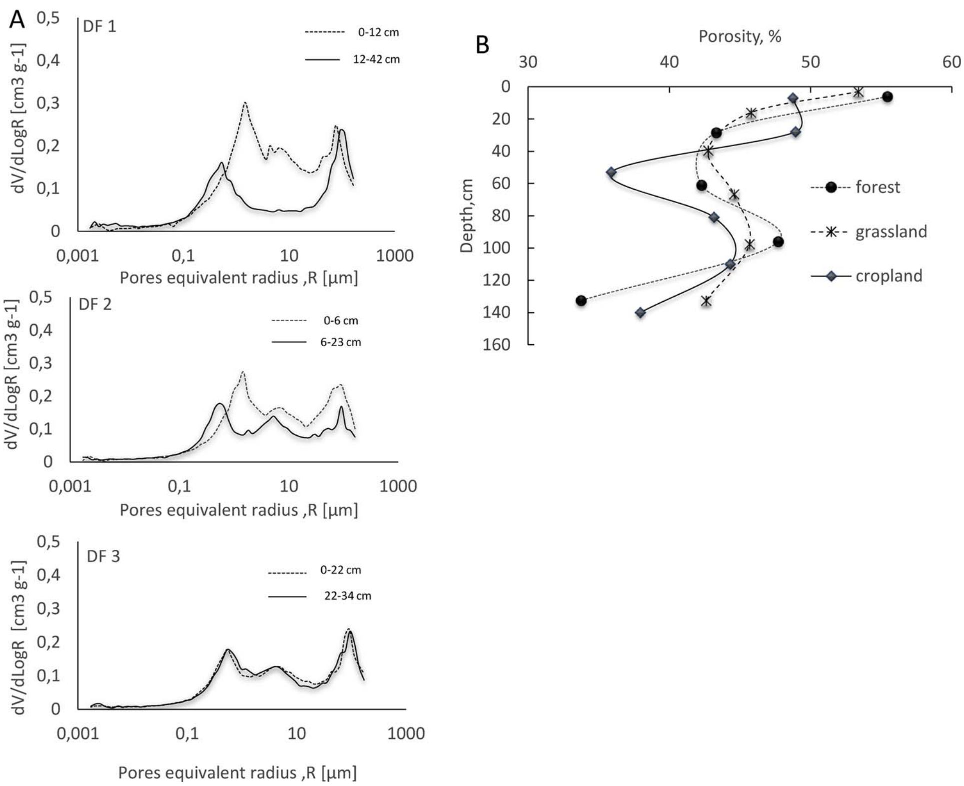

Fig. 4. Pore size distribution. A- Differential curve of pore volume vs. equivalent pore radius of soils with different land use (Deciduous forest-DF-1; Grassland -DF-2; Cropland - DF-3). B – Total porosity profile distribution.

broad range of values: 0–16% for OC and 0–0.8% for N. In some cases, the maximal concentrations of OC and N were found in this fraction. The stable large values were found for clay fractions, for which all values are within the small range: 4–6% OC and 0.4–0.8% for N. For all studied soils C/N values are the smallest for clay fractions and are increasing with the increasing of the particle size. As a rule, the largest C/N has the fraction > 100 μm. Large N concentrations and small C/N values found for clay fractions (natural organo-minerals complexes) from all studied soils can be explained by the large affinity of N-compounds towards the surfaces of clay minerals (Alekseeva et al., 2010; Mikutta et al., 2010; Alekseeva and Zolotareva, 2013).

4. Discussion

The different land use for the period near 50–150 years demonstrates the considerable variations in soils characteristics and ecosystem climatic parameter within the studied catchment. The main factor of observed changes is caused by the soil – plants interaction. The type of land use with different type of vegetation influences the metabolic and geochemical activity in soils.

Land use change result in the variations of emissions of greenhouse gases that may result in a positive feedback loop to climate change by increasing flux of CO_2 to the atmosphere. Soil influence climate on a

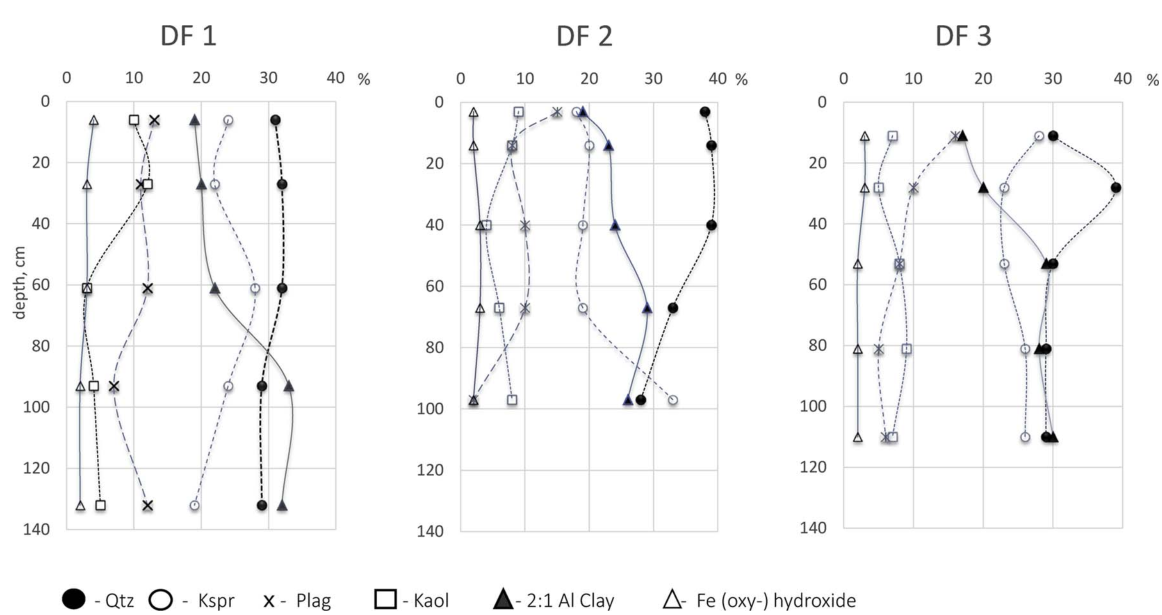

Fig. 5. Bulk mineralogy distribution along the soil profiles (Deciduous forest-DF-1; Grassland -DF-2; Cropland -DF-3).

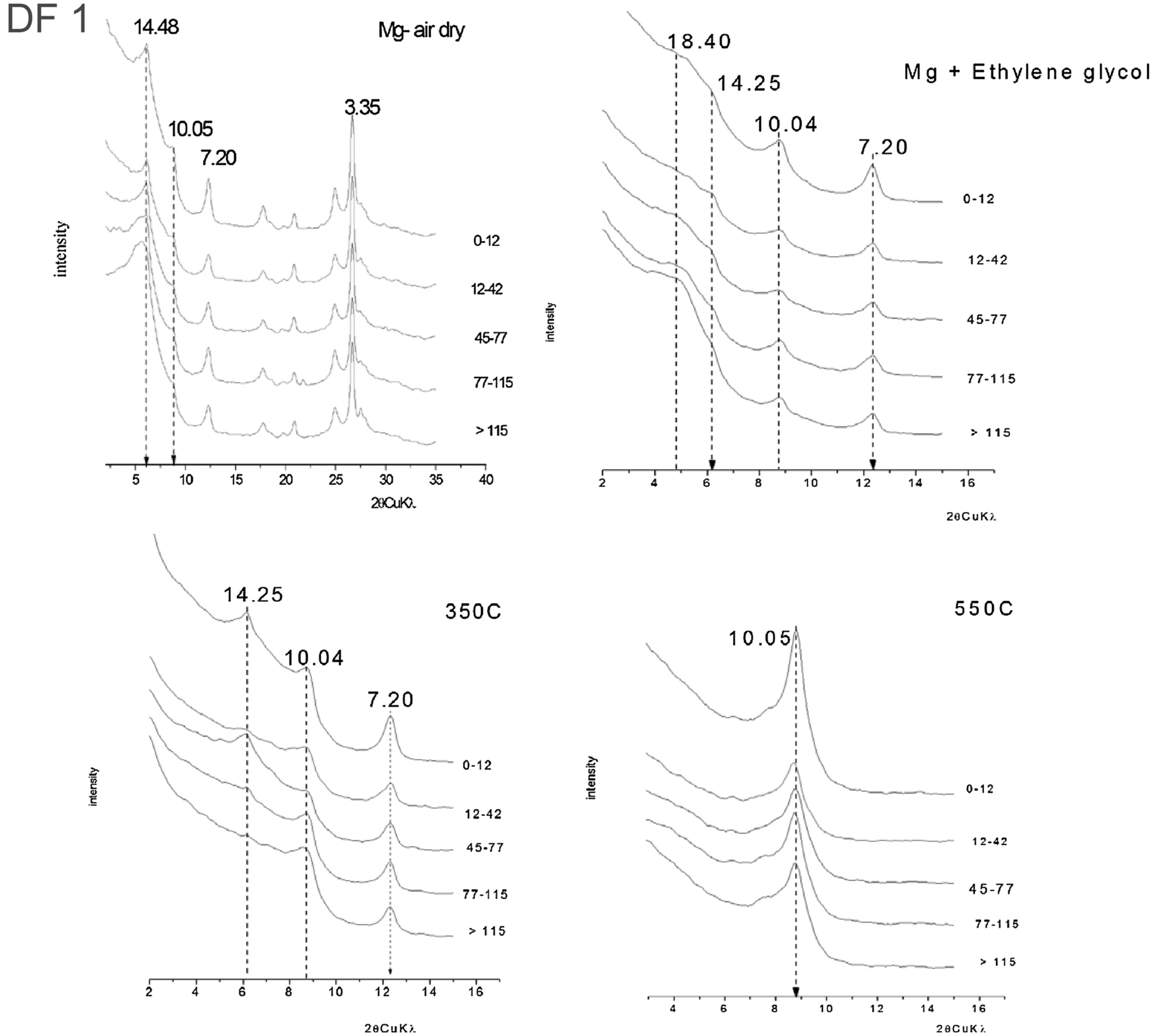

Fig. 6. Example of XRD patterns of < 2 μm fraction for the soil profile under the forest DF-1.

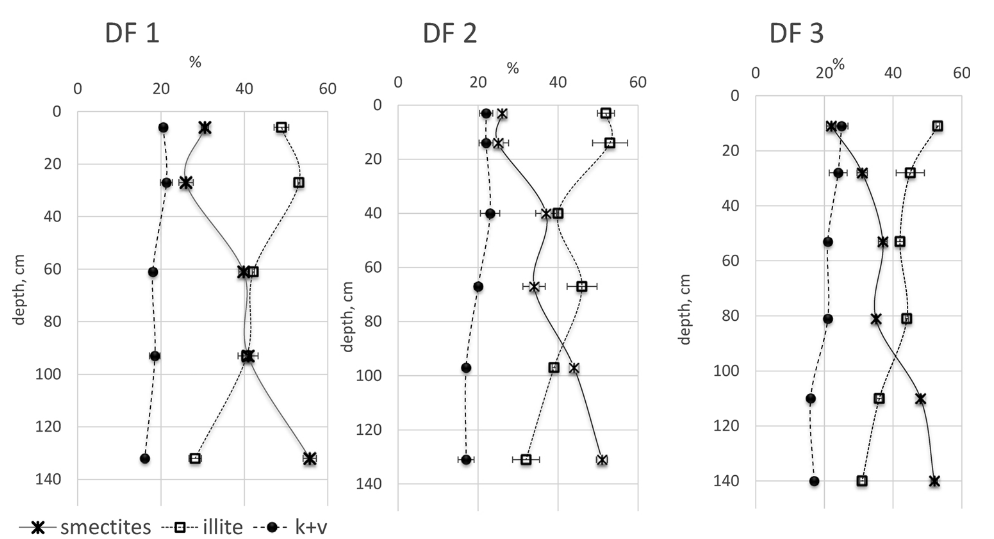

Fig. 7. Clay mineralogy distribution along the soil profiles (Deciduous forest-DF-1; Grassland -DF-2; Cropland -DF-3).Standard deviation values are based on three replications.

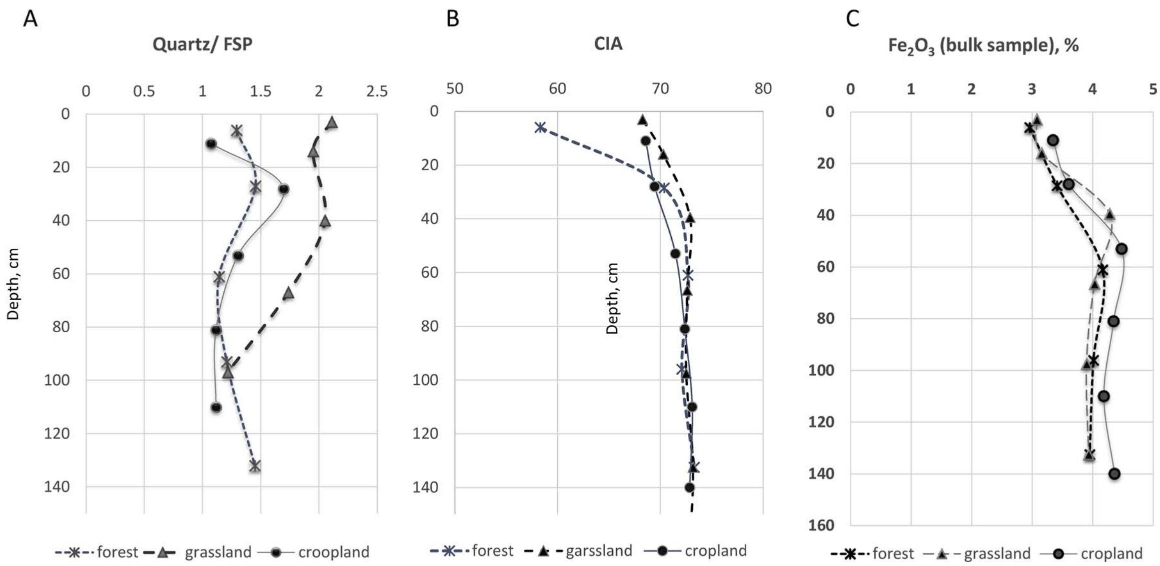

Fig. 8. Weathering index distribution along soil profiles: A – Quartz/FSP ratio. B – Chemical Index of Alteration (CIA). C - Iron distribution along the soil profiles,bulk soil samples.

smaller local scale (soil climatic gradients), ecosystem in responses to land use change the parameters of CZ especially CO_2 emission, soil humidity, temperature of soils, biological activity (Fig. 2, 3). The forest in a comparison with grassland and cropland soils contains the highest number of roots, the greatest microbial biomass, and the largest pool of organic matter. The main gradients at ecosystem level correspond to the CO_2 emission rate (soil respiration), soil microbial biomass and respiratory activity of soil microorganisms. This biologically derived soil CO_2 drives a soil gas concentrations to levels several orders of magnitude higher than in the atmosphere and forms carbonic acid, which attacks the mineral matrix of soils (Amundson et al., 2007). Biological activity, root penetration, abiotic processes, soil cultivation or possible shrinking and swelling of clay materials concern the observed changes in soils porosity and pore size distribution. This result implies that the abundant organic matter in soil within forest and grassland ecosystems may improve water-holding capacity for plant growth. Local scale soil climatic gradients (CO_2 emission, humidity, temperature biological activity) at ecosystem scale with land use differences resulted in basic soil properties, weathering intensity, mineralogical and geochemical changes in soils.

We suppose that the observed differences in bulk and clay mineralogy can be explained by both and redistribution of mineral components within the soil profile and the mineral transformations. The eluviation of clay with the development of the eluvial-illuvial kind of the profiles is supported by granulometry. The transportation of fine dispersed material is accompanied by the preferential transfer of fine colloids enriched in smectite from A-horizons which resulted in the accumulation of mica in the upper parts of soil profiles. Clay minerals distribution within a soil profile with decreasing of smectites in the upper parts of profiles and the increasing of illite, appearance of

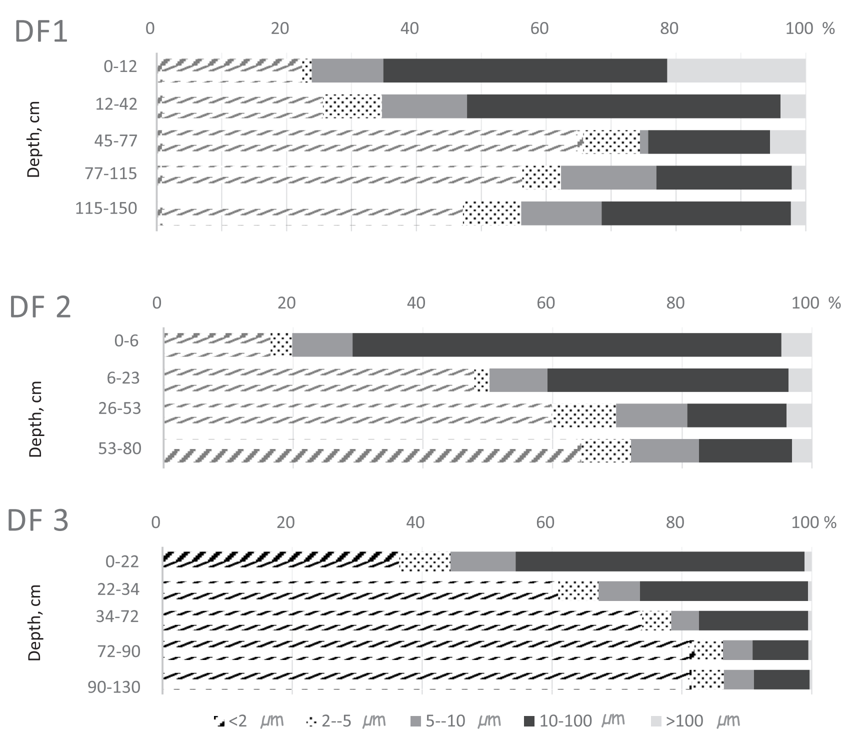

Fig. 9. Iron distribution along the soil profiles in different particle size fractions (Deciduous forest-DF-1; Grassland -DF-2; Cropland -DF-3).

vermiculite. The vermiculite enrichment can be attributed to rhizosphere effects (respiration, humic acids) which caused the decreasing of pH in soils under the forest. The observed acidification of the upper soil profile under forest is typical for non-arable soils. Soil vermiculite may also derive from muscovite, very fine-grained muscovite particles of high specific surface area and reactivity seem necessary for transformation into vermiculite in soil (Golan, 2006). Aoudjit et al. (1996) presented vermiculitization of muscovite in an acidic soil, showing HTREM images of the particles with a muscovite core and a vermiculite rim consisting of about 15 layers. The specific feature of the vermiculite from forest soil profile is the slightly development of the hydroxyl-interlayes (Barnhisel and Bertsch, 1989). This process takes place within the upper 80 cm of the forest soil profile and has not observed in soils developed under grassland and cropland. The intensity of the given process and depth in soil profile is increasing as the following: forest soil < grassland < cropland.

The water holding capacity was found to be positive and significantly correlated with organic carbon content, a weak or non-existent relationship for clay content. Unusual insignificant correlation of WHC with clay fraction probably connected with mineralogical peculiarities of studied soils. In top horizons, the decrease of smectiite and high content of dispersed quartz in clay fractions was detected (Fig. 6).

Changes in mineralogical composition and soil texture for soils with different land use are reflected as results in pore size distribution (PSD). PSD affects numerous soil functions and root growth. The most distinct peak in forest and grassland soils at pore radius of approximately 1.4 μm may favor retention of plant available water, stored in pores of 15–0.1 μm radii, in spite of not different total porosity. This result implies that the abundant organic matter in soil within forest and grassland ecosystems may improve water-holding capacity. Porosity is an additional factor that influences aggregate stability. Earlier studies revealed that the mechanical strength of natural soil aggregates generally increases with decreasing total porosity (Horn, 2004). The increasing volume of smaller pores at the expense of larger pores results in a greater number of contact points between soil particles (Lipiec et al., 2012, Arthur et al., 2013). Taken together, the results imply that greater OC content can be a key factor strengthening the internal bonds between components and stability of the soil aggregates. The stability of natural soil aggregates can be related to the morphology of pores within both micro- and macro-aggregate pore spaces. In cropland soils, we observe the densification of soils due to higher loads at the surface. The number of coarse pores is reduced, the amount of fine pores is increasing relatively and the number of contact points between the soil particles is growing. Perhaps this is a negative effect of bad agricultural practice.

As final point, we have to take in mind the time needed for soils to feedback to climate and land use changes. Generally, for CZ, this time decreases when moving up from the deep underground zone to the shallow subsurface zone to the surface zone and to the aboveground zone (Arnold et al., 1990, Lin, 2010).

The 50–150 years of different land use resulted in these feedbacks with maximum in aboveground zone and soils as main point of surface of a given CZ. The future perspective of present study is attributed to conversion of croplands to native vegetation and vice versa. Critical changes in land use caused by disintegration of the USSR, followed by economic crisis and abrupt shifts in agricultural policy, took place in the end of last century and led to radical decrease of cropland area. This was the most widespread and abrupt land use changes in the 20th century in the northern hemisphere. The spontaneous withdrawal of croplands caused several benefits for environment including substantial C sequestration in post-agrogenic ecosystems. Preliminary study of removal of lands (Luvic Phaezoem) from agricultural use for 20–30 years results in a gradual restoration of their natural structure, improvement of soil agronomical properties, and carbon sequestration in the upper part of the soil profile. (Baeva, et al., 2017).

5. Conclusions

Ecosystem in responses to land use change the parameters of CZ (CO_2 emission, humidity, biological activity). Land use change result in climate parameter on a smaller scale (soil climatic gradients) and formd feedback in weathering intensity and basic soil properties - organic matter, acidity, bulk density, WHC, surface properties and porosity, mineralogy and geochemical changes.

In studied soils of subzone of deciduous forest, the decreasing of smectite in the upper parts of profiles and the increasing of illite and vermiculite contents takes place. Montmorillonite into vermiculite transformation, which took place only under the forest, can be attributed to rhizospheric effect, respiration; humic acids that caused the decreasing of pH, soil vermiculite may also derive from muscovite. The intensity of the given process and depth in soil profile is increasing as the following: forest soil < grassland < cropland. The given tendency can be explained by both the mineral transformations and redistribution of mineral components within soil profiles. Unusual insignificant correlation of WHC with clay fraction probably connected with mineralogical peculiarities of studied soils. In top horizons, the decrease of smectite and high content of dispersed quartz in clay fractions was detected.

The redistribution of chemical elements between the different subfractions of silt and clay is in relationship to the land use. The maximum intensity of weathering and as results the redistribution of elements from silt fractions to the clay fraction is characteristic of cropland soil profile.

The 50–150 years of different land use resulted in these feedbacks with maximum in aboveground zone and soils as main point of surface of a given CZ.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.still.2018.02.008.

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