



Humic substances elemental composition of selected taiga and tundra soils from Russian European North-East

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Abstract: Soils of Russian European North were investigated in terms of stability and quality of organic matter as well as in terms of soils organic matter elemental composition. Therefore, soil humic acids (HAs), extracted from soils of different natural zones of Russian North-East were studied to characterize the degree of soil organic matter stabilization along a zonal gradient. HAs were extracted from soil of different zonal environments of the Komi Republic: south, middle and north taiga as well as south tundra. Data on elemental composition of humic acids and fulvic acids (FAs) extracted from different soil types were obtained to assess humus formation mechanisms in the soils of taiga and tundra of the European North-East of Russia. The specificity of HAs elemental composition are discussed in relation to environmental conditions. The higher moisture degree of taiga soils results in the higher H/C ratio in humic substances. This reflects the reduced microbiologic activity in Albeluvisols soils and subsequent conservation of carbohydrate and amino acid fragments in HAs. HAs of tundra soils, shows the H/C values decreasing within the depth of the soils, which reflects increasing of aromatic compounds in HA structure of mineral soil horizons. FAs were more oxidized and contains less carbon while compared with the HAs. Humic acids, extracted from soil of different polar and boreal environments differ in terms of elemental composition which reflects the climatic and hydrological regimes of humification.

Key words: Russian Arctic, Komi, soils, humic acids, fulvic acids, taiga, tundra.

Introduction

Soils of boreal and polar environments now has been considered as key components of global carbon cycle (Yu *et al.* 2014; Bruun *et al.* 2015; Peng *et al.* 2015; Wasak and Drewnik 2015; Szymański *et al.* 2016). This is especially important for Arctic soils, because they contain maximum stocks of soil organic matter (SOM) within the whole pedosphere (McGuire *et al.* 2009; Oliva *et al.* 2014; Zubrzycki *et al.* 2014; Fritz *et al.* 2015; Ping *et al.* 2015). Low temperature, high precipitation rate and appearance of continuous or discontinuous permafrost in cold boreal and polar environments results in favourable conditions for huge amounts of organic matter accumulations. At the same time, the climate warming and other global changes appearing during the last decades results in biodegradation and mineralization of soil and permafrost organic matter for the first time in millennia. In order to asses the implication of global climate changes of soil organic matter sequestration rate and its stability, both – amount and structural stability of soil organic matter should be investigated for polar and cold boreal environments (Fritz *et al.* 2015). At the current state of knowledge, soil organic carbon (SOC) stocks is estimated of 1307 petagram (Pg), different estimates range between 1140 and 1476 Pg, throughout the northern circumpolar region (Hugelius *et al.* 2014). However, the stability of this organic carbon pool is underestimated because of very clustered information sources for different sectors of Eurasian and North American Arctic.

While content and stocks of soil organic matter are very important, stability of humus in changing conditions is also very informative index, especially for soils of cold environments. There are a few indexes established for assessment of humus stability: ratio of humic acids to fulvic acids (Kononova 1984), degree of aromaticity (Ejarque and Abakumov 2015), content of free radicals in molecules (Chukov *et al.* 2017) and elemental composition of both groups of humic substances (Lodygin *et al.* 2014).

Elemental composition of humic substances (HSs) is an important inventory and informative characteristic, which indicates humification level, oxidation degree of humic acids (HAs) and fulvic acids (FAs), and indirectly assesses their condensation degree. It is also possible to asses the level of soil organic matter stabilization by assessment of atomic ratios and degree of HAs oxidation. Elemental composition is a basic characteristic of humic substances which show the degree of soil organic matter stabilization and humification (Schnitzer 1982). Nowadays, HAs and FAs are considered to be groups of high-molecular weight compounds with unregular molecular and elemental composition. Their elemental composition is characterized by averaged content of groups and quite different in terms of structural compounds. Elemental composition of humic substances reflects the main environmental conditions, climate, hydrological regime, soil texture and humification precursors composition (Kononova 1984; Rice and

MacCarthy 1991; Kechaikina *et al.* 2011; Bazhina *et al.* 2013; Gorbov and Bezuglova 2014). HAs and FAs form an inherent humus part which maintains the ecosystem stability by regulating various ecological functions (Frimmel and Christman 1987; Bayer *et al.* 2006; Farenhorst 2006; Baken *et al.* 2011). HAs are involved into cycle of matter and energy flow, affect growth and development of soil living organisms, regulate soil processes and regimes, and inhibit dangerous compounds. Being a system of organic macromolecules, HAs and FAs retain their functions and elemental composition in time (Dergacheva 2001; Dergacheva *et al.* 2012); their composition, structure, and properties reflect the specificity of bioclimate where they form (Abbt-Braun *et al.* 2004; Abakumov 2009; Zavyalova and Konchits 2011; Motuzova *et al.* 2012; Klavins *et al.* 2012).

Carbon distribution in HAs and FAs of one soil type is approximated by the normal distribution law where variation coefficients depend on soil type (Orlov 1990). Mean carbon content values in humic substances for the main soil types are more or less stable. However, carbon, hydrogen, oxygen, nitrogen, and sulfur are not the only components of humic substances which also consist of inorganic part, *i.e.* ash elements (normally metals, silicon and aluminum oxides). Soil geographical characteristic in wide scale of the East European plain should be based not only on background morphological indexes, but also on the main properties of the humic substances, namely on the data on elemental composition of humus acids.

Properties of HSs related to their ecosystem functions can be evaluated by C, H, N and O elements concentrations. They regulate the stability and biodegradability of soil organic matter and provide important information about the role of pedoenvironment in formation of humic substances structure (Schnitzer 1991; Preston 1992; Frund *et al.* 1994; Gonzalez-Perez *et al.* 2004; Wang *et al.* 2016). That is why this study aimed for investigation between elemental composition of humic and fulvic acids and types of key environments of pristine soils of the boreal (taiga) and polar (tundra) ecosystems of the European North-East of Russia.

The objectives of this study were (i) to evaluate the differences in soil organic matter of selected benchmark soils of Russian European North on examples of Komi Republic, and (ii) to evaluate the soil humic substances elemental composition for various zonal soils.

Materials and Methods

Study area and soil morphology. — The soils of the south taiga Albeluvisols according to WRB (2006), the middle taiga (Albeluvisols and Stagnic Albeluvisols), the north taiga (Stagnic Albeluvisols), and the south tundra subzone (Stagnic Cambisols, Histic Gleysols and Cryosols) of the Komi Republic

(Fig. 1) have been studied. Soil sampling was done at different types of landscapes: watersheds (automorphic well drained soils) to geochemically dependent landscapes (depressions, hydromorphic soils). Climate description for the study regions is given in Table 1. Morphological descriptions of soils is given in Table 2. Horizons identification were performed according to Russian Soil classification (Shishov *et al.* 2004) with correlation to the WRB. Soils types were identified according to WRB (2006). Short description of the soils profiles and their images are given in Table 2 and Fig. 2.

The south taiga soils were studied at the Letka permanent monitoring station. By the soil-geographical zone division (Dobrovolsky *et al.* 2008), the territory belongs to the Letka region of soddy-podzolic soils (Albeluvisols) at the Central Russian Province. Soil pit was sampled at a distance of 1 km northwestwards from the Krutotyła village of the Priluzsky district. It is a west-oriented gentle hill slope in birch-aspen-spruce forest (59°38'N, 49°21'E; 180 m a.s.l.). Slope angles do not exceed 2°. Nano- and micro relief formations vary within 23 cm, on slope – within 20 cm. They insignificantly increase by size and depth in hollow due to stem hillocks and wind erosions. Cover vegetation is dominated by *Vaccinium myrtillus* L., *Rubus saxatilis* L., *Pyrola* L., and *Oxalis acetosella* L. plants. Green mosses are few.



Fig. 1. Locations of sampling points. 1 – Umbric Albeluvisols, 2 – Haplic Albeluvisols, 3 – Stagnic Histic Albeluvisols, 4 – Stagnic Albeluvisols, 5 – Stagnic Histic Albeluvisols, 6 – Stagnic Cambisols, 7 – Histic Gleysols, 8 – Histic Cryosols.

Table 1

Climate parameters of the study regions.

Climate parameters	South taiga	Middle taiga	North taiga	South tundra
Mean annual air temperature (°C)	+1.3	+0.5	-1.1	-5.5
Mean air temperature (°C): of the warmest month (July) of the coldest month (January)	+17.0 -14.3	+16.7 -15.3	+16.0 -17.8	+13.4 -20.1
Number of days with mean daily air temperature: above 0°C above 5°C above 10°C	202 151 110	190 140 100	175 135 92	125 90 43
Freezing depth (cm)	43	89	101	139
Snow thickness (cm)	61	60	64	74
Annual precipitation (mm) in summer (mm)	622 218	560 195	590 201	548 172

Table 2

Morphological descriptions of soils.

Soil	Horizon	Depth of Sampling (cm)	Soil horizon description
South taiga			
Albeluvisol (a)	A	0–4	7.5YR 8/1, mull humus, friable, silt loam
	AEL	4–28	10YR 7/1, compacted, ortsteins, silt loam
	BEL	28–43	5Y 2/1, ortstiens, consolidated, silt clay
	Bt	43–70	7.5YR 2/1, siltans, silt clay
	Bt	70–100	7.5YR 2/1, silt clay
	BC	100–130	7.5YR 2/1, consolidated, clay with cracks
	C	130–170	7.5YR 2/1, consolideated unstructured clay
Middle taiga			
Stagnic Albeluvisol (b)	Oe	0–5	2.5YR, friable organic material without histic features
	AEh	5–7(10)	7.5YR 6/1, friable, contain many roots and humus cutans, silty loam
	EL1	7(10)–18	5YR 8/1, iron cutans and segregations, loam
	EL2	18–35	5YR 8/1, iron cutans and segregations, consolidated, loam

Table 2 continued

Soil	Horizon	Depth of Sampling (cm)	Soil horizon description
Stagnic Albeluvisol (c)	Oe	0–12	7.5YR, undercomposed with fresh organic remnants
	Ehg	12–15	7.5YR 5/6, friable, many nodules of iron oxides, loam
	Eg1	15–23	10YR 5/2, with many pores and vesicular voids, cutans and nodules, consolidated, sandy loam
	Eg2	23–31(40)	10YR 5/1, many voids, nodules, overconsolidated, silty loam
North taiga			
Stagnic Albeluvisol (d)	O	0–5	2.5YR 5/4, slightly decomposed organic material with coals and wood remnants
	Eg	5–16	7.5YR 6/1, with diffusial accumulation of iron oxides, loam
	EB	16–35	7.5YR 4/2, with cutans, silt loam
	Bt	35–75	10YR 5/3, loamy, many voids and nodules of iron and magnesium oxidation, clay loam
	Bt	75–105	10YR 5/3, with many accumulation of manganese in different morphological forms, silt loam
	BCg	105–140	10YR 5/3 – 2.5YR 8/3, unhomogenous in color, silt loam
	Cg	>140	10YR 4/3, with features of gleyification, silt loam
Planosol (e)	O	0–12	2.5YR 4/3, weak decomposed forest floor
	Elhg	12–15	5YR 4/1, with features of gleyification, loam
	Elg	15–20	5YR 4/1, with iron spots and coatings, iron nodules, silt loam
	ElBt	20–50	7.5YR 5/6, unhomogenous, silt loam
	Btg	50–85	7.5YR 5/6, unhomogenous, consolidated, clay loam
	Btg	85–120	5YR 8/6, consolidated, clay loam
	BCg	120–145	2.5YR 8/3, consolidated, clay loam
	Cg	145–200	2.5YR 8/3, consolidated, clay loam
South tundra			
Stagnic Cambisol (f)	O	0–5	10YR 4/2, undercomposed litter
	O	5–10	10YR 4/2, slightly decomposed material
	E	10–28	2.5YR 4/3, loam
	Bw	28–55	2.5YR 8/3, loam with gleyic features
	Bwg	55–87	2.5YR 8/3, clay loam, many siltans accumulations

Table 2 continued

Soil	Horizon	Depth of Sampling (cm)	Soil horizon description
	Bwg	87–120	2.5YR 8/3, clay loam with some siltans and skeletans
	BCg	120–150	10YR 5/3, clay loam, consolidated with accumulations of iron oxides
Histic Gleysol (g)	T1	0–7	2.5YR 4/1, undercomposed organic material
	T2	7–14	2.5YR 4/2, histic material
	T3	14–17	2.5YR 4/2, histic material with admixture of loamy spots
	C	17–40	2.5YR 4/3, silt loam, consolidated
	Cgw	40–55	2.5YR 4/3, clay, with cambic and cryic features
	Bw	55–90	10YR 5/3, clay, many formation of manganese and iron oxide
Cryosol (k)	O1	0–10	10YR 4/2, histic undercomposed material
	O2	10–26	10YR 4/2, histic slightly composed material
	A	26–28	10YR 5/2, loamy silt, unhomogenous in composition and color
	CR	28–40	2.5YR 2/3, overmoisted clay loam
	CR	40–50	2.5YR 2/3, clay loam with features of former permafrost affected cryogenic processes
	G	50–70	7.5YR 4/2, clay loam, consolidated, diffusion accumulations of organic matter

The middle taiga soils were studied at the Maximovsky research station of the Institute of Biology. By the soil-geographical zone division, the territory belongs to the Sysolsky *okrug* of typically podzolic soils and weakly peaty-podzolic-weakly gley soils at the Sysola-Vycheгда Province (Dobrovolsky *et al.* 2008). Soil pit (Albeluvisol) was dug at a distance of 8 km westwards from the city of Syktyvkar on a top of watershed hill on a back of microdepression being 1.5 m high (61°39'N, 50°41'E; 160 m a.s.l.). Vegetation is bilberry-green moss birch-spruce forest with many fallen trees. Soil pit (weakly peaty-podzolic-weakly gley soil) was dug at a distance of 74 m from the previous one (61°39'N, 50°41'E; 160 m a.s.l.). It is a microhollow between low and flat elevations. Vegetation is long moss-sphagnum birch-spruce forest. Near pit, there is a sphagnum cover.

The north taiga soils were studied at a distance of 3 km westwards from the Troitsko-Pechorsk settlement. By the soil-geographical zone division, the territory belongs to the Izhma-Pechora *okrug* of illuvial-humus-iron podzols, weakly

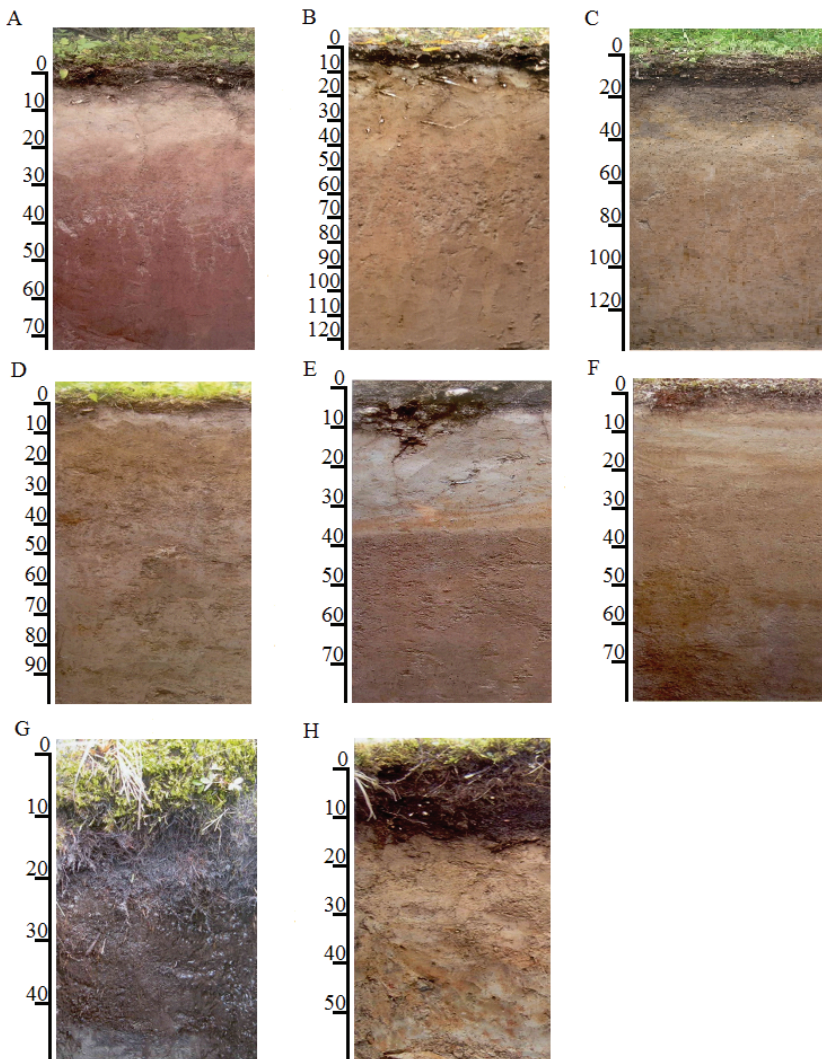


Fig. 2. Soil profiles: 1 – Umbric Albeluvisols, 2 – Haplic Albeluvisols, 3 – Stagnic Histic Albeluvisols, 4 – Stagnic Albeluvisols, 5 – Stagnic Histic Albeluvisols, 6 – Stagnic Cambisols, 7 – Histic Gleysols, 8 – Histic Cryosols.

peaty-and peaty-podzolic-gley illuvial-humus, gley podzolic and boggy-podzolic soils of the Timan-Pechora Province (Dobrovolsky *et al.* 2008). According to WRB (2006), these soils can be identifies as Stagnic Albeluvisols or Planosols. The above soil types occupy a flat top of watershed hill. Gley podzolic soils under green-moss spruce forests take a periphery part of polypedon. Weakly peaty-podzolic-weakly gley soils develop under long moss and Sphagnum-long moss spruce forests near the centre of hill. Gley podzolic soil pit was dug on

a top of a flat inter-stream hill (62°41'N, 56°08'E; 140 m a.s.l.). Vegetation is bilberry-green moss spruce forest. Floor vegetation is dominated by *Vaccinium myrtillus* L. and green mosses. Soil pit (weakly peaty-podzolic-weakly gley soil) was dug at a distance of 60 m from the previous cut on a gentle slightly drained near-top hill slope (62°41'N, 56°08'E; 140 m a.s.l.). Vegetation is sphagnum-long moss spruce forest. Vegetation cover is dominated by hypnum mosses, *Vaccinium vitis-idaea* L., *Equisetum* L., *Carex globularis* L., and *Rubus chamaemorus* L.

The tundra soils were studied in the Bolshezemelskaya tundra area in the Vorkuta region of the Komi Republic with massive-island permafrost distribution. By the soil-geographical zone division, the territory belongs to the Vorkuta *okrug* of tundra surface-gley, weakly peaty- and peaty-tundra gley permafrost soils of the Bolshezemelskaya Province (Dobrovolsky *et al.* 2008). The area is a gently undulating plain covered with silty loams being less than 10 m thick. Typical soil formation processes in the tundra zone are gleyzation (stagnic processes) and peat accumulation (Lodygin *et al.* 2014). Soil pit (tundra surface-gley soil) was dug on a gentle slope of the Nerusovei-musyur moraine hill (67°31'N, 64°07'E; 220 m a.s.l.). It is a willow and dwarf birch mossy small-hummock tundra area. Vegetation is dominated by hypnum and some *Polytrichum* mosses, *Vaccinium vitis-idaea* L., rare *Carex* L. and single *Betula nana* L. representatives. Soil pit (Stagnic Cambisol) was dug in the centre of the south-western slope, slope angle is 3° (67°35'N, 64°09'E; 150 m a.s.l.). Vegetation is presented by *Polytrichum* and *Sphagnum* mosses, lichens, *Empetrum nigrum* L. and *Ledum* L. plants. Hummocks are covered with *Rubus chamaemorus* L. and *Vaccinium uliginosum* L. Hummocks are up to 40 cm high and 1.5 m in diameter. There is an inter-hummock depression. Soil pit (Cryosol) was dug in the centre of the south-western slope, slope angle is 3°, at a distance of 100 m southwards from the previous pit (67°35'N, 64°09'E; 140 m a.s.l.). Soils were sampled in three replications from the peat land polypedon.

Extraction of humic acids. — Humic acids were extracted from each SOM humic substance solution according to the procedure of Schnitzer (1982). The humic acids were extracted with 0.1 M NaOH (soil : solution mass ratio 1 : 10) under nitrogen gas. After 24 h of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1516xg for 20 min and acidified to pH = 1 with 6 M HCl to induce the precipitation of the humic acids. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at 1516xg for 15 min. The humic acids were then redissolved in 0.1 M NaOH and shaken for 4 h under N₂ before the suspended solids were removed by centrifugation. The solution was acidified again with 6 M HCl to pH = 1, and the humic acids were separated by centrifugation and demineralised by shaking overnight in 0.1 M HCl = 0.3 M HF (solid/solution ratio 1 : 1).

Next, they were repeatedly washed with deionised water until pH = 3 was reached; and then they were finally freeze-dried. Extraction yields of humic acids were calculated as the percentage of carbon recovered from the original soil sample used for extraction.

Elemental analyses. — Humic acids were characterized for their elemental composition (C, N and H) using a EA-1110 analyzer. Water content was measured by gravimetric method, while ash content was evaluated in the base of ignition loss. Data were corrected for water and ash content. Oxygen content was calculated by difference taking into account the ash content. The elemental ratios (C/N, H/C and O/C) reported in this paper are based on weight percentages.

Statistics. — One-way analysis of variance (ANOVA) was carried out in order to identify the relationships between obtained data elemental composition. This method is based on estimation of the significance of average differences between three or more independent groups of data combined by one feature (factor). The null hypothesis of the averages equality is tested during the analysis suggesting the provisions on the equality or inequality of variances. In case of rejection of the variances equality hypothesis basic analysis is not applicable. If the variances are equal, F-test Fisher criterion is used for evaluation of intergroup and intragroup variability. If F-statistics exceeds the critical value, the null hypothesis is rejected considering inequality of averages.

Results and discussion

Elemental composition of humic acids. — Soil organic matter mineralization as well as possible CO₂ emission from soils has been paid great attention for its important effect on the global carbon cycle and ecosystems stability (Roulet 2000; Zamolodchikov *et al.* 2005). Permafrost thaw and degradation nowadays is the global process, which results in soil organic matter redistribution, alteration and mineralization (Takakai *et al.* 2008). Recent studies provide evidence of a high and long-term mineralisation potential of Arctic SOM under increased temperatures (Elberling *et al.* 2013; Schädel *et al.* 2014; Schuur *et al.* 2015). The possible alteration of organic matter depends on the degree of its stabilization, and the last one can be assessed by various indexes. The atomic ratios and elements content indicates the SOM and HAs stabilization rate in conditions of various climatic scenarios and following environmental changes (Ejarque and Abakumov 2016).

Data on elemental composition of humic substances, isolated from the soils investigated (Tables 3 and 4), shows that carbon content in humic acids is higher than that in fulvic ones. At the same time, in the HAs, the molar ratio (x) of carbon comprises 32.2–42.9% against 26.4–37.5% in FAs, molar ratio of oxygen x (O) varies within 12.5–22.0 for HAs and 12.5–22.0% for FAs. Previously,

Table 3

Distribution and elemental composition of soil humic acids (above line – weight ratio, under line – molar ratio (x); all estimations were done for absolutely dry and ash-free preparations).

Horizon	Depth (cm)	Content (%)				Atomic ratios			(H/C) _{corrected} *	Oxidation degree (ω)
		C	H	O	N	H/C	O/C	C/N		
South taiga										
Albeluvisol (a)										
A	0–4	53.5±1.7 38.3±1.2	4.5±0.4 39±4	38±4 20.2±2.4	4.37±0.29 2.68±0.18	1.01	0.53	14.3	1.72±0.05	+0.04
AEL	4–15	54.1±1.7 39.0±1.2	4.4±0.4 38±4	36±4 19.4±2.3	5.7±0.4 3.53±0.24	0.97	0.50	11.0	1.64±0.05	+0.02
AEL	15–28	56.1±1.8 39.3±1.3	4.7±0.4 40±4	33±4 17.2±2.0	6.4±0.4 3.83±0.26	1.01	0.44	10.3	1.60±0.05	-0.14
BEL	28–43	48.9±1.6 35.8±1.1	4.3±0.4 38±4	40±5 22.0±2.6	6.6±0.4 4.15±0.28	1.06	0.61	8.6	1.88±0.06	+0.17
Middle taiga										
Albeluvisol (b)										
Oe	0–5	54.5±1.7 35.6±1.1	5.7±0.5 45±4	36±4 17.8±2.1	3.45±0.23 1.96±0.13	1.25	0.50	18.4	1.92±0.06	-0.25
A _{Eh}	5–7	53.8±1.7 35.2±1.1	5.7±0.5 45±4	37±4 18.0±2.1	3.78±0.25 2.12±0.14	1.27	0.51	16.6	1.96±0.06	-0.25
E1	7–10	52.9±1.7 36.5±1.2	5.0±0.5 42±4	39±5 20.3±2.4	2.79±0.19 1.65±0.11	1.14	0.56	22.1	1.89±0.06	-0.02
E2	18–35	53.7±1.7 36.3±1.2	5.3±0.5 43±4	39±8 20±4	2.0±0.4 1.16±0.21	1.18	0.54	31.2	1.91±0.06	-0.09
Stagnic Albeluvisol (c)										
Oe	0–8	52.6±1.7 34.5±1.1	5.7±0.5 45±4	38±5 18.9±2.3	3.24±0.22 1.82±0.12	1.30	0.55	18.9	2.03±0.06	-0.20

Table 3 continued

Horizon	Depth (cm)	Content (%)				Atomic ratios			(H/C) _{corrected} *	Oxidation degree (ω)
		C	H	O	N	H/C	O/C	C/N		
Ehg	12–20	58.8 ± 1.9 32.2 ± 1.0	8.2 ± 0.8 54 ± 5	30 ± 4 12.5 ± 1.5	2.62 ± 0.18 1.23 ± 0.08	1.68	0.39	26.2	2.20 ± 0.07	-0.91
Eg1	20–28	56.8 ± 1.8 33.0 ± 1.1	7.3 ± 0.7 51 ± 5	33 ± 4 14.3 ± 1.7	3.20 ± 0.21 1.60 ± 0.11	1.55	0.43	20.7	2.12 ± 0.06	-0.68
Eg2	28–37	55.1 ± 1.8 35.2 ± 1.1	6.0 ± 0.6 46 ± 4	36 ± 4 17.0 ± 2.0	3.36 ± 0.23 1.84 ± 0.12	1.31	0.48	19.1	1.96 ± 0.06	-0.34
North taiga										
Stagnic Albelvisol (d)										
O	0–5	58.0 ± 1.9 38.5 ± 1.2	5.4 ± 0.5 43 ± 4	33 ± 4 16.2 ± 1.9	3.97 ± 0.27 1.26 ± 0.15	1.12	0.42	17.1	1.68 ± 0.05	-0.27
Eg	5–10	59.5 ± 1.9 37.5 ± 1.2	6.1 ± 0.6 46 ± 4	30 ± 4 14.0 ± 1.7	4.8 ± 0.3 2.58 ± 0.17	1.23	0.37	14.5	1.73 ± 0.05	-0.48
EB	10–16	54.2 ± 1.7 35.6 ± 1.1	5.6 ± 0.5 44 ± 4	34 ± 4 16.8 ± 2.0	6.0 ± 0.4 3.40 ± 0.23	1.25	0.47	10.5	1.88 ± 0.06	-0.30
B1	16–35	54.1 ± 1.7 37.7 ± 1.2	4.8 ± 0.5 41 ± 4	37 ± 4 19.5 ± 2.3	3.73 ± 0.25 2.23 ± 0.15	1.07	0.52	16.9	1.77 ± 0.05	-0.04
Planosol (e)										
O	0–10	57.2 ± 1.8 38.4 ± 1.2	5.3 ± 0.5 43 ± 4	34 ± 4 17.1 ± 2.0	3.47 ± 0.23 1.99 ± 0.13	1.11	0.45	19.2	1.71 ± 0.05	-0.22
O	10–12	51.6 ± 1.7 35.9 ± 1.1	5.0 ± 0.5 41 ± 4	41 ± 8 21 ± 4	2.6 ± 0.5 1.53 ± 0.28	1.15	0.59	23.4	1.95 ± 0.06	-0.04
Eg	12–15	49.7 ± 1.6 32.9 ± 1.1	5.6 ± 0.5 45 ± 4	42 ± 5 20.7 ± 2.5	3.02 ± 0.20 1.72 ± 0.11	1.36	0.63	19.2	2.20 ± 0.07	-0.10
B1	15–20	53.0 ± 1.7 36.1 ± 1.2	5.2 ± 0.5 42 ± 4	39 ± 5 19.8 ± 2.4	3.04 ± 0.20 1.77 ± 0.12	1.17	0.55	20.4	1.91 ± 0.06	-0.07

Table 3 continued

Horizon	Depth (cm)	Content (%)				Atomic ratios			(H/C) corrected*	Oxidation degree (ω)
		C	H	O	N	H/C	O/C	C/N		
B2	20–25	54.7±1.7 36.8±1.2	5.3±0.5 43±4	37±8 19±4	2.6±0.5 1.49±0.27	1.16	0.51	24.8	1.85±0.06	-0.13
BCg	35–40	61.2±2.0 42.9±1.4	4.6±0.4 39±4	31±4 16.1±1.9	3.61±0.24 2.17±0.15	0.91	0.38	19.8	1.41±0.04	-0.15
South tundra										
Stagnic Cambisol (f)										
O	0–5	53.2±1.7 36.8±1.2	5.0±0.5 41±4	38±5 19.5±2.3	4.23±0.28 2.51±0.17	1.12	0.53	14.7	1.83±0.05	-0.06
H	5–10	58.1±1.9 37.6±1.2	5.7±0.5 45±4	31±4 14.9±1.8	5.4±0.4 2.98±0.20	1.18	0.40	12.6	1.72±0.05	-0.39
G	10–28	58.9±1.9 38.0±1.2	5.7±0.5 44±4	30±4 14.5±1.7	5.4±0.4 2.98±0.20	1.17	0.38	12.8	1.68±0.05	-0.41
Histic Gleysol (g)										
O	0–14	55.1±1.8 37.1±1.2	5.3±0.5 43±4	36±4 18.1±2.2	3.74±0.25 2.16±0.14	1.15	0.49	17.2	1.81±0.05	-0.18
G	17–25	55.5±1.8 37.3±1.2	5.3±0.5 43±4	34±4 17.2±2.1	5.0±0.3 2.88±0.19	1.14	0.46	13.0	1.76±0.05	-0.22
Cryosol (d)										
O	0–26	54.7±1.7 36.1±1.2	5.6±0.5 44±4	36±4 17.7±2.1	4.04±0.27 2.28±0.15	1.22	0.49	15.8	1.88±0.06	-0.24
Gf	28–40	56.1±1.8 36.1±1.2	5.8±0.5 45±4	33±4 16.1±1.9	4.6±0.3 2.55±0.17	1.25	0.45	14.2	1.85±0.06	-0.36
P One-way ANOVA	Not det	<0.05	<0.03	<0.07	<0.05	Not det	Not det	Not det	Not det	Not det

Note: * $(H/C)_{corrected} = (H/C) + 2 \times (O/C) \times 0.67$ (Orlov 1990).

Table 4

Distribution and elemental composition of soil fulvic acids

(above line – weight ratio, under line – molar ratio (x); all estimations were done for absolutely dry and ash-free preparations).

Horizon	Depth (cm)	Content (%)				Atomic ratios			(H/C) corrected*	Acidification degree (to)
		C	H	O	N	H/C	O/C	C/N		
South taiga										
Albeluvisol (a)										
A0Asoddy	0–4	47.8±1.5 34.6±1.1	3.85±0.26 39±4	44±5 24±2.8	3.85±0.26 2.39±0.16	1.13	0.69	14.5	2.05±0.06	+0.24
A2'	4–15	44.8±1.4 34.9±1.1	3.7±0.3 35±3	49±10 28±6	2.9±0.5 1.9±0.3	0.99	0.81	18.1	2.08±0.06	+0.63
A2''	15–28	30.2±1.0 26.4±0.8	2.83±0.26 29.6±2.8	65±13 42±9	2.1±0.4 1.59±0.29	1.12	1.61	16.6	3.27±0.10	+2.09
A2B	28–43	39.2±1.3 29.7±1.0	4.1±0.4 38±4	53±6 30±4	3.45±0.23 2.24±0.15	1.27	1.02	13.3	2.63±0.08	+0.77
Middle taiga										
Albeluvisol (b)										
A0	0–5	45.6±1.5 33.3±1.1	4.5±0.4 39±4	48±10 26±5	2.3±0.4 1.42±0.26	1.17	0.78	23.4	2.22±0.07	+0.39
A1A2h	5–7	45.3±1.4 33.0±1.1	4.5±0.4 40±4	49±10 27±5	1.21±0.22 0.76±0.14	1.20	0.81	43.7	2.28±0.07	+0.42
A2'	7–10	44.9±1.4 34.3±1.1	4.0±0.4 36±3	50±10 29±6	0.93±0.17 0.61±0.11	1.06	0.84	56.3	2.18±0.07	+0.62
A2''	18–35	45.2±1.4 34.7±1.1	3.9±0.4 36±3	50±10 29±6	0.82±0.15 0.54±0.10	1.04	0.83	64.3	2.15±0.06	+0.62
Stagnic Albeluvisol (c)										
O1	0–8	45.6±1.5 33.9±1.1	4.2±0.4 38±4	48±10 27±5	2.4±0.4 1.54±0.28	1.12	0.79	22.0	2.17±0.07	+0.45

Table 4 continued

Horizon	Depth (cm)	Content (%)				Atomic ratios			(H/C) corrected*	Acidification degree (ω)
		C	H	O	N	H/C	O/C	C/N		
A2hg	12–20	41.8±1.3 33.3±1.1	3.6±0.3 3.4±0.3	53±11 32±6	1.7±0.3 1.18±0.21	1.02	0.95	28.2	2.29±0.07	+0.88
A2g'	20–28	40.2±1.3 31.0±1.0	4.0±0.4 3.7±0.3	54±11 31±6	1.36±0.24 1.90±0.16	1.19	1.02	34.5	2.55±0.08	+0.85
A2g''	28–37	43.4±1.4 30.8±1.0	4.9±0.5 4.2±0.4	50±10 26±5	2.1±0.4 1.30±0.23	1.35	0.86	23.7	2.50±0.07	+0.36
North taiga										
Stagnic Albelvisol (d)										
A0	0–5	49.1±1.6 35.5±1.1	4.5±0.4 3.9±0.4	44±9 24±5	2.7±0.5 1.7±0.3	1.10	0.67	21.3	2.00±0.06	+0.24
A2g'	5–10	49.8±1.6 37.4±1.2	4.1±0.4 3.7±0.3	44±9 25±5	2.2±0.4 1.44±0.26	0.98	0.66	26.0	1.86±0.06	+0.34
A2g''	10–16	48.5±1.6 37.5±1.2	3.7±0.3 3.5±0.3	45±9 26±5	2.5±0.4 1.63±0.29	0.92	0.70	23.0	1.86±0.06	+0.48
A2B	16–35	47.2±1.5 34.5±1.1	4.4±0.4 3.9±0.4	46±9 25±5	2.6±0.5 1.62±0.29	1.12	0.73	21.4	2.10±0.06	+0.34
Planosol (e)										
O1	0–10	43.9±1.4 33.6±1.1	3.9±0.4 3.6±0.3	49±10 28±6	2.7±0.5 1.8±0.3	1.08	0.84	19.1	2.21±0.07	+0.61
O2	10–12	41.3±1.3 32.1±1.0	3.8±0.4 3.6±0.3	53±11 31±6	1.58±0.28 1.05±0.19	1.11	0.97	30.5	2.41±0.07	+0.82
A2hg	12–15	33.0±1.1 27.8±0.9	3.16±0.29 3.2±0.3	63±13 40±8	1.03±0.19 0.74±0.13	1.15	1.42	37.4	3.06±0.09	+1.70
A2g	15–20	38.8±1.2 32.5±1.0	3.05±0.28 3.0.7±2.9	57±12 36±7	1.27±0.23 0.91±0.16	0.94	1.10	35.7	2.42±0.07	+1.26

Table 4 continued

Horizon	Depth (cm)	Content (%)			Atomic ratios			(H/C) corrected*	Acidification degree (ω)
		C	H	O	H/C	O/C	C/N		
A2Bg	20–25	34.7±1.1 29.7±1.0	2.94±0.27 30.2±2.8	61±13 39±8	1.25±0.23 0.92±0.17	1.02	1.32	32.3	2.78±0.08 +1.62
A2Bg	35–40	41.9±1.3 34.2±1.2	3.3±0.3 32±3	53±11 32±6	2.1±0.4 1.48±0.27	0.94	0.94	23.1	2.20±0.07 +0.95
South tundra									
Stagnic Cambisol (f)									
A0	0–5	49.1±1.6 35.8±1.1	4.4±0.4 38±4	44±9 24±5	2.4±0.4 1.47±0.27	1.07	0.68	24.3	1.98±0.06 +0.28
A0Ah	5–10	38.1±1.2 30.4±1.0	3.6±0.3 35±3	56±12 34±7	1.9±0.3 1.29±0.23	1.14	1.11	23.6	2.63±0.08 +1.09
G	10–28	37.4±1.2 28.2±0.9	4.3±0.4 39±4	56±11 32±6	2.4±0.4 1.52±0.27	1.37	1.12	18.6	2.88±0.09 +0.87
Histic Gleysol (g)									
O	0–14	46.3±1.5 33.8±1.1	4.4±0.4 39±4	48±10 26±5	1.8±0.3 1.10±0.20	1.15	0.77	30.7	2.19±0.07 +0.39
G	17–25	38.3±1.2 28.5±0.9	4.4±0.4 39±4	55±11 31±6	2.1±0.4 1.36±0.24	1.38	1.08	21.0	2.82±0.08 +0.78
Cryosol (k)									
O	0–26	45.9±1.5 34.0±1.0	4.3±0.4 38±4	48±10 26±5	2.2±0.4 1.42±0.26	1.12	0.78	23.9	2.16±0.06 +0.44
Gf	28–40	41.0±1.3 29.0±1.0	5.0±0.5 42±4	52±11 28±6	1.9±0.3 1.16±0.21	1.45	0.95	25.1	2.73±0.08 +0.46
P One-way ANOVA	Not det	<0.05	<0.03	<0.05	<0.05	Not det	Not det	Not det	Not det Not det

Note: * $(H/C)_{corrected} = (H/C) + 2 \times (O/C) \times 0.67$ (Orlov 1990).

for more northern soils of Russian Siberia, Abakumov *et al.* (2015) showed that differences between HAs and FAs are less pronounced. This was related to poorer composition of humification precursors and more severe conditions. Nitrogen concentrations in humic acids is normally twice higher than that in fulvic ones (the C/N atomic ratio – varies in frames 8.6–31.2 for HAs and 13.3–64.3 for FAs). Nitrogen content in HA and FA substances decreases downwards in soil profile. Humic and fulvic acids of soddy-podzolic soils are more enriched with nitrogen in contrast with the other studied soil types. This corresponds well with data on soils of adjacent Yamal region (Ejarque and Abakumov 2016), where the conditions of humification are comparable with those in northern Komi.

Results of elemental composition analysis show that the HAs of Albeluvisols soil are more humified (low H/C and high O/C atomic ratios) than over moistened soils with stagnic horizons. These differences are statistically significant (table 3). In middle- and north-taiga soils, HAs first increase H/C values on transition from organic to mineral horizons because of migration HAs with high content of oxygen-containing functional groups. However, in deeper soil horizons, HAs show the increased humification accompanied with decarboxylation and reduction of carbohydrate and amino acid fragments in their structure. These processes lead to decreasing of H/C values (Lodygin and Beznosikov 2010). High moisture content in taiga soils, especially in stagnic horizons increases H/C values due to low microbiological activity of peat-podzolic soils (Khabibullina *et al.* 2014), which favors conservation of carbohydrate and amino acid fragments in HA structure. For every tundra soil type, the H/C values decrease downwards soil profile evidencing HAs in mineral horizons contain more aromatic fragments. There are no statistically significant differences between H/C values for HAs of differently-moistured tundra soils. The differences between soils of different zones are higher than those which have been revealed for soils of different zones of the Gydan Peninsula and Arctic Islands (Ejarque and Abakumov 2016; Abakumov and Tomashunas 2016). This is caused by more expressed differences in climatic and hydrological regime between soil zones in Russian European North than in different zones of northern Siberia. It is also possible that greater humification rate in Albeluvisols is related to possible anthropogenic impact in Vorkuta region, as it was published previously (Walker *et al.* 2003; Walker 2005). Indirect chemical effect may be pronounced in increased humification rate.

Degree of oxidation. — Data on molecules oxidation degree (ω) shows that HAs are weakly reduced from -0.91 to -0.02) except for HAs of Stagnic Albeluvisols ($\omega = +0.17$). FAs are more oxidized with ω from +0.24 to +2.09. HSs of mineral soil horizons are more oxidized which is related to a high migration rate of acidified, *i.e.* water-soluble FAs down soil profile. High reduction degree of HA and FA preparations in organic soil layers affected to increased fresh organic precursors and their low humification rate in the cold environments.

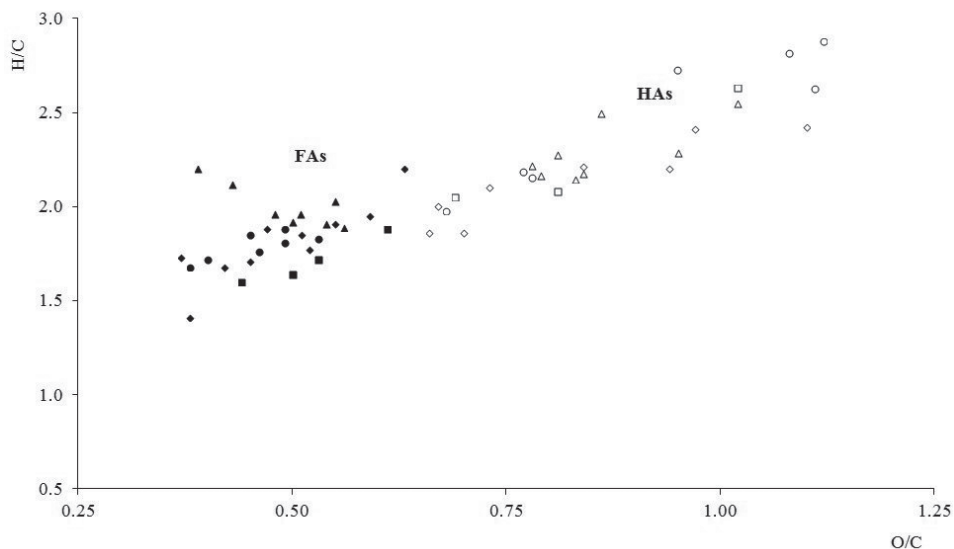


Fig. 3. Atomic ratios of elements in preparations of soil humic and fulvic acids in the south (HA■, FA□), middle (HA▲, FA△), north taiga (HA◆, FA◇) and south tundra subzones (HA●, FA○).

Atomic ratios. — Diagrams of D. van Krevelen (Kleinhempel 1970) serve a very popular method for numerical description of HS structure. This method is a graphical data presentation in H/C – O/C coordinates and illustrates how oxidation and condensation modify elemental composition of HA and FA preparations. By D. van Krevelen diagram (Fig. 3), humification of plant residues decreased both H/C and O/C ratios, *i.e.* enlarges share of aromatic structures in HS molecules. According to the results of graphical-statistic analysis, FAs contain more acids and less carbon in contrast to HAs and so have remarkably substituted aromatic rings and developed side aliphatic chains. The obtained results generally agree with data available for tundra soils (Dai *et al.* 2001, 2002) and for podzolic and boggy-podzolic soils (Simpson *et al.* 1997; Kechaikina *et al.* 2011).

Consequently, data obtained for the first time for the Komi republic allows to estimate the humification rate of soil organic matter in this landscape cluster of Russian Arctic, which is quite informative and were underestimated in previous global stocks and organic matter quality investigations. This investigation shows the humification process provide formation of different composition of humic acids in different types of cold boreal and polar pedoenvironments. Zonal climatic aspect as well as soil hydrology and permafrost appearance regulates such a basic humic acids characteristics as elemental composition and atomic

ratios. In more severe condition of Arctic and Antarctic HAs became more similar with FAs (Chukov 2015; Abakumov *et al.* 2015) due to composition of humification precursors and short vegetation period. But, in case of European East, in its easternmost part, there is longitude differentiation of humification process, which results in formation of two different groups of HSs: HAs and FAs, which are also different in pedoenvironment sequences. There are essential differences between elemental composition of soils HAs in gradient ecotone south tundra – north taiga – middle taiga – south taiga. These differences are most pronounced in atomic ratios, namely in H/C ratios, which indicates that degree of the molecules stabilization decreases in northern soils in comparison with southern ones. The specific characteristics of HAs of overmoisted soils with stagnic features are increment of aliphatic compounds in molecules. The specificity of humification in cold northern environments is the decreases of the differences between HAs and FAs characteristics, which was previously suggested by Orlov (1999), by other words humic substances became more homogenous group of macromolecular compounds. The prevalence of carbohydrate compounds and decreased values of carbon make the humic substances vulnerable for possible mineralization risks in case of the climate change. That is why further work on investigation of molecular composition of HSs along zonal transect with use of spectroscopic methods are need.

Conclusions

Elemental composition of HSs from different soil types of cold boreal and polar environment were investigated with aim to characterize the difference in soil organic matter stabilization mechanisms in different pedoenvironments. It was shown that humification leads to formation of two groups different in elemental composition, *i.e.* HAs and FAs with evident zonal trends in differentiation of elemental composition. Humic and fulvic acids of soddy-podzolic soils contain more nitrogen in contrast with those of the other soil types. Nitrogen content in HA and FA preparations tends to decrease down soil profile. High moisture content for taiga soils increases H/C values due to low microbiological activity of peat-podzolic soils and, consequently, good conservation of hydrocarbon and amino acid fragments in HA structure. Elemental composition analysis for tundra soils shows that the H/C ratios for every soil type decrease downwards within the soil profile and there is evident increasing of aromatic fragments in HAs of mineral soils layers. There are no statistically significant differences between H/C values for HAs of differently-moistured tundra soils. On the base of the graphical-statistical analysis, it was shown that FAs are more oxydized and less carbonized compared with HAs which evidences remarkably substituted aromatic

rings and developed side aliphatic chains. The differences between humic acids of different natural zones of Russian European North is higher than in North of Western Siberia. More pronounced differences in this case are caused by more evident differences in climatic and hydrological regimes.

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