

ELEMENTAL COMPOSITION OF HUMIC AND FULVIC ACIDS IN THE EPIPEDON OF SOME ESTONIAN SOILS

Loit REINTAM^a, Jüri KANN^b, Tiiu KAILAS^b, and Raja KÄHRIK^a

^a Institute of Soil Science and Agrochemistry, Estonian Agricultural University, Viljandi mnt., Eerika, 51014 Tartu, Estonia

^b Institute of Chemistry, Tallinn Technical University, Akadeemia tee 15, 12618 Tallinn, Estonia

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Abstract. The elemental composition of active humic and fulvic acids, bound with mobile sesquioxides, was studied in the mollic epipedon of Rendzic Leptosols and arable Calcari–Chromic Luvisols of different ages, as well as in the umbric epipedon of forest Stagnic Luvisols. In general, no essential differences were observed in the elemental composition of humus acids in the studied soils. A particularly uniform and stable composition of both humus acids is characteristic of the mollic epipedon of Rendzic Leptosol with age differences up to 7000 years, while the compositions of humic and fulvic acids are similar with only H content being more expressed in fulvic acids. The humic acids of the umbric epipedon of forest Luvisol have not changed with time either. However, an increase in the content of C, H, and N, accompanied by a decrease in the O content, has taken place in fulvic acids after clear-cutting, and obvious changes have occurred in their structural and chemical status. In the mollic epipedon of arable Luvisols, only a slight tendency of decrease in the content of C and N, and an increase in the O content of humic acids has developed during three decades as a result of alternating application of extensive and intensive management in agriculture. An evident decrease in the content of C, H, and N, accompanied by an increase in the O content, is opposite to changes in forest soils and appears to be common for the impacts of a cereal monoculture and weak agrotechnology on soil humus in general. The elemental composition of humic acids in all studied Luvisols was the following: C 53–56%, N 4–5%, H about 6%, O 33–36%, and C:N 10.7–14.5. The respective data for fulvic acids were: C 35–50%, N 2.5–4.5%, H 3–7%, O 40–58%, and C:N 10.2–18.6.

Key words: elemental composition, humus acids, Luvisol, Rendzic Leptosol.

INTRODUCTION

Organic matter always represents a driving force for pedogenesis on any mineral substrate in any place. The specific role of humus acids (humic and fulvic) in the formation and development of soils and in their production capacity is well known since the dawn of genetic soil science. The peculiarities, differences, and importance of the group, fractional, and elemental composition of humus

substances, especially of humus acids, have been discussed and illustrated with abundant data in many fundamental publications [1–9]. When the group and fractional composition of humus has been presented and discussed in almost every contemporary publication on soil genesis and/or humus chemistry, then the elemental composition has been less addressed; moreover, mainly in connection with metal–humic–fulvic interactions [10–15]; clay and mineral particle size [14, 16–18]; herbicides and other organic reagents [19–23]; humic substances in solution [24]; analytical techniques, modelling, and processing [25–32]; and methodology [18, 33]. Besides different reference and commercial samples, IHSS (International Humic Substances Society) standards and extractions from fossil organic sediments, humic and fulvic acids, extracted from various soil horizons (epipedons, spodic Bh), have been used in most of the above-mentioned laboratory modelling investigations. In some cases humus acids extracted from transformation products of straw have been studied [28, 29].

Besides the works by Tyurin [1], Kononova [3], Schnitzer & Khan [8], Orlov [6], Alexandrova [9], and other classics of soil humus research, relatively few studies contain data characterizing the elemental composition of humus acids in different soils [26, 34–39]. We did not find any information on temporal changes in the elemental composition of either humic or fulvic acids within the same genetic taxon and/or area. Temporal and multi-aged comparisons of changes in the content and group and fractional composition of humic acids did not contain data on their elemental composition [40]. Still, the impact of conventional tillage compared with no-tillage on humus status, including the elemental composition of humus, has been studied in some soils [41, 42]. Stearman et al. [41] suggested that no-tilled and tilled treatments were similar with respect to the structural properties of humic acids, and differences in the composition of humic acids were related more to depth than to differences in tillage. Martin et al. [43] studied differences in humic substances between forest soils and cultivated soils at various altitudes and found essential differences in elemental composition, dependent both on cultivation and altitude.

Our investigations in Estonia, aimed at providing a quantitative and a qualitative characterization of humus in forest and arable soil types and their horizons, have also dealt with peculiarities of humus formation and with seasonal differentiation of the group and fractional composition of humus both in forest soils [44, 45] and, within a special experiment, under herbaceous vegetation [46], as well as with changes in the humus status of arable soils [47, 48] and in the content, composition, and pool of humus substances in forest Luvisol [49]. To date, there is no information on the elemental composition of the humus acids of any Estonian soil, apart from the unpublished data of the graduation paper by Kaia Kaupmees (1970), which characterizes briefly functional groups (COOH and phenolic OH) in the humic and fulvic acids of the ground litter and in the humus horizon of some forest soils (Rendzic Leptosol, Calcaric Cambisol, Calcari-Haplic and Stagnic Luvisols). According to these data, the total acidity ($5\text{--}10\text{ mol kg}^{-1}$) of both humus acids in ground litter and in the mollic and umbric epipedons of Estonian soils is lower than that presented in the literature [10, 19, 25, 26, 28, 29], while within functional

groups $-\text{COOH}$ either prevails over or is almost equal to $-\text{OH}$ (phenolic) of humic acids. Contrary to the data given by Grossl & Inskeep [28] and Chen et al. [29], the content of phenolic $-\text{OH}$ exceeds that of $-\text{COOH}$ several times in the fulvic acids of Estonian forest soils.

To obtain more information on the humus of at least some of the Estonian soils, this paper focuses on elemental composition and its temporal changes in arable and forest Luvisols covering about 16% of the total territory and 42% of the automorphic territory of Estonia. Although Rendzic Leptosols on limestone account for only slightly more than 1%, they represent geological, historical, and pedogenetic uniqueness in the Ordovician–Silurian plateau.

MATERIAL AND METHODS

Layout, area, soils, and sampling

Arable Calcari–Chromic Luvisols (LVcx), formed on reddish-brown (5YR4/4) calcareous till, were studied within the Sakala Upland near the village of Mõnnaste (25°46' E, 58°18' N). The Ap–Ew–Bt–C profile is characteristic of these soils. For the first time, both the morphological description and sampling by genetic horizons were carried out in 1964. A demonstration of the profile and a discussion of related analytical data took place during the tour of the Third USSR Soil Congress in 1966 [50]. Repeated investigations were performed at the study site in 1986 and 1996 after extensive and intensive agricultural management had been alternatively applied there. The morphology revealed no significant changes. Only, as a result of deep ploughing, the mollic Ap-horizon (10YR3/3 moist and 10YR4/3 dry) had increased by about one-third in 1986 and mixed with underlying Ew. The thickness of the latter had simultaneously decreased. The colour indices had not changed essentially. The results of these field and laboratory studies were discussed at two international conferences and published in the corresponding transactions [47, 48].

Investigations in the forest were carried out in one of the areas of the International Biological Programme (IBP) at the Vooremaa Forest Ecology Station, Jõgeva County (26°44' E, 58°43' N) on the northeastern slope of the Kallivere drumlin covered with a nemoral spruce forest rich in ground vegetation [51]. The first studies of Chromi–Stagnic Luvisol (LVxj), formed also on reddish-brown (5YR4/4) calcareous till, though more deeply leached, were conducted in 1972. The A–Bw (Baf)–Ewg–Bt–C profile characterized the site. The obtained field and analytical results were published in the series *Estonian Contributions to the IBP* [52]. Repeated investigations were performed in the same pits in 1994, some years after clear-cutting and timber transportation activities. No major changes were established in soil morphology and profile structure. Still, the depth of the umbric humus horizon (10YR3/3 moist and 10YR5/3 dry) had almost doubled and it had compacted slightly, but to a smaller extent than on the drumlin summit [49]. The changes that had taken place in the composition and properties of forest Stagnic Luvisol during two decades were similar to those described in Saskatchewan,

Canada [53] and Oregon, USA [54]. The obtained results were presented at the 7th Estonian Conference on Ecology in 1997 and published [49, 55].

Rendzic Leptosols of Late-Yoldian–Early-Ancylian age (9000 years BP) on fallowed limestone alvar and on the limestone barrow walls (Photo 1) of ancient fields from 2000–2500 years BP were studied on the North-Estonian Plateau near the village of Rebala (25°02' E, 59°29' N), about 20 km to the east of Tallinn and 0.5 km to the south of the Baltic klint on the territory of the Rebala Archaeological Reserve. The difference in the age of the two investigated objects was some 6500–7000 years. The mollic epipedon (5YR3/2 moist and 7.5YR4/4 dry), extremely rich in organic matter, was underlain directly by the Ordovician bedrock (A–D profile). The data obtained for these and other archaeological objects were presented and discussed at the 15th World Congress of Soil Science and published in the Congress Transactions [56].

The content of organic carbon and nitrogen, the group and fractional composition of humus, and the mineral composition of decalcinate (solution of 0.05 M sulphuric acid) have served as key objects of all these studies; their dynamics and changes are discussed in the above publications. All the analysed samples are preserved in the Soil Collection of the Institute of Soil Science and Agrochemistry, Estonian Agricultural University, which has made it possible to use them for extraction of humus acids and for measurement of their elemental composition. For this purpose, only the epipedon (humus horizon) was used, although samples from deeper horizons were available as well.



Photo 1. Rendzic Leptosol on ancient field barrow (2000–2500 BP) and fallowed alvar (at the barrow foot) of Yoldian–Ancylyus age at Rebala. Photo by L. Reintam.

In addition, two samples of humic acids from the *mull* and *moder* types of spruce forest floor on Rendzic Leptosol and Stagnic Luvisol, respectively, and two samples of humic acids from the umbric A-horizons (10YR3/3 moist and 10YR4/3 dry) of two Stagnic Luvisols, prepared by Kaia Kaupmees already in 1969/70 and preserved up to the present, were used in elemental analysis.

Analyses

Humus acids were extracted at the laboratories of the Institute of Soil Science and Agrochemistry, Estonian Agricultural University, in 1997 with 0.1 M NaOH according to the technique used in other analogous studies [3, 8, 33, 57]. Precipitation of humic acid from an alkaline solution was repeatedly carried out with 0.5 M H₂SO₄ and finally purified from S with bidistilled water. Purified humic precipitation was air-dried and preserved in glass vials.

Fulvic acids in the acidified solution were collected in the Büchner filter, purified from acid with bidistilled water, extracted once again with 0.1 M NaOH, neutralized with H₂SO₄ up to pH 5.8–6.0, condensated at the temperature of 40–50°C, dialysed, and air-dried for preservation in vials. The same techniques were used by Kaia Kaupmees in 1969/70.

Elemental analysis was performed in 3–4 replications, with the accuracy prescribed for analyser, at the laboratories of the Institute of Chemistry at Tallinn Technical University, using the Elemental Analyser PE 2400 Series II CHNS. Combustion temperature was 975°C, reduction temperature 640°C. Dry combustion at 600°C was used for measurement of total ash. The results obtained were expressed in percentages of dry ash-free material. The contents of C, H, and N were measured directly, the content of O was obtained from the difference. Standard deviation did not exceed 1%.

In our previous studies with these samples and soils, the total percentages of organic carbon and nitrogen were established by the Tyurin and Kjeldahl methods, respectively. The group and fractional composition of humus was determined by alternate acid–alkaline treatment after the Tyurin–Ponomareva volumetric method [58]. The obtained results were expressed in percentages of organic carbon. Humic and fulvic acids, extractable directly in alkali, are bound with mobile sesquioxides and can be qualified as active [3, 58]. As they represent the fraction subjected to elemental analysis in our study, the percentage of humic acids in the following tables corresponds to that of the first fraction given in earlier publications. Among fulvic acids, this paper deals with the first fraction together with free fulvic acids (1a) extractable altogether in alkali. Humic–fulvic complexes, bound with alkaline earths (second fraction) and clay minerals (third fraction), were not extracted for elemental analysis.

RESULTS AND DISCUSSION

In general, the elemental composition of humic acids was quite similar in all the studied soils, although there were significant differences in the quantitative and qualitative indices of humus (Tables 1–4). Still, a clear tendency of decrease in the content of carbon and nitrogen, simultaneous with an increase in the content of oxygen, appeared to be accompanied with a decrease in the total content of carbon and nitrogen and an increase in the fulvicity of arable Luvisol under a cereal monoculture during the last decade. Such changes have been significant in case of fulvic acids (Table 1). According to Grossl & Inskeep [28] and Chen et al. [29], fulvic acids prevailed in wheat straw; they were poor in nitrogen and were characterized by a large C:N ratio. It is evident that not only changes in the general status of humus [48] but also changes in the elemental composition of the mollic epipedon of Calcari–Chromic Luvisol are due to intensification of mineral fertilization and deepening of tillage from 1964 to 1986, as well as to poorer agrotechnology and increasing importance of low-productivity cereal monoculture from 1986 to 1996. Changes in the elemental composition of both humic and fulvic acids were found to be similar under cultivation compared with the natural forest situation [43].

Table 1. Elemental composition of alkali-extractable humic (HA) and fulvic (FA) acids as percentage of dry ash-free material in the mollic epipedon of arable Calcari–Chromic Luvisol at Mönnaste

Humus acid	Year	Percentage in total soil					Percentage of humus acid				
		C	N	C/N	HA/FA	1st fr. of C	C	H	O	N	C/N
HA	1964	1.14	0.13	8.8	0.5	19	55.1	6.2	33.7	5.0	11.1
	1986	1.09	0.11	9.9	1.0	18	53.9	6.1	35.0	5.0	10.7
	1996	0.98	0.08	12.3	0.4	16	53.1	6.0	36.1	4.8	11.2
FA	1964	1.14	0.13	8.8	0.5	36	45.1	4.6	45.9	4.4	10.2
	1986	1.09	0.11	9.9	1.0	18	43.9	4.8	47.3	4.0	11.7
	1996	0.98	0.08	12.3	0.4	29	35.5	2.6	58.7	3.2	11.1

Table 2. Elemental composition of alkali-extractable humic (HA) and fulvic (FA) acids as percentage of dry ash-free material in the umbric epipedon of forest Chromi–Stagnic Luvisol at Voore

Humus acid	Year	Percentage in total soil					Percentage of humus acid				
		C	N	C/N	HA/FA	1st fr. of C	C	H	O	N	C/N
HA	1972	2.79	0.21	13.5	0.4	15	54.7	6.0	35.1	4.2	13.1
	1994	2.59	0.13	19.9	0.3	12	54.1	6.0	35.4	4.5	12.1
FA	1972	2.79	0.21	13.5	0.4	28	47.1	5.8	44.6	2.5	18.6
	1994	2.59	0.13	19.9	0.3	25	50.1	6.7	39.6	3.6	13.9

Table 3. Elemental composition of alkali-extractable humic (HA) and fulvic (FA) acids as percentage of dry ash-free material in the mollic epipedon of alvar Rendzic Leptosol at Rebala

Humus acid	Age, years	Percentage in total soil					Percentage of humus acid				
		C	N	C/N	HA/FA	1st fr. of C	C	H	O	N	C/N
HA	9000	10.0	1.3	7.7	0.5	18	53.6	5.4	36.0	5.0	10.6
	2000	13.8	1.4	9.6	0.5	13	53.5	5.5	36.0	5.0	10.8
FA	9000	10.0	1.3	7.7	0.5	18	57.2	7.3	31.0	4.5	12.7
	2000	13.8	1.4	9.6	0.5	13	57.3	6.9	31.1	4.7	12.1

Table 4. Elemental composition of alkali-extractable humic acids as percentage of dry ash-free material in *mull* (OH) and *moder* (OF) forest floors and in the A-horizon of forest Stagnic Luvisols at Reola (1) and Mooste (2)

Object		Percentage in total soil					Percentage of humus acid				
		C	N	C/N	HA/FA	1st fr. of C	C	H	O	N	C/N
Forest floor	OH	49.3	1.58	31.6	0.22	18	58.4	5.9	33.2	2.5	23.1
	OF	53.0	1.31	40.5	0.43	17	56.6	6.0	34.3	3.1	18.5
A-horizon	1	1.67	0.12	13.9	0.43	15	56.2	5.7	34.2	3.9	14.5
	2	1.93	0.12	16.1	0.41	17	56.0	6.3	33.7	4.0	14.0

According to the C:N ratio, there appears a trend towards a slight deterioration in the maturity of total humus as well as humic acids. This may be caused by deficiency of organic nitrogen and weakening of nitrogenous bridges in the phenolic molecules of humic acids rich in carboxydes [5], which can take place even under conditions of high level tillage and balanced nutrition [59]. A more or less similar decrease in the content of carbon and nitrogen in fulvic acids did not affect the essential change in the C:N ratio during the last decade, although a slight tendency towards status deterioration was ascertained. The rise in the oxidation rate (against the background of decreasing hydrogen and increasing oxygen) of fulvic acids can be interpreted as a result of intensified polycondensation in conditions of changeable temperature [27]. The impact of slightly increased solubility and fulvicity [47, 48] on these phenomena cannot be excluded either, as is demonstrated by several data on the H:O ratio for fulvic acids from spodic formations [10, 25].

Compared with arable soils, both humic and fulvic acids from the umbric epipedon of forest Luvisols are more carbonized but poor in nitrogen (Table 2). At the same time, practically no temporal changes were observed in humic acids. Changes in the content of O and H in fulvic acids at the end of the last quarter of the 20th century after clear-cutting seem to have been caused by an increase in topsoil compaction and acidity, by development of reductomorphic processes, and by a decrease in base exchange capacity [49]. According to Baes & Bloom [26], phenolic OH groups are more H⁺-bonded in fulvic acid than in humic acid. The

unpublished analytical data by Kaia Kaupmees, presented in her graduation paper, show that in an analogous umbric epipedon of Stagnic Luvisols, fulvic acids contain up to 7.7 mol kg^{-1} of phenolic OH groups against $0.3\text{--}0.4 \text{ mol kg}^{-1}$ of COOH groups. Under conditions of increased seasonal perched water, processes of polymerization and polycondensation, as well as transformation of fulvic acids into humic acids, are apparently inhibited, as has been suggested in theoretical debates [3, 6]. Moreover, in his last papers, Orlov [60, 61] showed that fulvic acids do not represent an individual group of substances but are formed as a result of the analysis, causing partial hydrolysis of high molecular compounds. Hence, the described peculiarities of fulvic acids are to be expected at our human-affected study site.

Considering the C:N ratio, the maturity of the humic acids of the first fraction was almost the same as in the entire humus in 1972 (Table 2). However, the status of fulvic acids bound with them was different. Up to 1994, soil humus maturity decreased owing to a greater decrease in the content of nitrogen compared with the decrease in the content of carbon, but also owing to an increase in total fulvicity. The increase in the content of nitrogen in both humic and fulvic acids studied can be interpreted as accelerated mineralization of clear-cut residues and damaged ground vegetation, mobilization of nitrogenous products of albumen transformation, and insertion of released nitrogen in the structure of the formed active humic–fulvic acids. Because of their relative rapidity, these processes did not evidently involve the more stable third fraction. However, Ca–fulvic complexes (second fraction of fulvic acids) had been removed, because dissolved hydrophilic humus acids [62] are fulvic in their origin, having previously been also complexable with alkaline earths delivered in the process of mineralization [9]. Guggenberger & Kaiser [63] suggested on the basis of Typic Dystric Eutrochrept and Typic Haplorthod that the proportion of organic acidity, percolating with dissolved organic matter from the forest floor into mineral horizons, is about the same as the proportion of total inorganic acidity. As organic solutes are lignocellulose degradation products [64], rich in phenolic OH [19], removal of fulvic acids and fulvates is favoured, resulting in changes in the elemental composition of fulvic acids in the umbric epipedon of our Chromi–Stagnic Luvisol.

The mollic epipedon of Rendzic Leptosol is extremely rich in organic carbon and nitrogen, being comparable even to the best Chernozems of forest-steppes and steppes or prairies [1, 3, 6, 8]. The elemental composition of humic and fulvic acids of Yoldian–Ancyclus age is the same as that of the soil formed on human installations up to 7000 years later (Table 3). At the same time, in both cases fulvic acids are somewhat richer in carbon and hydrogen but poorer in oxygen and nitrogen compared with humic acids. Since brown humic acids (the first fraction extracted and analysed) prevail in humus [56], a dark brownish colour is characteristic of both soil formations. High similarity of the elemental composition of humic and fulvic acids, at least in Rendzic Leptosols, confirms Orlov's suggestion [60, 61] about the natural uniformity of these acids.

According to the C:N ratio, in both cases the molecules of humic acids are to a greater extent bound with nitrogenous bridges than the molecules of fulvic acids. From the aspect of elemental composition, these data confirm once more our earlier postulate that formation of qualitative pedogenetic indices, including characteristics of humus status, is a rapid process as a result of which diagnostic attributes can be established within quite a short time [56]. Seasonal aridity, high base saturation of the weathering products of limestone, and a prevalent proportion of underground phytomass favour rapid deposition of the quantitative and qualitative properties of humus in Rendzic Leptosols, which have been relatively stable during several millennia demonstrating excellent soil memory [65]. Cyclicity, characteristic of pedogenesis in general, appears to be less expressed in relatively stable Rendzic Leptosol.

The elemental composition of humic acids both of the *mull* and *moder* types of the forest floor is similar to that occurring in the mollic as well as in the umbric epipedons (Tables 1–4). In spite of the rich ground vegetation and presence of hazel (*Corylus avellana*) in the underwood, the humic acids of both forest floors are poorer in nitrogen than those of the umbric epipedon (Table 4), being even comparable to fulvic acids in the forest soil epipedon (Table 2). This is also reflected in the large C:N ratio and in the relative immaturity of litter humus. According to the unpublished data by Kaia Kaupmees, the total acidity (5–6 mol kg⁻¹) of humic acids in the forest floor is lower than in the corresponding epipedons (7–9 mol kg⁻¹), while the share of COOH groups and OH groups is more or less equal. As mentioned above, in fulvic acids the content of phenolic OH exceeded that of the carboxylic (COOH) several times. The situation demonstrates an intensive accumulation of N-free compounds in ground litter, accompanied by the release and removal of nitrogen from it, and formation of N-enriched more condensated humic complexes in the underlying humus horizon. The above interpretation can be associated with several explanations found in the literature [39, 63].

CONCLUSIONS

Against the background of variability in the content and group and fractional composition of the humus of different soil types, the elemental composition of humic and fulvic acids, bound with mobile sesquioxides and extractable directly in alkali, is in general extraordinarily similar, even between the mollic and umbric epipedons of any soil in any area. Still, a tendency towards decrease in the content of carbon in humic acids and of carbon, hydrogen, and nitrogen in fulvic acids in the mollic epipedon of arable Luvisol appears to have arisen as a result of agricultural activity of alternating intensity during about three decades. Simultaneous changes in the content of carbon and nitrogen have led, according to the C:N ratio, to a relative stability of structural maturity of both humic and fulvic acids. Compared with the entire soil humus, the status of carbon and nitrogen in active humic and fulvic acids has been less changeable, although slight tendencies to proportional impoverishment and/or deterioration appeared with time.

Temporal uniformity and stability of the elemental composition are characteristic of humic acids both in the umbric epipedon of forest Luvisols and in the mollic epipedon of Rendzic Leptosols of different ages. This regularity applies also to the fulvic acids of Rendzic Leptosols, confirming an earlier postulate about rapid formation and subsequent stabilization of qualitative diagnostic attributes of soils. Uniformity of the group, fractional, and elemental composition of humus on natural limestone as well as on slabs of human installations is characteristic of the soils studied.

As a result of intensified mineralization of organic residues, release of nitrogen and its participation in the increase in the nitrogen content of fulvic acid have occurred after clear-cutting in the umbric epipedon of forest Luvisol. Therefore, the C:N ratio in fulvic acids became comparable to that in humic acids but was smaller than that in the entire soil humus.

Irrespective of mineral soil strata, the elemental composition of both *mull* and *moder* forest floors is similar for spruce stands. Evidently, nitrogen-free organic residues are predominant here, although the ground vegetation and underwood are rich in varieties that produce albumens. Major complexation of nitrogen appears to have taken place under the forest floor in epipedons of both mollic and umbric origin.

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HUMIIN- JA FULVOHAPETE ELEMENDILINE KOOSTIS EESTI MÕNEDE MULDADE HUUMUSHORISONDIS

Loit REINTAM, Jüri KANN, Tiiu KAILAS ja Raja KÄHRIK

Liikuvate poolteisthapenditega seotud aktiivsete (0,1 M naatriumhüdrosiidis lahustuvate) humiin- ja fulvohapete elemendilist koostist uuriti erivanuseliste paepealsete rendsiinade ning pruunide näivleetunud metsa- ja leetjate põllumuldade huumushorisondis. Vaadeldud muldade mõlema huumushappe elemendilises koostises põhimõttelisi erinevusi ei täheldatud. Eriti ühtlane ja ajaliselt stabiilne koostis iseloomustab paepealsete rendsiinade huumushappeid, vaatamata kuni 7000 aastani ulatuvaile erinevustele objektide vanuses. Seejuures on humiin- ja fulvohapete koostis hämmastavalt ühesugune ning üksnes vesinikku sisaldavad fulvohapped mõnevõrra rohkem. Ka pruuni näivleetunud metsamulla humiinhapete elemendiline koostis on vähemalt viimase veerandsaja aasta jooksul püsitud peaaegu muutumatuna. Samas on aga fulvohapete C, H ja N hulga suuremine ning O sisalduse vähenemine ilmselt seotud lageraie tulemusel arenenud muutustega mulla füüsikalises seisundis ning ülavee režiimis. Leetja põllumulla huumushorisondi humiinhapetes ilmneb tendents C ja N sisalduse vähenemiseks ja O sisalduse suurenemiseks seoses kolmekümne aasta jooksul vaheldunud intensiivse ja ekstensiivse agrotehnoloogia ning teravilja monokultuuriga. See on erinev metsamulla humiinhapetes juhtunust. Kõigi uuritud leetjate ja näivleetunud muldade humiinhapete elemendiline koostis oli: C 53–56%, N 4–5%, H ligikaudu

