

Topsoil Acidity of Forested Mineral Lands in Estonia

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Abstract

The active acidity (pH) of forested mineral land topsoil, its relationships with alternative soil acidity characteristics and the influence of soil acidity on forest soil profile fabric and functioning are analysed in the pedo-ecological conditions of northeastern Europe. The active acidity of the forest floor (O-horizon) was taken as the baseline for this analysis. The acidity of the forest floor was studied in accordance with the underlying soil horizons, which are humus and/or raw-humus horizons in the more fertile soils, whereas in less fertile soils, they are podzolized horizons. The data on soil acidity are presented by main soil types, forest site types, forest humus cover types (pro humus forms) and forest stand groups. In this work, the influences of forest floor acidity on mineral topsoil fabric, soil processes and peculiarities of carbon sequestration are explained. The active acidity of the forest floor provides a great indicative value in elucidating the regularities of the forest soil cover, as a whole, formation and functioning. For evaluating the normality of soil functioning, or the absence of disturbances in ecosystem functioning, the intervals of soil type-specific reference pH levels have been established.

Keywords: forest floor, active acidity, humus cover, humus cover type (pro humus form), soil cover

Introduction

Soil reaction is a valuable pedo-ecological characteristic that reflects the actual status and development direction of the forest ecosystem as well as its soil cover (SC). To understand the nature of the acidity of forest soils in the function of the whole ecosystem, it is necessary to study the vertical distribution of soil acidity in the topsoil of the SC in detail. In this work, the baseline or starting point of this analysis is the active acidity (pH) of the forest floor (FF). The FF's (or O-horizon's) active acidity is studied in accordance with humus (A) or/and raw-humus (AT) horizons, as an essential component of humus cover (HC). HC may be taken as a transitional space between plant cover and SC (Ponge 2013, Kõlli and Köster 2018). In soils, where the humus horizon is absent, the interactions of the FF were studied with respect to the mineral soil horizons that were contacted with it from underneath (and not belonging to the HC); these were podzolized (Ea) horizons in most cases (Chertov 1981, Rozanov 1983).

In this work, the data on soil acidity are analysed by main soil types, forest site types, forest HC types (*pro* humus forms) and forest stand groups. For explaining the mutual relationships of the FF's active acidity with alternative soil acidity characteristics in soil functioning, a correlation analysis is performed.

The importance of soil reaction in characterizing soil development and functioning was previously empha-

sized by several authors (Müller 1887, Hüttle and Schneider 1998, Boruvka et al. 2007, Zanella et al. 2011). The detailed research, which focused on the acidity of soils and on mechanisms of complete soil profile acidification, was conducted for both cases, i.e. in the conditions of agricultural (Eidukeviciene et al. 2011) and silvicultural land uses (Iwald 2016). In connection to the HC's acidity of forest soils, only the exchangeable ($H_{5,6}$) and hydrolytic ($H_{8,2}$) acidities, mobile aluminium (Al), and the stage of basic cation saturation were previously analysed (Kõlli 1992). At the same time in Estonia, the relatively abundant initial data on both arable and forest soil pH (Estonian Agri-project 1983, 1985a, 1985b) are not yet sufficiently analysed and generalized scientifically. Rare exceptions in this field are the statistically elaborated pH distribution curves of model soils, which were calculated on the basis of soil diagnostic horizons, and separately for arable and forest soils. These models were made available online (CD Kõlli et al. 2008).

For the basis of this work are different origin databases about acidity of FF and about agrochemical characteristics of, contacted with FF, soil mineral horizons. The results from these data, for the main tasks of the research are the following: (1) to present the generalized data on the topsoil acidity of Estonian mineral forest lands by the dominated forest soil groups, by forest site types, by HC types and by forest stand groups, (2) to distinguish the correlation and interaction of active acidity with different alternative parameters (reflecting soil

acidity), (3) to explain the influences of the FF's acidity on mineral topsoil fabric, on proceeding of soil processes, and on peculiarities of carbon sequestration, and (4) to emphasize the great indicative value of active acidity in forest soil ecology and in the formation of SC as a whole of mineral forest lands.

Materials and Methods

General pedo-ecological characterization of soil cover of Estonian forest lands

The SC of Estonian forest landscapes is typical to northeastern Europe. Locating the transition area between continental and marine climates in mild and wet pedo-climatic conditions of the temperate zone, in natural areas of Estonia, the coniferous, mixed (coniferous-deciduous) and deciduous forests are developed. Presently, the forests occupy approximately half of whole Estonian SC. To Estonia, the *frigid udic* (49 %), *frigid aquic* (47 %) and *frigid aridic* (4 %) pedo-climatic conditions (Soil Survey Staff 2014) are inherent.

The present research is limited by mineral soils, which form 63.3 % of the total forested area (Kokk 1995). The main parts of parent materials in mineral soils are derived from the glacial and aquaglacial *Quaternary* deposits (Raukas and Teedumäe 1997). Approximately 35 % of forest mineral soil parent materials are *Pleistocene* tills. The glaciofluvial, glaciolacustrine, alluvial and aeolian sediments re-worked from tills are alternatively distributed with tills.

The greatest share (56.4 %) of the mineral forest soils forms *Gleysols*, of which half have *eutric* (calcareous) and a quarter *dystric* character. To the wet (*epigleyic*) mineral soil group belong the *Histic Podzols* (~5 %) as well. The share of automorphic soils is only 38.5 % from the whole area of mineral forest soils, whereas among them the *Retisols* (12.5 %), *Cambisols* (10.3 %) and *Podzols* (9.5 %) are dominant. A modest part belongs to *Luvvisols* (3.8 %), *Leptosols* (1.3 %) and *Regosols* (1.1 %) (Kõlli et al. 2009).

The dominating texture of mineral forest soils is sand (56 %). With the best forest growing potentiality loams form only 25 %, but the shares of loamy sands and clays are 14 % and 5 % respectively. According to the moisture conditions, 62 % of forest soils are characterized as wet mineral (*epigleyic*), 21 % automorphic fresh, 14 % moist (*endogleyic*) and 3 % dry aridic.

Databases and datasets

Pedon Database (DB). The dominating part of the databases used in this work data on soils originate from the Pedon DB, which contains data on forest-, crop- and grassland soils. The research areas (RAs) established for studying forest soils are located in scattered areas of

the territory of Estonia. The main part of the Pedon DB was created during 1967-85; it was updated and revised in 1986-95. The Pedon DB enfolds all of the main forest soil types of Estonia.

Pedon-1 Dataset (DS) is an excerpt from the Pedon DB, which contains only mineral forest soils, where their characteristics are given by individual RAs. Pedon-1 enfolds a total of 189 RAs. On the basis of Pedon-1, it was possible to resolve task 1, but could only partially resolve the other tasks, as the soil acidity data are linked with a great number of other forest soil pedo-ecological characteristics, which characterize soil functioning, and are important for forest management.

DS Pedon-2 is an excerpt from the Pedon DB in the form of a summarized table, which contains the averaged data for 13 mineral forest soil groups. This DS enables the study of different kinds of interrelationships on the basis of generalized data (by soil groups).

DS Pedon-3 is an excerpt on the FF acidity data of these 30 RAs, which have a multi-layered fabric and where the data are given by FF' sub-horizons. Pedon-3 is used for explaining regularities in the formation of multi-layered FF fabric and its acidity.

EMA DB (Soils of Estonia in Numbers) was formed as result of large scale soil mapping of Estonia (Estonian Land Board 2012). The EMA DB contains, among others, the statistically analysed data on forest soil agrochemical properties, presented by soil diagnostic horizons and soil species or/and varieties (Estonian Agri-project 1983, 1985a, 1985b).

DS EMA used in this work is an excerpt from the EMA DB on the acidity of forest lands topsoil. The highly appreciable sides of the EMA DS are: (1) the data are summarized (generalized) by the most detailed level of Estonian soil classification (ESC) i.e. on the level of soil species and/or soil varieties, and (2) the model soil profiles are linked to different quantitative characteristics and available online, which enables the explanation of the relationship of soil acidity with other pedo-ecological characteristics (see CD-6 about forest soils in Kõlli et al. 2008). The main shortcoming of the EMA DS is the absence of data on the O-horizons' properties of these soils, which have been formed on calcareous soil parent materials.

DS Comp. This DS was compiled on the basis of scientific works data on Estonian forest soils published during the last half century. The aim of forming the DS Comp was to study the interrelationships between pH_{KCl} and pH_{H_2O} in the FF (Comp-1) and subjacent FF mineral soil horizons (Comp-2). These DSs enable the elaboration of the pedotransfer functions (PTF) for determining soil pH_{H_2O} on the base of their pH_{KCl} .

For all statistical analyses the STATISTICA version 13.4 (StatSoft Inc.) software package was used. One-

way ANOVA were applied to test the effect of soil type on mean pH. The level of statistical significance was set at $P < 0.05$.

Methodological principles and terms

The main soil organic matter (SOM) or carbon (SOC) rich constituents in mineral forest soils may be: (1) mixed or single layer FF or O-horizon, (2) stratified or multi-layered FF or O-horizon, (3) thin (10–30 cm) peat or histic (T) horizon, (4) humus (A) horizon, and (5) raw-humus (AT) horizon. The sub-horizons of FF or O horizons are separated as: (1) O1 horizon as weakly (slightly) decomposed or undecomposed forest litter, (2) O2 as moderately decomposed FF, and (3) O3 as well-decomposed FF. The soils with thin (<30 cm) peat layers belong to the mineral soil (as transitional soils between mineral and organic soils); their T-horizon is treated here as a certain type (histic) of O-horizon. Used in ESC, the AT-horizon is a transitional horizon between humus (A) and peat (T) horizons. The AT-horizon is determined on the basis of SOM or SOC content, for which percentages are in the limits of 7–35 and 4–20 respectively (Astover et al. 2013). The AT- and T-horizons were formed first in *epigleyic* and *epihistic* soils. The O- and T-horizons are classified as exo-organic (belonging to the FF), whereas the A- and AT-horizons are classified as endo-organic (i.e. the SOM has been sequestered into the mineral soil of the HC).

On the basis of topsoil fabric and already formed soil horizon properties, a different kind of epipedon classification has already been explored (Zanella et al. 2011, Soil Survey Staff 2014, IUSS Working Group WRB 2015). In Estonia, the topsoil complex enriched with the SOM is called HC, which is the superficial part of the SC. The SC's HC classification for Estonian natural areas contains 27 HC types in total (Kõlli 1992). The internationally recognized term for HC type is humus form (Müller 1887, Zanella et al. 2018). The subsequent to the HC (but not belonging to it) horizons in podzolized soils are Ea-horizons. In calcareous soils, the endo-organic horizons (A, AT) belonging to the HC are mostly followed by B-horizons. The HC of weakly developed soils is commonly under-layered by different transitional (BC) or by parent material (C, Cg, CG) horizons.

The basic indicator of soil acidity was taken as the active acidity or pH determined in neutral salt (KCl) solution (pH_{KCl}). Alternatively, the data on the soil horizon $\text{pH}_{\text{H}_2\text{O}}$, exchangeable acidity ($\text{H}_{5,6}$), hydrolytic acidity ($\text{H}_{8,2}$), and mobile aluminium (Al) concentration and stocks were used.

In the case of both DBs (Pedin and EMA), the pH_{KCl} was determined in 1M KCl solution in relation to soil/solution with a ratio of 1:2.5, and materials from the O- and peat horizons at a ratio of 1:5 electrometrically by means of pH-meters, whereas the used method is ade-

quate to ISO 10390. In determining the $\text{pH}_{\text{H}_2\text{O}}$, pure water was used instead of 1 M KCl solution. The content of clay ($\phi < 0.01$ mm) was analysed by the pipette method (Kachinsky 1965). The SOC/SOM contents were determined by the method of Tjurin with dichromate oxidation using external heating (Arinouskina 1970) and the total nitrogen by Kjeldahl digestion. The $\text{H}_{5,6}$ (exchangeable H^+) and mobile Al (Al^{+++}) were extracted with 1 M KCl solution with afterwards separated titration of total exchangeable acidity ($\text{H}^+ + \text{Al}^{+++}$) and of H^+ using the Sokolov method. The $\text{H}_{8,2}$ and basic cations (BC) were extracted with 1 M NaCH_3COO and determined by titration or by the Kappen method (Arinouskina 1970). The cation exchange capacity (CEC) was calculated by summing BC and $\text{H}_{8,2}$, but the base saturation percentage (BS %) using the formula below:

$$\text{BS}(\%) = \text{BC}/\text{CEC} \times 100 \quad (1)$$

The quantitative evaluation of acidity per SC layer ($\text{H}_{5,6}$ and $\text{H}_{8,2}$ in kmol ha^{-1} , mobile Al in kg ha^{-1}) was performed using their concentration ($\text{H}_{5,6}$ and $\text{H}_{8,2}$ in mmol kg^{-1} , mobile Al in mg kg^{-1}) and of the layer volume weights. The soil names, which are given in national DS by ESC, were converted into the World Reference Base (WRB) soil classification system (IUSS Working Group WRB 2015). The same was done with particle size distribution, since in both DBs (Pedin and EMA), the soil texture was characterized by Kachinsky.

The baseline or starting point in this work is the pH_{KCl} of the O-horizon. In the case of multi-layered FF, the baseline was taken as the pH of the O2-horizon. In explaining the vertical distribution of pH_{KCl} in HC, the A-horizon pH was measured (or sample was taken) from the middle of the A-horizon. Therefore, in most of the cases, the A- and AT-horizon acidity were determined in relation to a 5 cm soil layer, which was located at the depth of 5–10 cm from the surface of the mineral soil. In the case of soils without A (AT)-horizons, the acidity parameters or their vertical distribution were compared with the Ea-horizon as the first mineral horizon and with followed it B-horizons. The A-, AT- and Ea-horizons with thickness less than 2 cm were not taken into account. Therefore, the Ea acidity was determined in the soil layer which was located mostly in the depth of 3–8 cm from the surface of the mineral soil. The layering depth of the B-horizon was variable as this depends on the soil podzolization stage, which is 8–12 cm in weakly podzolized soils, or 23–27 cm in strongly podzolized soils (Kõlli et al. 2008).

Results

Active acidity (pH_{KCl}) of forest floor and adjacent to it mineral horizons

The average pH_{KCl} of mixed FFs, formed on calcareous parent materials and in aeromorphic conditions soils

Table 1. Active acidity (pH_{KCl}) of the forest floor and the underlying mineral horizons on the basis of the Pedon-1 DS

ESC code ¹⁾	WRB name	n	Mean pH_{KCl} of FF ²⁾	Mineral horizon ³⁾	Mean pH_{KCl} ²⁾	Difference with FF ⁴⁾
Soils with A or AT horizons						
Kh ¹⁾	Rendzic Skeletic Leptosols (Loamic, Hyperhumic)	6	5.05 ^{ab}	A	5.98 ^c	0.93*
K ¹⁾	Calcaric Skeletic Cambisols (Loamic, Humic)	9	4.90 ^d	A	6.09 ^c	1.19*
Ko ¹⁾ &Kog ¹⁾	Endogleyic Endoskeletal Calcaric Cambisols (Loamic, Humic)	15	5.02 ^{ab}	A	5.97 ^c	0.95*
Kf ¹⁾ &Klg ¹⁾	Endogleyic Endocalcaric Lamellic Luvisols (Loamic, Cutanic, Humic)	13	4.78 ^d	A	5.18 ^b	0.40
LP ¹⁾	Dystric Stagnic Fragic Glossic Retisols (Abruptic, Humic)	26	4.1 f	A	4.20 ^f	0.09
Lk	Dystric Albic Arenosols (Humic, Protosodic)	12	3.67 ^{ab}	A	4.08 ^b	0.41
Lkg	Dystric Endogleyic Albic Arenosols (Humic, Protosodic)	28	3.85 ^{bc}	A	4.04 ^b	0.19
Go	Calcaric Reductic Mollic Gleysols (Loamic/Siltic)	4	5.62 ^a	AT	5.48 ^{bc}	-0.08
GI	Dystric Reductic Umbric Gleysols (Luvic)	5	5.12 ^{ab}	AT	5.06 ^b	-0.06
LkG	Dystric Umbric Reductic Spodic Gleysols (Loamic/Arenic)	4	3.12 ^e	AT	4.12 ^e	1.00*
Soils with sequence of Ea-B horizons						
L	Albic Rustic Podzols (Arenic)	27	3.23	Ea B	3.7 ^f 4.34	0.48* 1.11*
Lg	Endogleyic Carbic/Rustic Albic Podzols (Arenic)	16	3.1 ^{fb}	Ea B	3.57 ^{ab} 4.05 ^b	0.46* 0.94*
LG	Epigleyic Carbic/Rustic Albic Podzols (Arenic)	5	2.74 ^a	Ea B	3.32 4.20 ^b	0.58* 1.46*
LG1	Histic Epigleyic Ortsteinic/Carbic Albic Podzols (Arenic)	15	2.89 ^a	Ea B	3.7 ^f 4.12 ^e	0.90* 1.23*

¹⁾ The fabric of these soils is characterized by the model profiles in the following way: Kh – M-1, K – M-2, Ko – M-4, KI – M-5, LP – M-7 and M-8, and Kog – M-15; for models see Digital collection of Estonian soils: CD-6, 2008; ²⁾ Different letters within columns indicate a significant difference ($p < 0.05$) between soils; ³⁾ Horizons: A – humus, AT – raw-humus, Ea – podzolized, and B – illuvial horizon; ⁴⁾ The significant difference is denoted by an asterisk (*).

(*Leptosols*, *Cambisols* and *Luvisols*) are within the limits of 4.8–5.1 (see Table 1). The differences between these soils FF and subsequent to it A horizons, which pH_{KCl} are in the limits of 5.2–6.1, varied from 0.4 units to 1.2, being higher in more calcareous soils. The FF pH_{KCl} of *epigleyic* and calcareous loamy soils (i.e. *Gleysols*) is relatively high (5.1–5.4), whereas the AT pH_{KCl} is practically similar to the FF pH.

The most acidic FFs are formed in wet conditions on *epigleyic* sandy soils (pH_{KCl} of 2.7–2.9), but the FF pH_{KCl} is low in aeromorph *Podzols* (3.1–3.2) and in *Arenosols* (3.6–3.9) as well. The difference between the *Podzols* FF and Ea-horizons' pH_{KCl} is on average 0.4–0.9 pH units, but the same with B-horizons is 0.9–1.5 units. This means that the difference in pH_{KCl} between Ea and B is 0.3–0.9 pH units.

Besides presentation of FF pH_{KCl} by soil types it is shown by forest site types as well, by HC types and by forest stand groups (Figure 1). It should be mentioned that in Figure 1 and in Table 1, the pH_{KCl} data on FFs and mineral horizons that are contacted with them from below are given by soil groups or to a certain extent in a generalized way, whereas these data originated from the Pedon DB. The DS presented in Table 2 originated from the EMA DB, whereas the data on forest soil acidity are given by soil varieties of ESC. Unfortunately soils formed on calcareous conditions are absent in this DS, with the exception of *Mollic* and *Umbric Gleysols*. With great value in understanding ecology of FF acidity have the linked with this DS (Table 2) generalized Estonian forest soil models available online (CD-6 in Kölli et al. 2008).

The EMA DS data on acidity of forest topsoils show similar tendencies with the Pedon DS. The most acidic

are FFs of not only *Epigleyic Podzols* (pH_{KCl} 2.6–2.8), but also of *Endogleyic Podzols* (pH_{KCl} 2.8–3.1). It is remarkable that the soil species, which are by their diagnostic properties very similar each to other, do not differ essentially by their FF and subsoils (Ea-horizon) acidity. Therefore, it is meaningful to calculate average pH_{KCl} , i.e. acidity data, separately for soil groups L(k), L and Lg, for which the FF pH_{KCl} are 3.28, 2.90 and 2.90 respectively. It was elucidated as well that the FF of south Estonian *Arenosols* have substantially lower pH_{KCl} compared to ones from north Estonia (Table 2).

Relationships between active acidities (pH) determined in 1M KCl solution and in water

Besides pH_{KCl} , several alternative indicators can be used for characterization of FF and subjacent with it mineral soil horizons. Most frequently, the pH_{H_2O} indicator is used, as it strongly correlates with pH_{KCl} in the case of both materials, i.e. FF and in mineral topsoil layers (Figure 2). A high correlation coefficient between pH_{KCl} and pH_{H_2O} (Table 3) enables the use of the pedotransfer function (PTF-2) for the determination of FF pH_{H_2O} and PTF-3 for the determination of mineral topsoil horizon pH_{H_2O} by their pH_{KCl} (see Figure 2):

$$pH_{H_2O} \text{ of FF} = 0.82 \text{ (ff)}pH_{KCl} + 1.52, \tag{2}$$

$$pH_{H_2O} \text{ of mineral soil} = 0.88 \text{ (ms)}pH_{KCl} + 1.54, \tag{3}$$

where (ff) pH_{KCl} is the pH_{KCl} of FF, and (ms) pH_{KCl} is the pH_{KCl} of mineral soil.

Since DS Comp was used as the base of PTFs 2 and 3, it should be mentioned that the PTFs 2 and 3 should be taken as suitable for the Estonian forested mineral land topsoil.

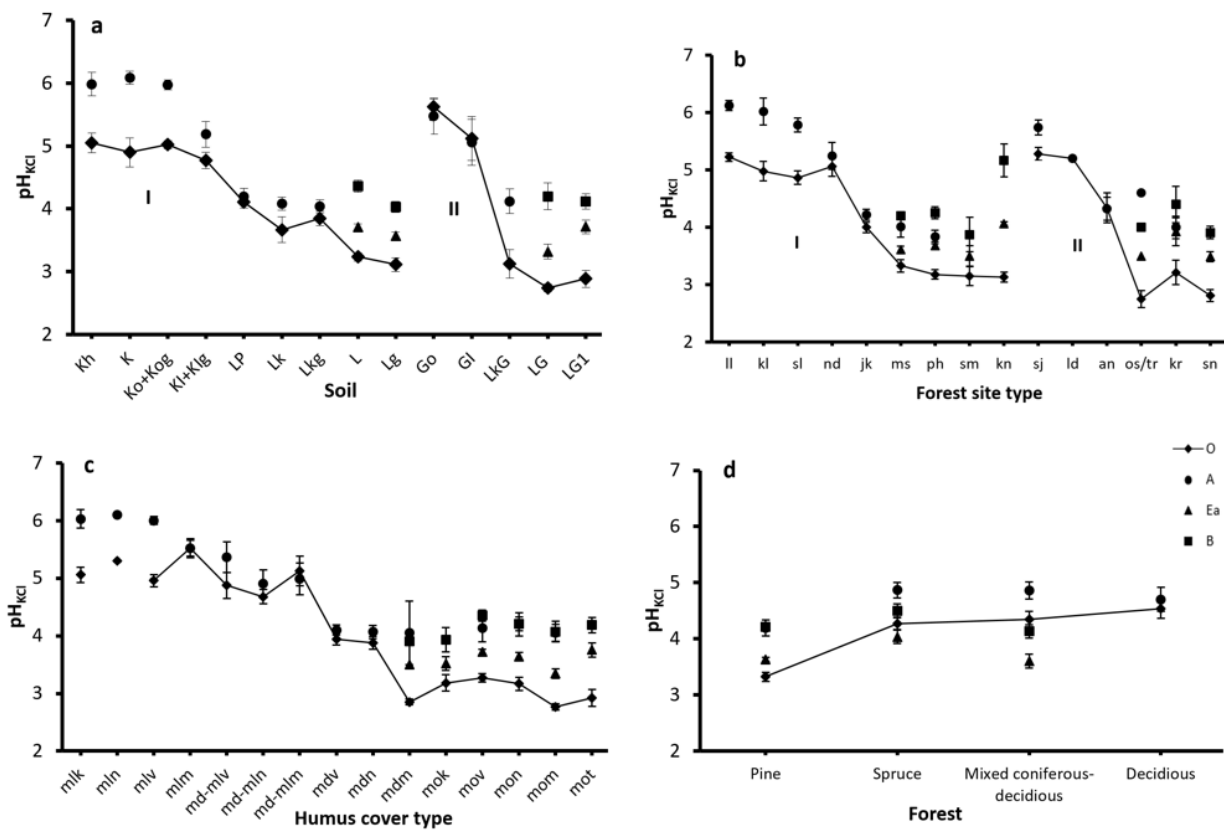


Figure 1. Active acidity (pH_{KCl}) of the forest floor and the underlying it mineral horizons of soils:

- a) By soil groups. For the Estonian soil code and the WRB name, see Table 1; soil sequences are: I – aeromorphic and II – hydromorphic soils
- b) By forest site types. Forest site type codes and names: II – *Arcostaphylos*-alvar, kl – *Calamagrostis*-alvar, sl – *Hepatica*, nd – *Aegopodium*, jk – *Oxalis*, ms – *Myrtilus*, ph – *Rhodococcum*, sm – *Cladonia*, kn – *Calluna*, sj – *Dryopteris*, ld – *Alder*, an – *Filipendula*, os – *Equisetum*, tr – *Carex*, kr – *Polytrichum* and sn – *Vaccinium uliginosum*; forest site type sequences: I – site types on aeromorphic soils and II – site types on hydromorphic soils.
- c) By humus cover types or humus forms. Humus cover type codes and names: mlk – dry mull, mln – moist mull, mlm – wet mull, md-mlv – fresh moder-mull, md-mln – moist moder-mull, md-mlm – wet moder-mull, mdv – fresh moder, mdn – moist moder, mdm – wet moder, mok – dry mor, mov – fresh mor, mon – moist mor, mom – wet mor, mot – peaty mor.
- d) By forest stand composition, whereas dominating species in pine forests was Scots pine (*Pinus sylvestris* L.), in spruce forests was Norway spruce (*Picea abies* L.), in deciduous forests were birch (*Betula pendula* Roth.), aspen (*Populus tremula* L.) and alder (*Alnus glutinosa* L. and *A. incana* L.).

Correlation of FF's active acidity with alternative indices of soil acidity in FF and in other topsoil horizons

The highest correlations ($r = 0.95-0.97$) of FF pH_{KCl} were mentioned along with the FF $\text{pH}_{\text{H}_2\text{O}}$ in Table 3. From the other alternative soil acidity indices, the highest correlation of FF active acidity corresponded to exchangeable acidity, which were followed by the hydrolytic acidity, and finally by the presence of mobile aluminium in different soil layers. In most cases, the FF pH_{KCl} has the higher correlation with alternative index concentrations as compared to their quantities per area. The FF pH_{KCl} correlation with the subjacent horizon pH is the highest in the case of A- and AT-horizons as com-

pared to Ea-horizons. The correlation of FF active acidity with acidity parameters of the complete HC is weak and nonsignificant in most cases.

Correlation of FF acidity with chemical and ecological characteristics of humus cover

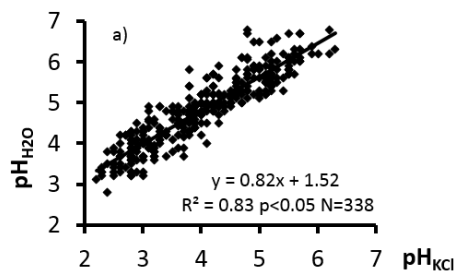
The Pedon DB reveals that the FF active acidity has a significant negative correlation with the amount of FF, which is characterized by the FF thickness and by its stocks per area (Table 4). At the same time, however, the FF acidity correlates positively with the thickness of the HC, and therefore with SOM/SOC and nitrogen stocks within it. A high positive correlation of the FF pH_{KCl} with a litho-genetic scale of Estonian normal soil matrix shows

Table 2. Active acidity (pH_{KCl}) of the forest floor and the underlying it mineral horizons on the basis of the EMA DB

ESC code	WRB name	O-horizon			Mineral horizons			Diffe- rence ²⁾	Model soil ³⁾		
		n	Mean	±SE	n	Hor- izon	Mean			±SE	Tex- ture ¹⁾
LP	Fragic Stagnic Glosic Retisols (Abruptic, Humic)	14	3.86	0.16	38	A	3.78	0.04	LS	-0.08	M-6
LPg	Endogleyic Glosic Stagnic Fragic Retisols (Abruptic)	15	3.42	0.13	34	A	3.59	0.06	LS	0.17*	M-16
Lk ⁴⁾	Dystric Albic Arenosols (Humic, Protosodic)	23	3.16	0.08	26	A	3.99	0.06	LS	0.83*	M-9
L(k)I	Entic Umbric Podzols (Arenic)	10	3.99	0.22	17	A	3.85	0.09	LS	-0.14	M-10
L(k)II	Albic Umbric Carbic Podzols (Arenic)	13	3.31	0.14	17	A	3.55	0.10	S	0.24*	M-11
L(k)IIg	Endogleyic Umbric Carbic Albic Podzols (Arenic)	16	3.25	0.07	21	A	3.28	0.05	S	0.03	M-12
LI	Entic Podzols (Arenic)	21	3.32	0.07	26	A	3.39	0.05	S	0.07	M-17
LII	Albic Carbic Podzols (Arenic)	46	2.89	0.04	47	Ea	3.52	0.04	S	0.63*	M-13
LIIg	Endogleyic Entic Podzols (Arenic)	37	2.91	0.04	40	Ea	3.58	0.06	S	0.67*	M-14
LIIIg	Endogleyic Albic Carbic Podzols (Arenic)	21	3.10	0.06	21	EaA	3.48	0.06	S	0.38*	M-18
LIIIg	Endogleyic Albic Rustic/Carbic Podzols (Arenic)	29	2.85	0.05	16	EaAT	3.53	0.09	S	0.68*	M-19
Go	Endocalcaric Reductic Mollic Gleysols (Loamic)	26	2.80	0.07	14	EaAT	3.44	0.12	S	0.64*	M-20
GI	Epidystric Reductic Umbric Gleysols (Luvic, Loamic)	28	4.79	0.15	34	AT	5.95	0.09	L	1.16*	M-21
LPG	Epigleyic Dystric Glosic Retisols (Abruptic)	8	3.78	0.12	26	AT	4.25	0.11	L	0.47*	M-22
LkG	Epigleyic Dystric Glosic Retisols (Abruptic)	12	3.46	0.06	14	AT	3.61	0.07	L	0.15*	M-23
LGN	Reductic Umbric Dystric Spodic Gleysols (Endoaerenic)	22	3.24	0.14	24	AT	3.13	0.09	LS	-0.11	M-24
LGN	Epigleyic Ortsteinic Albic Podzols (Arenic)	15	2.77	0.07	16	Ea	3.49	0.08	S	0.72*	M-25
LGI	Epigleyic Carbic Albic Podzols (Arenic)	19	2.62	0.06	22	Ea	3.46	0.05	S	0.84*	M-26
LGI	Histic Epigleyic Ortsteinic Albic Podzols (Arenic)	15	2.59	0.07	15	EaG	3.52	0.08	S	0.93*	M-27

1) Soil texture: LS – loamy sand, S – sand, L – loam; 2) The significant difference is denoted by an asterisk (*); 3) For model soils profile fabric see Kölli et al. 2008, <http://mullad.emu.ee>; 4) Upper row characterizes South-Eastern Estonian, but the lower row North-Estonian forest Arenosols' acidity; 5) In soils mentioned by codes Lk, L(k), L(k)g, L and Lg the I means weak, II moderate and III strong podzolization stage.

Forest floor



Mineral soil

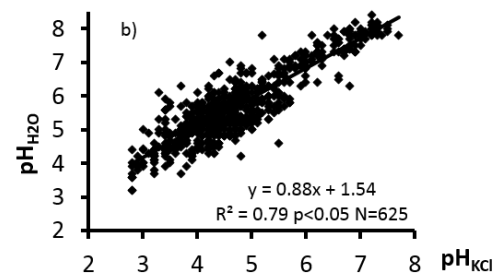


Figure 2. Relationships between active acidities (pH) determined in 1M KCl solution and in water

- a) $\text{pH}_{\text{H}_2\text{O}}$ of forest floor as a function of pH_{KCl}
- b) $\text{pH}_{\text{H}_2\text{O}}$ of forest mineral topsoil as a function of pH_{KCl}

that accumulation of multi-layered FF is intensified with soil podzolization and with increasing sand content in the soil cover.

Regularities of soil acidity in sub-horizons of forest floor

The acidity of the FF sub-horizons is presented by four soil groups in Table 5. Besides the baseline data (pH_{KCl}), the characterizing FF sub-horizons acidity alternative indices and some ecological data are presented. It is revealed that FF acidity depends on soil groups, i.e. from the specific properties of the soil type. The highest pH (or smallest acidity indices) are characteristics of the

Calcaric Cambisols (Table 5), which have been formed on calcareous parent materials and in aeromorph conditions. On these soils, the falling litter is rich by basic chemical elements, it is readily decomposable, and it has relatively high biological activity and base saturation stage. In connection to this, the stocks of the ash-free SOM and SOC, which may be taken as endo-organic matter of the FF, are low, as most of SOM/SOC were accumulated into the A-horizon of these soils.

With respect to *Calcaric Cambisols*, the FF sub-horizons acidity of *Dystric Retisols*, *Endogleyic Albic Podzols* and *Histic Epigleyic Podzols* are increased, i.e. exchangeable acidity, mobile Al and hydrolytic acidities are increased, but the pH and base saturation stages are decreased. In relation to these changes, the stocks of SOM/SOC are also increased, most importantly in sub-horizons O2. In the course of *Retisol* and *Podzol* FF formations by the sequence of sub-horizons from O1 to O3 the FF acidity is increased, but the C to N ratio is decreased.

Discussion

The fabric and acidity of humus cover

The SOM rich constituents of HC and their acidity were formed in accordance with existing pedo-ecological conditions and land management practice. Among the pedo-ecological conditions of forested areas, the leading role belongs to the soils' mineral-textural composition, its moisture conditions, and to adapted with soil properties plant cover and soil organisms (Hüttle and Schneider 1998, Boruvka et al. 2007). In agricultural areas, where the FF is absent, the HC fabric and its properties depend, besides of natural prerequisites, very much on soil tillage, liming and fertilization intensities (Eidukeviciene et al. 2010).

The dominating part of forested land HCs consists of the exo-organic (FF and thin superficial peat horizons) and of endo-organic (A- and AT-) horizons (Chertov 1981). The HC may be independently described as a FF

Table 3. Correlation of forest floor pH_{KCl} with alternative acidity characteristics of topsoil on the basis of the Pedon and EMA DS

Characteristics	Horizon ¹⁾ , layer ²⁾	Pedon-1		Pedon-2		EMA	
		n ^{1 3)}	r	n ^{1/n^{2 4)}}	r	n ^{1/n²}	r
pH _{H2O}	O	140	0.95* ⁵⁾	140/13	0.96*	491/- ⁶⁾	0.97*
Exchangeable acidity (concentration), mmol kg ⁻¹	O	–	–	140/13	-0.88*	491/29	-0.77*
Exchangeable acidity (quantity per area), kmol ha ⁻¹	O	–	–	140/13	-0.88*	–	–
Hydrolytic acidity (concentration), mmol kg ⁻¹	O	–	–	140/13	-0.91*	491/29	-0.82*
Hydrolytic acidity (quantity per area), kmol ha ⁻¹	O	–	–	140/13	-0.72*	–	–
Mobile Al (concentration), mg kg ⁻¹	O	–	–	140/13	-0.87*	491/29	-0.65*
Mobile Al (quantity per area), kg ha ⁻¹	O	–	–	140/13	-0.79*	–	–
pH _{KCl} of the subsequent to FF horizon	A(AT)	130	0.71*	88/9	0.92*	307/13	0.85*
pH _{KCl} of the subsequent to FF horizon	Ea	63	0.24	52/4	0.00	355/14	0.69*
pH _{KCl} of the subsequent to Ea horizon	B	64	0.19	52/4	0.35	310/12	-0.17
Exchangeable acidity (concentration), mmol kg ⁻¹	A(AT)	112	-0.43*	88/9	-0.88*	307/13	-0.30
Exchangeable acidity (concentration), mmol kg ⁻¹	Ea	45	-0.23	52/4	-0.26	355/14	0.24
Exchangeable acidity (concentration), mmol kg ⁻¹	B	49	-0.37*	52/4	-0.22	310/12	0.14
Exchangeable acidity (quantity per area), kmol ha ⁻¹	HC ³⁾	145	-0.43	140/13	-0.16	–	–
Hydrolytic acidity (quantity per area), kmol ha ⁻¹	HC	145	0.07	140/13	0.15	–	–
Mobile Al (quantity per area), kg ha ⁻¹	HC	145	-0.12	140/13	-0.13	–	–

1) Horizons: O – forest floor, A – humus, AT – raw-humus, Ea – podzolized, and B – illuvial horizon; 2) HC – humus cover; 3) n¹ - quantity of individual research areas or soil pits; 4) n² - quantity of formed soil groups; 5) the significant correlation is denoted by an asterisk (*); 6) by “-” noted ones are not determined.

Table 4. Correlation of forest floor pH_{KCl} with some ecological characteristics of topsoil on the basis of the Pedon and EMA DS

Characteristics	Horizon ¹⁾ , layer ²⁾	Pedon-1		Pedon-2		EMA	
		n ^{1 3)}	r	n ^{1/n^{2 4)}}	r	n ^{1/n²}	r
Forest floor thickness, cm	O	160	-0.53* ⁵⁾	140/13	-0.73*	491/29	0.00
Forest floor stock, Mg ha ⁻¹	O	127	-0.54*	140/13	-0.79*	– ⁶⁾	–
SOC content in forest floor, %	O	–	–	–	–	491/29	-0.66*
Total nitrogen content in forest floor, %	O	–	–	–	–	491/29	0.78*
C:N in forest floor	O	–	–	140/13	-0.61*	491/29	-0.78
Thickness of A-horizon, cm	A(AT)	–	–	93/9	0.32	307/13	0.32
Thickness of humus cover, cm	HC	145	0.51*	140/13	0.74*	491/16	0.74*
SOM stock, Mg ha ⁻¹	HC	145	0.54*	140/13	0.80*	–	–
SOC stock, Mg ha ⁻¹	HC	145	0.54*	–	–	–	–
Total nitrogen stock, Mg ha ⁻¹	HC	145	0.61*	140/13	0.74*	–	–
C:N of humus cover (HC)	HC	145	-0.37*	–	–	–	–
Position on the hydroscalar	HC	194	-0.28*	–	–	–	–
Position on the litho-genetic scalar	HC	194	-0.80*	–	–	–	–

1) Horizons: O – forest floor, A – humus and AT – raw-humus horizon; 2) HC – humus cover; 3) n¹ - quantity of individual research areas or soil pits; 4) n² - quantity of formed soil groups; 5) the significant correlation is denoted by an asterisk (*); 6) not determined.

Table 5. Active acidity (pH_{KCl} and pH_{H2O}) of forest floor (FF) sub-horizons and the pH relationships with alternative indices of FF acidity on the basis of the Pedon-3 DS

Soil group	Position in relation to scale of ¹⁾		Sub-horizon ²⁾	n	pH _{KCl}	pH _{H2O}	Exchange-able acidity	Mobile Al ³⁺⁾	Hydrolytic acidity	Base saturation stage	C:N	SOMa ⁴⁾	SOC ⁴⁾
	moisture	genesis											
<i>Calcaric Cambisols</i> (K – see Table 1)	18	23	O1	2	4.6	5.4	2.1	13	36	56	49	3.4	2.0
			O2	2	5.4	6.6	0.8	6	15	78	34	5.0	3.7
			O3	1	5.3	6.6	0.4	2	15	74	14	2.1	0.9
<i>Dystric Retisols</i> (LP Lk Lkg)	31	51	O1	10	4.1	5.1	3.4	19	44	39	51	5.7	3.3
			O2	9	3.9	4.9	2.9	17	46	33	30	11.8	6.9
			O3	5	3.0	4.0	4.4	28	53	19	23	5.5	3.1
<i>Endogleyic Albic Podzols</i> (L Lg)	18	73	O1	11	3.5	4.6	6.0	35	55	21	67	6.6	3.7
			O2	12	3.2	4.2	5.1	32	84	17	38	17.7	10.6
			O3	8	2.9	3.9	4.8	31	82	16	33	8.3	5.2
<i>Histic Epigleyic Podzols</i> (LG LG1)	50	65	O1	6	3.6	4.5	7.3	50	64	30	55	25.0	12.5
			O2	5	3.0	4.0	10.5	77	131	21	36	68.5	31.9
			O3	3	3.0	3.9	14.3	117	134	16	31	26.0	15.5

1) see Kölli et al. 2008; 2) Sub-horizons of FF: O1 – slightly or undecomposed forest litter, O2 – moderately decomposed, and O3 – well-decomposed; 3) Ash free soil organic matter; 4) Soil organic carbon.

with various peaty (histic) variants that were formed in wet moisture conditions (Astover et al. 2013). However, having a more complex understanding regarding the formation of SOM-rich topsoil layer or HC on the SC, the O- and T-horizons are researched in accordance with endo-organic A- and AT-horizons. The Estonian HC type clas-

sification for forest soils is based also on such kind principle (Kölli 1992, Kölli and Rannik 2018). Using this classification, the HC types are determined and named by their moisture conditions (i.e. dry, fresh, moist, wet, peaty and peat), and by their development character and trophic status (CD-3 in Kölli et al. 2008). Zanella et al. (2011)

proposed to name the HC formed on mineral soils as humipedon, and the HC formed on peat soils as histopedon. This proposal will be probably used in the next version of the Estonian HC classification.

In determining HC type and in elucidating the role of active acidity (as well of alternative to it characteristics) in soil functioning, it is important to study it in accordance with the subjacent horizons of HC (Ponge 2013, Zanella et al. 2018). More calcareous, and to a lesser extent acidic and more fertile soils for this are mostly B-horizons, but to an even lesser extent, the BC- and C-horizons as well. On more acidic and sandy soils, where the A and/or AT have been not formed, is important to study the characteristics of E (leached) and Ea (podzolized) horizons and, if possible, to follow the properties of the sequence E-B, i.e. the relationships between eluvial and illuvial horizons (Rozanov 1983).

In Estonian pedo-ecological conditions, where the precipitation periodically exceeds evapotranspiration, the acidification takes place as an essential soil degrading process and as a result of this the leaching of soil cover can occur (Estonian Agri-project 1983, 1985a, 1985b). The natural podzolization process is most intense in poor sand-containing soils in conditions of non-calcareous wet forest soils under pure pine forests. Strong soil acidity is accompanied with increased quantities of mobile Al in the SC, which is toxic to lots of plant species (Rout et al. 2001).

The evaluation of active acidity by pH

In most cases, the pH_{KCl} of these O-horizons, which are under-layered by Ea-horizons, have a pH_{KCl} less than three. Unfortunately, there are not presently available a

suitable scale for the evaluation of such a kind of strong acidity in soil by its pH (Soil Survey Division Staff 1993, FAO 2006, Astover et al. 2013).

The generalized by us baseline or reference level limits of O and of subjacent mineral horizon pH_{KCl} are presented in the Table 6. As these generalized levels of pH originated from the Pedon and EMA DBs, they should be represent very well the Estonian forest mineral soils. The pH intervals, given by soil groups (I-IX), may be taken as the reference pH level for belonging to the group of soil species. These intervals, i.e. soil type specific reference levels of pH, are by their issue the individual soil type mean values minus and plus (-/+) their standard deviation. This kind of soil type-specific approach for evaluating the soil varieties functioning normality enables to assess the probability of being soil functioning in equilibrium state, or to discover the presence of disturbances in ecosystem functioning. The critical status with respect to equilibrium is reached when the normal pH of the soil type is surpassed (increased/decreased) by the quantity of units equal to one standard deviation. This is roughly 0.2-0.5 pH units on average. In the case of surpassing the normal pH limits, more than 0.4 pH units in O- and Ea- horizons and more than 0.5 units in A-horizon means serious disturbances in the functioning of forest ecosystems (Table 6).

The topsoil acidity may be taken as a soil type-specific intrinsic property. However, the evaluation of its status by the general pH scale only provides information in relation to the concrete pH scale. For example, if the *Glossic Retisol* active acidity indices (pH_{KCl}) of O- and A-horizons are 3.4 and 3.7, respectively, they may be classified by the USDA Soil Survey Manual (Soil Sur-

Table 6. Reference and indicating disturbance (threshold) levels of forest floor pH_{KCl} and of underlying it mineral soil horizons classified by forest soil groups

Soil group	Horizon ¹⁾	Reference pH_{KCl}	Indicating disturbance pH_{KCl}		Pedo-ecological characterization of belonging to group soils ²⁾
			min	max	
I	O	4.4 – 5.5	≤3.8	≥6.1	(1) Kh Kr K; (2) Cambisols/Leptosols - skeletal, rendzic, calcaric, loamic; (3) fresh calci-mull; (4) <i>Arcostaphylos-alvar</i> and <i>Calamagrostis-alvar</i> .
	A	5.4 – 6.7	≤4.9	≥7.2	
II	O	4.3 – 5.3	≤3.7	≥6.0	(1) Ko Kl Kog KlG; (2) Luvisols/Cambisols – humic, loamic, endocalcaric, endogleyic; (3) fresh and moist forest-mull and moder-mull; (4) <i>Hepatica</i> and <i>Aegopodium</i> .
	A	4.7 – 5.7	≤4.0	≥6.4	
III	O	3.0 – 4.5	≤2.5	≥5.1	(1) LP LPg; (2) Retisols – glossic, stagnic, abruptic, humic; (3) fresh and moist moder; (4) <i>Oxalis</i> and <i>Myrtillus</i> .
	A	3.2 – 4.6	≤2.8	≥5.2	
IV	O	2.9 – 4.2	≤2.5	≥4.8	(1) Lk Lkg; (2) Arenosols – albic, humic, dystic, endogleyic, protosporic; (3) fresh and moist moder and moder-mor; (4) <i>Rhodococcum</i> , <i>Oxalis</i> and <i>Myrtillus</i> .
	A	3.1 – 4.5	≤2.7	≥5.1	
V	O	4.2 – 5.8	≤3.6	≥6.3	(1) Go; (2) Gleysols – mollic, endocalcaric, loamic/siltic; (3) wet forest-mull; (4) <i>Dryopteris</i> and <i>Filipendula</i> .
	AT	5.0 – 6.2	≤4.4	≥6.8	
VI	O	3.6 – 5.1	≤2.9	≥5.8	(1) Gt; (2) Gleysols – umbric, epidystic, luvic, reductic; (3) wet moder-mull; (4) <i>Filipendula</i> .
	AT	4.0 – 5.3	≤3.3	≥6.0	
VII	O	3.2 – 3.9	≤2.7	≥4.4	(1) LPG Lkg; (2) Retisols/Gleysols – dystic, albic, umbric, reductic, spodic; (3) wet moder; (4) <i>Polytrichum</i> .
	AT	3.3 – 4.1	≤2.9	≥4.6	
VIII	O	2.6 – 3.5	≤2.2	≥4.0	(1) L Lg; (2) Podzols – albic/entic, endogleyic, arenic; (3) fresh and moist mor and moder-mor; (4) <i>Cladonia</i> , <i>Calluna</i> and <i>Rhodococcum</i> .
	Ea	3.1 – 4.5	≤2.7	≥5.0	
IX	O	2.3 – 3.2	≤1.9	≥3.7	(1) LG LGn LG1; (2) Podzols – epigleyic, histic, albic, arenic; (3) wet mor and peaty mor; (4) <i>Vaccinium uliginosum</i> .
	Ea	3.1 – 4.1	≤2.7	≥4.6	

¹⁾ Soil horizons: O – forest floor, A – humus horizon, AT – raw-humus horizon, Ea – podzolized horizon; ²⁾ Sequence of characteristics: (1) Soil codes by ESC (Astover et al. 2013), (2) WRB soil reference group and most important qualifiers (IUSS Working Group WRB 2015); (3) Humus cover types by ESC (Kölli 1992) and (4) Dominating forest site types (Löhmus 2006).

vey Division Staff 1993) as ultra and extremely acidic, respectively. But according to this information, it is impossible to evaluate the normality of soil type-specific functioning. Therefore, it is recommended to use the reference levels of pH indices in this kind of evaluation. By comparing the presented pH levels of O- ($\text{pH}_{\text{KCl}} = 3.4$) and A- ($\text{pH}_{\text{KCl}} = 3.7$) horizons with reference levels for this soil, it may be concluded that there is the existence of a relatively normal active acidity in the HC.

Moreover, the data presented in Table 6 indicates the presence of possible disturbances in the functioning of certain soil types by the critical (threshold) levels of O-, A- and Ea-horizons' pH_{KCl} . For example, the flying dusts of cement factory Kunda has an increased pH_{KCl} of Podzols O-horizons as compared with control areas by 3.4-3.7 pH units as a function of the distance (2.75-6.75 km) from the factory (Teras 1984).

Conclusions

On the basis of three different databases on Estonian forested mineral land topsoil acidity, the classifications of pH_{KCl} reference level limits (from *min* to *max*) and indicating soil disturbance threshold levels of forest floor and underlying it mineral soil horizon were elaborated. These levels of pH_{KCl} are given by nine Estonian forest soil groups, which together form the sequence or catena from the fresh calcareous loamy soils to the wet acid sandy soils (Table 6). The pedo-ecological character of belonging to sequence soil groups is explained (1) by soil names of ESC, (2) by reference groups and qualifiers of WRB, (3) by local humus cover types, and (4) by forest site types.

With increasing forest floor acidity or decreasing its pH_{KCl} from 5.5-5.8 to 2.3-2.6 the soil humus accumulation horizons (humus (A) horizons in fresh and moist conditions, and raw-humus (AT) horizons in wet conditions) are changed by podzolized (Ea) horizons, which indicated to the presence of podzolization process and to the accumulation of formed mobile humus substances into the subsoil i.e. into the humus-rich illuvial (Bh) horizon.

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