

Analysis of the Indices of Acidity in the Soil Profile and Their Relationship with Pedogenesis

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Abstract—A new notion—an acidic trace of pedogenesis in the field of soil acidity—is suggested. This notion implies a three-dimensional representation of the distribution of soil acidity in the soil profile and can be graphically shown in three two-dimensional projections that can be combined on a common *V*-diagram. Such *V*-diagrams are individual for each particular soil profile. At the same time, they have some common phenomenology in their shapes and in the position in the acidity field. A tendency for the S-shaped form of acidic trace is manifested by a sharp decrease in pH upon the reduction of base saturation at the high and low values of this index and by small changes in pH at the moderate values of base saturation in the area of acid buffering of the soil profile. This phenomenon is related to the weak acidity and polyfunctionality of the soils as ionite systems. An acidic trace can be subdivided into several characteristic parts related to different pedogenetic processes in their interaction. Its position in the field of acidity is largely determined by the acidity of parent material. Acidic traces of different types of soils in the northwestern Russia are discussed. It is argued that *V*-diagrams should be analyzed together with other soil characteristics.

Keywords: soil profile, actual and potential soil acidity, acidity field, base saturation, *V*-diagram, acidic trace of pedogenesis, shape and analysis of acidic trace, acid buffering of the soil profile

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INTRODUCTION

Soil acidity is one of the most significant manifestations of pedogenesis in the humid zone with the formation of the particular soil profiles (soil horizonation). Soil acidity and its quantitative chemical and agrochemical characteristics are being actively studied and discussed in literature [7, 12–15]. New data on the acidity of different soils require thorough analysis and generalization. It is of particular interest to trace the relationships between the characteristics of soil acidity and the character of pedogenesis and the organization of soil profiles.

Routine soil studies usually include the determination of the following characteristics of soil acidity: pH of the water and salt extracts, hydrolytic (total) acidity ($A_{c_{tot}}$), and base saturation of the exchange complex determined as the ratio of exchangeable bases to the cation exchange capacity (CEC) (V_{bs}). Their general physicochemical meaning was discussed in our previous paper [2].

The results of the studies of soil acidity are usually presented in a tabulated form showing the distribution of soil acidity characteristics by the soil horizons. The same data can also be represented in a graphical form showing the changes in the acidity characteristics in the soil profiles.

The studies of soil acidity in separate soil horizons provide us with data on the average characteristics of soil acidity in these horizons in a discreet form. They discrete data can be used to construct the curves of the distribution of the particular characteristics in the entire soil profile; such curves interpolate discrete information on separate horizons and can be referred to as “horizonograms.”¹ In some cases, discreet information on soil horizons is supplied with more detailed layer-by-layer studies of soil horizons.

A notion of *the three-dimensional acidity field* was introduced by us on the basis of general ideas on the acidity of ion-exchange systems [2]. This field is characterized by three interdependent values: the pH of the salt and water extracts and the base saturation (V_{bs}); it can be visualized in the form of three two-dimensional projections.

In this study, we argue that the same data can be combined on one plot, so that each of the studied soil

¹ In geology, analogous curves are usually constructed on the basis of virtually continuous information on the geological profiles (sections). Such curves can be referred to as “profilograms.” They are rarely applied in soil science [3]. The methods of continuous analysis of core samples are being developed. This direction of studies seems to be promising for soil science in general and, in particular, for soil mapping purposes.

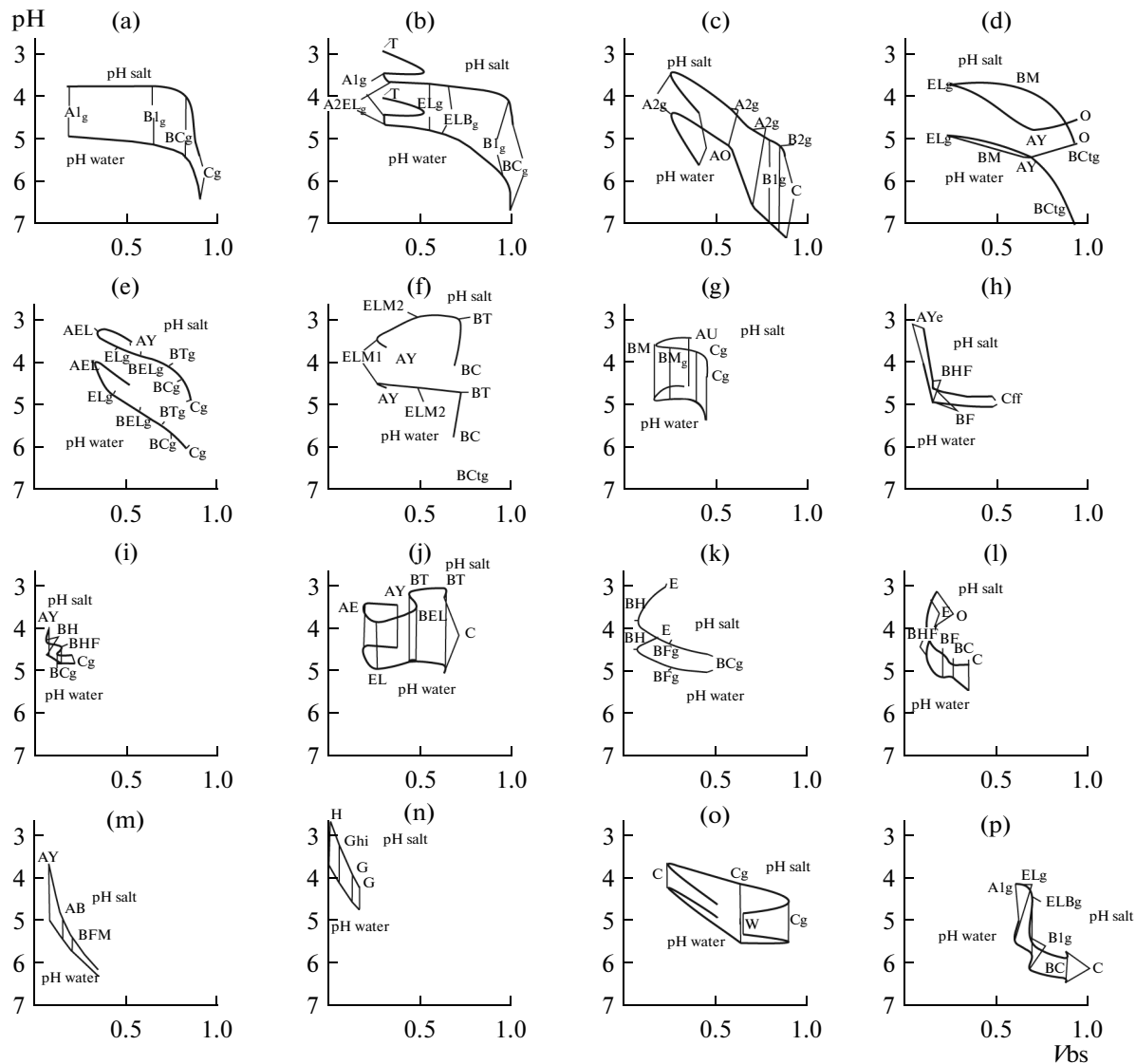


Fig. 1. Acidic traces of the soils of northwestern Russia: (a) soddy surface-eluvial gley soil developed from varved clay (pit 196 [3]), (b) peaty surface-eluvial gley soil developed from varved clay (pit 198 [3]), (c) gleyed podzolic soil developed from sandy silt loams (pit 2357 [3]), (d) raw-humus eluvial-metamorphic clay-illuvial gley soil developed from glaciolacustrine loams (pit 11-04 [1]), (e) gleyed soddy-podzolic soil developed from moraine loams (pit 2-96 [1]), (f) texture-metamorphic soil developed from moraine loams underlain by lacustrine loams (pit 7-99 [1]), (g) podzolized gleyic burozem developed from moraine loams (pit 13-99 [1]), (h) podzolized soddy podbur developed from lacustrine sands (pit 5-05 [1]), (i) humus-illuvial gleyic soddy podbur developed from loamy sandy moraine underlain by granite (pit 3-02 [1]), (j) soddy-podzolic soil developed from glaciolacustrine sediments (pit 12-99 [1]), (k) humus-illuvial gleyic podzol developed from glaciofluvial loamy sand underlain by moraine loams (pit 11-99 [1]), (l) mucky tonguing podzol developed from ancient alluvial sands (pit 3-04 [1]), (m) podzolized rzhavozem developed from kame sands (pit 16-00 [1]), (n) mucky humus-impregnated peaty gleyzem developed from glaciolacustrine sediments (pit 7-05 [1]), (o) gleyic pelozem developed from Cambrian clay (pit 3-00 [1]), and (p) soddy surface-eluvial gley soil developed from varved clay (pit 64 [6]).

profiles can be characterized by a two-dimensional horizonogram describing the changes in the three major characteristics of soil acidity in the acidity field of soil horizons (Fig. 1). Ordinates of the points on the plot (Fig. 1) correspond to the pH values of salt extract (upper line) and water extract (lower line) for separate soil horizons. The distance between the curves characterizes ΔpH values. The abscissa axis displays a dimen-

sionless variable of V_{bs} (base saturation), which, in essence, is an analogue of the portion of acid titrated with an alkali during the titration procedure applied in the analytical and physical chemistry. On these plots, each horizon is characterized by the particular point (with its letter symbol and, if necessary, with figures specifying its position in the profile). These points are connected with continuous interpolation curves. The

plots describe changes in the relationships between the three values (pH_{salt} , pH_{water} , and V_{bs}) in the horizons of a given soil profile. Such plots can be referred to as the diagrams of soil acidity, or as V -diagrams. In fact, they include pH-diagrams discussed in [2]. When separately considered, pH-diagrams are less informative than V -diagrams. In fact, each V -diagram can be considered the trace of pedogenesis in the acidity field.²

The shape of V -curves displays both general regularities of pedogenesis in the humid zone and its local manifestations. The analysis and comparison of V -diagrams for different soil profiles allow us to reveal their common and specific features, judge their possible reasons, and better understand the nature of soil acidity.

The results of such an analysis for a given soils should be taken into account in soil classification procedures; they may help us to determine characteristic features of the given soil types [2]. Thus, the acidic trace can be considered one of the most important typomorphic features of soils.

Even for two soils of the same taxonomic position, their V -diagrams may differ significantly, because they reflect individual features of the development of pedogenesis in the given soil profile.

In other words, the acidic trace of each soil reflects both common and individual features of the soil development.

In this study, we shall analyze V -diagrams for a number of different soils of the humid zone (Fig. 1) with the aim to reveal some general regularities in their behavior and the rules for their interpretation.

Published data on the acidity of major genetic soil types in the northwestern Russia are used in our study [1, 3, 5]. Soil names and designations of genetic soil horizons given in the original publications are preserved. These data have been used to plot V -diagrams of the soils belonging to different soil types (Fig. 1).

RESULTS AND DISCUSSION

The diversity of V -diagrams obtained by us corresponds to the complexity of soil morphology and the genetic diversity of the studied soils. They differ in the

general shape of the curves and in their particular position in the acidity field. These diagrams indirectly reflect some common and specific local features of pedogenesis in the considered places through the characteristics of soil acidity.

The analysis of the entire set of the obtained V -diagrams leads us to a hypothesis about some common tendency in the shapes of the particular acidic traces. This tendency is also reflected in the distribution of the particular genetic horizons in the soil acidity field and in the shape of the entire area occupied by the given soils in the acidity field [2].

If consider the entire set of the curves for the particular soil horizons (horizonograms), we can see that some soil horizons are characterized by the low values of V_{bs} ; their acidic traces are allocated to the left part of the diagrams and are characterized by a sharp decrease in both pH values (pH_{water} and pH_{salt}) upon the decrease in the base saturation V_{bs} . In other soils, the same tendency for a sharp decrease in both pH values upon the decrease in the base saturation is observed in the right part of the diagram at the high values of V_{bs} . Finally, there is a transitional area with the plateau-like shape of the curves (the changes in pH upon changes in V_{bs} are small). As a rule, middle-profile soil horizons belong to this area. In some soil types, the V -diagrams of all their horizons also belong to this area. Within the plateau-like part of the curves, both pH values are within the range of 3.5–5.5 corresponding to the moderate values of the soil acidity. In this area, the leaching of bases that takes place in the neighboring horizons has little effect on the acidity characteristics of the soil. Thus, this area can be referred to as the area of acid buffering of the profile. It can be supposed that each of the soils belonging to this part of V -diagrams occurs in its own acid buffering range. In some cases, this range is extended towards the low values of V_{bs} (down to 0.1). A well-pronounced plateau-like part of the curves is typical of the heavy-textured soils with gley features and of the middle-profile metamorphic (in-situ transformed) soil horizons.

In general, it can be supposed that the acidic trace of most of the particular soils can be considered as a part of one of the families of hypothetical S-shaped curves.

The S-shaped pattern of the curves and its deformations are the key to understanding and interpretation of the acidic traces of the soils.

It is important to understand the meaning of the S-shaped pattern of all the diagrams. To explain this pattern, the properties of the aluminosilicate mineral components of the soils, as well as the properties of soil humic substances, and the amphoteric nature of soil hydroxides should be taken into account. S-shaped patterns are typical of the curves characterizing the reaction of neutralization of a weak acid with a strong alkali in the one-phase system of the soil solution. To explain this pattern, we should analyze weakly acidic properties of the aluminosilicate compounds of the mineral soil matrix and some humic compounds, as

² Sometimes, instead of the routine index of base saturation (V_{bs}) calculated from data on the total cation exchange capacity (CEC), a somewhat different characteristic (V_{ebs}) calculated from data on the effective cation exchange capacity ECEC is used. The latter is determined as the sum of exchangeable bases and exchangeable (salt-replaceable) acidity. The difference between these characteristics consists of the fact that the hydrolytic (total) acidity taken into account in V_{bs} includes weakly acidic and slightly dissociated acidic groups of the soil that do not participate in ion exchange processes at low pH values; these groups do not affect the exchangeable acidity. The use of V_{ebs} instead of V_{bs} can change the shape of two projections of the acidity field ($\text{pH}_{\text{salt}} = F(V)$ and $\text{pH}_{\text{water}} = F(V)$, though it does not affect the third projection ($\text{pH}_{\text{salt}} = F(\text{pH}_{\text{water}})$). In this case, the V -diagram should be somewhat different.

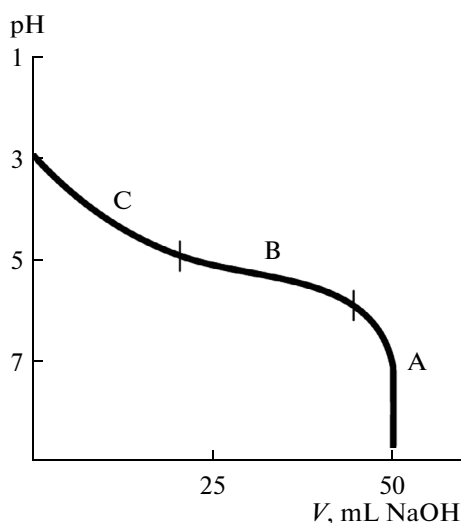


Fig. 2. Curve of the titration of 50 mL of 0.1 n CH_3COOH with 0.1 n NaOH (according to [11]).

well as amphoteric properties of soil hydroxides. The S-shaped pattern is typical of the curves of neutralization of a weak acid by a strong alkali in the one-phase system of the water solution that can be described by corresponding equations [11]. On the titration curve, we can clearly distinguish three different areas: sharply inclined areas A and C and a gently inclined area B (Fig. 2). This characteristic pattern is even more pronounced upon the titration of a mixture of weak acids slightly different in their strength.

For two-phase systems, an analogous S-shaped curve is observed for titration curves of some ionites, e.g. for weakly acidic monofunctional carbonyl and bifunctional polymeric cationites of phosphoric acid [6]. In some cases, it is also clearly seen on the soil titration curves [4], especially when the latter are given as the dependence of the soil pH on the degree of base saturation [12].

According to the ion exchange theory, all the soils (with a few exceptions) can be considered polyfunctional weakly acidic cationites. In the course of neutralization of hydrogen ions by bases in the cationites, a unidirectional (sympate) shift of all the three characteristics of the soil acidity (pH_{water} , pH_{salt} , and V_{bs}) towards their increase is observed. This shift is clearly seen on the corresponding titration curves. The leaching of bases from the soil and the soil acidification are the manifestations of the process reciprocal to the process of neutralization of a mixture of weak acids. This process might follow a similar pattern. The shape of V -diagrams reflects this process at different stages of soil neutralization.

The particular manifestation of the S-shaped pattern of the acidic trace in the given soil profile can be distorted, because we deal with the samples from the different soil horizons. These samples may differ in their textures and mineralogical compositions, exchange

capacities, and the natures of humic substances. These factors may deform the S-shaped pattern of model curves. However, these deformations are largely compensated for by the use of a dimensionless characteristic V_{bs} that levels the differences in the texture, humus content, and exchange capacity of the analyzed samples.

Our analysis indicates that the acidic trace of the studied soils can be separated into the following parts (branches).

The lower mineral branch of the acidic trace. This part of the diagrams is typical of the C, D, and transitional BC horizons of the soil profiles. It is closely associated with the acidic properties of parent materials. In the heavy-textured soils, it begins from the nearly neutral soil horizons with the high base saturation (Figs. 1a and 1b). The S-shaped pattern of the curves is most distinctly pronounced for these horizons. A tendency for the soil acidification in the steep part of the curves is clearly seen for the upper layer of the parent material, especially when the parent material contains carbonates in the deep layers. The gradient of acidity in the lower mineral part of the soil profiles cannot be explained by the specific influence of organic substances. It attests to a continuous leaching of cations from the soils as a unidirectional continuous geological process that takes place simultaneously with the pedogenesis proper or even precedes it.

The analysis shows that parent materials of soils in the humid zone differ in their acidity characteristics. A greater acidity and lower base saturation are typical of the coarse-textured noncalcareous soils. Thus, low base saturation (<0.5) and low pH_{water} and pH_{salt} values are characteristic of sandy parent materials. The acidic trace of the soils developing from these materials is characterized by the sharp rise of the curve in the left part of the acidity field.

The position of the acidic trace in the field of acidity and, largely, its shape are greatly influenced by the acidic characteristics of the parent material, especially by its base saturation. Therefore, the analysis of the acidic trace of soils should be performed “from the bottom,” i.e., from the C and D horizons of the soil profiles.

The upper organomineral branch of the acidic trace. The upper organomineral and humus-rich horizons of the soil profile are the zone of the most active pedogenesis. The upper parts of the soil profiles differ for different soils. Their behavior is largely dictated by the properties of the soil humus. For some of the soils, the curve of the acidic trace sharply rises in agreement with its general S-shaped pattern. This is usually typical of the coarse-textured strongly acid soils (Figs. 1c, 1e, 1m, and 1n). In other soils, the curve descends down, so that a loop is formed (Fig. 1d). Often, the V_{bs} values increase in the upper horizons, whose pH values may both increase and decrease. The behavior of the curve depends of the properties of humic substances of the soil against the background of a general tendency for the saturation

of the exchange complex in the topmost horizons with biogenic bases (Ca, Mg, K, etc.) released from plant debris during their mineralization. An opposite tendency for the removal of bases from the upper soil layers during their leaching with water solutions and their uptake by the roots. A competition between these oppositely directed tendencies dictates the behavior of the acidic trace in the upper organomineral horizons.

It is also important that organic acids of the soil humus in the upper and deeper horizons sharply differ in their nature from the acids of the mineral substrates. The organic acids may be strong acids with a higher base saturation in comparison with the acidic groups of the mineral substrate at similar pH levels. At the same time, there are also weak slightly dissociated organic acids responsible for the high hydrolytic acidity and low base saturation of the soil horizons rich in humic substances.

The proper organic (peat and litter) branch of the acidic trace (upper part of the curve shown in Fig. 1b) should be separately considered. For peat soils, it can be analyzed as a separate acidic trace.

The plateau-like branch of the acidic trace is typical of the middle-profile horizons (B, BEL, BF, BFH, BT, and BM). It is generally characterized by the *high acid buffering*, i.e., by small changes in the pH values upon significant changes in the degree of base saturation. The acidity of this part of the soil profiles is dictated by the properties of the mineral soil matrix partly saturated with bases and by the properties of the soil humus. In general, this branch belongs to the middle part of the S-shaped pattern. It is differently pronounced in different soil profiles. In some soils, virtually the entire profile lies in this zone of the high acid buffering (Figs. 1g, 1h, and 1j). In other soils, this part of the acidic trace is absent (Figs. 1m and 1n).

The eluvial horizons composed of the slightly humified mineral material should be separately considered. However, with respect to their acidity characteristics, they occupy a transitional place between the discussed branches of the acidic trace; as a rule, they can be attributed to one of these branches.

The value of ΔpH is important in the analysis of acidic traces. As shown in [2], this value is determined by the coefficient of the interphase distribution of hydrogen ions on different parts of the isotherm of sorption of these ions by the soil. The values of ΔpH depend on the exchange capacity of the soil and the shape of the exchange isotherm. In general, ΔpH values decrease in the soils with a low exchange capacity and upon saturation of the exchange complex with hydrogen ions in the area of low pH values. The logarithmic nature of the pH scale should be taken into account. It implies that the total concentration of hydrogen ions in the water and salt extracts changes by several orders of magnitude. The values of ΔpH in the soil horizons belonging to the left part of the acidity

field are relatively small in comparison with those in the middle and right parts of the acidity field.

The values of ΔpH should be relatively large in the soils with the high exchange capacity, i.e., in the heavy-textured and humus-rich soils. They are generally higher for the loamy and clayey soils than the sandy soils. The middle-profile metamorphic horizons are characterized by the higher values of V_{bs} .

The presence of the gently inclined or plateau-like part of the acidic trace is clearly pronounced in many soils; in general, it is typical of the middle-profile metamorphic horizons.

The plots of the acidic trace shown in Fig. 1 demonstrate its complicated and diverse patterns. As shown in [2], the ΔpH values of the middle-profile horizons may differ significantly: from about 2 pH units to an almost zero value in some horizons of the Al-Fe-humus soils. As this value depends on the exchange capacity of the soils, it is higher for the heavy-textured and acid soil horizons, e.g., for the BT and BM horizons. The acidic trace of the relatively coarse-textured and strongly acid soil horizons (BH horizons) should be shifted towards the left part of the acidity field and have lower ΔpH values. Minimum values of ΔpH should be typical of the BF horizons with a low exchange capacity.

These regularities explain the complicated pattern of the acidic trace in the area of its plateau-like part.

The considered branches of the acidic trace have their individual distinctions depending on the properties of the given soil material and on the local specific features of pedogenesis.

The disturbance of the general regularities discussed above may take place because of changes in the properties of the soil material in the upper humus horizons and in the middle-profile metamorphic horizons. The transition of the anions from the low molecular-weight weak organic acids into the soil solution [8–10] may also contribute to changes in the acidic trace, because it affects the coefficient of the distribution of hydrogen ions between the solid and liquid soil phases and, hence, the ΔpH value [2].

It should be noted that the considered regularities of the acidic trace are typical of the group of postlithogenic soils.

We had no opportunity to study the acidic traces of synlithogenic soils. It can be expected that their acidic traces should have more complex shapes with sharp changes in the curves explained by the spasmodic transformations of the soils in the course of pedogenesis because of the accumulation of the new portions of the soil-forming material. Some manifestations of such changes might be also typical of the postlithogenic soils developed from the heterogeneous parent materials.

Among the considered soils, an unusual shape of the acidic trace was found for a soddy-podzolic soil developed from the layered glaciolacustrine sediments

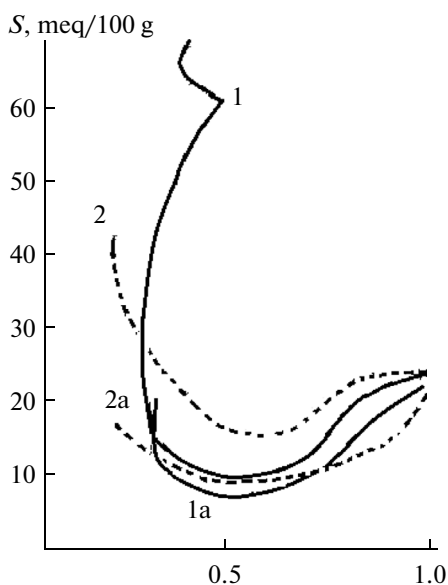


Fig. 3. Horizonograms for CEC and ECEC values of the peaty surface-eluvial gley soil (1 and 1a) and soddy eluvial-gley soil (2 and 2a). Designations: (1 and 2) CEC (S) and (1a and 2a) ECEC.

(Fig. 1p). This soils is characterized by the low position of the plateau-like part of the curve (for the middle-profile horizons) in the area of close to neutral pH values (both pH_{water} and pH_{salt}) and relatively high base saturation values. These facts attest to the very weak acidity of the soil material. Such horizons are really present in the soils of the humid zone [2]. An example of their acidic traces calculated for the two base saturation values (V_{bs} and V_{ebs}) is shown in Fig. 3. Upon the transition to higher values of base saturation (V_{bs}) in the eluvial horizon, a sharp rise in the pH values is observed. Such a behavior is typical of the titration curves of ionites with two functional groups sharply different in their strength (bifunctional ionites) and attests to considerable differences of the acidic functional groups in different parts of the soil profile.

An usual shape of the acidic traces was found for a pelozem (clayey soil) developed from the blue-colored Cambrian clay (Fig. 1o). In contrast to other gleyed soils, gleyzation in this soil affects relatively acid parent material. The degree of base saturation of the gleyed horizons increases in the upper humus horizon; the most acid layer with the minimum base saturation is the layer transitional to the nongleyed parent material. Among the considered soil profiles, this variant of the acidity pattern was only found in this particular soil. Its specific features are explained by the location of the outcrop of Cambrian clay on the slope of a plateau composed of limestone. Thus, soil formation in this place is influenced by the lime-saturated water. It is important that calcification of the initially acid parent rock led to the gleyzation of the soil. Note that the weakly developed humus horizon (W) with a different

nature of acidity is less saturated with bases than the underlying soil layer.

A comparative study of acidity traces of the virgin, plowed, and fallow soils within a relatively small region is of particular interest. It can be expected that the patterns of the acidic trace in the upper horizons, including the eluvial horizon, should differ in these soils because of the impact of tillage, lime application, and durable growing of the particular plant species; the cessation of these impacts in the fallow soil should also be reflected in their acidity trace. A study of the acidic trace of various anthropogenic soils is also of great interest.

In general, it can be supposed that the acidic trace of the soils carries valuable information on the character of pedogenesis and on various kinds of the disturbances of the normal development of natural soils.

The acidic trace can be compared with horizonograms for various other soil characteristics, including the characteristics of the soil acidity showing the distribution of these characteristics in the soil profiles. For this purpose, the values of V_{bs} can be shown on the common abscissa axis of the horizonograms, and the characteristics of the particular properties should be shown along the ordinate axis. Such data can be plotted on V -diagrams via introducing an additional (right-hand) ordinate axis.

This method is particularly interesting for the comparative analysis of all the characteristics of soil acidity. For example, V -diagrams can be analyzed together with data on the contents of exchangeable aluminum in the soil horizons.

V -diagrams can also be compared with data on changes of both values of the exchange capacity (CEC and ECEC) (Fig. 2). These data reflect the heterogeneity of the soil profile with respect to its exchange capacities and, hence, the heterogeneity of the soil texture and the content and composition of humus.

A comparison of horizonograms for the two values of the exchange capacity (CEC and ECEC) in two soils of the Volkhov–Ilmen Lowland (Fig. 3 and Figs. 1a and 1b) shows that sharp changes in the exchange capacity are not reflected in the general pattern of the acidic trace of these soils in the right and middle parts of the S-shaped pattern. This can be explained by the “leveling” properties of the V_{bs} index. It is evident that the difference between CEC and ECEC in the considered soils characterizes the value of nonexchangeable acidity. This index is important for understanding soil acidity and its changes upon the soil liming. Weakly acidic groups are present in all the soils. However, their participation in the ion-exchange processes are only significant in the soils with the V_{bs} values close to 1.0 and with the high pH_{salt} and pH_{water} values. This situation is typical of the weakly developed humus horizon (W) and of the middle-profile and lower horizons of some heavy-textured soils.

CONCLUSIONS

(1) Data on the characteristics of a given soil with a graphical representation of their distribution in the soil profile can be considered the traces of pedogenesis in this soil profile. In particular, data on changes in the characteristics of soil acidity in the soil profile can be considered the acidic trace of pedogenesis in this soil profile.

(2) The acidic trace of pedogenesis can be shown on the plots with coordinates of the acidity field in the form of pH diagrams and *V*-diagrams.

(3) Each soil is characterized by its individual acidic trace reflecting the character of pedogenesis; the shape of the acidic trace is dictated by the properties of the soil horizons.

(4) The acidic trace should be analyzed from the lower soil horizons beginning from the parent material. Acidity characteristics of the parent material, including, in particular, the degree of base saturation affect the shape of the acidic trace and its position in the acidity field.

(5) The study of acidic traces of many soils from humid regions attests to their common S-shaped pattern, though its particular characteristics are different for different soils. The S-shaped pattern of the acidic trace is typical of the titration curves for heterogeneous and homogeneous weakly acidic systems with a strong alkali. It can be considered a model of changes in the acidity characteristics of the soils of humid regions subjected to the leaching of bases released upon weathering of the parent material.

(6) The acidic trace can be analyzed together with other diagrams showing the relationships between different soil properties and the degree of base saturation of the soil horizons.

(7) The representation of data on the soil acidity in the form of the acidic trace and, in particular, in the form of *V*-diagrams is a helpful tool for the comparative analysis of experimental data on the soil acidity and its role in the pedogenesis.

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