===== **SOIL CHEMISTRY** =====

In Honor of the 120th Birthday of A.A. Rode

Contributions of Separate Reactions to the Acid−Base Buffering of Soils in Brook Floodplains (Central Forest State Reserve)

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Abstract—The acid−base buffering of gleyic gray-humus soils developed in brook floodplains and undisturbed southern-taiga landscapes has been characterized by the continuous potentiometric titration of soil water suspensions. During the interaction with an acid, the major amount of protons (>80%) is consumed for the displacement of exchangeable bases and the dissolution of Ca oxalates. In the O and AY horizons, Mn compounds make the major contribution (2−15%) to the acid buffering. The buffer reactions with the participation of Al compounds make up from 0.5 to 1−2% of the total buffering capacity, and the protonation of the surface OH groups of kaolinite consumes 2−3% of the total buffering capacity. The deprotonation of OH groups on the surface of Fe hydroxides (9−43%), the deprotonation of OH groups on the surface of illite crystals (3−19%), and the dissolution of unidentified aluminosilicates (9−14%) are the most significant buffer reactions whose contributions have been quantified during the interaction with a base. The contribution of the deprotonation of OH groups on the surface of kaolinite particles is lower (1−5%) because of the small specific surface area of this mineral, and that of the dissolution of Fe compounds is insignificant. In the AY horizon, the acid and base buffering of soil in the rhizosphere is higher than beyond the rhizosphere because of the higher contents of organic matter and nonsilicate Fe and Al compounds.

INTRODUCTION

The acid−base buffering is a fundamental property of the soil, determining the resistance to acidic and alkaline reagents for not only the soil itself, but also for the entire ecosystem. The nature of buffer reactions proceeding during the interactions of the taiga soils with acids and bases is mainly understood for the soil cover components occupying autonomous positions in the landscape.

It is established that the interactions of the organic horizons of forest soils with acids mainly involve the following buffer reactions: cation exchange; the decrease in basicity and the dissociation of Al, Fe, and Mn organomineral complexes; the dissolution of salts of strong bases and weak organic acids followed by the protonation of the organic anion; and the protonation of the functional groups of organic acids [4, 9, 12, 21, 38, 40, 47−50]. In the interaction of organic horizons with bases, the deprotonation of the functional groups of organic acids and the increase in the basicity of the Al, Fe, and Mn complexes with organic ligands are the leading buffer reactions [6, 7, 26, 41].

The interactions of mineral horizons with an acid involve the displacement of exchangeable bases by protons, the dissolution of the finest mineral particles, the decrease in the basicity of metal complexes and hydroxo complexes with organic ligands [6, 47], and the protonation of OH groups on clay crystallites [36, 37]. The interaction with a base results in the neutralization of exchangeable proton and exchangeable aluminum. The deprotonation of pH-dependent exchange sites, i.e., the neutralization of weaker acid components, is of similar importance. Along with organic acids, mineral soil components (mainly amorphous iron and aluminum hydroxides) and clay minerals can be carriers of pH-dependent acidity. Deprotonation involves the singly coordinated hydroxide groups occurring on the surface of iron and aluminum hydroxides [43, 45], as well as specific types of hydroxyl groups on the surface of clay minerals [36, 46].

The acid−base buffering of gleyic gray-humus soils developed in the floodplains of small brooks within the southern-taiga subzone is less studied. Rusakova et al. [22] showed that the acid buffering of the mineral

horizons in gleyic gray-humus soils exceeds that of the mineral horizons of podzolic soils in the eluvial and transitional-eluvial positions by 2−10 times. It was found that the treatment with the Tamm reagent significantly reduces the base buffering because of the removal of buffer components, primarily mobile Al compounds.

The present work deals with the quantification of the contributions of separate buffer reactions proceeding during the continuous acid or base potentiometric titration of samples from the genetic horizons of the soils developed in the floodplains of small brooks in the Central Forest State Nature Biosphere Reserve (CFSNBR), which can be considered as standards of undisturbed landscapes in the southern taiga [20].

Although the soils of the brook floodplains occupy <1% of the CFSNBR area [3], their buffering role in the landscape can be significant, because they occur in the transitional-accumulative positions and the soil- and ground-water flows feeding the brooks pass through these soils. Therefore, the buffering properties of floodplain soils can significantly affect the composition of surface water and determine the resistance of landscape components to unfavorable chemical effects.

OBJECTS AND METHODS

Soils in brook floodplains develop under thin forest vegetation with the predominance of Norway spruce (*Picea abies*), Norway maple (*Acer platanoides*), European white elm (*Ulmus laevis*), and bird cherry (*Prunus padus*). The ground cover consists of abundant herbs: ostrich fern (*Matteucia struthiopteris*), northern wolfsbane (*Aconitum septentrionale*), yellow archangel (*Galeobdolon luteum*), cabbage thistle (*Cirsium oleraceum*), dog's mercury (*Mercurialis perennis*), etc.

The soil profiles are clearly differentiated into horizons. A shallow O litter horizon is underlain by a gray-humus AY horizon about 10 cm thick; a transitional AYB horizon occurs in some profiles; it is absent in other profiles, where a BMg horizon about 10 cm thick occurs immediately under the AY horizon. These horizons are developed within the cover loam layer. At a depth of 40−50 cm, the cover loam gives place to heavy loamy morainic deposits (denoted as Dg) with obvious gleying signs, which can contain carbonate fragments and dispersed carbonates. In some cases, the deposit occurs directly under the AY or AYB horizon.

The taxonomic position of the studied soils is not quite clear. The above combination of the horizons classifies them as gleyic gray-humus soils (the trunk of postlithogenic soils) according to the 2004 classification of Russian soils [10], soddy-gley soils according to the 1977 classification [11], and as Gleyic Umbrisols (Ruptic) according to the WRB classification [24].

The studied soils occur in the floodplains of brooks; therefore, signs of alluvial processes could be supposed to be present, but these signs are morphologically revealed as buried horizons only in isolated profiles. The soils with such indices should belong to the trunk of synlithogenic soils and be classified as gray-humus alluvial gleyic soils. However, they should contain no BM horizon [10], which is present in all of the studied profiles. Therefore, the soils under study are defined as gleyic gray-humus soils, except profile 4-2010, which contains a buried humus horizon. This soil would be more correctly classified as an alluvial gleyic gray-humus soil, although it also contains a BMg horizon. The absence or weak manifestation of alluvial processes in most profiles is primarily related to the presence of woody plants and thick sod layer in the soils of floodplains and slopes of small waterways, which hampers the transport and redeposition of solid particles.

Test samples were taken from the genetic horizons in five profiles of gleyic gray-humus soils developed in the floodplains of small brooks in the CFSNBR (5-2007, 7-2007, 2-2010, 3-2010, 4-2010). The brooks are Mezha River tributaries of the first and second orders. The data on the general properties and buffering for two profiles (5-2007 and 7-2007) were reported earlier [8, 22]; they are not presented in this paper but are included in the general set of samples for the statistical processing of data. The reported data on the mineralogy of the soils [23] are also not given in this paper, but they are used for calculating the contributions of separate reactions to the acid−base buffering of soils.

In profile 4-2010, rhizosphere and non-rhizosphere soil samples were also separately taken from the AY horizon. This profile has no forest litter, because the profile was established on the plot without trees. The samples were taken using the following procedure.

A general sample was first taken from the AY horizon, and roots with adhered soil were separated. The soil "beads" remaining on the roots after shaking were considered rhizosphere soil. The resting sample was regarded as non-rhizosphere soil.

The chemical properties of soils were determined using conventional procedures [2]. The contents of mobile Fe and Al compounds in the Tamm solution were determined by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent ICP-MS 7500A instrument.

To assess the acid−base buffering properties, water suspensions of the soil samples were prepared at solid-to-liquid phase ratios of 1 : 10 for the mineral horizons and 1 : 25 for the organic horizons. The acid−base buffering was determined by continuous potentiometric titration of the water suspensions on a Mettler Toledo DL 58 titrator from the initial titration point (ITP) to pH 3 for the acid titration and from the ITP to pH 10 for the base titration (in the latter case, before and after the Tamm treatment). The titration was performed in steps of 0.2 mL; the pH values were recorded 2 min after the addition of each titrant portion under CO_2-free atmosphere, with 0.1 M HCl and NaOH solutions being used as titrants. The acid−base

Table 1. Some chemical properties and acid and base buffering of the studied soils

Horizon	C_{org}, %*	pH		Exchangeable acidity	Base buffering between ITP and pH 8.3	Base buffering between ITP and pH 10		Acid buffering between ITP and pH 3	Total exchangeable bases	In Tamm solution, mmol/kg	
		H_2O	KCl			before Tamm treatment	after Tamm treatment			Fe	Al
						mmeq/kg					
Profile 2-2010											
O	89.3	6.4	5.9	24.2	32.4	359.5	424	575.2	305.9	10.7	23.7
AY	5.5	6.3	5.1	1.0	27.9	145.3	72.5	101.5	109.4	59.4	87.7
AYB	1.3	6.3	4.8	0.3	17.0	91.3	32.1	43.3	60.8	55.8	59.9
BMg	1.2	6.6	5.0	0.2	13.9	76.4	24.5	37.7	59.7	73.1	54.3
Dg	0.9	6.9	5.4	0.2	6.1	30.0	25.2	34.4	52.0	12.0	31.8
Profile 3-2010											
O	90.2	6.4	6.0	20.6	48.6	440	515	595	302	1.7	1.7
AY	2.7	5.9	4.5	0.6	25.0	98.6	55.2	45.9	59.7	57.5	51.8
AYB	1.2	6.2	4.5	1.2	11.1	60.1	21.4	27.9	37.1	87.5	53.1
BMg	0.6	6.6	4.7	0.5	8.9	50.6	32.0	32.2	58.5	64.4	49.9
Dg	1.0	6.8	5.0	0.2	10.2	67.1	45.9	52.5	114	138	75.0
Profile 4-2010											
AY	5.1	5.9	5.0	0.6	18.4	128	83.1	84.0	82.3	105	70.2
AYBg	3.1	5.9	4.6	1.0	31.2	103	65.8	53.7	69.3	65.3	60.2
AYg**	4.5	5.9	4.7	0.8	22.0	139.2	65.0	68.2	68.4	62.0	58.4
BMG	2.7	6.3	4.78	0.5	11.6	92.5	53.6	45.5	65.5	94.0	78.9

* In all organic horizons, ignition loss. ** Buried humus horizon.

buffering capacity was expressed in mmeq/kg soil as the amount of the titrant necessary to change the suspension pH from the ITP to 3 at the acid titration and from the ITP to 10 at the base titration. The contents of Al, Fe, Si, Mn, Mg, Ca, Na, and K in the filtered liquid phase of suspensions after the acid and base titration and in the water extracts from the initial samples were determined by ICP-MS after the addition of several drops of concentrated HNO_3.

The statistical processing of data [5] (correlation analysis and analysis of variance) was performed using Excel software.

RESULTS AND DISCUSSION

Chemical properties of the soils. A slightly acid reaction is observed throughout the profiles of the soils under study, and the pH values increase with depth, probably because of the former presence of carbonates (leached later on) in the lower horizons (Table 1). The increase in the pH of water and salt suspensions in the organic horizons compared to the lower horizons is related to the biogenic accumulation of bases.

The humus horizon in the studied soils begins from forest litter, except for profile 4-2010 developed under herbaceous plants. A humus-accumulative AY horizon with a high content of C_{org} (2.5–5.5%) occurs below. As noted above, profile 4-2010 has a buried humus horizon. The maximum content of exchangeable bases is observed in the litters. The second maximum of exchangeable bases in profile 3-2010 is confined to the lower mineral horizon because of heaved texture.

Exchangeable acidity in the organic horizons varies in the range of 5–10% of the effective cation exchange capacity (CEC); it is formed due to exchangeable H^+, which mainly occurs in the functional groups of organic compounds. In the upper mineral horizons, the exchangeable acidity makes up 1–1.5% of the CEC and is due to exchangeable Al. In the lower mineral horizons, the exchangeable acidity is absent or very low in value.

In general, the gleyic gray-humus soils developed in the floodplains of small brooks have a significantly less acid reaction and a higher saturation of the soil exchange complex (SEC) than the podzolic and bog-podzolic soils developed on watersheds and slopes.

The contents of oxalate-soluble Al and Fe. The content of oxalate-soluble aluminum (Al_{OX}) is minimum in the litters, because their ignition loss is 90%, and the calculation was performed for air-dry samples (Table 1). In the mineral horizon, it varies from 30 to 88 mmol/kg. It was shown earlier that, when carbonates are present in the lower part of the profile of gleyic gray-humus soils or in the bed rock, the content of Al_{OX} in the mineral horizons can exceed 200 mmol/kg because of its accumulation over the carbonate barrier [22]. It was supposed that Al_{OX} is accumulated in these profiles in the forms of Al−organic complexes and, probably, amorphous aluminosilicates precipitating from solutions [25]. An accumulative distribution of Al_{OX} with a maximum in the humus-accumulative horizon and gradual decrease down the profile in accordance with the distribution of Al−organic complexes (the main sources of mobile Al in these soils [25]) is observed in profile 2-2010. In profile 3-2010, the content of Al_{OX} in the mineral horizons is poorly differentiated, except the parent rock, where it abruptly increases. The same horizon is characterized by the heaviest texture. In profile 4-2010, the content of Al_{OX} decreases with depth in accordance with the distribution of Al−organic complexes, but it appreciably increases in the lowest horizons with the heaviest texture.

The content of oxalate-soluble iron (Fe_{OX}) is also minimum in the litters, because the calculation was performed for air-dry samples. In the mineral horizons, it irregularly varies among the horizons between 12 and 138 mmol/kg. The nonsilicate Fe partially occurs in the crystallized forms: goethite is found in the clay fractions from all horizons of profile 2-2010; goethite and lepidocrocite are found in the BMg horizon. Goethite is also identified in the clay fraction from the Dg horizon of profile 3-2010 [23]. The profile distribution of Fe_{OX} also has no general regularities in the studied soils, because it depends on several factors. The content of organic matter and the redox conditions are the most important factors. All of the studied soils show morphological signs of gleying and Fe segregation in the form of nodules, rusty spots, and patches irregularly distributed in the soils.

In general, the content of Fe_{OX} in all of the studied profiles and the content of Al_{OX} in some of the studied profiles of soils in the floodplain brooks exceed those in the podzolic and gleyic peaty-podzolic soils of eluvial and transitional-eluvial positions. This can be related to the additional input of Fe and Al compounds from the soils of autonomous positions and slopes with the lateral flows of soil solutions.

Acid−base buffering of the studied soils. In all of the studied profiles, forest litters have the maximum acid and base buffering, because they contain 90% organic matter, the main carrier of functional groups capable of protonation and deprotonation in a wide pH range [17, 44]. In the mineral horizons, the acid−base buffering generally decreases from the AY horizon to the AYB horizon in accordance with the appreciable decrease in the content of C_{org} and varies in the ranges of 43−101 and 60−145 mmeq/kg, respectively. In the lower horizons, their values increase again because of the heavier texture and the increased content of nonsilicate Fe and Al compounds in profile 3-2010 and in the buried humus horizon of profile 4-2010.

In all of the studied profiles, the base buffering exceeds the exchangeable acidity by an order of magnitude and more in the pH range up to 8.3. This is due to the participation of weakly acidic components (with *pKa* in the range between the pH_{KCl} and 8.3) present in the solid phase of suspension in the buffer neutralization reactions. These weakly acidic components include functional groups of weak organic acids and OH groups on the surface of Fe and Al hydroxides. The significant contribution of nonsilicate Fe and Al compounds to the base buffering in all of the mineral horizons due to the deprotonation of surface OH groups is confirmed by the significant (in some horizons, by 2−3 times) decrease of buffering after the Tamm treatment. It is known that the pH of the zero charge point for Fe and Al hydroxides lies in the pH range >7 [19, 32, 45]; therefore, these groups exhibit base-buffering properties during the titration to pH 10.

In the forest litters of profiles 2-2010 and 3-2010, the acid buffering significantly exceeds the content of total exchangeable bases, which is related to the presence of other buffering mechanisms than the displacement of exchangeable bases by protons. This can be the dissolution at the interaction of Ca oxalate with an acid followed by the protonation of oxalate anions. The content of Ca oxalates in the litters of forest soils of the temperate zone can reach 80 g/m², or 1250 mmeq/m² [29, 33]. The reserve of litter in podzolic soils is 3−4 kg/m²; thus, the content of Ca oxalates can reach 300−400 mmeq/kg. Oxalates probably incompletely dissolve at the short-term interaction with the titrant, but the contribution of their dissolution to the acid buffering can be significant. In the mineral horizons, the acid buffering capacity is comparable to (although slightly lower than) the content of total exchangeable bases; in some cases, these values coincide. In the mineral horizons, the displacement of exchangeable bases by protons is obviously one of the main buffer reactions.

Another aspect of the work was the comparative analysis of the acid−base buffering of soil material from the rhizosphere and non-rhizosphere soil of the AY horizon in profile 4-2010 (Table 2). It can be seen that the acid−base buffering in the rhizosphere soil is higher than in the non-rhizosphere soil. This is related to the higher contents of organic matter and oxalate-soluble Fe and Al compounds.

Results of correlation analysis. The revealed relationships between the acid−base buffering of the stud-

Table 2. Some chemical properties and acid–base buffering of the rhizosphere and nonrhizosphere soil in the AY horizon of profile 4-2010 (averages from five replicates)

Sample	pH		C_{org}, %	Buffering			In Tamm solution, mmol/kg	
	H$_2$O	KCl		to bases between ITP and pH 10	to acids between ITP and pH 3	total exchangeable bases	Fe	Al
				mmeq/kg				
Rhizosphere	6.16	5.22	5.05	233.7	135.9	78.5	103.8	64.6
Nonrhizosphere	6.16	5.00	2.87	189.4	92.5	80.2	97.2	57.3

Table 3. Pair correlation coefficients between the buffer parameters and some properties of the studied soils

Pairs of correlated parameters	N	r*
Acid-buffering capacity − total exchangeable bases (all horizons)	21	0.91
Acid-buffering capacity − total exchangeable bases (mineral horizons)	14	0.77
Acid-buffering capacity − C_{org} (horizons AY, AYBg, BMg)	9	0.97
Acid-buffering capacity − Al$_{OX}$ (all horizons except O and Dg)	14	0.71
Acid-buffering capacity − Fe$_{OX}$ (all horizons except O and Dg)	14	0.67
Acid-buffering capacity − (Al$_{OX}$ + Fe$_{OX}$) (all horizons except O and Dg)	14	0.73
Base-buffering capacity − C_{org} (all horizons except O)	19	0.84
Base-buffering capacity − Fe$_{OX}$ (all horizons except O)	19	0.82
Base-buffering capacity − Fe$_{OX}$ (horizon Dg)	5	0.99
Base-buffering capacity − Al$_{OX}$ (all horizons except O)	19	0.67
Base-buffering capacity − Al$_{OX}$ (horizons BMg, Dg)	10	0.86
Base-buffering capacity − Al$_{OX}$ + Fe$_{OX}$ (all horizons except O)	19	0.66
Base-buffering capacity − Al$_{OX}$ + Fe$_{OX}$ (horizons BMg, Dg)	10	0.90

* Significant at $P = 0.99$.

ied soils and their chemical parameters are confirmed by correlation analysis data (Table 3).

Acid buffering. For the entire sample set, including the mineral and organic horizons, a reliable correlation is found between the acid-buffering capacity and the total exchangeable bases; the coefficient of correlation is 0.91 (significant at $P = 0.99$). For the mineral horizon, it is 0.77 (significant at $P = 0.99$). In the mineral horizons of podzolic soils in the CFSNBR, no reliable correlation between the acid-buffering capacity and the total exchangeable bases was found [14]. These differences between the soils can be explained as follows. The gleyic gray-humus soils have higher pH values and are more saturated with bases than the podzolic soils. The content of exchangeable bases is high; therefore, they occupy many exchange sites, including low-selective ones, and are displaced by protons during titration.

The proton-buffering properties of organic matter are due to the following reactions: the protonation of the acid groups of organic acids in accordance with their pKa values, the dissociation and decrease in the basicity of Al-, Mn-, and Fe-organic complexes followed by ligand protonation, and the dissolution of Ca^{2+}, Mg^{2+}, and K^+ salts with organic anions followed by anion protonation. The above-noted close correlation between the acid-buffering capacity and the total exchangeable bases in the upper horizons is directly related to the displacement of exchangeable bases in the functional groups of organic acids by protons. Therefore, a close correlation can be expected between the acid-buffering capacity and the content of organic matter, which is confirmed by the high correlation coefficient (0.97, significant at $P = 0.99$) for the sample set containing the main mineral horizons.

The acid buffering cannot be provided by the protonation of OH groups on the surface of Fe and Al oxides and hydroxides, because the pH of the zero charge point is higher than 7 for these minerals [19, 32, 45]; i.e., it exceeds the soil pH. Therefore, the acid-buffering role of nonsilicate Fe and Al compounds is realized through other mechanisms. First, the finest particles of these compounds can be subjected to dissolution under acidic conditions. Second, the dissoci-

ation of Fe- and Al-organic complexes followed by the protonation of organic ligands occurs under acidic conditions, as noted below. These complexes (at least in the upper horizons) make up a significant portion of Fe and Al compounds, which pass to the Tamm solution and are defined as nonsilicate compounds. The coefficients of correlation between the total acid-buffering capacity and the contents of Al_{OX}, Fe_{OX}, and total Al_{OX} and Fe_{OX} are 0.71, 0.67, and 0.73, respectively (significant at $P = 0.99$).

Base buffering. A high correlation ($r = 0.84$, significant at $P = 0.99$) was also revealed between the base-buffering capacity and the content of organic matter. As noted above, the base-buffering effect of organic matter involves several different reactions and mechanisms. In the course of continuous titration, the functional groups of specific and nonspecific organic acids with the corresponding pKa values are subjected to deprotonation: the weakest acid carboxylic groups, the NH_2 groups of amino acids, and phenolic hydroxyls. The addition of OH groups also results in an increase in the basicity of Fe- and Al-organic complexes up to their complete dissociation and the precipitation of metal hydroxides, as well as the dissolution of hydroxides with the formation of negatively charged metal hydroxo complexes under still higher pH values.

In the mineral horizons, the base buffering of soils is primarily provided by the deprotonation of hydroxyl groups on the surface of Fe hydroxide particles and some Al compounds in accordance with the pH > 7 in the point of zero proton charge. Therefore, a reliable correlation between the base-buffering capacity and the content of nonsilicate Al and Fe compounds in both organic and mineral horizons can be expected, as confirmed by the results of correlation analysis. The relationship between the base-buffering capacity and the content of Fe_{OX} for the set of samples from all horizons, except the litters, is characterized by a correlation coefficient of 0.82, significant at $P = 0.99$. The closest correlation is found for the Dg horizon with the minimum content of organic matter.

Analogous relationships are also revealed between the total base-buffering capacity and the content of Al_{OX}, although the corresponding correlations are slightly lower. For the entire sample set except the litters, the correlation coefficient is 0.67; for the set of samples from the BMg and Dg horizons, it increases to 0.86 (significant at $P = 0.99$).

In accordance with the established relationships, a correlation is revealed between the total base-buffering capacity and the total Al_{OX} and Fe_{OX}; the correlation coefficient is 0.66 (significant at $P = 0.99$) for the set of samples from all horizons (except the litters) and 0.90 (significant at $P = 0.90$) for the set of samples from the BMg and Dg horizons.

The obtained correlations and the significant decrease in buffering after the Tamm treatment suggest that nonsilicate Fe and Al compounds in the studied soils are among the most important factors controlling the values of acid−base buffering, especially in the BMg and Dg horizons.

Analysis of data on the composition of filtrates after the acid and base titrations. The dissolution of some of the finest components of the solid phase is another type of buffer reaction proceeding during the interactions of the mineral horizons of the studied soils with an acid and a base. The compositions of the suspension filtrates separated from the solid phase immediately after the end of titration are given in Tables 4 and 5. The concentrations of elements in the water extracted at a similar dilution are also given for comparison. During the acid titration, the abrupt increase in the concentrations of Ca, Mg, and Mn in the liquid phase and the appreciable increase in the concentration of K are primarily related to the above-mentioned displacement of these exchangeable cations by protons.

In the filtrates after acid titration, the concentration of Al also increases compared to that in the water extract (except for the two lower horizons in profile 3-2010), as well as the concentrations of Fe and Se in some samples. The maximum concentration of Al in the filtrates is found in different genetic horizons of soil profiles. No correlation was revealed between the Al and Si concentrations in the filtrates after the acid filtration.

After the base titration, a significant increase in the concentrations of Al, Fe, and Si is observed in the filtrates; the differences with the water extract reach an order of magnitude in many cases. A high linear correlation between the Al and Si concentrations ($r = 0.87$, significant at $P = 0.99$) is observed in the filtrates for the set of samples from the mineral horizons in profiles 2-2010 and 3-2010. In the samples from all mineral horizons, except the two upper horizons in profile 4-2010, the Al : Si molar ratios in the filtrates after titration are close to 2.

The data obtained for the composition of filtrates can be interpreted as follows. In the litters and some underlying mineral horizons, the increase in the Al and Fe concentrations during the acid titration to pH 3 is due to the dissociation of Al- and Fe-organic complexes with the formation of Al^{3+} [1, 43] and Fe^{3+} and their hydroxo monomers in the solution. The solubility and basicity of Al- and Fe-organic complexes increase during the base titration, which results in an increase in the Al and Fe concentrations in the filtrates.

An increase in the total Al and Si concentration in the filtrates is also observed during the acid and base titration for the mineral horizons. Al and Si in the filtrates can partly occur in the fine particles of clay silicates, because the liquid phase was separated by filtering through a blue-ribbon filter with a pore diameter of 2−3 μm under water aspirator vacuum. Although the pores were rapidly filled and the filtrates were crystal-clear, some amount of finest silicate particles could be present in the filtrates. Therefore, concen-

Table 4. Contents of Ca, Mg, K and Na in water extracts and filtrates after acid and base titrations, mmeq/kg

Horizon	Ca			Mg			Na		K		
	H$_2$O	HCl	NaOH	H$_2$O	HCl	NaOH	H$_2$O	HCl	H$_2$O	HCl	NaOH
Profile 2-2010											
O	12.4	298.3	1.8	0.6	13.0	0.6	1.4	1.8	0.9	1.0	0.7
AY	1.4	106.5	1.8	0.2	7.6	0.6	1.3	1.3	0.1	1.2	0.1
AYB	0.6	29.6	1.5	0.3	6.0	0.5	1.3	1.2	0.3	0.7	0.1
BMg	0.7	24.0	0.7	0.3	6.0	0.3	1.1	1.3	0.1	1.6	0.7
Dg	06	21.9									
Profile 3-2010											
O	17.9	277.6	2.6	0.4	8.8	0.9	1.4	1.3	0.2	0.9	0.9
AY	0.8	57.3	2.2	0.3	3.8	1.0	1.0	0.9	0.1	0.5	0.3
AYB	0.6	19.3	1.3	0.3	5.5	0.5	1.1	1.1	0.1	0.7	0.1
BMg	0.6	20.0	1.2	0.3	8.3	0.5	1.1	1.7	0.2	1.0	0.2
Dg	0.6	30.8									
Profile 4-2010											
AY	1.4	45.6	1.7	0.3	5.4	0.6	1.1	1.5	0.1	1.3	0.1
AYBg	0.8	35.6	3.1	0.5	9.4	1.2	1.1	1.4	0.9	1.4	0.2
AYg*	1.2	42.2	2.0	0.3	6.9	0.7	1.4	0.9	0.8	0.9	0.4
BMG	0.8	27.5	1.8	0.6	13.0	0.6	1.4	1.8	0.9	1.0	0.7

* Buried humus horizon.

Table 5. Contents of Al, Fe, Si and Mn in water extracts and filtrates after acid and base titrations, mmeq/kg

Horizon	Al			Fe			Mn			Si		
	H$_2$O	HCl	NaOH	H$_2$O	HCl	NaOH	H$_2$O	HCl	NaOH	H$_2$O	HCl	NaOH
Profile 2-2010												
O	0.9	3.9	4.5	0.5	9.3	1.4	0.2	10.5	0.2	4.4	5.2	27.4
AY	0.2	2.2	17.7	0.1	0.4	0.5	0.01	1.7	<0.1	0.5	1.3	8.6
AYB	0.2	0.9	19.5	0.2	0.3	1.0	0.01	0.3	<0.1	1.2	1.5	9.5
BMg	0.4	0.7	14.3	0.2	0.2	1.1	0.01	0.2	<0.1	1.2	1.7	8.9
Dg	0.8	1.4	4.7	0.3	0.5	0.4	0.01	0.1	<0.1	2.0	3.2	4.4
Profile 3-2010												
O	0.4	0.9	0.5	0.6	8.7	0.5	0.27	9.9	0.2	4.0	2.6	28.0
AY	0.5	1.1	20.7	0.4	0.2	1.0	0.03	2.4	0.1	1.6	2.6	10.6
AYB	0.6	2.0	12.5	0.4	0.2	1.0	0.01	0.2	<0.1	1.4	0.9	6.6
BMg	1.1	0.6	10.0	0.6	0.1	0.6	0.02	0.1	<0.1	2.7	1.7	5.7
Dg	0.9	0.3	9.0	0.5	0.2	0.6	0.03	0.2	<0.1	2.9	3.4	3.9
Profile 4-2010												
AY	0.3	1.7	17.1	0.2	0.3	0.9	0.03	3.9	0.1	1.4	1.9	2.6
AYBg	0.4	1.9	15.9	0.3	0.3	0.8	0.02	4.1	0.1	1.2	1.4	2.7
AYg*	0.1	1.5	18.9	0.1	0.3	0.9	0.01	2.2	0.1	0.7	2.1	8.5
BMG	0.3	1.0	19.9	0.2	0.2	0.7	0.03	1.2	<0.1	1.1	1.6	9.0

* Buried humus horizon.

Table 6. Contributions of separate reactions to the total acid buffering of soils during the titration to pH 3, % of the total buffering capacity

Hori-zon	Displacement of			Dissolution of			Protonation of kaolinite OH groups	Unaccounted reactions
	exchangeable Ca	exchangeable Mg	exchangeable K	Ca oxalates	Al compounds	Mn compounds		
Profile 2-2010								
O	29	14	4	31	1	2	0	19
AY	64	12	<0.5	40	1	3	1	Not det.
AYB	67	17	3	0	1	1	2	9
BMg	62	15	1	0	1	1	2	18
Dg	62	17	4	0	1	<0.5	2	14
Profile 3-2010								
O	32	6	2	60	<0.5	4	0	0
AY	53	18	1	8	1	10	3	6
AYB	67	13	2	0	3	1	3	11
BMg	60	16	2	0	<0.5	0	3	19
Dg	58	15	2	0	<0.5	1	2	22
Profile 4-2010								
AY	53	9	2	0	1	9	1	25
AYBg	65	9	2	0	2	15	2	5
AYg*	61	13	1	0	1	6	2	15
BMG	59	14	<0.5	0	1	5	2	19

* Buried humus horizon.

trated nitric acid is added to the solution for the determination of the total concentration of the elements by ICP MS. The total concentration of the elements in the solution, including in fine solid particles, is obtained in this case [30]. The higher content of silicate particles in the filtrates after the base titration than in the filtrates after the acid titration is due to the additional dispersion of the solid phase in the presence of Na.

At the same time, the above-mentioned molar Al : Si ratio close to 2 suggests the presence of other compounds in the alkaline filtrates, because this ratio is 1 in kaolinite and some chlorites and varies from 0.2 to 1.3 in other clay minerals [15, 16]. In the alkaline filtrates, Al and Si can partly occur in the truly dissolved forms $Al(OH)_4^-$ and H_4SiO_4 and products of H_4SiO_4 polymerization. The constant molar Al : Si ratios and the high correlation between Al and Si in the alkaline extracts suggest that the base titration is accompanied by the dissolution of amorphous aluminosilicates like allophanes, which have molar Al : Si ratios of 2. They can occur in the soils not as independent spherical particles and their aggregates but form films on the surface of different mineral particles [34].

Along with all the above-considered buffering mechanisms, the protonation–deprotonation of hydroxyl groups on the edges of clay minerals can contribute to the acid–base buffering in the mineral hori-zons [27, 28, 36, 39]. Therefore, the higher clay content and the related increase in the content of reactive hydroxyl groups on the surface of clay minerals can be a reason for the increased values of acid–base buffering capacity in the Dg horizon of profile 3-2010 [23].

Quantification of the contributions of separate reactions to the acid–base buffering of the studied soils. An attempt was made to quantify the contributions of separate reactions to the acid–base buffering of soils on the basis of the obtained data with consideration for the content of nonsilicate Fe and Al compounds and the mineralogy of the fine fractions [23] and some suppositions. The computation scheme for the quantification of the percentage-based contributions of separate reactions and the results of calculation are given below.

In the calculations, the concentration of each element in the liquid phase of suspension before the addition of the titrant was subtracted from its concentration in the filtrate after the acid or base titration (Tables 6, 7) in order to determine the content of protons and hydroxyl groups consumed for the buffer reactions.

Acid Buffering: Principles of Calculation

Displacement of exchangeable Ca and the dissolution of Ca oxalates. In the organic horizons, the content of calcium in the filtrate after acid filtration calculated

Table 7. Contributions of separate reactions to the total base buffering of soils during the titration to pH 10, % of the total buffering capacity

Horizon	Dissolution of			Deprotonation of OH groups on			Unaccounted reactions
	Al	Fe	Si	Fe hydroxides	kaolinite	illite	
Profile 2-2010							
O	1	<0.5	1	<0.5	0	0	98
AY	8	<0.5	1	9	1	3	78
AYB	14	1	3	13	2	6	61
BMg	12	1	3	27	2	8	47
Dg	9	<0.5	4	24	5	17	41
Profile 3-2010							
O	<0.5	<0.5	<0.5	<0.5	0	0	99
AY	14	<0.5	3	9	3	4	67
AYB	13	1	3	29	3	5	46
BMg	12	<0.5	3	26	4	15	40
Dg	8	<0.5	1	43	4	19	25
Profile 4-2010							
AY	9	<0.5	<0.5	15	1	5	70
AYBg	10	<0.5	1	12	2	6	69
AYg*	9	<0.5	2	11	2	6	70
BMG	14	<0.5	2	10	2	6	66

* Buried humus horizon.

for unit soil mass was significantly higher than the content of exchangeable Ca in the horizon (Table 1). Therefore, it was taken that all the exchangeable Ca from the organic horizons was displaced by protons into the solution, and the difference between the content of Ca in the filtrate and that of exchangeable Ca was attributed to the dissolution of Ca oxalates followed by the protonation of oxalate anions. The content of exchangeable Ca and the difference between the content of Ca in the filtrate and the content of exchangeable Ca were expressed in percentage of the total acid-buffering capacity. Ivanova et al. [7] and Shamrikova et al. [26] earlier used an analogous calculation scheme. For the mineral horizons, it was taken that the content of Ca in the filtrate is equal to the content of exchangeable Ca displaced by protons from the SEC.

Displacement of exchangeable Mg and K. For the samples from all horizons, it was taken that these cations in the filtrates are completely displaced by protons from the SEC during the buffer reaction. Their content was expressed in percentage of the total acid buffering.

Dissolution of Al compounds. In the organic horizons, aluminum passes into the solution during the titration with an acid to pH 3 due to the dissociation of Al−organic complexes with the formation of Al^{3+} particles in the liquid phase. The initial pH values of the studied soils were about 6; therefore, it may be sup-

posed that Al in these complexes initially had the basicity $Al(OH)_2^+$, and the equivalent number of Al was taken equal to 2. For the mineral horizons, this number was also taken equal to 2, although the nature of the buffer reactions resulting in the release of Al into the acid solution is less clear. The titration can be accompanied by the dissolution of the finest aluminosilicates, including kaolinite, with the predominant release of Al into the solution [28, 37]. In the calculations, the content of Al in the filtrate in mmol/kg soil was multiplied by 2 and expressed in percentage of the total acid-buffering capacity.

Analogous calculations were made for Fe and Si found in the filtrates, but their contents in all soils and horizons were insignificant; therefore, the results of calculations were not included in the summary table.

Dissolution of Mn compounds. During the acid titration, Mn could pass into the solution due to different reactions: the displacement of exchangeable Mn from the SEC by protons and the dissociation of Mn−organic complexes followed by the protonation of ligands in the upper horizons. It was taken that Mn had a valence of 2 in the both cases; therefore, the content of Mn in the filtrate expressed in mml/kg soil was multiplied by 2 and expressed in percentage of the total acid buffering.

Protonation of the surface hydroxyl groups of kaolinite. The calculation was based on the experimental work of

Huertas et al. [36], who performed the potentiometric titration of the pure kaolinite suspension and concluded that two types of surface OH groups occur on the surface of kaolinite particles: the groups titrated with an acid and confined to the external aluminol groups of the gibbsite layer (stronger acidic), and those on the edges of crystallites (weaker acidic). The reported titration curves [36] show that 1.1 μmol/m^2 of protons are consumed for the protonation of surface OH groups during the acid titration of kaolinite suspension in the pH range from the ITP to 3.

Taking the specific surface area (SSA) of kaolinite equal to 10 m^2/g [46] and expressing the percentage of kaolinite [23] in the whole soil with consideration for the content of the clay and fine silt fractions, we calculated the surface of kaolinite particles in m^2/kg soil. The obtained value was multiplied by 1.1 μmol/m^2 to obtain the content of protons consumed for the protonation of surface hydroxyl groups of kaolinite particles. The obtained result was expressed in mmol/kg and normalized to the total base buffering capacity.

Acid Buffering: Results of Calculation

It can be seen (Table 5) that most of the protons (>80%) are consumed during titration for the displacement of exchangeable bases in the mineral horizons and for the displacement of exchangeable bases and the dissolution of Ca oxalates in the organic horizons of all the studied profiles. In the O and AY horizon, a significant contribution (2–15%) to the acid buffering is made by Mn compounds, which agrees with the published data [6, 50]. The buffer reactions with the participation of Al compounds make up <0.5 to 1–2% of the total buffering, and the protonation of the surface OH groups of kaolinite makes up 2–3%.

It was shown in some works that the same buffer reactions also occur during the interaction with an acid in different genetic horizons of podzolic soils, but their contribution to the total acid-buffering capacity is significantly smaller, and the reactions with the participation of Al compounds play a significant role, especially in the mineral horizons [4, 9, 12, 13]. In the more acid gleyic peaty-podzolic soils, the buffer reactions of dissociation of Al-organic complexes play the main role and are capable of completely providing the acid buffering during the titration from the ITP to pH 3. In the mineral horizons of these soils, the total acid-buffering capacity is lower than in the alluvial soddy-gley soils by about an order of magnitude [13].

Thus, the studied soils are characterized by higher acid buffering, the larger contribution of the displacement of exchangeable bases by protons to the acid buffering, and the smaller contribution of the reactions with the participation of Al compounds. The contribution of the protonation of the surface hydroxyl groups of kaolinite obviously does not depend on the soil type, but it is a function of soil texture and mineralogy.

It is also seen (Table 6) that 0 to 25% of the total acid-buffering capacity is accounted for in the reactions that were not quantified in this study. In the O horizon of profile 3-2010, the total contribution of all reactions calculated according to the above scheme exceeded 100%, obviously due to the spatial variation of all characteristics, because the buffer properties, the composition of exchangeable bases, and other properties were determined from different samples. The fact that, in spite of the assumptions made, the proportion of the unaccounted reactions in most horizons is lower than 20% of the total acid-buffering capacity allows considering the calculations performed as generally satisfactory. The total contribution of all reactions in all cases except one (mentioned above) is smaller than the experimentally determined acid buffering; therefore, it is hardly correct to attribute this difference to the effect of random factors. It can be supposed that the unaccounted buffer reactions primarily involve the strongest acid functional groups of organic compounds and the protonation reactions of other clay minerals than kaolinite, probably interstratified illite–chlorite and chlorite–vermiculite. This supposition could not be verified, because no literature data are available on the potentiometric acid titration of these minerals.

Base Buffering: Principles of Calculation.

Among the buffer reactions identified in this work, the dissolution of Al, Fe, and Si compounds and the deprotonation of the surface hydroxyl groups of Fe hydroxides, kaolinite, and illite were quantitatively characterized.

Dissolution of Al and Fe compounds. In the organic horizons, Al passes into the solution during the base titration to pH 10 because of the dissociation of Al–organic complexes with the formation of Al(OH)$_4^-$ particles in the liquid phase. The initial pH values of the studied soils were about 6; therefore, Al in these complexes had the initial basicity Al(OH)$_2^+$, and the equivalent number of Al was taken equal to 2. In the mineral horizons, this number was also taken equal to 2. Therefore, the Al concentration in the filtrate after the base filtration was expressed in mmol/kg, multiplied by 2, and normalized to the total buffering capacity. Analogous suppositions and calculations were made for the content of Fe in the filtrates after titration.

Dissolution of Si compounds. The sources of Si under alkaline conditions can include various compounds, in particular, phytolitharia and different aluminosilicates. If phytolitharia were the main sources of Si, the content of Si in the filtrates should decrease with depth, but the data in Table 6 indicate an opposite tendency. At the dissolution of aluminosilicates, a reliable correlation could be expected between the contents of Si and Al in the filtrates, which is confirmed by the results of correlation analysis for the set of samples

containing those from the mineral horizons of profiles 2-2010 and 3-2010 ($r = 0.87$, significant at $P = 0.99$). Thus, during the base titration, Si and Al pass into the solution, most probably due to the dissolution of the finest aluminosilicates, probably allophanes.

In the calculation of the contribution of the dissolution of Si compounds to the total buffering during the titration, the equivalent number of Si was taken equal to 1 in accordance with the buffer reaction

$$Si(OH)_4 + (OH)^- = H_3SiO_4^- + H_2O.$$
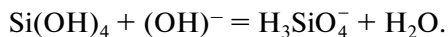
Deprotonation of OH groups on the surface of Fe hydroxide particles. The calculation was based on the supposition that the density of surface hydroxyl groups on Fe oxides and hydroxides is 5 sites/nm^2 (according to Sparks [42], this value can vary from 2 to 22 sites/nm^2) and that the SSA of these minerals is 100 m^2/g (a similar value for finely dispersed goethite was reported by Stumm [45]). Then, the density of functional groups is 5×10^{18} sites/m^2. The division of this value by the Avogadro number to express it in moles and multiplying by 1000 to convert to millimoles give $((5 \times 10^{18})/(6.022 \times 10^{23})) \times 1000 \sim 1$ mmol/m^2. The content of Fe in the Mehra−Jackson solution found in mmol/kg (our data) was converted to g/kg and multiplied by the SSA value (100 m^2/g) and the density of hydroxyl groups (1 mmol/m^2) to obtain the content of the functional hydroxyl groups capable of deprotonation on the surface of Fe hydroxide particles. The obtained value was normalized to the total base-buffering capacity.

Deprotonation of OH groups on the surface of kaolinite crystallites. The calculation was based on the experimental works of Huertas et al. [36] and Tertre et al. [46], which showed by the titration of kaolinite suspensions that the content of the OH groups capable of deprotonation on the surface of kaolinite during the titration to pH 10 is 2.3 µmol/m^2. From our earlier data [23], the content of kaolinite was calculated in g/kg, and the SSA of kaolinite was taken equal to 10 m^2/g [46]; the total surface area of kaolinite particles in the clay and fine silt fractions was calculated in m^2/kg soil. The obtained value was multiplied by 2.3 µmol/m^2, divided by 1000 to covert micromoles to millimoles, and normalized to the total buffering capacity.

Deprotonation of OH groups on the surface of illite crystallites. According to the results of the potentiometric titration of an illite suspension with a SSA of 20 m^2/g [31], the content of the OH groups capable of deprotonation during the titration to pH 10 is 0.11 mmol/g. From the reported data [23], the content of illite was calculated in g/kg. The value was multiplied by 0.11 and normalized to the total base buffering.

Base Buffering: Results of Calculation

It can be seen (Table 7) that, in all of the studied profiles, three reactions—the deprotonation of OH groups on the surface of Fe hydroxides, the deprotonation of OH groups on the surface of illite crystallites, and the dissolution of presumably amorphous silicates—are the most important quantified buffer reactions. The smaller contribution of the deprotonation of OH groups on the surface of kaolinite particles to the base buffering can be related to the small SSA of these particles; the contribution of the dissolution of Fe compounds is insignificant.

It can be seen (Table 7) that, in contrast to the acid buffering, a significant proportion of base-buffering capacity in the studied soils is due to the reactions unaccounted in this work. This proportion approaches 100% in the organic horizons and varies from 25 to 80% in the mineral horizons, where it decreases with depth in all three studied profiles. This is primarily related to the involvement of organic matter as an essential buffer component, whose role was not experimentally quantified in this work. The high correlation between the base-buffering capacity and the content of organic matter due to the deprotonation of functional groups with the corresponding pKa values of specific and nonspecific organic acids was noted above. The values of soil pH in most horizons are close to 6; therefore, the weakest carboxyl groups, the NH$_2$ groups of amino acids, and the phenol hydroxyls should participate in the deprotonation reactions occurring during the titration.

According to the data of Russian and foreign authors, the amount of these functional groups strongly varies depending on the type of the groups and among the soils and horizons; however, it is generally in the range 2−10 mmol/g C$_{org}$ for carboxylic groups and phenol hydroxyls [17, 18, 35, 44]. The content of C$_{org}$ in the AY and buried AY horizons is 3−5% and thus can ensure the base-buffering capacity of 60 to 500 mmeq/kg, which is comparable to the experimentally found value of the total base-buffering capacity (100−150 mmeq/kg).

In the lower horizons, the content of organic matter decreases to 1% or even lower, because the Tyurin method of determining C$_{org}$ assesses the oxidizability that in the gleyed horizons is related not only to the presence of organic matter. This amount of organic matter cannot ensure the base buffering, which varies from 30 to 90 mmeq/kg in the AYB, BMg, and Dg horizons. Hence, other buffer reactions (unidentified in this work) also occur in these horizons during the base titration. These reactions can include the deprotonation of other clay minerals than kaolinite and illite, in particular, interstratified illite-chlorites and chlorite-vermiculites, whose contents could not be determined by the used procedure and for which no literature data are available on the titration of suspensions. If the supposition about the presence of amor-

phous and poorly crystallized aluminosilicates in the mineral horizons is true, their surface hydroxyl groups can also participate in deprotonation.

In addition, the calculation was based on the supposition that the SSA is 100 m^2/g for Fe hydroxides and 20 m^2/g for illite. In reality, both of these values and, hence, the contributions of the corresponding reactions to the base buffering could be significantly higher.

From the obtained results, it may be concluded that the calculated contributions of separate reactions to the base buffering of the studied soils should be considered as preliminary.

CONCLUSIONS

(1) In gleyic gray-humus soils developed in brook floodplains, reliable direct correlations are revealed between the acid-buffering capacity and the content of exchangeable bases and between the acid-buffering capacity and the content of C_{org}, which is atypical for podzolic and bog-podzolic soils. This tendency can be related to the high saturation degree of the SEC in gleyic gray-humus soils and, hence, the low binding energy of exchangeable bases to the soil solid phase, which favors their displacement by protons during the titration.

(2) At the interaction with an acid, the major amount of protons (>80%) is consumed for the displacement of exchangeable bases in the mineral horizons and for the displacement of exchangeable bases and the dissolution of Ca oxalates in the organic horizons. In the O and AY horizons, Mn compounds make a significant contribution (2−15%) to the acid-buffering. The buffer reactions with the participation of Al compounds make up from 0.5 to 1−2% of the total buffering, and the protonation of the surface OH groups of kaolinite consumes 2−3% of the total buffering capacity.

(3) The deprotonation of OH groups on the surface of Fe hydroxides (9−43%), the deprotonation of OH groups on the surface of illite crystals (3−19%), and the dissolution of unidentified, probably amorphous, aluminosilicates (9−14%) are the most significant buffer reactions, whose contributions were quantified during the interaction with a base. The contribution of the deprotonation of OH groups on the surface of kaolinite particles is lower (1−5%), probably because of the small specific surface area of this mineral, and that of the dissolution of Fe compounds is insignificant.

(4) The obtained correlations and the significant decrease in buffering after the Tamm and Mehra−Jackson treatments indicate that nonsilicate Fe and Al compounds in the studied soils are among the most important factors controlling the values of acid−base buffering, especially in the BMg and Dg horizons, due to the deprotonation of the surface hydroxyl groups.

(5) In the AY horizon, the acid−base buffering capacity of soil in the rhizosphere is higher than beyond the rhizosphere because of the higher contents of organic matter and nonsilicate Fe and Al compounds.

REFERENCES

1. O. A. Amel'yanchik and L. A. Vorob'eva, "Acid components of water and salt extracts from podzolic soils," Eurasian Soil Sci. **36** (3), 266−276 (2003).

2. L. A. Vorob'eva, *Chemical Analysis of Soils* (Moscow State University, Moscow, 1998) [in Russian].

3. N. Yu. Goncharuk, "Soil map of the Central Forest Nature Reserve and regularities of the spatial distribution of soils," Tr. Tsentr.-Lesn. Zapoved., No. 4, 195−219 (2007).

4. L. A. Grishina and T. A. Baranova, "The impact of acid rains on the properties of soils of forest ecosystems in the southern taiga zone," Pochvovedenie, No. **10**, 121−136 (1990).

5. E. A. Dmitriev, *Mathematical Statistics in Soil Science* (Moscow State University, Moscow, 1995) [in Russian].

6. S. E. Ivanova, Candidte's Dissertation in Biology (Moscow, 1999).

7. S. E. Ivanova, D. V. Ladonin, and T. A. Sokolova, "Experimental study of acid-base buffering reactions in pale-podzolic soil," Eurasian Soil Sci. **35** (1), 61−70 (2002).

8. I. V. Ishkova, E. S. Rusakova, I. I. Tolpeshta, and T. A. Sokolova, "Soils of slopes and bottomland positions of a small stream valley in the Central Forest Reserve: chemical properties and clay mineralogy," Moscow Univ. Soil Sci. Bull. **65** (3), 99−106 (2010).

9. *Acid Precipitations and Forest Soils,* Ed. by V. V. Nikonov and G. N. Koptsik (Kola Scientific Center, Russian Academy of Sciences, Apatity, 1999) [in Russian].

10. *Classification and Diagnostic System of Russian Soils* (Oikumena, Smolensk, 2004) [in Russian].

11. *Classification and Diagnostics of Soils of the Soviet Union* (Kolos, Moscow, 1977) [in Russian].

12. G. N. Koptsik and E. D. Silaeva, "Buffer capacity of forest substrates to acid atmospheric precipitation," Pochvovedenie, No. **8**, 954−962 (1995).

13. Y. G. Maksimova, Candidate's Dissertation in Biology (Moscow, 2013).

14. Y. G. Maksimova, N. N. Maryakhina, I. I. Tolpeshta, and T. A. Sokolova, "The acid-base buffer capacity of podzolic soils and its changes under the impact of treatment with the Mehra-Jackson and Tamm reagents," Eurasian Soil Sci. **43** (10), 1120−1131 (2010).

15. *Minerals: Handbook* (Nauka, Moscow, 1992), Vol. 4, No. 1.

16. *Minerals: Handbook* (Nauka, Moscow, 1992), Vol. 4, No. 2.

17. D. S. Orlov, *Humic Acids of Soils and a General Theory of Humification* (Moscow State University, Moscow, 1990) [in Russian].

18. D. S. Orlov, *Soil Chemistry* (Moscow State University, Moscow, 1992; Oxford & IBH, New Delhi, 1992).

19. D. L. Pinskii, *Ion-Exchange Processes in Soils* (Pushchino, 1997) [in Russian].

20. *Regulatory Role of Soil in the Activity of Taiga Ecosystems,* Ed. by G. V. Dobrovolskii (Nauka, Moscow, 2002) [in Russian].

21. A. A. Rode, "Some data on physicochemical properties of water-soluble substances in forest substrates," Pochvovedenie, No. 3, 103−125 (1941).

22. E. S. Rusakova, I. V. Ishkova, I. I. Tolpeshta, and T. A. Sokolova, "Acid-base buffering of soils in transitional and transitional-accumulative positions of undisturbed southern-taiga landscapes," Eurasian Soil Sci. **45** (5), 503−513 (2012).

23. T. A. Sokolova, I. I. Tolpeshta, E. S. Rusakova, and Yu. G. Maksimova, "Clay minerals in the stream floodplain soils in undisturbed landscapes of the southern taiga (with the soil of the state Central Forest Reserve as an example)," Moscow Univ. Soil Sci. Bull. **68** (4), 154−163 (2013).

24. V. O. Targulian and M. I. Gerasimova, *World Correlation Database of Soil Resources as the Base for International Classification and Correlation of Soils* (KMK, Moscow, 2007) [in Russian].

25. I. I. Tolpeshta, Doctoral Dissertation in Biology (Moscow, 2010).

26. E. V. Shamrikova, T. A. Sokolova, and I. V. Zaboeva, *Acid-Base Buffer Capacity of Podzolic and Wetland Podzolic Soils of the Northeast of European Russia* (Ural Branch, Russian Academy of Sciences, Yekaterinburg, 2005) [in Russian].

27. J. Chorover and G. Sposito, "Surface charge characteristics of kaolinitic tropical soils," Geochim. Cosmochim. Acta **59** (5), 875−884 (1995).

28. J. Chorover and G. Sposito, "Dissolution behavior of kaolinitic soils," Geochim. Cosmochim. Acta **59** (15), 3109−3121 (1995).

29. K. Cromack, "Calcium oxalate accumulation and soil weathering in mats of the hypogeus fungus *Histerangium corassium*," Soil Biol. Biochem. **11** (5), 463−468 (1979).

30. C. T. Driscoll, "A procedure for the fractionation of aqueous aluminum in dilute acidic waters," Int. J. Environ. Anal. Chem. **16**, 267−283 (1984).

31. Q. Du, Z. Sun, and H. Tang, "Acid-base properties of aqueous illite surfaces," J. Colloid Interface Sci. **187**, 221−231 (1997).

32. M. E. Essington, *Soil and Water Chemistry* (CRC Press, Boca Raton, FL, 2004).

33. W. C. Graurstein, K. Cromack, and P. Solling, "Calcium oxalate: occurrence in soils and effect on nutrient and geochemical cycle," Science **198** (323), 1252 (1977).

34. J. Harsh, J. Chorover, and E. Nizeyimana, "Allophane and imogolite," in *Soil Mineralogy with Environmental Application,* Ed. by J. B. Dixon and D. G. Schulze (Soil Science Society of America, Madison, WI, 2002), pp. 291−322.

35. M. H. B. Hayes, "Influence of acid/base status on the formation and interactions of acids and bases in soil," in *Transactions of the 13 Congress of International Society of Soil Scientists* (Hamburg, 1986), Vol. 5.

36. F. J. Huertas, C. Lei, and R. Wollast, "Mechanism of kaolinite dissolution at room temperature and pressure: Part 1. Surface speciation," Geochim. Cosmochim. Acta **62** (3), 417−431 (1998).

37. F. J. Huertas, C. Lei, and R. Wollast, "Mechanism of kaolinite dissolution at room temperature and pressure: Part II. Kinetic study," Geochim. Cosmochim. Acta **63** (19/20), 3261−3275 (1998).

38. B. S. James and S. J. Riha, "pH buffering in forest soil organic horizons: relevance to acid precipitation," J. Environ. Qual. **15**, 229−234 (1986).

39. A. M. L. Kraepiel, K. Keller, and F. M. M. Morel, "On the acid-base chemistry of permanently charged minerals," Environ. Sci. Technol. **32**, 2829−2838 (1998).

40. N. Paxeux and M. Wedborg, "Acid-base properties of aquatic fulvic acid," Anal. Chim. Acta **169**, 87−98 (1985).

41. G. S. P. Ritchie and A. M. Posner, "The effect of pH and metal binding on the transport properties of humic acids," J. Soil Sci. **33**, 233−247 (1982).

42. D. L. Sparks, *Soil Physical Chemistry,* 2nd ed. (CRC Press, Boca Raton, FL, 1999).

43. G. Sposito, *The Environmental Chemistry of Aluminum* (CRC Press. Boca Raton, FL, 1989).

44. F. J. Stevenson, *Humus Chemistry, Genesis, Composition, Reactions* (Willey, New York, 1982).

45. W. Stumm, *Chemistry of the Solid-Water Interface* (Wiley, New York, 1992).

46. E. Tertre, S. Castet, G. Berger, M. Loubet, and E. Giffaut, "Surface chemistry of kaolinite and Na-montmorillonite in aqueous electrolyte solutions at 25 and 60°C: experimental and modeling study," Geochim. Cosmochim. Acta **70**, 4579−4599 (2006).

47. B. Ulrich, "An ecosystem approach to soil acidification," in *Soil Acidity,* Eds. by B. Ulrich and M. E. Summer (Springer-Verlag, Berlin, 1991).

48. B. Ulrich, "Soil acidity and its relation to acid deposition," in *Effects of Accumulation of Air Pollutants in Forest Ecosystems* (D. Reidel, Dordrecht, 1983), pp. 127−146.

49. B. Ulrich, R. Mayer, and P. K. Khanna, "Chemical changes due to acid precipitation in a loess-derived soil in Central Europe," J. Soil Sci. **130** (4), 193−199 (1980).

50. G. F. Vance and M. B. David, "Spodosol cation release and buffering of acid inputs," J. Soil Sci. **151** (5), 363−368 (1991).

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