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Articles

Spatial heterogeneity of soil acidity properties in peatlands of Western Siberia

Tatiana V. Raudina — National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia
Georgyi I. Istigechev — National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia
Sergey V. Loiko — National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

The formation of significant amounts of low molecular weight (LMW) water-soluble organic compounds, which are highly reactive compounds of a non-specific nature, is a feature of the biogeocenoses of the North. Soil acidity, which in turn depends on LMW organic acids content, regulates the migration ability of compounds in landscapes and the bioavailability of nutrients. With an increase in the active layer thickness of peat soils in Western Siberia in the course of climate warming, new portions of LMW water-soluble organic compounds will enter, which will be quickly processed by microorganisms into CH4 and CO2. Five key sites were considered, located within thawed oligotrophic, frozen mound and polygonal bogs. The analysis of zonal patterns of acidity changes in the waters of peat soils indicates an increase in the pH in the series: northern taiga<forest tundra<southern tundra. A feature of the most acidic soils of the northern taiga is the high content of low molecular weight organic acids, the accumulation of which is determined by the species diversity of the vegetation cover and high humidity. The decrease in the content of acids in the soils of the southern tundra is due to changes in climatic conditions and, accordingly, the quality and quantity of organic material involved in the processes of mineralization and humification. Relationships between the pH of the soil solution and such parameters as the specific conductivity, the content of dissolved organic carbon, and the specific UV-absorbency (SUVA245) were revealed. Comparison of the acidity indices of peat soils of the zonal series of the European Northeast with similar ones obtained for the study area of Western Siberia showed that, at the same values of actual acidity, the exchangeable acidity values of peat soils of Western Siberia are slightly lower.

Corresponding author: Tatiana V. Raudina (tanya_raud@mail.ru)

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Keywords

Soil acidity, zonal patterns, Histosols, soil waters, frozen mound and polygonal bogs, Western Siberia Lowland

Introduction

West Siberian wetlands significantly affect the fluxes of dissolved organic matter and related elements from land to surface waters and further to the Arctic Ocean. The impact of warming on bog landscapes is manifested primarily through the active layer thickness (ALT), which, as a result, will affect the chemical parameters of the watercourses draining them (Tank et al. 2012, 2016; Striegl et al. 2005; Rember and Trefry 2004; Prokushkin et al. 2011; Mann et al. 2012; Grosse et al. 2016; Holmes et al. 2013). An increase in the ALT and a change in the hydrological regime is especially important for frozen bogs, which occupy up to 29% of the catchment area in the southern tundra and up to 40–70% in the northern taiga (Liss et al. 2001; Novikov et al. 2009; Ilina et al. 1985) and have a significant potential for further ALT growth due to the thawing depth increasing. For these reasons, peat soils, which are the initial link in the formation of the runoff of substances and elements from bogs, are given significant attention when solving this problem (Olefeldt and Roulet 2012; Charman et al. 2013; Quinton and Baltzer 2013; Muller et al. 2015; Morison et al. 2017; Raudina et al. 2017, 2018).

To assess the current state of soils, the characteristic of organic matter is important. A feature of the biogeocenoses of the North is the formation of significant amounts of water-soluble low-molecular-weight organic compounds (LMWOCs), which determine soil acidity. The LMWOCs are the most reactive compounds of a non-specific nature among organic substances, which are rapidly degraded by heterotrophic bacteria causing net heterotrophic conditions and CO2 emission to the atmosphere (Ask et al. 2009; Lapierre et al. 2013). Between 10% and 40% of these organic compounds in the surface and soil waters in the boreal zone may be available for bacterial uptake over a time frame of several weeks (Berggren et al. 2010; Roehm et al. 2009).

The importance of the composition and content of the LMWOCs in peat soils (Histosols according to IUSS WRB, 2014) is indicated by the fact that the amount of dissolved organic carbon largely determines pH and specific conductivity due to low molecular weight organic acids. In turn, acidity regulates the migration ability of compounds in landscapes and the bioavailability of nutrients. In this regard, knowledge of the nature of soil acidity is of general biological and theoretical significance, since it allows one to determine the processes of functioning of terrestrial ecosystems and their stability. On the territory of the European North, it has been shown that the acid properties and water-soluble low-molecular-weight organic acids (LMWOAs) content of peat soils change from north to south, and are also quite contrasting within the bog microtopography elements (Shamrikova et al. 2012, 2015). Therefore, this work is aimed at studying the spatial heterogeneity of acidity and the factors that form it within the frozen bog's ecosystems along the latitudinal gradient.

Materials and methods

Sampling was performed along the latitudinal transect of Western Siberia Lowland (WSL) whose northern part is comprised of taiga zone with sporadic (Kogalym, Kg), discontinuous permafrost (Khanymey, Kh; Pangody, Pg; Urengoy, Ur) and forest-tundra biome with continuous permafrost (Tazovsky, Tz) (Fig. 1). The first key area occupies the northern part of the range of thawed ombrotrophic bogs. The next three are flat-mound bogs, and the third is located in the southern part of polygonal bog areas. The main mineral substrates underlying frozen peat layers of the WSL are quaternary clays, sands, and alevrolites, which were subjected to strong influence of aeolian processes at the beginning of the Holocene (Velichko et al. 2011). From the south to the north, the average annual temperature ranges from -4.4°C to -9.1°C with an annual precipitation of 594 to 365 mm. Vegetation of three studied bog types is essentially oligotrophic (poor in nutrients) which indicates ombrotrophic conditions (i.e. lack of groundwater input and lateral surface influx).

The bog waters were sampled in 2014 and 2015 from a 40×40×80 cm pit at the active layer – permafrost boundary. In mounds and dry depressions, the pit was usually filled with water after digging. In hollows and fens, 20×20×20 cm pits were filled immediately by the surrounding water. The time of filling the pit and the volume of inflowing water were smaller on mounds. The surface of depressions is always 0.5 to 0.7 m below that of mounds, and the difference in the active layer water horizon between mounds and depressions is between 0.3 and 0.4 m. As such, the input of water from depressions to mounds is not possible. The water-table depth (from the soil surface) was between 0 and -10 cm in depressions and between -15 and -40 cm in mounds. Collected waters were filtered through single-use Minisart filter units (0.45 µm poresize, Sartorius, acetate cellulose filter). The first 20 mL of filtrate was discarded. The pH and specific conductivity were measured in the field using a combined electrode with uncertainty of ±0.02 units (WTW MULTI 3430 SET). The dissolved organic carbon (DOC) was analyzed using a Carbon Total Analyzer (Shimadzu TOC VSCN) with an uncertainty better than 3%. The UV absorbance of the filtered samples was measured at 245 nm using 10-mm quartz cuvette on a Cary-50 spectrophotometer. The specific UV-absorbency (SUVA245, L mg−1 m−1) was used as a proxy for aromatic C, molecular weight and source of dissolved organic matter (DOM) (Weishaar et al. 2003; Ilina et al. 2014; Peacock et al. 2014 and references therein).

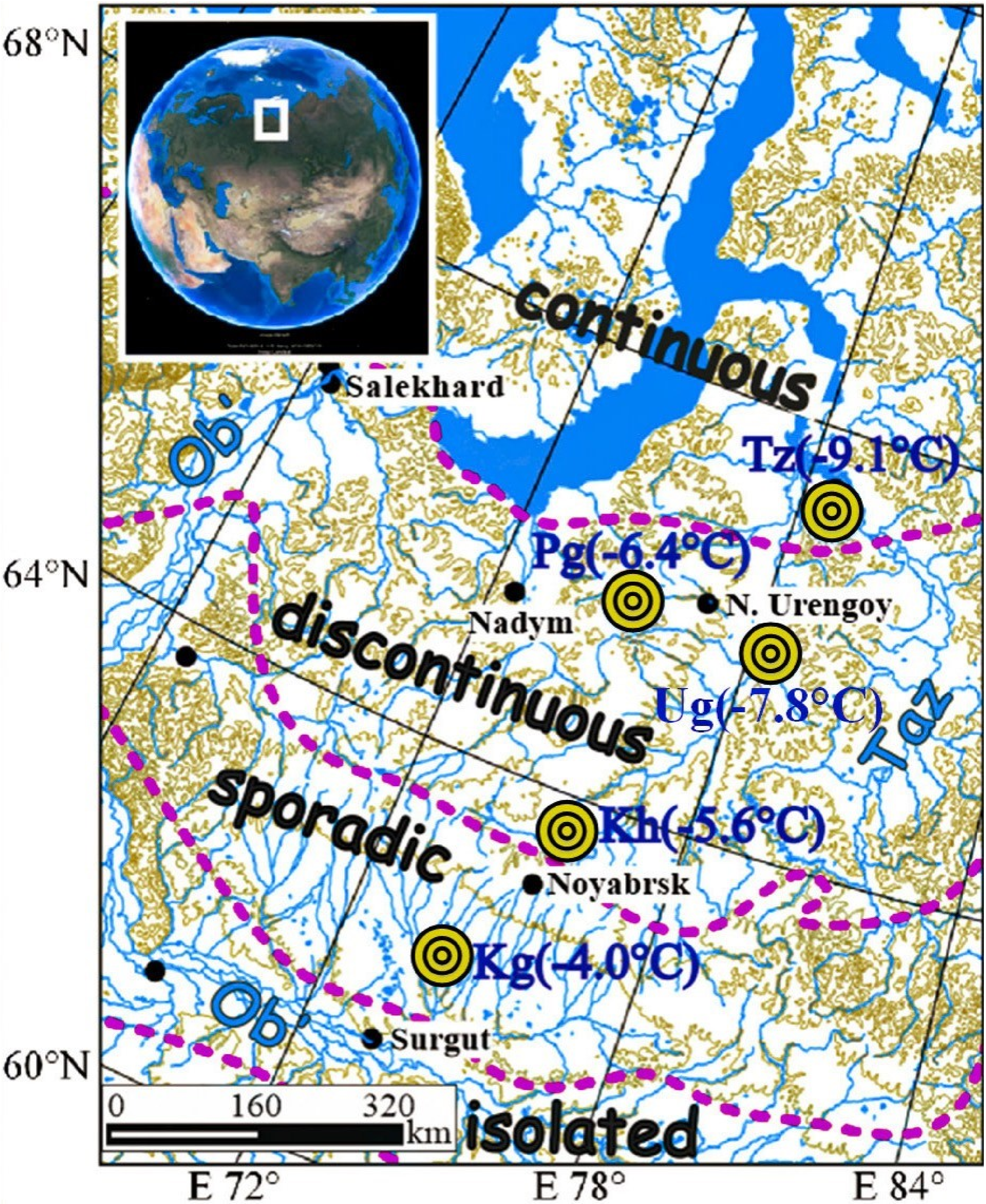

Figure 1. *Map of the study sites with permafrost boundaries: Kogalym (Kg), Khanymey (Kh), Pangody (Pg), Urengoy (Ur), and Tazovsky (Tz). The mean annual temperatures are given in parentheses.*

Results and discussion

In the waters of peat soils, the main source of acidity is the protons released during the dissociation of organic acids in dissolved or undissolved form, as well as in the form of colloidal organic matter. The pHH2O values in all samples turned out to be higher than pHKCl. The values of the integral indicators of acidity (pHH2O and pHKCl) indicate that in the studied zonal series, the northern taiga–forest tundra– southern tundra showed a tendency to increase the pH (Fig. 2). Peat soils of the northern taiga are characterized by the lowest values (pHH2O 3.2–4.1, pHKCl 2.4–3.1), while soils of the southern tundra have the maximum values (pHH2O 3.9–5.6, pHKCl 2.7–4.4). This conclusion agrees with the results obtained in the study of zonal series of automorphic soils on loose silicate rocks (typical podzolic, gley-podzolic, and surface-gley tundra soils) of the European northeast from the middle taiga to the southern tundra (Shamrikova et al. 2013). In particular, it was shown that the subzonal feature of the most acidic soils of the northern taiga is the high content of LMOAs, including aliphatic hydroxy acids. Automorphic loamy soils are characterized by a high content and diversity of low molecular weight aliphatic unsubstituted acids (pKa 4.5–6.0). An increase in soil moisture both in the latitudinal-zonal direction and within individual zones (subzones) determines the accumulation of low molecular weight acids. This feature can be explained by the slowdown in the reactions of dehydration of hydroxy acids to unsaturated acids, as well as their oxidation to polybasic acids under conditions of higher humidity. The decrease in the content of acids in the soils of the southern tundra is due to a sharp decrease in the species diversity and abundance of acid-forming microorganisms, which is associated with low temperatures, as well as changes in the quality and quantity of organic material involved in the processes of mineralization and humification.

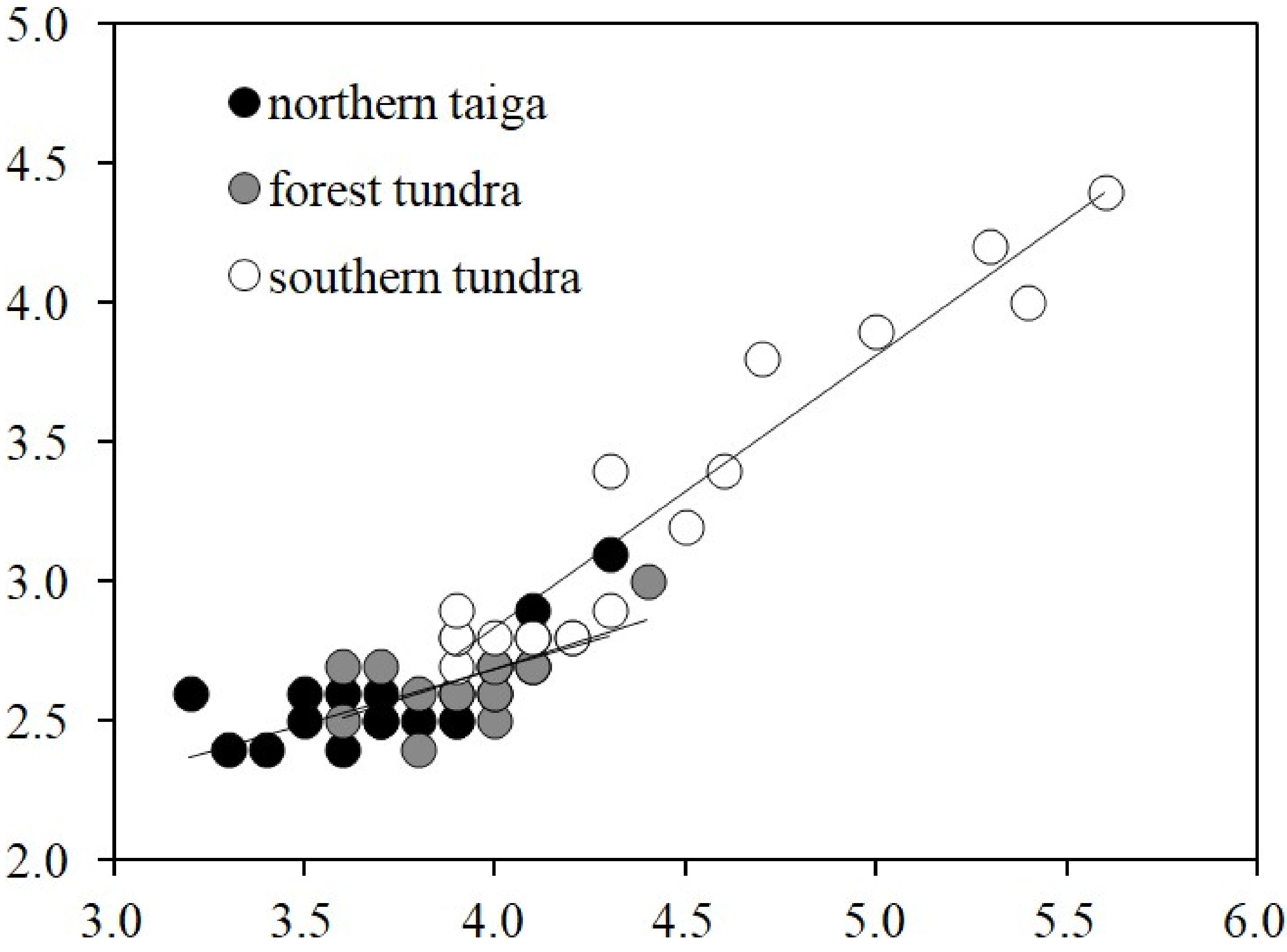

Figure 2. *Relationship between pHH2O values (x-axis) and pHKCl (y-axis).*

Previously proposed approaches were used to reveal the heterogeneity of the acidic properties of peat soils in Western Siberia. The methodology was developed by analyzing the parameters of the compiled database of taiga and tundra loamy soils of the European Northeast (Shamrikova et al. 2013). In particular, for soils of the zonal series, we analyzed the parameters of the equations of linear pair regressions, as well as the tightness of the relationships between the indicators of the acid-base state. It is shown that the entire set of organic horizons of peat soils is characterized by a close direct linear correlation between the considered indicators (pHKCl=0.89*pHH2O–0.75, *r*= 0.92), which can be explained by the cation exchange reaction. The content of any cation in the exchange form increases with its concentration in the equilibrium solution (Orlov 1992). Since in this case H+ is displaced by K+ (monovalent cation), a linear dependence between the concentration of H+ in the solution and in the soil-absorbing complex can be expected. Moreover, the tangent of the slope to some extent reflects the selectivity of the soil in relation to H+ compared to K+. The closeness of the slope tangent to 1 indicates approximately equal selectivity of organic horizons for K+ and H+.

An analysis of the zonal patterns of changes in acidity indicators revealed that the highest correlation coefficients between pHH2O and pHKCl are observed in the organogenic horizons of the soils of the southern tundra (pHKCl=0.97pHH2O-1.04, *r*= 0.96). In the KCl extracts of these objects, all compounds that pass into aqueous extracts, and additionally exchangeable acidic components, are probably dissolved. For the soils of the forest-tundra and northern taiga, the relationship between the pHH2O and pHKCl values remains direct and can formally be approximated by a linear regression equation. In this case, there is a decrease in *r* between these indicators to 0.67, and the tangent of the slope of the straight line decreases to ~ 0.4. The equations for the soils of the forest-tundra and northern taiga are as follows: pHKCl=0.44pHH2O+0.95 и pHKCl=0.40pHH2O+1.11. The lower values of the correlation coefficient for more acid soils compared to other soils were already noted earlier (Shamrikova et al. 2013) and are associated with the transfer of additional amounts of Al3+ and Fe3+ into solution under conditions of a strongly acidic reaction of KCl extracts from organometallic complexes. The presence of strongly acidic exchange components in salt extracts in the relationship equations reflects the free term. The presence of strongly acidic exchange components in salt extracts in the relationship equations reflects the free term. The maximum content of such components was noted in the soils of the northern taiga; their transition to the liquid phase of KCl suspensions (in contrast to aqueous suspensions) is facilitated by the high ionic strength of the solution and cation exchange reactions.

The revealed differences between pHH2O and pHKCl, as well as the relationships between them, are explained by the difference in the concentration of elements in soil solutions (Fig. 3). The organogenic horizons of more acidic soils contain much less bases, and much more exchangeable H+ passes into the salt extract, which ensures a decrease in pHKCl. It was also found that more acidic soils contain stronger LMWOCs in water extracts from organic horizons. A significant part of the points characterizing the pHKCl of soils in the northern taiga and southern tundra (Fig. 2) lies below the critical pH value for Al3+ and Fe3+ mobility (4.2 and 3.2 respectively according to Ulrich 1983). In these samples, Al3+ and, possibly, Fe3+ are released from complexes with organic ligands and pass into solution, where they enter into a hydrolysis reaction with the formation of H+. Thus, the trigger mechanism for the differences between the studied objects is the different amount of H+ displaced by K+ into the salt extract. According to Tolpeshta and Sokolova (2009), the content of Al3+ in the organic horizons of automorphic podzolic soils, determined directly in the KCl extract by the ICP method, is 1–3 orders of magnitude lower compared to (semi)hydromorphic, more acidic soils. Therefore, in automorphic soils of the northern taiga and southern tundra, in addition to cation exchange, another mech- anism of Al3+ transfer to the salt extract plays a significant role. Namely, its release from organoaluminum complexes leads to a decrease in the correlation between pHH2O and pHKCl.

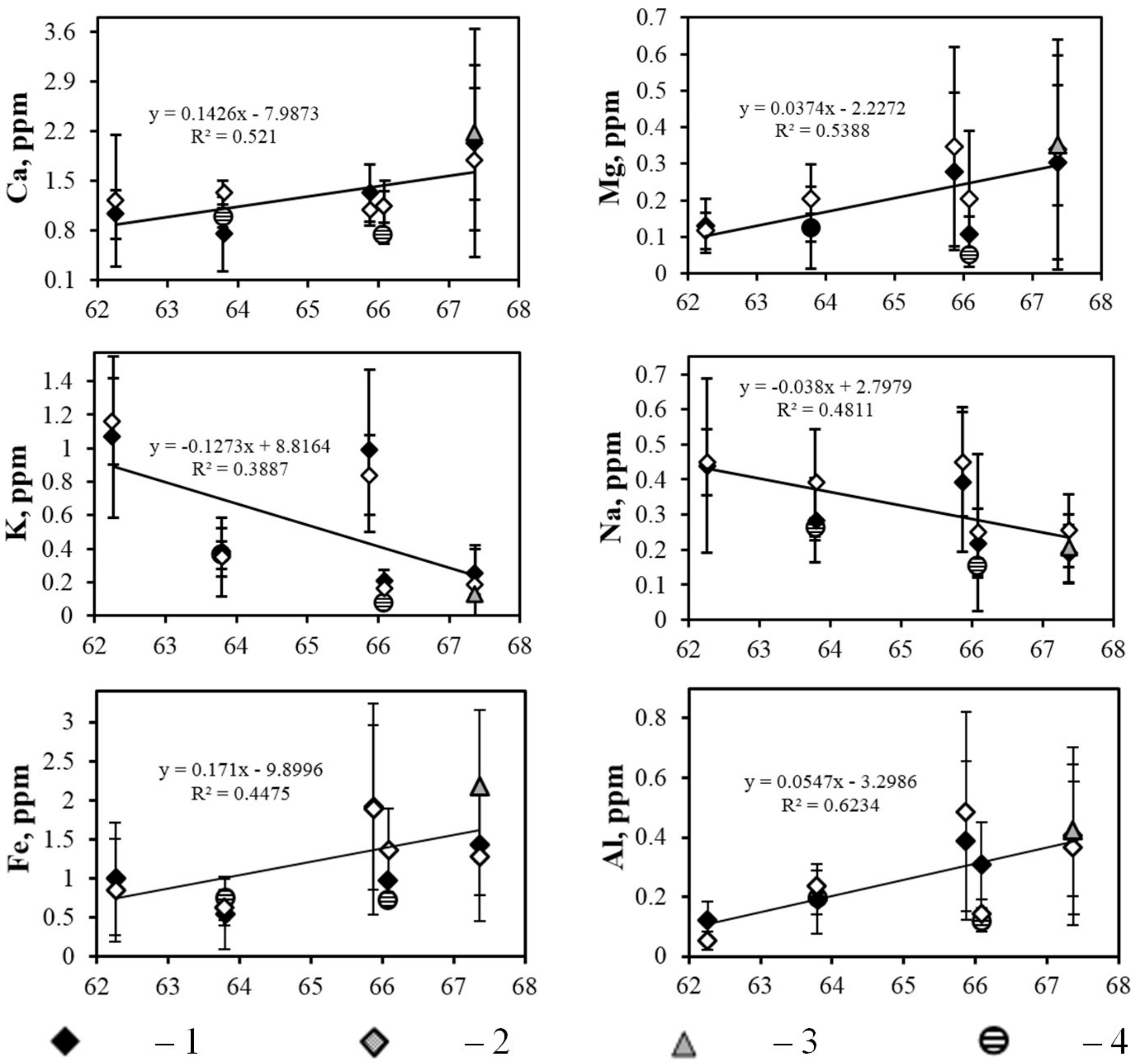

Figure 3. *Latitudinal trends in average concentrations of elements in soil solutions, taking into account bog microtopography:* ***1*** *– mounds/polygons;* ***2*** *– hollows;* ***3*** *– interpolygonal cracks of polygonal bog;* ***4*** *– thermokarst subsidence.*

Using a previously compiled database, we built a relationship between the acidity indices for peat soils of a similar zonal series in the European Northeast and compared it with the results obtained for the studied territory of Western Siberia. The dependence equations are as follows pHKCl=0.94pHH2O-0.58, r = 0.95 (n=150) and pHKCl=0.89pHH2O-0.75, r= 0.92 (n=56), respectively. The tangents of the slopes of both dependences are close (~ 0.9). However, the value of the free term for the sample characterizing the peat soils of the Komi Republic is ~0.2–0.3 pH units higher (Fig. 4). At the same values of actual acidity (pHH2O), the exchangeable acidity (pHKCl) values of peat soils in Western Siberia are slightly lower compared to similar soils in the European part of Russia. Probably, protons in salt extracts appear as a result of an exchange reaction upon replacement by potassium cations. Moreover, in the solid phase, the source of such protons can be acids that do not pass into the liquid phase. Increased content of protons in the solid phase capable of exchanging with potassium ions may be, among other things, a consequence of the low amount of Ca^{2+} and Mg^{2+} capable of neutralizing acidic compounds. One of the reasons for the lower pHKCl values may be the low content of various forms of basic cations involved in the neutralization of acidic compounds. In addition, the soils of Western Siberia generally contain a higher content of acidic agents, such as organic acids and inorganic components (Al^{3+} and Fe^{3+} ions). In the studied frozen peat deposits of Western Siberia, the reserves of iron and aluminum in the upper part are higher than in the lower part. In the northeast of the European part of Russia, the opposite picture is observed.

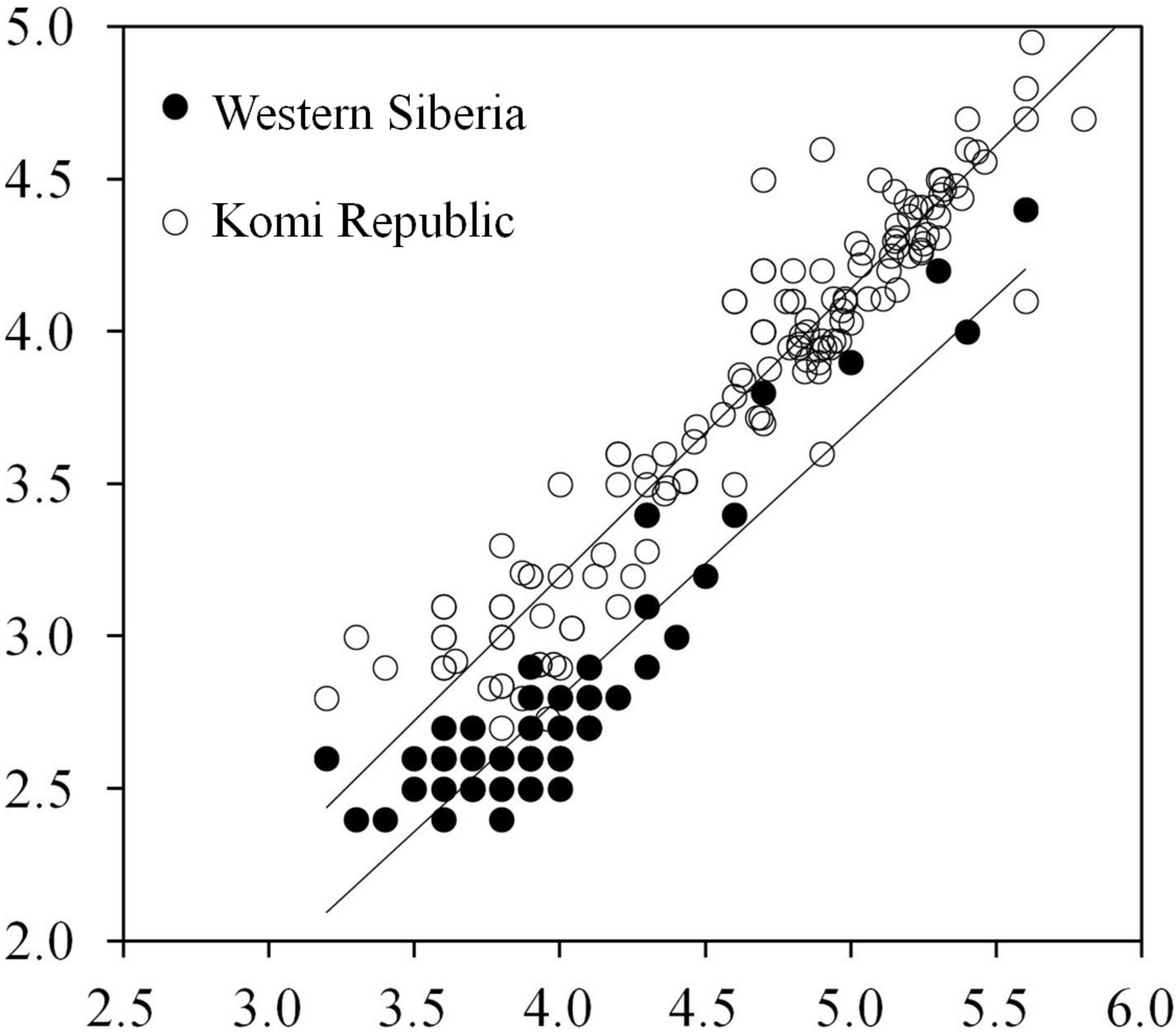

Figure 4. *Relationship between pHH2O values (x-axis) and pHKCl (y-axis).*

Statistical relationships were also identified between individual soil parameters and pH values for the studied key areas. Figure 5 shows the relationship between the content of dissolved organic carbon and specific conductivity. According to the degree of correlation of these parameters, the studied key areas can be divided into four groups: 1) $R^2 \geq 0.9$; 2) $0.9 > R^2 \geq 0.6$; 3) $0.6 > R^2 \geq 0.4$; 4) $R^2 < 0.4$.

The greatest relationships are typical for the key site "Kogalym", the northern part of the area of thawed oligotrophic bogs (Fig. 5). Soil waters are characterized by an almost linear relationship

($R2$=0.96) between the considered parameters (the higher the DOC content, the greater the specific conductivity). In the waters of these soils, the specific conductivity is entirely determined by the content of organic matter, and the influence of other charged particles is minimal. Such a relationship also indicates the composition of DOC, which is mainly represented by fulvic acids, as indicated by the SUVA254 value (from 2 to 4) (Fig. 6). With an increase in specific conductivity, an increase in SUVA254 is noted, which indicates an increase in the role of weakly converted high-molecular protohumic substances.

The next group ($0.9>R2\geq0.6$) combines the key areas "Khanymey" and "Urengoy" with mound bogs. Figures 5 and 6 show that with increasing specific conductivity comes an increase in DOC and SUVA254 (except for the "Urengoy" site).

The third group includes the key sites "Khanymey" with a flat-mound bog and "Tazovsky". About half of the sample is characterized by the presence of a relationship between the DOC content and specific conductivity. This may indicate both a strong influence of inorganic ions and a significantly more hydrophobic organic matter.

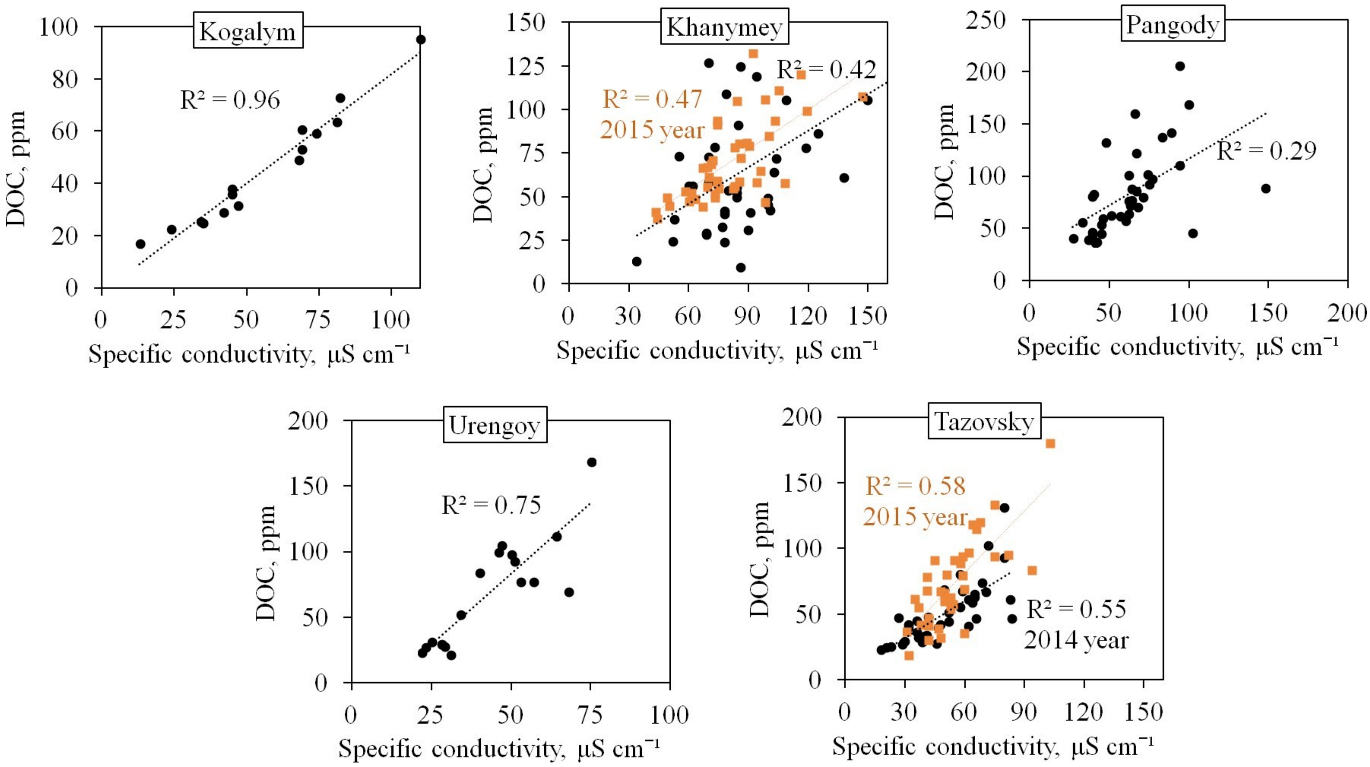

Figure 5. *Relationship between DOC content and soil water conductivity in five key sites*

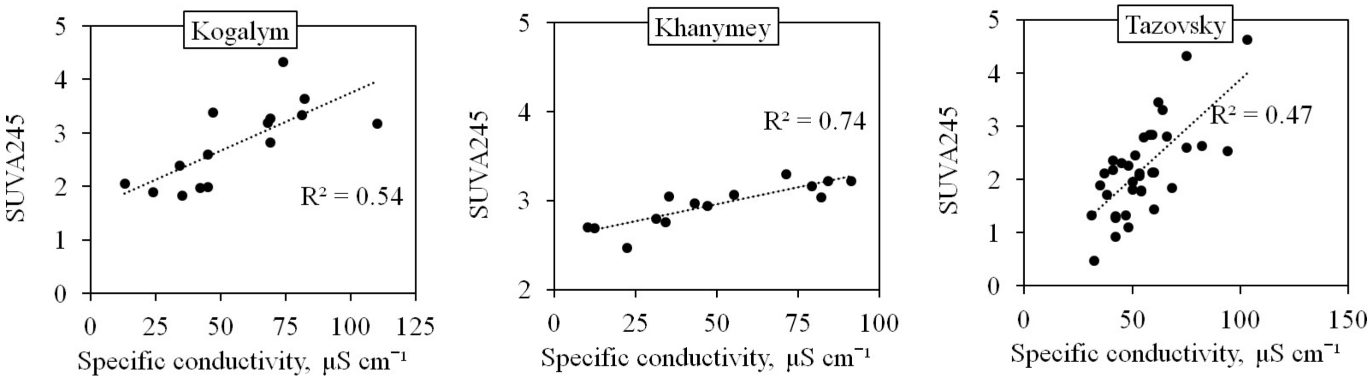

Figure 6. *Key sites showing the relationship between SUVA254 and soil water conductivity.*

For the "Pangody" site, no significant relationship was found between the parameters under consideration, which means that the specific conductivity is determined not by organic matter, but by inorganic charged particles. Mainly highly or medium decomposed peat (hemic or sapric) occurs in this area, like the others. At the same time, it has the smallest average peat thickness, and the mineral horizons have a loamy composition, which leads to a significant contribution of the inorganic component to the water composition.

Obviously, the presence of a relationship between the DOC content and specific conductivity should also lead to the presence of a relationship between the pH and DOC. However, only two key sites showed relationships between these parameters for soil waters (Fig. 7). At the site "Kogalym" with an increase in the content of DOC, the pH value decreases ($R2$=0.58) in soil water. This result indicates that, in contrast to specific conductivity, pH values depend to a lesser extent on the content of organic substances. Perhaps this is due to the contribution of aluminum and iron compounds to the formation of soil acidity (mentioned above), as well as hydrocarbonates. At the same time, their significantly colloidal status may cause their lesser effect on specific conductivity than on pH (Pokrovsky et al. 2016).

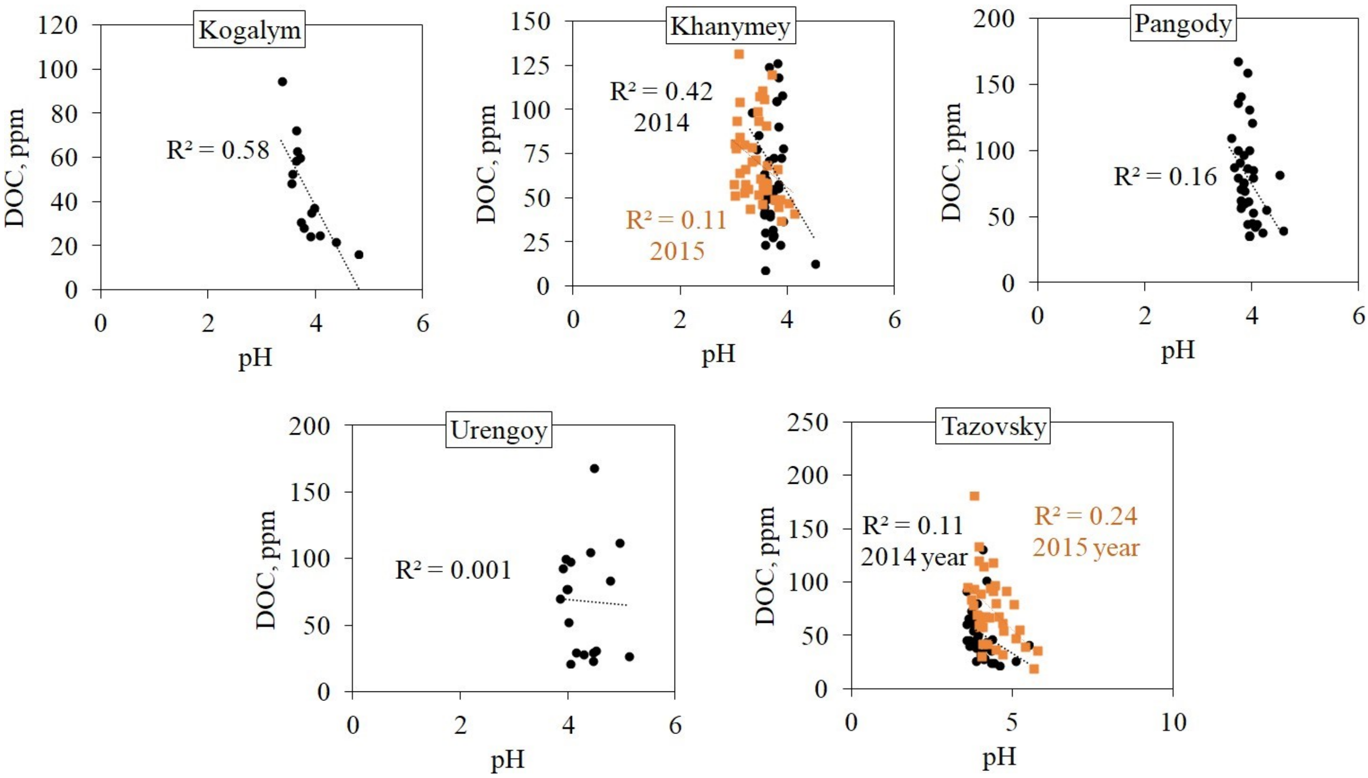

Figure 7. *Relationship between DOC content and pH in soil waters of five key sites.*

The relationship between specific conductivity and pH is mediated through dissolved organic matter and is characterized by an intermediate form of the patterns described above. In general, an increase in electrical conductivity is accompanied by a decrease in pH. In addition, there are significant differences between the water parameters obtained in different years. This is probably due to the different conditions of the year. For example, it was previously shown that in some years the temporal (seasonal, interannual) variation in the indicators of the acid–base state of soils can be significantly higher than the spatial one (Shamrikova et al. 2011). The next reason may be differences in the genesis of soils in key areas. The bog massifs are somewhat different geomorphologically and, in addition, in 2014 the "Khanymey" site was less watered compared to the "Tazovsky" one.

Conclusions

It is shown that changes in the acid properties of peat soils in Western Siberia have zonal features. The values of the integral indicators of acidity indicate a trend towards an increase in the pH value in the studied zonal series: northern taiga<forest tundra<southern tundra. An increase in soil moisture both in the latitudinal-zonal direction and within individual zones (subzones) determines the accumulation of low molecular weight acids (primarily aliphatic hydroxy acids and phenolcarboxylic acids). The decrease in the content of acids in the soils of the southern tundra is due to a sharp decrease in the species diversity and abundance of acid-forming microorganisms due to severe temperatures, as well as a change in the quality and quantity of organic material. The revealed differences between pHH2O and pHKCl of soils, as well as the relationships between them, are explained by the difference in the element concentrations in soil solutions. The organogenic horizons of more acidic soils contain much less bases, and much more exchangeable H+ passes into the salt extract, which ensures a decrease in pHKCl. The obtained data also made it possible to establish a number of relationships between the pH of the soil solution and such parameters as specific conductivity, dissolved organic carbon content and the specific UV-absorbency (SUVA245). According to the degree of correlation of these parameters, the studied key areas can be divided into four groups: 1) $R2 \geq 0.9$; 2) $0.9 > R2 \geq 0.6$; 3) $0.6 > R2 \geq 0.4$; 4) $R2 < 0.4$. The amount of dissolved organic carbon in peat soils is largely determined by specific conductivity, and also partially by pH due to low molecular weight organic acids. Comparison of the acidity indices of peat soils of the zonal series of the European Northeast with similar ones obtained for the study area of Western Siberia showed that, at the same values of actual acidity, the exchangeable acidity values of peat soils of Western Siberia are slightly lower.

Acknowledgements

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