Redox potential and acidity of peat are key diagnostic physicochemical properties for the stratigraphic zones of a boreal raised bog

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SUMMARY

Redox potential and acidity are widely used to describe soil processes and to assess the state of soils, including peat soils. This study aimed to identify the main trends in the change of peat physicochemical properties with depth below the surface of a peat deposit. The research was carried out on the Ilas bog complex, Russia, which is typical for the South White Sea bog province. Changes in peat indicators (Eh, pH, botanical and elemental composition, the number of viable cells of the main groups of aerobic and facultative anaerobic microorganisms) with depth demonstrated that the redox regime of the studied peat deposit corresponded to the moderately reduced class of organogenic soils with Eh range 100–400 mV. There was an increase in pH (from 3.3 to 4.3) and a non-monotonic decrease in Eh (from 340 to 220 mV) with increasing depth within the deposit (up to 360 cm). These results were consistent with data on the elemental composition of peat and the number of viable cells of a typical boreal raised bog will serve as a theoretical basis for assessing the transformation of wetland ecosystems resulting from anthropogenic pressure or climatic changes within this geographical region.

KEY WORDS: acrotelm, Brusovitsa, catotelm, Ilas bog, ombrotrophic mire, peat microbial characteristics

INTRODUCTION

The land in northern latitudes is extensively covered by mires (Minayeva & Sirin 2012, Sirin et al. 2017, Tomson et al. 2018), with a predominance of raised bogs. Natural bogs are complex, self-regulating and evolving systems. constantly Their main components (e.g., flora and fauna, microbiota, aquatic environment, peat deposits) are closely interrelated, such that changing any of them can lead to a significant transformation of the entire system (Kuznetsov 2018). Recent environmental trends require the development of rapid assessment methods for the status of wetland ecosystems in terms of changes in their natural state, whether the changes are a consequence of global climatic processes (Gorham 1991, Heimann & Reichstein 2008) or triggered by direct intervention associated with human economic activity (Lindsay 2010, Luscombe et al. 2016, Heras & Infante 2018).

Currently, biological approaches in which the main source of information is the vegetation cover (Yurkovskaya 2018, Böhner *et al.* 2019, Kutenkov & Philippov 2019) are the most widely used assessment methods for wetlands. The composition of plant communities is determined primarily by

climatic and hydrological conditions, as well as by the regime and nature of mineral nutrition in the locality (Ivanov 1975, 1981). The transformation of bog plant communities can indicate changes in the aerated surface layer (acrotelm), but it cannot provide information rapidly because the response is often delayed; nor does it easily allow a reliable assessment of processes occurring in the underlying peat deposit (catotelm) (Rogova *et al.* 2011, Gonzalez *et al.* 2016, Zubov *et al.* 2019).

The functioning of bog ecosystems is based on the interactions of individual elements and a combination of chemical and biochemical processes (Rakovsky & Pigulevskaya 1978, Lishtvan et al. 1989, Bambalov 2005). This affects how the physical and chemical properties (e.g., bulk density, ash content, elemental composition, redox potential, pH, salinity) of their component peat and water change. Therefore, a combination of chemical and physicochemical methods can provide effective information on the state of the ecosystem as a whole, as well as on its individual components at different levels of the dimensional hierarchy; for example, on the state of a peat deposit by depth. Some physicochemical methods (for example, direct potentiometric and conductometric measurements)



do not require sample preparation, which opens the possibility of making fast measurements on undisturbed material in situ and thus avoiding the multiple disadvantages associated with transporting and storing samples (Zubov *et al.* 2019).

Considering the nature of processes and transformations occurring in peat (Lishtvan et al. 1989, Inisheva et al. 2016), the redox potential of the deposit is a clear candidate indicator for assessing its state. Redox potential (Eh) reflects the totality of factors responsible for the redox regime (e.g., oxygen content of the deposit, the state of soil chemical redox systems, and biochemical redox processes; Potter 1911, Kemmou et al. 2006, Tokarz & Urban 2015). It also depends, to some extent, on the acidity (pH) and mineralisation of pore water, which are the diagnostic properties used for gradation of mires according to the type of mineral nutrition (Shishov et al. 2004, Samoylik 2016). Eh and acidity can be measured directly in the natural environment, which makes them appropriate metrics for rapid assessment of the state of wetland ecosystems.

Redox potential and acidity are used widely in describing soil processes and assessing soil conditions (Snakin *et al.* 2001, Sabiene *et al.* 2010), in particular for hydrogenic soils (Tokarz & Urban 2015), which include peat deposits. Previous studies have associated fluctuations in acidity and redox potential values with changes in moisture content during periods of drying and flooding of the soil (Cogger *et al.* 1992, Balakhnina *et al.* 2010) and noted that they appear only in the acrotelm (Urquhart & Gore 1973). Smith & Patrick (1983) attributed the accelerated transformation of organic matter under such conditions to a change in redox potential.

An additional interest in the redox potential of peat bogs arises because it is sensitive to stresses on ecosystems such as pollution (Coleman *et al.* 1992, Fernandez *et al.* 2009, Frohne *et al.* 2011, Szafranek-Nakonieczna & Stepniewska 2015), so can be used to assess the processes occurring in characteristic layers of bogs in poorly studied areas such as the northern parts of European Russia (Urquhart & Gore 1973, Zhang *et al.* 2002, Szafranek-Nakonieczna & Stepniewska 2015).

A number of studies note relationships between Eh, soil pH and the number and structure of soil microbial communities (Billen 1973, Snakin & Dubinin 1980, Brzezinska 2004, Kimbrough *et al.* 2006). On one hand, certain pH values and amplitudes of fluctuation in redox potential are suitable indicators for the vital activity of particular types of microorganisms (Rabotnova & Schwarz 1962, Pett-Ridge & Firestone 2005, Fierer & Jackson 2006, Lauber *et al.* 2009, Seo & DeLaune 2010). On the other hand, microorganisms can alter the Eh and pH of soils; for example, by reducing oxygen consumption (Bohrerova *et al.* 2004) or increasing acidity (Rabotnova & Schwarz 1962, Twining *et al.* 2004). Such studies have been carried out mainly in middle-latitude wetlands (Urquhart & Gore 1973, Lishtvan *et al.* 1989, Bennicelli *et al.* 2006, Tokarz & Urban 2015, Inisheva *et al.* 2016). It should also be noted that physicochemical measurements have been carried out mainly in the upper layers of peat deposits, to maximum depths of 30–40 cm (Urquhart & Gore 1973, De Mars & Wassen 1999, Tokarz & Urban 2015).

This study hypothesises that, with increased human pressure and/or a change in climatic conditions, irreversible transformations will occur in the peat deposits of raised bogs, and in the early stages of the process these will be expressed as an increase in redox potential. The aim is to identify the main trends of change in physicochemical properties with depth in the peat deposit of an undisturbed boreal raised bog; and thus to establish a baseline for assessing the transformation of wetland ecosystems under any future anthropogenic pressures or climatic changes.

METHODS

Location

The study was conducted within the observation area of the Brusovitsa bog meteorological station (Popova & Ruzhnikova 2007), which is located in an undisturbed part of the Ilas bog complex in the Primorsky district of Arkhangelsk Region, Russian Federation (64° 19' 43" N, 40° 36' 45" E; Figure 1). The area has an Atlantic-Arctic boreal coastal climate with pronounced influence of the White and Barents Seas. At the Arkhangelsk weather station the annual mean temperature is +1.3 °C, the mean air temperature in January is -12.7 °C, the mean air temperature in July is +16.3 °C, the growing season sum of the daily mean temperature excess above the threshold 10 °C is about 1400 °C, the growing season usually lasts for 80-100 days, mean annual precipitation is 606 mm, the duration of snow cover is about 180 days and the mean maximum snow depth is 102 cm (Pogoda i klimat 2019).

The Ilas bog complex is located in the waterlogged part of the taiga forest zone 30 km south-southwest of Arkhangelsk, on the watershed of three rivers (Brusovitsa, Shukhta and Babya) that drain part of the Northern Dvina basin. The bogs





Figure 1. Location of the experimental sites within the Ilas bog complex

belong to the south White Sea bog province, which is the most northerly of the group of sub-oceanic mire types that occupies the entire Baltic lowlands (Elina 1974, Yurkovskaya 1992). Bogs of this type dominate the wooded tundra zones of northern taiga forests, where they are found alongside Pechora-Onega type bogs and Aapa-bogs. The Ilas complex is a raised bog mesotope (Ivanov 1981). It has a combination of typical microtopes for raised bogs of the taiga zone, which can be classified as complex hummock-hollow-pool and complex hummock-pool microtopes with raised bog vegetation on hummocks and in hollows (Figure 2). Microtopes with oriented belt-hummock relief are common in waterlogged parts of the boreal forest zone.

The study was established on three test sites $(4\times4 \text{ m})$, located 25 m from one another on the hummocks of the hummock-hollow complex within the zone indicated by the yellow outline in Figure 1. Geobotanical description of the test sites was carried out according to the guidelines and standard methods of Sukachev & Zonn (1961), Yaroshenko (1961) and Borisova & Bogachev (2009), i.e. the vegetation layers were differentiated and then described by species (Ignatov & Ignatova 2003, Noskova 2016).

Eh and pH measurements

Eh and pH data were obtained simultaneously at all three test sites on each of three days (the 5th, 15th and 25th of July 2019), by the method of direct potentiometry (Lishtvan *et al.* 1989, Zubov *et al.* 2019) using an Expert-001 universal analyser (Econiks-Expert, Russia) with an ERP-105 combined platinum electrode for measuring Eh values in liquid and heterogeneous media and a combined electrode ESK-10603 for measuring pH. Representative peat samples were obtained by coring layer-by-layer, using a stainless steel peat sampler (Eijkelkamp, The Netherlands) with chamber diameter 52 mm. Immediately after removal from the body of the deposit, each 20 cm peat core section was placed in a hermetic cell from which air was removed and into which the electrodes and a thermal sensor were introduced. After allowing five minutes for stabilisation, five replicate Eh and pH values were recorded. This procedure was repeated for each 20 cm layer down to 350 cm depth. The arithmetic mean of each indicator per depth interval was then calculated across the three test sites.

Recalculation of the obtained Eh values to standard conditions (t = $25 \text{ }^{\circ}\text{C}$ and pH = 4.0) was carried out according to Urquhart & Gore (1973) using the following equations:

$$E_t = E + 197 - 0.76 \times (t - 25)$$
[1]

$$E_h = E_t + 56.2 \times (\text{pH} - 4)$$
 [2]

where E (mV) is the measured redox potential value; 197 (mV) is the correction coefficient for a silver chloride saturated half-electrode, to make the reading equivalent to that of a normal hydrogen electrode at 25 °C; and t (°C) is the peat temperature at the time of measurement. Values of redox potential provided in the Results section here represent Eh4 values (i.e., the value of Eh reduced to the value corresponding to pH 4) unless explicitly stated otherwise.





Figure 2. Examples of the hummock-hollow-pool microscale landscape of Ilas bog: hollow (left); hummock (right).

Properties of peat

After making the pH and Eh measurements, averaged samples from three test sites were used for laboratory studies. Averaging of the peat samples was carried out over the corresponding layers (0-20, 20-40, 40-60 cm, etc.). The degree of decomposition was determined in the field by the method of visual assessment of the presence of undecomposed plant residues and the properties of the decomposed part of peat (the colour of peat, the colour of the manually squeezed water, etc.) described by Lishtvan & Korol' (1975), Tyuremnov (1976) and Randall et al. (2011). The data obtained in the field were subsequently verified microscopically in the laboratory where mixed wet peat samples were used to determine the botanical composition and degree of decomposition. The five replicate determinations of degree of decomposition were carried out using transmitted light microscopy for each studied layer (0-20, 20-40, 40-60 cm, etc.). The degree of decomposition was determined as the ratio of the relative area occupied by decomposed particles in a liquefied peat sample on a slide.

Plant residues (macrofossils) were identified according to Levesque *et al.* (1988) and Noskova (2016). To study the ash content and elemental composition, air-dry peat samples were used, which were preliminarily homogenized in a laboratory mill. Considering their high homogeneity and high convergence of results, the determination was carried out in three replications for each studied layer (0-20, 20-40, 40-60 cm, etc.). The moisture content of three replicate air-dry peat sub-samples per 20 cm layer was determined by oven drying at 105 ± 5 °C until a constant mass was achieved (O'Kelly & Sivakumar 2014). Ash content was determined by the loss on ignition (LOI) method. For this, three replicate sub-samples (1.0-3.0 g) of

oven-dried peat were placed in a muffle furnace at $800 \text{ }^{\circ}\text{C}$ for 3 h (Parfenova *et al.* 2016) then the ash content (A) was calculated as:

$$A = (m - m_{800}) \times 100 / m_{a.d.m.}$$
[3]

where $m_{a.d.m.}$ is the mass of the dry peat sample, *m* is the mass of the dry sample plus crucible, and m_{800} is the mass of the crucible and its contents after ignition at 800 °C.

The content of C, H and N in the three replicate sub-samples was determined using a EuroEA 3000 CHN elemental analyser (Eurovector, S.p.A.). Oxygen content was determined as the difference between the total mass and the sum of other elements. Then, the oxidation level (ω) of peat organic matter was calculated according to (Orlov 1992) using the formula:

$$\omega = (2O - H) / C \qquad [4]$$

where *C*, *H* and *O* are the atomic percentages of these elements. The higher the oxidation level (ω) value, the more resistant the organic matter is to atmospheric oxygen.

Microbial analysis

The process of peat genesis encompasses the decomposition of substances that make up peatforming plants. One part of peat genesis is the decomposition of nitrogen-containing organic substances, which involves a large number of different physiological groups of microorganisms. The main groups are obligate aerobes, which are nitrifying and oligotrophic bacteria, and ammonifying and saccharolytic bacteria that might normally be anaerobic with a facility to metabolise aerobically. To obtain a first indication of how



microbial processes may vary with depth in the peat deposit, the number of viable cultivable cells of the main groups of aerobic and facultative anaerobic bacteria in selected 10 cm layers of the peat deposit was measured using classical plate-counting methods from microbiology (e.g., Zvyagintsev 1991, Tepper *et al.* 2004, Elliott *et al.* 2015). The layers were selected for their contrasting redox regimes.

Peat for microbiological analysis was collected during a separate field visit. This time six cores were extracted from sequentially increasing depths to sample the peat layers at depths of 0–10, 40–50, 100–110, 150–160, 200–210 and 300–310 cm). Then, using sterilised gloves, peat was taken from the central part of each core into a sterilised container (for microbiological studies) and a plastic bag (for determination of moisture content).

Homogenised sub-samples (1 g) of peat were transferred to flasks containing sterile water and extracted by ultrasonic treatment (ultrasonic disperser UZDN-1) for two minutes at a current strength of 0.44 A and an oscillation frequency of 22 kHz. Standard serial dilutions followed, and 100 μ l aliquots of each dilution (10⁻², 10⁻³, 10⁻⁴, 10⁻⁵) were inoculated (in triplicate, giving an uncertainty of 5–20 %) onto agar-based culture media augmented to select for different physiological types.

Ammonifying bacteria utilising organic forms of nitrogen were estimated on nutrient agar (NA) (5 g L⁻¹ peptone, 3 g L⁻¹ beef extract, 15 g L⁻¹ agar; in distilled water), while bacteria assimilating mineral forms of nitrogen was estimated on starchand-ammonia agar (SAA) (10 g L⁻¹ soluble starch, 2 g L⁻¹ (NH₄)₂SO₄, 1 g L⁻¹ K₂HPO₄, 1 g L⁻¹ MgSO₄, 1 g L⁻¹ NaCl, 3 g L⁻¹ CaCO₃, 20 g L⁻¹ agar; in distilled water). The number of saccharolytic bacteria was estimated on glucose-and-peptone agar (GPA) (1 g L⁻¹ peptone, 1 g L⁻¹ glucose, 1 g L⁻¹ yeast extract, 1 g L⁻¹ casein hydrolysate, 5 g L⁻¹ CaCO₃, 20 g L⁻¹ agar; in distilled water) and the number of raised autochthonous bacteria was estimated on starvation agar (SA) (15 g L⁻¹ agar in natural bog water). The inoculated agar plates were incubated in the dark at 20 °C for 5–7 days (NA), 10-14 days (SAA), 10 days (GPA) or 21 days (SA). The counts were expressed as colony-forming units (CFU) per unit mass of dry peat (CFU g⁻¹).

The total number of microorganisms was determined by direct counting with 4',6-Diamidine-2'-phenylindole dihydrochloride (DAPI). Appropriate dilutions were filtered through 0.2 μ m black polycarbonate membranes (Millipore), stained with DAPI and examined on an epifluorescence microscope at ×1000 magnification following the method of Porter & Feig (1980). Since the moisture content of peat samples from different depths varied, in order to compare results, the number of colony-forming units in 1 g of the sample was recalculated per 1 g of dry peat using the formula:

$$N = (Nc \times 100\%) / (100\% - W)$$
 [5]

where Nc is the number of CFU per g of sample (i.e. peat with its initial water content), N is the number of CFU in 1 g of dry peat and W is water content (%).

It should be noted that the methods used here do not faithfully reproduce the bog environment from which the samples were taken and, therefore, cannot account for the full variety of viable bacteria within the studied peat deposit. However, these methods are sufficient to provide a general characterisation of the composition of the aerobic and facultativeanaerobic parts of the microbial community (Puspita *et al.* 2012, Elliott *et al.* 2015, Mosharova *et al.* 2019).

Statistical analysis

Statistical processing of the results was carried out using the Microsoft Excel analysis package and SPSS Statistics 11. The confidence interval for the mean values is displayed as $x \pm s.e.m.$, where x is the mean value and *s.e.m.* is the standard error of the mean. The significance of differences between certain groups of values was determined using the Student's t criterion and the Mann-Whitney U-test for two unconjugated homogeneous variances and the Kruskal-Wallis H-test for three and more unconjugated homogeneous variances.

RESULTS

Vegetation

The tree layer of the study site consists of sparse *Pinus sylvestris* f. *litwinovii* L. and *Betula pubescens* L., and the shrub layer is represented by *Betula nana* L. with cover of up to 10 %. The grass-dwarf shrub (field) layer reaches 40 % cover on hummocks and consists of *Ledum palustre* L., *Rubus chamaemorus* L., white *Andromeda polifolia* L., *Calluna vulgaris* L., *Empetrum nigrum* L., *Vaccinium vitis-idaea* L., *Drosera rotundifolia* L., *Drosera anglica* Huds., *Drosera medium* Hayne, *Oxycoccus microcarpus* Turcz. Ex Rupr., *Vaccinium uliginosum* L. and *Eriophorum vaginatum* L. The moss-lichen (ground) layer has 80 % cover and consists mostly of *Sphagnum fuscum* (Schimp.) H. Klinggr. with admixed *Sphagnum medium* Brid.,



S. tenellum (Brid.) Pers. ex Brid., S. rubellum Wilson and S. capillifolium (Ehrh.) Hedw., Dicranum undulatum Schrad. ex Brid., Pleorozium schreberi (Willd. ex Brid.) Mitt., Polytrichum strictum Hedw., Aulacomnium palustre (Hedw.) Schwägr. Lichens are represented by Cetraria islandica (L.) Ach. and Cladonia sp. In general, the plant community of the test site belongs to the pine-shrub-Sphagnum type.

Characteristics of the peat deposit

The thickness of the peat deposit in the study area was 3.4–3.6 m and the underlying mineral layers were quaternary non-calcareous clayey and loamy lacustrine-glacial sediments. The level of the water table (relative to ground level) fluctuated during the research season between 0 cm during active snowmelt and heavy rainfall and -30 cm during summer drawdown (mid-July).

Figure 3 shows the botanical composition of the studied peat deposit. The botanical composition of the peat was represented by raised bog plant residues (e.g. Schulz *et al.* 2019), and characterised by a high degree of homogeneity throughout the profile. The upper layers of the peat deposit (0–240 cm) were composed of raised bog and meso-raised *Sphagnum* species (*S. angustifolium*, *S. balticum*, *S. capillifolium*, *S. compactum*, *S. fuscum*, *S. lindbergii S. magellanicum*, *S. majus*, *S. papillosum*).

The percentage of herbaceous vegetation (*Ericaceae* sp., *Carex* sp., *Eriophorum vaginatum*, *Scheuchzeria palustre*) varied between 20 % and 30

%. The lower layers of the deposit (240–360 cm) were composed of transitional peat. The percentage of Sphagnum mosses did not exceed 40 %. Admixtures of pine wood and bark appeared at depths of 0-20, 70-180 and 280-320 cm. In the first two cases, the woody materials (e.g., roots of living bark litter. branches) were weakly trees. decomposed and their proportions ranged from 5 % to 20%. In the lower horizons, the proportion of pine wood reached 25 % and the degree of decomposition of wood residues was high.

Values of degree of decomposition, ash content and elemental composition per layer of the peat deposit are presented in Table 1. Ash content varied in the range 0.61-1.26 % (dry mass basis). The elemental contents were in the ranges: 47.6-57.3 % (C); 0.9–2.1 % (N); 6.9–7.5 % (H); and 33.2–44.6 % (O). The H/C quotient decreased non-linearly with depth, indicating some increase in the contribution of aromatic structures to the composition of organic matter (reflecting increasing biodegradation of plant residues) with increasing depth in the peat profile. C/N was in the range 31-60, which is typical for bog peats (Schulz et al. 2019). Based on elemental ratios (H/C and O/C) from Table 1, a Van Krevelen diagram was constructed (Van Krevelen 1950). The data presented in Figure 4 indicate the occurrence of reducing conditions (change from oxidising conditions to weakly reducing) in the catotelm, which is consistent with the results for Eh.

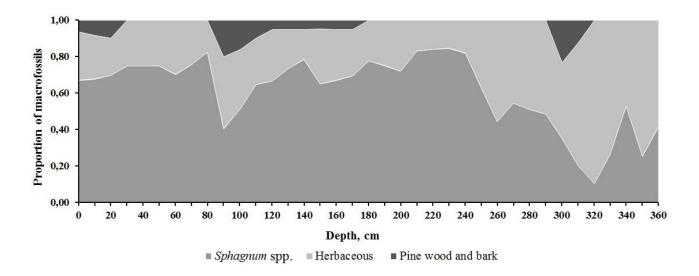


Figure 3. Depth profile of plant macrofossils for Ilas bog (hummocks): *Sphagnum* spp. (*S. angustifolium*, *S. balticum*, *S. capillifolium*, *S. compactum*, *S. fuscum*, *S. lindbergii*, *S. magellanicum*, *S. majus*, *S. papillosum*); Herbaceous (*Ericaceae* sp., *Carex* sp., *Eriophorum vaginatum*, *Scheuchzeria palustre*); Wood and bark (*Pinus sylvesrtis* wood and bark, *Betula* sp. bark).



Table 1. Change in the degree of decomposition, ash content and elemental composition of peat by depth. Degree of peat humification according to the Von Post
scale. Ranges (±) expressed as 95% confidence interval. Sample sizes per layer (n) for each analytical approach are given.

Layer, cm	Degree of decomposition R, % (H*) (n=5)	Ash content A, % (n=3)	Elemental composition, % of total organic matter content (n=3)				Oxidation level (ω)	
			Ν	С	Н	Ο		
0–20	0–5 (H1)	1.18 ± 0.02	0.93 ± 0.10	47.61 ± 0.76	6.87 ± 0.37	44.60	-0.44	
20–40	5–10 (H1)	0.72 ± 0.01	1.19 ± 0.14	51.41 ± 0.78	7.06 ± 0.14	40.34	-0.56	
40–60	5–10 (H1)	0.61 ± 0.01	1.13 ± 0.05	50.04 ± 1.40	6.98 ± 0.24	41.85	-0.51	
60–80	5–10 (H1)	0.85 ± 0.03	1.56 ± 0.02	55.13 ± 0.35	7.30 ± 0.07	36.01	-0.69	
80–100	10–15 (H2)	0.91 ± 0.02	1.76 ± 0.03	57.34 ± 0.57	7.58 ± 0.09	33.32	-0.80	
100–120	10–15 (H2)	0.92 ± 0.05	1.37 ± 0.13	54.86 ± 0.31	7.23 ± 0.03	36.54	-0.67	
120–140	12–17 (H2)	0.97 ± 0.01	1.33 ± 0.05	53.34 ± 0.76	7.24 ± 0.15	38.09	-0.65	
140–160	12–17 (H2)	0.78 ± 0.01	1.46 ± 0.20	54.95 ± 0.56	7.21 ± 0.10	36.38	-0.66	
160–180	15–20 (H3)	0.81 ± 0.02	1.35 ± 0.04	52.13 ± 0.31	6.98 ± 0.17	39.55	-0.56	
180–200	15–20 (H3)	0.76 ± 0.03	1.60 ± 0.16	53.85 ± 1.39	7.27 ± 0.22	37.27	-0.67	
200–220	15–25 (H3)	1.26 ± 0.02	1.58 ± 0.01	53.99 ± 0.36	7.13 ± 0.09	37.30	-0.65	
220–240	20–25 (H3)	0.83 ± 0.02	1.32 ± 0.06	52.18 ± 0.80	7.22 ± 0.23	39.28	-0.62	
240–260	20-30 (H4)	0.73 ± 0.01	1.82 ± 0.22	55.99 ± 0.42	7.37 ± 0.08	34.83	-0.73	
260-280	20-30 (H4)	0.90 ± 0.03	1.81 ± 0.18	56.44 ± 0.41	7.42 ±0.15	34.33	-0.75	
280-300	30–35 (H5)	0.95 ± 0.02	1.73 ± 0.02	56.57 ± 0.36	7.11 ± 0.09	34.59	-0.68	
320–340	35–40 (H6)	1.24 ± 0.05	1.78 ± 0.02	56.04 ± 0.08	7.31 ± 0.12	34.87	-0.73	
340–360	35–40 (H6)	1.20 ± 0.01	2.08 ± 0.19	55.07 ± 1.25	7.11 ± 0.27	35.74	-0.67	



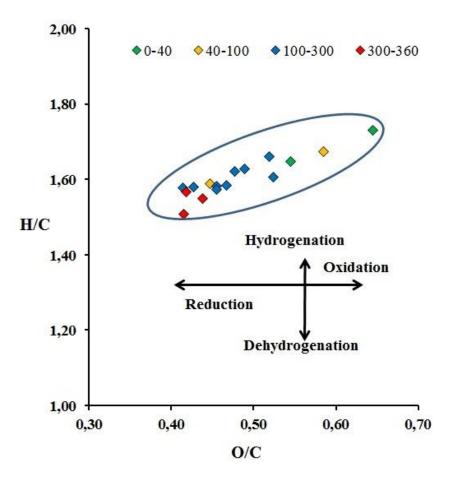


Figure 4. Van Krevelen diagram of studied peat samples. Coloured symbols denote peat depth (cm).

Changes in the physicochemical properties of peat with depth

The variations of Eh and pH with depth are presented in Figure 5. Trends were similar for all three test sites, and the values plotted are 3-site mean values. The Eh values ranged from 220 to 340 mV (Figure 5a) and the pH values from 3.3 to 4.3 (Figure 5b). Whereas Eh changed unevenly, there was a monotonic increase in pH with increasing depth. The greatest changes between consecutive 20 cm layers occurred in the uppermost 40 cm. Between 40 cm and 100 cm depth, Eh stabilised at about 300 mV and pH at 3.5-3.6. Below this (100-300 cm depth), Eh decreased in tandem with gradual deacidification (increasing pH values). In contrast, the continuing trend of deacidification in the bottom layer (300-350 cm depth) was accompanied by an increase in Eh values.

Microbiological characteristics of the peat deposit

The results of the microbial counts are presented in Table 2. The ranges of abundance (dry peat basis, CFU g⁻¹) were: 0.6×10^3 to 285.7×10^3 for ammonifiers; 0.4×10^3 to 29.6×10^3 for bacteria

assimilating mineral forms of nitrogen; 0.2×10^3 to 74.0×10^3 for saccharolytic bacteria; and 0.1×10^2 to 56.4×10^3 for oligotrophic bacteria (Table 2). The greatest abundance of all groups of both aerobic and facultative anaerobic microorganisms was found in the surface layer (0-10 cm). There was a sharp decrease in abundance with depth in the acrotelm. At a depth of 40–50 cm, the number of viable cells of ammonifiers and bacteria assimilating mineral forms of nitrogen was reduced by almost 60 times, saccharolytic bacteria by 60-80 times, and oligotrophic bacteria by about 15 times. Further changes in bacterial abundance with depth were not significant (Mann-Whitney U-tests, p > 0.05). It might be expected that the key factor determining the number of viable cells of all microorganisms capable of aerobic respiration would be the level of aeration of the peat deposit, which reduces substantially below the water table. At the time of sample collection, the water table in the bog was 30 cm below ground level, which seems compatible with our results. However, it is also important to note that viable cells belonging to all the aerobic and facultative anaerobic groups studied were recorded throughout the depth of the deposit.



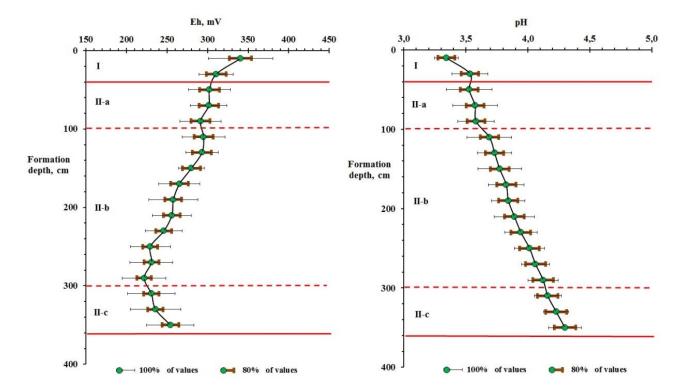


Figure 5. Changes with depth of mean values of the physicochemical properties of the peat deposit: Eh (in mV) (left) and pH (right).

	Viable cultivable b	Total number				
Depth (cm)	Bacteria utilising organic forms of nitrogen	Bacteria assimilating mineral forms of nitrogen	Saccharilytic bacteria	Oligotrophic bacteria	of bacteria, ×10 ⁶ cells per $g_{dry peat}$	C/N
0–10	285.7 ± 74.4	29.6 ± 4.7	74.0 ± 14.5	56.4 ± 8.0	185.1 ± 27.1	59.66
40–50	4.8 ± 1.4	0.5 ± 0.1	1.0 ± 0.3	3.7 ± 0.4	89.0 ± 27.0	51.71
100-110	2.2 ± 0.5	0.4 ± 0.1	1.0 ± 0.3	1.8 ± 0.4	47.6 ± 14.1	46.67
150–160	1.3 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	27.6 ± 8.0	43.83
200–210	0.6 ± 0.1	0.6 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	n/a	39.76
300-310	1.5 ± 0.3	0.6 ± 0.2	1.2 ± 0.2	0.1 ± 0.1	36.7 ± 6.2	35.90

Table 2. Bacterial concentrations in (dry) peat and C/N values of the studied peat samples.

DISCUSSION

At present, there is a rapid increase in the stress load on wetland ecosystems due to direct anthropogenic impacts and climate change. This load can become critical and lead to the transformation of individual elements of bogs and the ecosystem as a whole. Redox potential and acidity of peat deposits can be used to assess bog condition. To adequately assess the transformation of wetland ecosystems under any future anthropogenic impacts or climatic change, it is necessary to establish a baseline by estimating the dynamics of changes in ORP (Oxidation Reduction Potential) and acidity values.

The mineral nutrition of raised bogs is sourced mainly from the atmosphere (e.g., dissolved in rainwater, dry deposition), but this does not affect the mineralisation of the catotelm so long as the influx of mineral components from the atmosphere does not exceed the buffering capacity of the acrotelm. The increase in ash content observed at the base of the studied deposit (below 300 cm depth;



see Table 1) arises primarily from the formation mechanism of this bog (upland swamping) (Inisheva 2009), which caused the bog surface to become isolated from the mineral substratum in the early stages of peat deposition. Although upward migration of mineral components by diffusion is possible (Rudmin et al. 2020), it is likely that the rate of movement would be low and this potential mechanism requires additional research. A gradual replacement of minerotrophic vegetation by less nutrient-demanding species is confirmed by the predominance (60-80%) of herbaceous plant residues (Carex spp., Eriophorum vaginatum, Scheuchzeria palustre) typical of mesotrophic or eutrophic communities in the bottom layer of the deposit and their replacement by Sphagnum species above 300 cm depth (Figure 3). The degree of decomposition of peat, the composition of organic matter (Table 1) and the redox potential (Figure 5a) also change at this depth. This is consistent with the views of other authors that the mineral composition of the peat, especially the presence of metals with mixed valencies, determines the richness and abundance of microbiota involved in the decomposition of plant residues and the functioning of redox systems, and thus influences the biotransformation of organic matter (Lishtvan et al. 1989, Tokarz & Urban 2015, Inisheva et al. 2016).

The redox regime of the peat deposit at the Ilas bog complex (Eh ~200-370 mV) corresponds to the moderately-reduced class of organogenic soils (Eh 100-400 mV) identified for hummocks by other authors (Kaurichev & Shishova 1967, Tokarz & Urban 2015). The profiles of pH and redox potential (Figure 5), combined with the presence of aerobic and facultative anaerobic microorganisms throughout the depth of the peat deposit (Table 2), indicate that the mineralisation of organic matter occurs under both aerobic and anaerobic conditions. On the basis of these data, a stratigraphic zonation of the peat deposit is proposed. This is presented schematically in Figure 6.

The upper aerated layer (I) is confined by the (fluctuating) water table and is entirely included in the acrotelm (0-40+ cm). This layer has highly homogeneous botanical composition dominated by *Sphagnum* mosses (Figure 3) and is characterised by weakly oxidative conditions. This is evidenced by the maximum Eh values (310-340 mV) at the minimum pH values of the peat deposit (3.3-3.6) (Figure 5) and the highest degree of organic matter oxidation (Table 1). These features are explained by its good aeration and, as a consequence, viable cells of the studied groups of aerobic and facultative anaerobic microorganisms are most abundant in this

layer (Table 2) with a predominance of ammonifiers. According to the changes in the ash content of the peat (Table 1), the atmospheric flux of elements affects only the upper layer of the studied bog complex (Hansson *et al.* 2015). This is caused, firstly, by a significant increase in industrial emissions carried by atmospheric masses in recent decades; and, secondly, by the high sorption capacity of *Sphagnum* peat with a low degree of decomposition that composes the acrotelm (Shevchenko *et al.* 2015).

Within the catotelm (Layer II; starting below 40 cm), which is perennially waterlogged, the weakly-oxidative conditions (340-310 mV) of the conditionally active layer (with air entry only during the severest droughts) change to moderately-reduced (down to 200 mV), and pH values increase to 4.1-4.3, but the gradient of the change in Eh and pH with depth is less than in the acrotelm. In general, the values obtained are consistent with literature for raised peatlands in other parts of the Russian Federation (Shishov et al. 2004, Samoylik 2016). The change in Eh values could be associated with decreasing penetration of oxygen into the lower layers of the deposit (Tokarz & Urban 2015), due to the lack of downward water movement as well as the consumption of any downward-diffusing oxygen by active processes at the boundary between acrotelm and catotelm. The transformation of organic matter in the catotelm is slower than in the acrotelm because microbial assimilation must occur under anaerobic conditions (Urquhart & Gore 1973). This is confirmed by the distribution of the measured microbial groups with depth (Table 2), as well as by the decrease in the oxidation state of organic matter in the peat (Table 1, Figure 4). The nature of the changes in H/C, C/ N and O/C (Tables 1 and 2, Figure 4) confirms the transformation of organic matter by microbial communities and indicates the predominance of anaerobic processes in the main part of the deposit (i.e., reduction and dehydrogenation of organic matter) (Figure 4) with the formation of CH₄ and CO₂. At the same time, CO_2 is released only from the upper (aerated) horizons. A more detailed examination of the curves shown in Figure 5 enables us to distinguish three zones in the catotelm, denoted as II-a, II-b and II-c.

Zone II-a (transition zone) extends from the base of the acrotelm to a depth of 100 cm. This layer is again characterised by peat with high botanical homogeneity dominated by *Sphagnum* mosses (Figure 3). Diffusion of atmospheric oxygen into this horizon of the deposit rarely occurs, and its input in the dissolved form with rainwater is insignificant. It should also be noted that



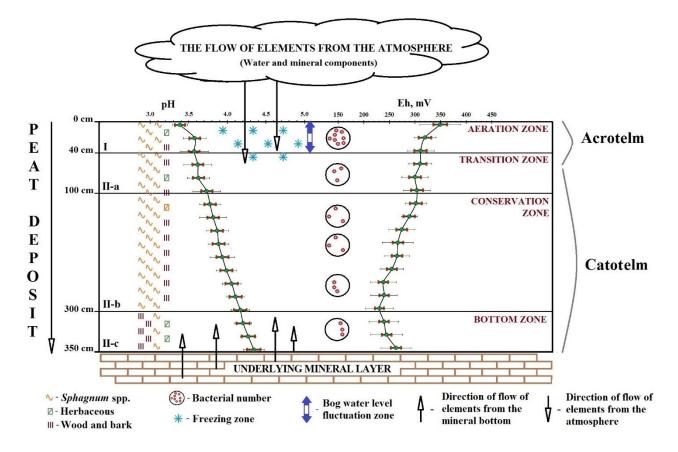


Figure 6. Schematic structure of the peat deposit of the raised bog.

aerenchymal vegetation (including, e.g., *Eriophorium* spp.) is found infrequently in the study area. As a result, there is a slight decrease in Eh (to 290 mV) in zone II-a, although the pH shows little change.

Zone II-b is located below the transition zone and occupies most of the peat profile. It is commonly accepted that a non-aerated layer is a conservation zone, where the processes of biotransformation of organic matter gradually subside (Dobrovol'skaya et al. 2013). A steady gradient of Eh values showing a gradual change in conditions from weakly-reduced to moderatelyreduced (Figure 5a), an increase in pH values (Figure 5b), as well as the data on microbial abundance (Table 2) indicate the occurrence of biotransformation processes throughout the depth of the deposit. The decrease in Eh values in the anaerobic zone of the deposit is explained by the accumulation in the peat of products from the anaerobic metabolism of microorganisms, which use oxidised mineral and organic compounds as electron acceptors in the respiratory chain, converting them into reduced forms (Tokarz & Urban 2015). In addition, organic acids, especially acetate, are formed as a result of fermentation reactions in the upper part of the catotelm. In the lower layers,

where methanogenesis occurs, acetate, formiate and hydrogen are consumed and this is associated with an increase in pH values (Garsia *et al.* 2000, Horn *et al.* 2003). These processes are accompanied by a change in the composition of the organic matter of peat (Parfenova *et al.* 2016, Lishtvan *et al.* 2021).

The bottom zone of the peat deposit (II-c), adjacent to the mineral substratum, is a clearly distinct part of the catotelm. The pH of this layer is in the range 4.0-4.5 and the redox potential increases slightly, relative to zone II-b, from 200 to 250 mV (Figure 5). A change in physicochemical properties in the bottom layer of peat has been noted elsewhere in fens and transitional mires (Inisheva et al. 2009, Wright et al. 2011, Larina et al. 2017) fed by mineral-rich groundwater. Inisheva et al. (2018) explain this in terms of the peculiarities of hydrology and the presence of geochemical barriers in the body of the peat deposit, whereas Wright et al. (2011) attribute it to the botanical composition of the peat-forming vegetation and an increase of carbohydrate content in the organic matter of peat. In the case of the Ilas bog complex, the increase of Eh in the bottom layer is probably associated with a change in botanical composition of the peat (Figure 3).



Thus, our study has shown that the redox potential and acidity of peat can serve as informative indicators for the status of a peat deposit. The high sensitivity and rapid response of redox potential to external influences, especially in the upper layers, confirms its potential usefulness as a diagnostic indicator. The studied bog complex is typical of the south White Sea bog province, which allows us to use the results and the proposed zonation from this study to set a baseline for other bogs in the region. This is especially important because changes in the hydrological regime as a result of future anthropogenic intervention or climatic changes could lead to a change in the depth of the aeration zone and therefore to significant changes in the redox regime and acidity of the peat deposit.

AUTHOR CONTRIBUTIONS

SS originated and planned the work; IZ wrote the first draft and is the lead author; AO and SZ undertook the laboratory work; AO, TP and IZ made the field observations.

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Submitted 02 Mar 2020, final revision 10 Mar 2022 Editor: Gareth Clay

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