

Characterisation of the organic components of peat and implications for the binding of toxic trace elements

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SUMMARY

We aimed to determine the distribution of toxic elements amongst the organic components of peat collected from raised bogs located in the Arkhangelsk region of Russia, and thus to gain new insights about the ability of peat to accumulate these elements. We separated peat samples into four fractions (bitumen, humin, humic acids (HA) and fulvic acids (FA)) using phased liquid-liquid extraction. We found that humin was the main component of the peat and its proportion varied from 87.5 % to 90.0 % of total mass. HA, FA and bitumen accounted for 1.7–5.7 %, 2.1–3.8 % and 3.8–5.2 % of the total mass of peat, respectively. Using spectroscopic techniques we found that the humin, HA and FA contained significant concentrations of carboxylic and amino groups capable of forming chemical bonds with elemental ions. Elemental concentrations in the peat fractions were analysed using inductively coupled plasma mass spectrometry (ICP-MS), focusing on the toxic elements arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and uranium (U). FA was the most active component in terms of binding trace elements in the peat, while the bituminous fraction had the lowest sorption capacity for all of the elements observed. The accumulation of toxic ions was dependent on the presence and concentration of active chemical centres and proceeded according to the chemisorption mechanism.

KEY WORDS: bitumen, fulvic acids, humic acids, humin, ICP-MS, IR, NMR, raised bog, spectroscopy

INTRODUCTION

Nowadays, environmental pollution by toxic trace elements is one of the most common negative consequences of human activities for natural and artificial ecosystems (Gogmachadze 2010). Whilst this causes great concern, it is at the same time an interesting focus for scientific study of how anthropogenic influence and pollutants spread in the environment. Peat is a good deposition matrix for several trace elements and is capable of accumulating them, which can reduce pollution of the wider environment. Raised bogs are unique indicators of air pollution, especially by trace elements, because they are fed only by rainwater, cover large areas, and contain a large number of organic substances (Golubina *et al.* 2019, Koziol *et al.* 2020, Miszczak *et al.* 2020) with copious carboxyl, phenol, carbonyl and amino groups that adsorb heavy metals through both physical and chemical sorption mechanisms (Orlov 1997).

Peat adsorbs a variety of toxic elements and can serve as a natural barrier to their spread in the

environment (Kyziol 2002, Ringqvist & Öborn 2002, Kalmykova *et al.* 2008). Published results of experiments on binding of heavy metals to peats (Twardowska & Kyziol 1996) generally confirm the high sorption capacity of peats, suggesting they have distinctive binding mechanisms depending on the kind of metal.

Peat can be separated into four main fractions, namely bitumen, humic and fulvic acids, and humin, using step-by-step liquid-liquid extraction (Popov 2004). These organic components of peat have specific chemical compositions and, therefore, can be expected to differentially adsorb metal and metalloid ions according to their different contents of the functional groups that are active sorption centres (Zhao *et al.* 2021). With a change in the depth of peat, the content of organic components also changes. For example, (Syrovetsnik *et al.* 2007) found significant differences in depth distribution between different metals bound in peat, which was partly due to the change in peat composition with depth. Although the majority of related research has been devoted to complex formation and sorption of



metals by humic acids (Levshina & Matyushkina 2021), some studies have demonstrated that different components of peat (peat moss, humin and humic acids) adsorb heavy metals differently; but the contribution of each peat component to the sorption of trace elements has not been studied previously (De la Rosa *et al.* 2003, Dai *et al.* 2021, Zhao *et al.* 2021).

NMR spectroscopy is one of the most widely applied methods for characterisation of the content and types of functional groups in organic components of peat. This method has been used successfully for the characterisation of humic and fulvic acids for a long time (Ruggiero *et al.* 1980, Tao *et al.* 1999). Infrared spectroscopy is also used for component characterisation, sometimes in combination with nuclear magnetic spectroscopy (Kim *et al.* 1990, Helal *et al.* 2011). However, simpler analytic methods such as elemental analysis and potentiometric titration (Rice & MacCarthy 1991, Bratskaya *et al.* 2008) can also provide important data for characterisation of the organic fraction of peat.

Peat soils are widespread in the Russian Federation. The country's total area of wetlands is about 369 million hectares, or 21 % of the territory (Inisheva 2005), and Arkhangelsk is one of the most extensively peat-covered regions in Russia. According to governmental data obtained by the "Arkhangelskaya" agrochemical service station, the average concentrations of various elements in the peats of Arkhangelsk Region are: Cu 7.4 ± 0.4 mg kg⁻¹, Zn 35.2 ± 1.8 mg kg⁻¹, Pb 2.8 ± 0.1 mg kg⁻¹, Ni 14.7 ± 0.7 mg kg⁻¹, Co 6.3 ± 0.3 mg kg⁻¹, Hg <0.1 mg kg⁻¹, Cd <1.0 mg kg⁻¹, As 0.5 ± 0.03 mg kg⁻¹, Mn 399 ± 20 mg kg⁻¹ (Popova 2014). It is noticeable that the concentrations of the most toxic elements, such as uranium (U), mercury (Hg), cadmium (Cd), silver (Ag) and arsenic (As) are at sub-mg kg⁻¹ and even sub- μ g kg⁻¹ levels. Therefore, accurate determination (and interpretation) is challenging, and modern analytical instruments are needed. Although As is a metalloid, for the sake of simplicity it will be included in the group "heavy metals" for the purposes of this article.

The primary objectives of the research reported here were to characterise raised bog peat that formed in the Arkhangelsk region of Russia in terms of its organic components, and to study of influence of the components on the distributions of the toxic elements As, Cd, Cr, Hg, Pb and U within the four main organic components (bitumen, humin, humic acids (HA) and fulvic acids (FA)). Thus we aimed to gain new insights about the storage and migration mechanisms of toxic contaminants in peat.

METHODS

Characteristics of raised bog peat in the study area

The Arkhangelsk region is typical of northern Europe in that peat bogs cover 19 % of the territory. About 20 % of the region's soils are hydromorphic with large amounts of surface and ground water. These include upland (14.2 %) and transitional peat soils, but there are raised bogs on the water divides. A typical example is the Ilas bog complex (64° 19' 43" N, 40° 36' 45" E), which has been studied intensively since 1941. Long-term records show that average annual precipitation is 882 mm, the total mineralisation is 27 mg L⁻¹ and the average concentrations of individual elements in pore water are: 2.1 mg L⁻¹ of iron (Fe); a pH of 4.3; 4.1 mg L⁻¹ of Ca²⁺ ions; 1.5 mg L⁻¹ of Mg²⁺ ions; 5.2 mg L⁻¹ of Na⁺ and K⁺ ions; 0.9 mg L⁻¹ of HCO₃⁻ ions; 1.2 mg L⁻¹ of SO₄²⁻ ions; 4.3 mg L⁻¹ of Cl⁻ ions; 0.44 mg L⁻¹ of NO₃⁻ ions; 0.033 mg L⁻¹ of NO₂⁻ ions; 0.38 mg L⁻¹ of NH₄⁺ ions; 0.03 mg L⁻¹ of PO₄³⁻ ions. These combined mean annual values of all data collected at the Ilas bog complex can be assumed to represent the generalised composition of bog peat in Arkhangelsk Region, because there are no statistically significant intra-annual differences in these properties of the oligotrophic microlandscapes of raised bogs. Seasonal fluctuations in the total mineralisation values do not exceed the statistical confidence limits. Seasonal changes in pH are characterised by a slight increase (10 %) during the spring flood and a decrease in the summer. Typically, the acidity decreases during floods owing to the dilution of acidic organogenic bog waters with melted snow and, conversely, the increase of acidity (decrease in pH) during the summer dry season can be explained by increased evaporation from the bog surface and the enrichment of waters with humic acids during this period. The seasonal dynamics of organic matter content are characterised by a statistically significant decrease during the spring flood and an increase during the summer–autumn period, which is also associated with the processes of dilution and concentration of humic acids in bog waters. For biogenic elements, a pronounced maximum of ammonium and nitrite nitrogen is observed in winter against the background of a surge in the concentration of mineral phosphorus at the beginning of the spring flood (Potapova *et al.* 2020).

Collection and characterisation of peat samples

Peat for this study was collected, between 25 May and 08 June 2018, at sampling locations in the south



of Arkhangelsk Region near the town of Velsk (61° 02' 21.7" N 42° 14' 37.5" E), in the central part near the settlement Yemetsk (63° 49' 47.09" N, 41° 61' 92.20" E), in the north-western part between the towns of Onega and Severodvinsk (64° 49' 23.74"N, 38° 44' 70.8"E), and near the city of Arkhangelsk itself (64° 33' 41.95" N, 40° 60' 97.19" E) (Figure 1). These four locations were chosen to achieve the best practical representation of the entire mainland part of Arkhangelsk Region. All of them were at least 300 m distant from highways to avoid local contamination, and all were on ombrotrophic peatlands (bogs) (Du Rietz 1954) where the presence of plant species such as *Ledum palustre*, *Calluna vulgaris*, *Drosera rotundifolia* and *Rubus chamaemorus* (among others) indicated that the bog

ecosystem was oligotrophic and acidic (Joosten & Clarke 2002).

To obtain representative samples, peat was collected from several points on each bog. At each sampling point, the top 35 cm of peat (below the uppermost green part of the profile) was collected using a manual soil sampler with drill bit for clay and wet soils ('mole with handle and bar' supplied by Bürkle GmbH, Bad Bellingen, Germany). This depth range was chosen because, according to numerous studies (e.g. Ukonmaanaho *et al.* 2004, Fiałkiewicz-Kozieł *et al.* 2011), the highest concentrations of trace elements in peatland soils are found in the upper layers of the profile; and our own previous study in Arkhangelsk Region (Sypalov *et al.* 2020) detected only trace levels of these



Figure 1. Locations of the four sampling points within the Arkhangelsk region of Russia.

elements below 35 cm depth. After collection the peat was described in the field according to IUSS Working Group WRB (2015). All samples from each site were mixed, homogenised, and placed in a metal-free ziplock bag for transport to the laboratory, where laboratory characterisations were carried out according to (Van Reeuwijk 2002).

Isolation of organic fractions

For the fractionation, peat was air-dried and sieved through a 2 mm sieve. Then 7.50 grams of each sample was extracted with a 1:1 mixture of hexane and ethanol in a Soxhlet apparatus for 6–8 hours. The extract was evaporated to dryness and the mass of the bitumen fraction was determined (Muristo *et al.* 2010). The remaining peat without bitumen was dried until the organic solvent had evaporated completely, then processed with 150 ml of 0.1 N sodium hydroxide solution in a plastic flask. The suspension was agitated on a laboratory shaker overnight and then centrifuged at 4000 rpm for 15 minutes. The supernatant was placed in a plastic flask while the residue was washed with de-ionised water (DI water) and centrifuged again. This washing process was repeated (3–4 times on average) until transparent DI water was obtained. At this stage, the residue (humic fraction) was dried and weighed. All of the supernatants were mixed together and acidified (to precipitate HA) with 10 % HCl, with constant stirring, until pH 1–2 was reached and persisted overnight. On completion of the precipitation process, the suspension was centrifuged at 4000 rpm for 20 minutes in a 100 ml glass vial. The residue (HA) was dried and weighed and the solution of FA was gently evaporated to a volume of exactly 50 mL. The mass of the FA fraction was calculated by subtracting the masses of the humin and HA fractions from the initial mass of peat weighed out for the extraction (Gondar *et al.* 2005). At least five parallel extractions were carried out for each sample of peat, and all components isolated per extraction were analysed for metal content at least three times.

Mobile forms of some of the studied elements could be lost during the extractions that were required to isolate the peat components. Unfortunately, it is not possible to assess such losses accurately. The non-polar organic solvent used to extract the bitumen fraction should not significantly influence any of the studied elements, so the metal content of the bitumen fraction can be assumed to represent the true value. During the alkali extraction to separate humic acids from humin, mobile forms of metals should not move from one fraction to another and, if they did, would mostly appear in the

residue (humic fraction). The most significant stage in this regard would probably be the acid extraction to separate humic and fulvic acids, as desorption of metals from humic acids might occur in an acid environment. There was no opportunity to estimate or measure such effects in the current study, but given the large number of parallel samples and the high repeatability of results showing convergence of the metals mass-balance in all fractions, we consider that any losses were non-significant.

Spectroscopy

The functional groups that are active sorption centres were determined using infrared (IR) spectroscopy. IR spectra were obtained by Fourier-transform infrared (FTIR) spectroscopy using a Vertex 70 IR Fourier spectrometer (Bruker, Germany) equipped with a GladiATR FTIR system (Pike Tech., United States) incorporating a diamond prism. The spectra were registered under the following conditions: spectral range 4000–400 cm^{-1} , resolution 4 cm^{-1} , 128 scans. The FTIR spectrum obtained underwent an extended ATR-correction. The instrument was controlled, and the spectra were processed, with OPUS software (Bruker, Germany). We also used ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE III NMR spectrometer with an operating frequency of 600 MHz for protons) to analyse the three organic components of peat (HA, FA, bitumen) that could be dissolved in deuterated NMR solvents. To do this, we dissolved a weighed portion of the sample in 0.6 ml of deuterated dimethyl sulfoxide (DMSO- d_6). The deuterated solvent was used to register the reference signal of deuterium nuclei for adjusting the maximum magnetic field homogeneity. A weighed portion of trioxane was added to the solution and its signal of carbon nuclei was used as an internal standard for quantitative calculations. To reduce the relaxation time of the samples, and thus reduce the experiment time, a solution of chromium tris-acetylacetonate (Cr(Ac)III) in DMSO- d_6 with a concentration of approximately 5 mg mL^{-1} was added to the sample. Then the sample was placed in a 5 mm sample tube. The spectra were registered using a standard proton-decoupled pulse program. The pulse in the decoupling channel was applied to the sample during the delay time and the pulse time in the observing channel (gated decoupling). Experimental parameters are shown in Table 1.

After registration, phase and baseline corrections were applied to all spectra. We integrated the intensity of carbon nuclei signals that corresponded to carbon nuclei in different functional groups of the samples and calculated the mass fraction of carbon

Table 1. Parameters of ^{13}C -NMR spectra register.

Parameter	Value
Sample temperature (K)	298
Pulse length (μs)	12
Acquisition time (s)	0.91
Relaxation delay (s)	2
Number of scans	16384

in each observed group. The formula for calculation of the mass fraction of carbon W_C (%) in the various functional groups according to NMR data is:

$$W_C = \frac{m_{IS} \times W_{C(IS)} \times I}{n_c} \times \frac{100}{m_s} \quad [1]$$

where m_{IS} is the internal standard mass; $W_{C(IS)}$ is the mass fraction of carbon in the standard, calculated as the quotient of the sum of relative atomic weights of carbon and the molecular weight of trioxane; I is the integrated intensity of the corresponding signal; n_c is the number of carbon atoms in trioxane (= 3); and m_s is the sample mass. All intensities were normalised on the intensity of the internal standard signal, taken as unity.

Elemental analysis

Sub-samples (0.1–0.25 g) of peat, bitumen, humin, HA and FA were separately dissolved in a mixture of 2.5 ml of extra pure concentrated HNO_3 and 7.5 ml of DI water with addition of 500 μL (0.5 mg L^{-1}) of internal standard (^6Li , Sc, Y, In, Tb and Bi) in a TOPwave laboratory microwave digesting system (Analytik Jena, Germany) at 200 $^\circ\text{C}$ for 45 minutes, according to the method developed by Sypalov *et al.* (2020). The laboratory blank was prepared by the same procedure but without adding a sample. For the elemental analysis of metals we used an Aurora Elite inductively coupled plasma mass spectrometer (ICP-MS) (Bruker, Germany). A seven-point calibration curve was constructed for each element (U, Pb, Hg, Cd, Ag, As, Zn, Cu, Ni, Co, Fe, Mn, Cr, V), covering the range 0.1–500 $\mu\text{g L}^{-1}$ (Sypalov *et al.* 2020).

During the determination of metals in five replicate peat fractions, considering the isolation of components and acid decomposition stages, the deviation of determined concentrations amounted to

no more than 17 % for each element. The mass balance of the metal content was calculated, and it was found that the sum of the metal fractions was equal to the total metal content of the peat within an error margin of 25 %.

The elemental (C, H, N, O) composition was determined by catalytic combustion using an EA-3000 CHNS-O analyser (EuroVector, Itlay).

RESULTS

Characteristics of the peat

The field characterisation of the peat was as follows. The studied soil was a thick Histic horizon consisting of organic material, and it was saturated with water for most of the year. It was classified as permanently submerged in water (Subaquatic), with more than two-thirds by volume of the organic material consisting of recognisable plant tissue after rubbing (Fibric), having a histic horizon saturated predominantly with rainwater (Ombric) and a field pH water value around 4 in 50 % or more of the part with organic material (Dystric). Thus, the field classification was Subaquatic Fibric Ombric Histosol (Dystric) (IUSS Working Group WRB 2015). The laboratory analyses confirmed pH values of 3.8–4.3. All organic fractions of peat were obtained from peat of this classification.

The proportions of the organic components were quite similar across the four sampling locations (Table 2). The content of humin (forming the bulk of the peat) was highest (87.5–90.0 %) and least variable (CV = 1 %), while the content of HA was lowest (1.72–5.72 %) and most variable (CV = 57 %). Moderate variations were found for bitumen and FA, with CVs of 13 % and 24 %, respectively. The Arkhangelsk sampling location was distinguished by its high content of HA (5.72 %) compared to the other three locations, where HA content ranged from 1.72 % to 2.90 %.

Spectroscopy

The IR spectra of the peat samples (Figure 2) and their fractions (Figures 3 and 4) indicate insignificant influence of sampling location on the structural features. All of the spectra are characterised by a number of absorption bands, which are typical for peat and its fractions, with insignificant variation in relative intensity. The intensity of absorption bands varies by no more than 10 %.

The spectra for peat samples (Figure 2) show clearly distinguishable peaks attributed to aliphatic (C-H) groups (2930 and 2850 cm^{-1}). The peaks of CO_2H (1708 cm^{-1}) and aromatic groups (1598 cm^{-1})

are also clearly distinguishable, and their relative intensity increases slightly between samples in the order Yemetsk < Severodvinsk-Onega < Velsk < Arkhangelsk, which is associated with a slight increase in the degree of humification. For a similar reason, there is a reciprocal decrease in the intensity of peaks in the region of C-O-C bonds of polysaccharides (1050–1170 cm^{-1}) (Niemeyer *et al.* 1992).

The bitumen samples (Figure 3a) are characterised by the presence of intense absorption bands at 2920 and 2854 cm^{-1} which correspond, respectively, to asymmetric and symmetric stretching C-H vibrations in $-\text{CH}_2-$. The absorption bands at 1598 and 866 cm^{-1} are related to vibrations of aromatic rings. Aliphatic vibrations are reflected at 1456 cm^{-1} (scissoring vibration of $-\text{CH}_2-$), 1375 cm^{-1} (umbrella vibration of $-\text{CH}_3$), and 723 cm^{-1} (sympathetic vibration of $[-\text{CH}_2-]_n$, $n \geq 4$) (Feng *et al.* 2013). The absorption bands at 1706 and 1049 cm^{-1} are associated with stretching vibrations of carbonyl (C=O) and sulfoxide (S=O), reflecting degree of oxidation of the bitumen molecules (Xiaohu & Isacsson 2002).

The IR spectra of the humin fractions (Figure 3b) contain typical absorption bands for humic materials (Helal *et al.* 2011). The main absorption bands are in the range 2940–2900 cm^{-1} (aliphatic C-H stretching), low-intensity bands at 1750 and 720 cm^{-1} (C=O stretching of $-\text{COOH}$), 1598 cm^{-1} (aromatic C=C, COO^- , H-bonded C=O), around 1375 cm^{-1} (C-O stretching and OH deformation of COOH) and 1040 cm^{-1} (C-O polysaccharide stretching). These spectra clearly demonstrate the predominance of OH and COOH groups, which are the most characteristic indications of soil humic materials.

The IR spectra of the HA and FA fractions demonstrate their homogeneity (Figure 4). Regardless of their origin, all FA and HA had similar IR spectra. This interpretation agrees with the concepts attributed to humus mixtures and data from other authors (Giovanela *et al.* 2004). FA are characterised by a higher degree of saturation in comparison to HA, which is confirmed by the presence of two peaks in the region of 2940–2850 cm^{-1} (asymmetric and symmetric stretching C-H vibrations in $-\text{CH}_2-$) and is typical for aliphatic and unsaturated cyclic hydrocarbons. For HA samples,

Table 2. The average proportions (%) of components, median values and coefficients of variation (CV) in the studied soils.

Components	Sampling points				Median (%)	CV (%)
	Arkhangelsk	Severodvinsk-Onega	Yemetsk	Velsk		
Bitumen	3.79	4.93	5.18	4.87	4.90	13
Humin	87.5	90.0	89.9	89.6	89.7	1
Humic acids (HA)	5.72	2.23	2.90	1.72	2.57	57
Fulvic acids (FA)	3.01	2.83	2.05	3.78	2.92	24

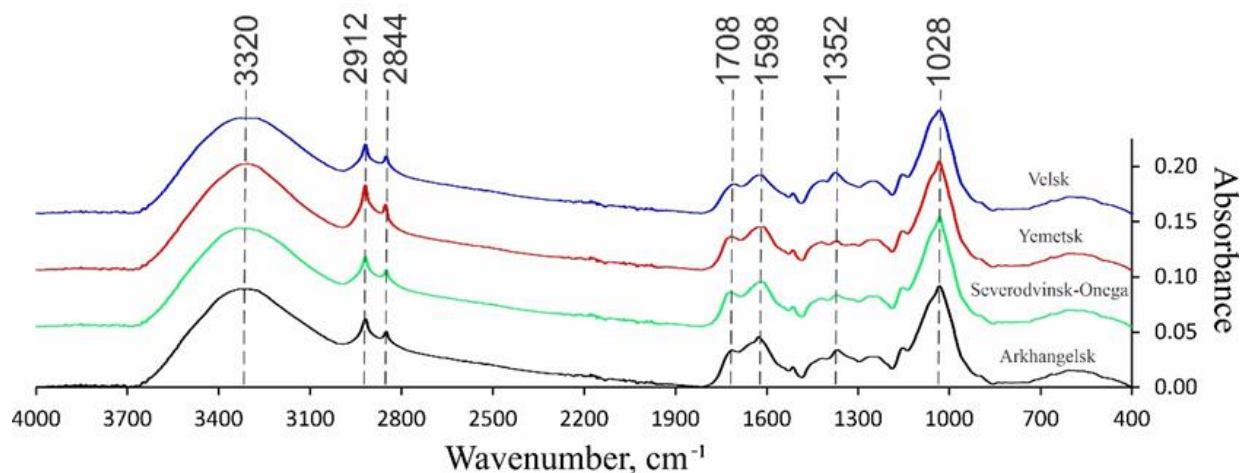


Figure 2. IR spectra of the peat samples.

only the peak at 2914 cm^{-1} (asymmetric C-H stretching of $-\text{CH}_3$ groups) is clearly observed. The difference in the IR spectra of FA and HA is seen primarily in peaks located in the wavelength range $1580\text{--}1720\text{ cm}^{-1}$. Thus, the absorption peak of the carboxyl C=O stretch is slightly stronger in the FA spectra than in the HA spectra. However, there is an overlap of this band at 1583 cm^{-1} associated with the aromatic C=C stretch. In the case of HA the bands at 1706 and 1612 cm^{-1} are more prominent, due to the C=O stretching of the amide group (RCONH_2) and the -NH amide bending, which is confirmed by the presence of nitrogen in the elemental composition.

The results of ^{13}C NMR spectroscopy are shown in Figures A1–A3 in the Appendix. The signal of

trioxane carbon nuclei is observed in the region of $90\text{--}95\text{ ppm}$. The intense signal in the region around 40 ppm corresponds to DMSO carbon.

Elemental analysis

For the purposes of this article, we focus on the distributions of the toxic elements As, Cd, Cr, Hg, Pb and U amongst the peat components, in order to characterise the ability of peat to retain these elements and thus prevent their release into the aquatic environment. The concentrations of the six focus elements are presented in Table 3 (for the full list of elements determined, see Table A1 in the Appendix). The lead (Pb) content ranged from 9.74 to 28.0 mg kg^{-1} , with the highest concentration found in the Severodvinsk-Onega peat sample. If

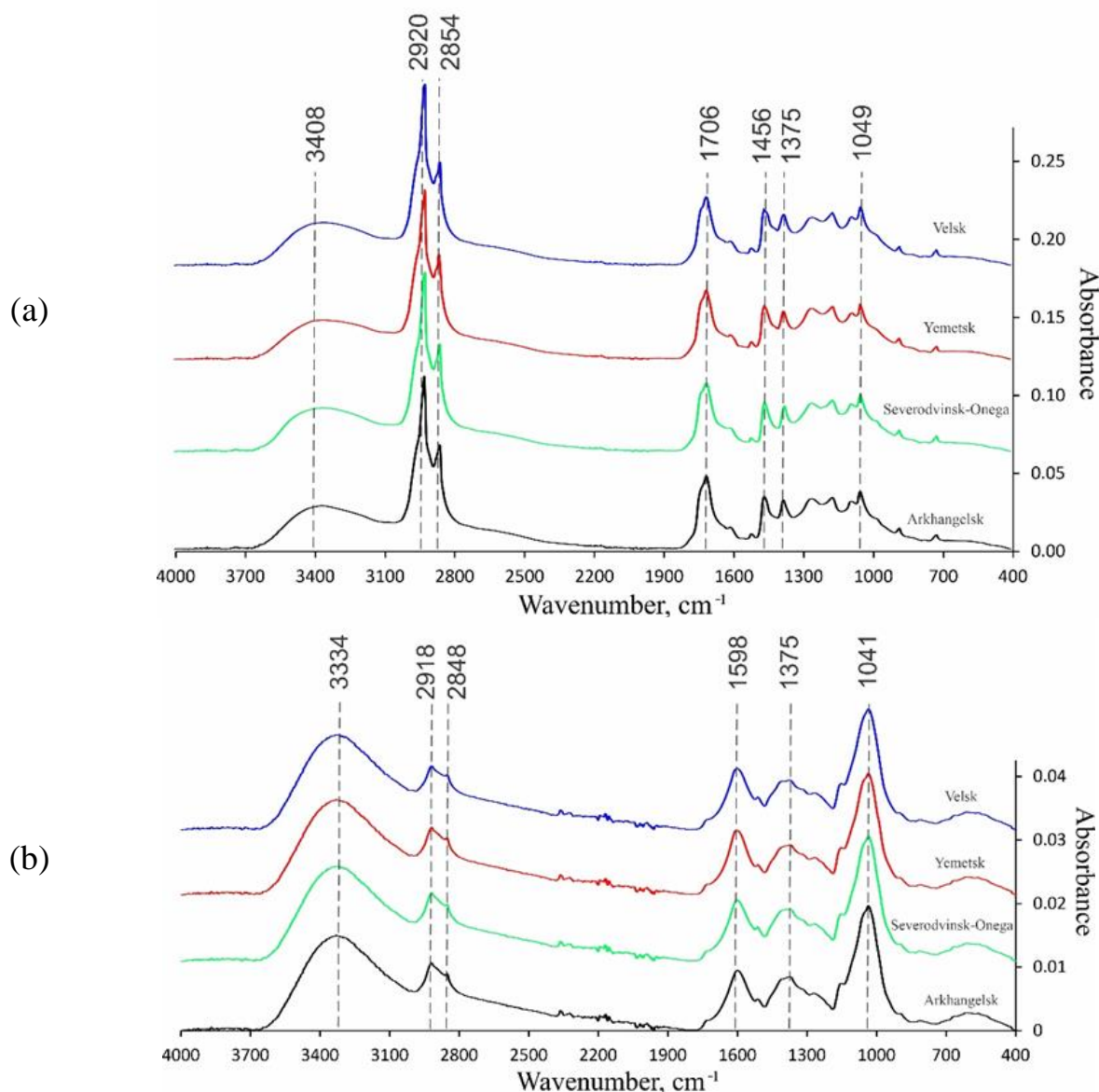


Figure 3. IR spectra of (a) the bitumen samples and (b) the humin samples.

assessed against background values for other soil types, the arsenic (As) concentrations (0.37–1.17 mg kg⁻¹) were significantly below the maximum permissible concentrations (Table A1). The concentrations of mercury (Hg) and uranium (U) in the peat samples were very low (0.01–0.10 mg kg⁻¹), with the highest concentrations observed in the Severodvinsk-Onega sample. Table 4 compares our results from different locations in Arkhangelsk Region with results from other studies in Russia and Europe (see also Table A2). The distributions of the focus elements in different parts of Arkhangelsk region were relatively similar, as discussed below.

Many studies have obtained and presented data on the content of elements in peat soils. It is more interesting to examine the distributions of elements between components (fractions) of peat that have differential tendencies to accumulate toxic elements. Our results for the average concentrations of C, H, N and O in peat and its fractions, and the results of the NMR analysis for C are presented in Tables 5 and 6. The proportions of the six toxic heavy metals

in each fraction of the peat are presented in Figure 5 (see Figure A4 and Table A3 for the full dataset).

The fraction with the highest element content was humin, which makes up a substantially greater fraction (89.7 %) of the total mass of peat than the other components. The bitumen fraction showed an ability to concentrate As. Despite the relatively low proportion of bitumen among the peat components (median value 4.90 %), the concentration of As in bitumen reached 16 % of the total concentration in the peat sample. HA mainly contained U and, to a lesser degree, Hg and As. While the median mass fraction of HA in the studied peat soils was 2.57 %, the proportion of chemical elements that this fraction contained could be several times higher. The median mass fraction of FA was 2.92 %, which is relatively low compared to the other peat components. FA contained the highest proportion of the studied elements (up to 56 % of the total concentration in the peat samples). FA contained the highest concentrations of As and high concentrations of other elements such as Cr and Pb.

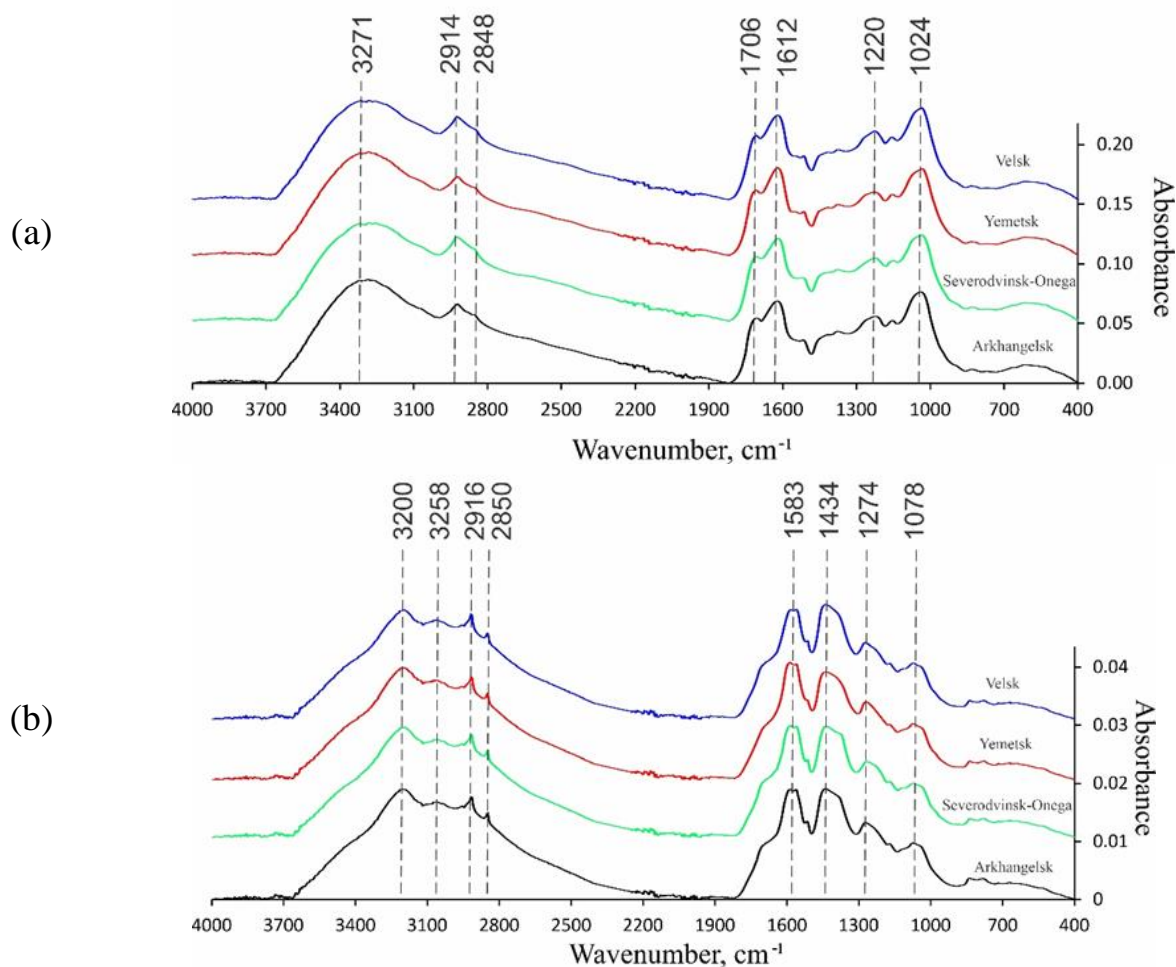


Figure 4. IR spectra of (a) the humic acids (HA) samples and (b) the fulvic acids samples.

Table 3. The average concentrations (mg kg⁻¹), median concentrations, and coefficients of variation (CV) of elements in the studied soils.

Elements	Velsk	Yemetsk	Severodvinsk-Onega	Arkhangelsk	Median (mg kg ⁻¹)	CV (%)
As	0.65	0.78	1.17	0.37	0.71	45
Cd	0.26	0.06	≤0.01	0.11	0.08	104
Cr	2.21	2.27	4.26	1.89	2.24	41
Hg	0.02	0.03	0.10	≤0.01	0.03	108
Pb	9.74	9.87	28.0	10.2	10.0	63
U	0.02	0.02	≤0.01	0.09	0.02	105

Table 4. Median concentrations of elements (mg kg⁻¹) and CV (%) values determined in this study (see Table 3) in comparison with average concentrations of elements reported in the literature for soils in Arkhangelsk region (Popova 2014) and for peat in the Russian Solovetsky Islands (Kozioł *et al.* 2020) as well as in other European countries: Estonia (Oru & Oru 2006); Hietajarvi, Finland (Ukonmaanaho *et al.* 2004); and Kistrand, Norway (Frontasyeva & Steinnes 2005).

Elements	Soil	Peat				
	Arkhangelsk	Arkhangelsk (this study)	Solovetsky Islands	Estonia	Hietajarvi	Kistrand
As	0.5	0.71 (45 %)	-	2.40	2.60	0.230
Cd	<1.0	0.08 (104 %)	0.80	0.12	-	-
Cr	-	2.24 (41 %)	1.27	3.10	-	1.600
Hg	<0.1	0.03 (108 %)	-	0.05	-	-
Pb	2.8	10.0 (63 %)	6.87	3.30	11.30	-
U	-	0.02 (105 %)	-	1.30	-	0.235

Table 5. Average concentrations (% ± SD) of the main elements in Arkhangelsk peat and its components.

Component	N	C	H	O	C/H	C/O
Peat	1.3 ± 0.1	54.5 ± 2.0	7.3 ± 0.3	36.8 ± 2.9	7.4	1.5
Humins	0.8 ± 0.1	55.0 ± 2.0	5.4 ± 0.3	38.8 ± 2.9	10.2	1.4
HA	8.7 ± 0.1	55.7 ± 1.9	6.8 ± 0.3	28.8 ± 2.9	8.2	1.9
FA	7.8 ± 0.1	57.7 ± 2.0	6.9 ± 0.3	27.0 ± 2.9	8.4	2.1
Bitumen	0.9 ± 0.1	81.4 ± 2.5	12.5 ± 0.3	5.2 ± 2.9	6.5	15.7

Table 6. Mass fraction of carbon (C) in the different functional groups of peat components (from NMR analysis).

Sample	Sample weight (mg)	Internal standard weight (mg)	Mass fraction of carbon atoms (%)						
			C(Alk)	C(Alk-O)	C(O-Alk-O)	C(Ar-C.H)	C(Ar-O)	C(COOH) + C(COOR)	C(C=O)
HA	32.235	4.207	2.12	2.31	0.47	1.93	1.06	1.13	0.30
FA	17.777	2.822	4.00	2.69	0.53	4.21	1.57	1.82	0.42
Bitumen	26.820	2.686	18.45	1.24	0.00	0.76	0.00	0.33	0.00

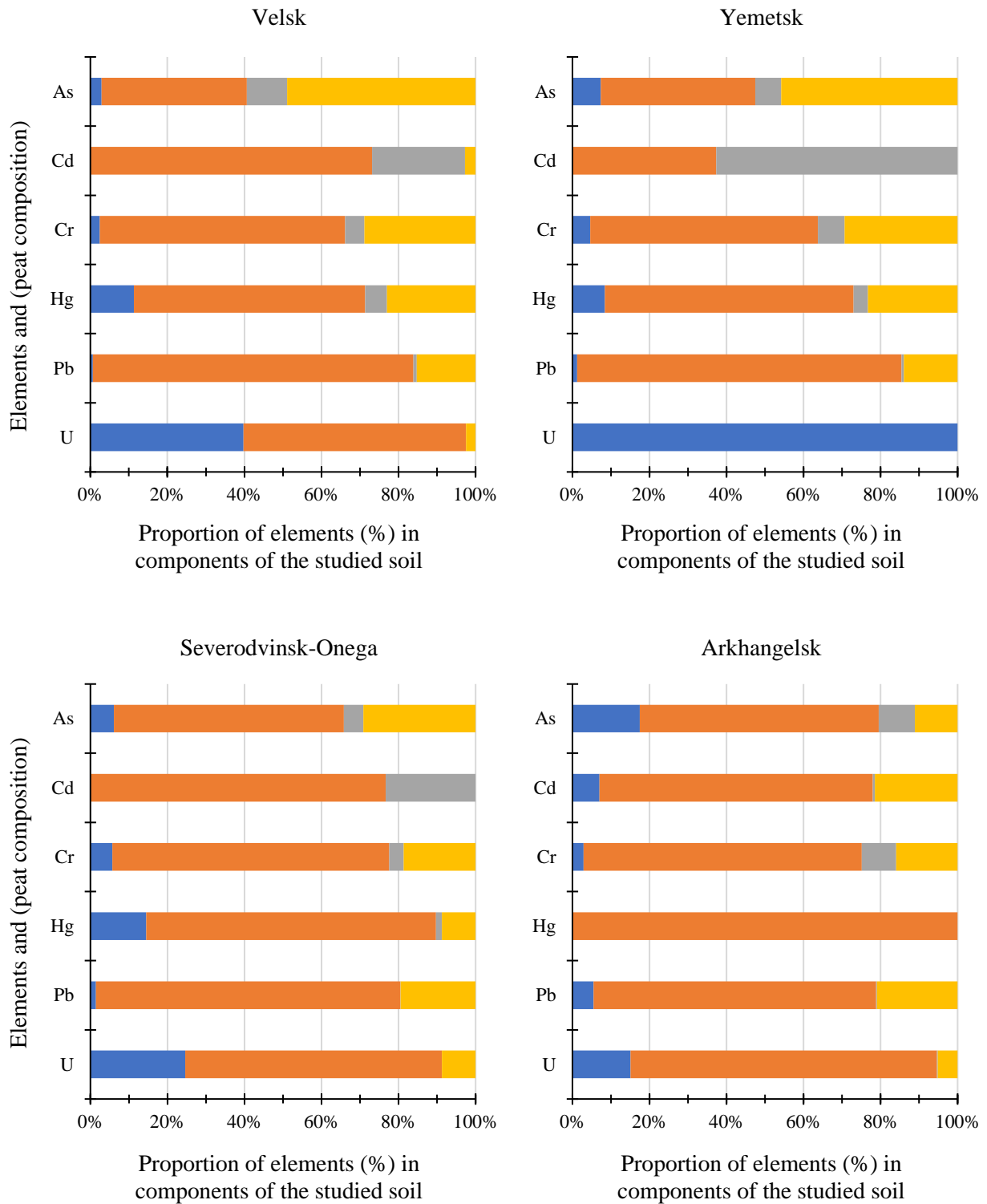


Figure 5. Distribution of elements between the components of peat at the four sampling locations: Velsk (top left); Yemetsk (top right); Severodvinsk-Onega (bottom left); and Arkhangelsk (bottom right). The components are, from left to right: humic acids (HA; blue), humin (orange), bitumen (grey) and fulvic acids (FA; yellow).



DISCUSSION

Levels of heavy metal pollution in Arkhangelsk Region

The concentrations of As, Cr, Hg and Pb were higher in the Severodvinsk-Onega peat sample than at our other three sampling locations (Table 3). In particular, the value for Pb in the Severodvinsk-Onega sample was three times higher than for the other locations, where the concentrations were similar to one another. This is probably a consequence of the shipbuilding industry located in Severodvinsk. In order to reduce this influence on our overall values, we calculated median rather than average concentrations to represent Arkhangelsk Region as a whole. On the whole, the concentrations in peat of the six toxic elements measured in our study were similar to (although not the same as) those measured in peat samples from the Solovetsky Islands and other countries in Europe by the authors whose data are summarised in Table 4.

The low mobility of Pb in peatlands is well established, such that Pb is used as a marker of human activity (Shotyk 1996, Shotyk *et al.* 1998, Le Roux *et al.* 2004, Bindler 2006). Even so, the highest concentration of Pb that we observed was below the maximum permitted level in soil (32 mg kg⁻¹) according to Russian regulations set out in The List of MAC and TAC № 6229-91 (1994). The median Pb concentration of 10.0 mg kg⁻¹ is consistent with results from previous studies (Ukonmaanaho *et al.* 2004, Koziol *et al.* 2020).

The As content was quite consistent in all studied samples, and the median concentration (0.71 mg kg⁻¹, CV = 45 %) was lower than the maximum permitted concentration for soil of 2 mg kg⁻¹ (The List of MAC and TAC № 6229-91 1994). These data agree with average As concentrations reported from other peatlands in Russia and Europe (Table 4), which have usually reported only trace amounts. Shotyk (1996) suggests that trends in As concentrations in peat may reflect an increase of human activities such as the use of As-containing pesticides and P fertilisers, and coal combustion. Redox conditions can also influence the behaviour of As because, by changing its bonding form and valency, it can transform into a mobile form that may redistribute by diffusion in water.

We recorded only trace levels of U in our samples, with a median concentration of 0.02 mg kg⁻¹, which was lower than the average concentrations of U reported from Norway and Estonia (Table 4). We also recorded trace levels of Hg with a median concentration of 0.03 mg kg⁻¹, which is in agreement with average concentrations

of Hg previously reported for soils in Arkhangelsk Region (Popova 2014) and in Estonia (Orru & Orru 2006). The content of Hg in peatlands is extremely low, and it is not a biogenic element. A positive correlation with other technogenic elements indicates its anthropogenic origin (Coggins *et al.* 2006).

Cd varied over a wider range; the median concentration was 0.08 mg kg⁻¹ and the coefficient of variation was 104 %. This is consistent with the average concentration of Cd reported from Estonia in Table 4, and lower than the concentrations reported from other locations in Russia (Popova 2014, Koziol *et al.* 2020). The Cd content of Arkhangelsk peat did not correlate with data for the other elements studied; Silamikele *et al.* (2011) also found no correlation between the concentrations of Cd and other elements. There are no sources of cadmium pollution in the region.

The median concentration of Cr in peat was 2.24 mg kg⁻¹ with a coefficient of variation of 41 %. This is highly consistent with the average concentration of Cr found in the other studies summarised in Table 4. The Cr content correlated with the content of several other elements, specifically iron, copper, zinc, arsenic, mercury and lead (Cr-Fe 0.952; Cr-Cu 0.987; Cr-Zn 0.983; Cr-As 0.927; Cr-Hg 0.985; Cr-Pb 0.984). Silamikele *et al.* (2011) also found correlations between the pairs Cr-Fe, Cr-Cu, Cr-Pb, Cr-As and others.

Distribution of pollutants amongst the components of peat

It has long been known that HA and FA have the ability to accumulate metals and metalloids (Gao *et al.* 1999). Thus, variations in the representation of these fractions within peat could lead to spatial variations in the ability of peat to accumulate elements. For example, the atypical predominance (within our sample set) of HA in peat collected from the vicinity of Arkhangelsk City (Table 2) could significantly influence the accumulation of chemical elements in the entire volume of peat. Our data do identify some trends in the distribution of elements between the four different peat components, suggesting significant tendencies for different elements to accumulate in specific peat components which are largely supported by previous studies reported in the literature.

Humins were the main component of the peat at all of our sampling locations, accounting for 87.5–90.0 % of total peat dry mass. Most of the toxic elements studied were contained in humins because it made up the largest fraction of the soil components. However, it can be seen from Figure 5 that, with



regard to all of the focus elements, humin was the peat component that showed the lowest sorption activity. For example, humin made up >90 % of the peat but accumulated only ~60 % of the As, which was more actively accumulated by the FA and HA components. We observed similar situations for Cr and Pb, whereas Cd accumulated most actively in bitumen.

The bitumen fraction predominantly accumulated As and Cr, holding 10 % of the total concentration of these elements despite the relatively low proportion (3.8–5.2 %) of bitumen in the peat. Arsenic was distributed amongst all four peat components but most of it was contained in the bitumen fraction. This is consistent with some (but not all) literature sources. Donner *et al.* (2019) found that most of the selenium and As in peat was contained in bitumen; Zherebtsov *et al.* (2008) found that As had a great affinity for bitumen isolated from coal; while Bicalho *et al.* (2017) noted the accumulation of V and Ni in bitumen whereas As and Cu accumulated in mineral fractions. The differences in distribution of elements reported from these studies can be explained in terms of differences in the concentrations and chemical forms of elements in the respective samples, and in the physical and chemical properties of the soils under study.

The HA fraction accumulated more elements than did the bitumen. The mass fraction of HA in the studied peat samples ranged from 1.7 % to 5.7 %, and this fraction showed a tendency to accumulate As, Hg and Cr. At the same time, we found no significant correlation between the content of HA and the content of trace elements in the peat. Zaccone *et al.* (2007) also noted that metal elements have affinity for organic matter in peat soil, namely HA. Martynyuk & Więckowska (2003) found that Pb, Ag, Hg and Cu ions have an affinity for HA under almost any conditions, whereas Cr is adsorbed only under certain conditions.

The mass fraction of FA varied from 2.1 % to 3.8 % and, of the four peat components, FA had ability to accumulate the greatest number of the focus elements, accumulating As, Cr, Zn and Pb very well. Borůvka & Drábek (2004) found that the Pb content in FA exceeded 80 % of the total amount of Pb in their peat samples, while Krajnc *et al.* (1995) reported that complexes of Cr with FA isolated from peat showed that FA accumulates Cr. In our study, Cr also accumulated preferentially in FA.

Mechanisms

The high sorption capacity of HA and FA is associated with their higher content of carboxyl

groups relative to the other two peat components. The high content of As and Cr in these fractions may be associated with large ionic radii, because these elements are mostly present as anions. Ions with large radii have a lower charge density and, as a result, a smaller hydrated radius. This leads to stronger forces of interaction with the surface, which is manifest as a higher sorption capacity. FA and HA also contain more nitrogen than the other peat components (Table 5), mainly due to amino groups, which also form complexes with metals. Covelo *et al.* (2008) noted that FA was mainly adsorbed on the surfaces of iron oxides in soils, and formed stable complexes with heavy metals. Wällstedt *et al.* (2010) showed that an upward trend in As adsorption was largely due to an increase in colloidal iron, which was stabilised by an increase in the proportion of FA. Possibly, the combination of these factors led to the accumulation of As by FA in the studied peats.

Humin contains non-humic components such as long-chain hydrocarbons, esters, acids, and even relatively polar structures of microbial origin such as polysaccharides and glomalin, which can be associated with non-polar fragments and soil minerals as well as with plant components that are highly resistant to decomposition (Hayes & Clapp 2001). Nonetheless, a characteristic that humin shares with HA and FA is the possession of a significant amount of functional groups and a certain amount of carboxyl groups that are capable of forming chemical bonds with the ions of heavy metals. These functional groups, along with the amino groups found in HA and FA, are capable of binding heavy metals most strongly into metal - organic ligand complexes. From the data presented in Figures 2–4 it can be seen that, despite the low content of FA in all peat samples, this is the most active component in terms of binding metals in the peat. At the same time, from the analysis of elemental composition, we can see that FA and HA have the largest numbers of amino groups and oxygen-containing groups. This is fully confirmed by the data shown in Figure 4. HA and FA immobilise the ions of trace elements by binding to them in the solid phase. Data obtained using IR spectroscopy and nuclear magnetic resonance spectroscopy also show that the amount of functional groups in FA and HA is higher than in the other organic components of peat (Table 6).

The bitumen fraction of peat had the lowest sorption capacity in relation to all elements, contained the lowest number of oxygen-containing groups, and had low nitrogen content. Thus, in terms of chemical composition, bitumen should

have the lowest affinity for heavy metals. This makes the formation of bitumen - element complexes in peat seem improbable, meaning that we might expect the proportion of elements found in bitumen to be minimal. Nonetheless, some metals were found in the bituminous part of the peat. The presence of a large number of low molecular weight organic acids, as well as nonpolar organics, can lead to methylation of the elements that are easily methylated under such conditions, namely Hg, As and - to a lesser extent - selenium. Therefore, it is possible to find these elements in the bitumen fraction, as well as for methylated forms of these elements to be captured along with bitumen during the first (organic solvents) phase of the extraction procedure. Cadmium is an exception, however, since we determined high cadmium content in bitumen. Probably, a different mechanism is at work here, and cadmium actually has an affinity for the non-polar organic fraction.

Thus, by considering the data in Table 2 in conjunction with Figure 5, we can conclude that the sorption of metals depends on the presence and concentration of active chemical centres and proceeds according to the chemisorption mechanism. Other researchers have indicated similar mechanisms of metal binding by bog peat through ion exchange and complexation (Kuznetsova *et al.* 2014). The absence of any statistically significant differences between sampling locations in the sorption of elements by peat components is attributed to differences in the component composition of the samples and errors in the determination of elements.

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AUTHOR CONTRIBUTIONS

SAS: project administration, methodology, writing original draft of manuscript, review and editing; AYK: conceptualisation, acquisition of funding, supervision, review and editing of manuscript; NLI, EVD, SLS, AVB: investigation, validation, formal analysis, visualisation of data.

REFERENCES

- Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J., Shoty, W. (2017) Determination of ultratrace (<0.1 mg kg⁻¹) elements in Athabasca Bituminous Sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). *Fuel*, 206, 248–257.
- Bindler, R. (2006) Mired in the past—looking to the future: Geochemistry of peat and the analysis of past environmental changes. *Global and Planetary Change*, 53(4), 209–221.
- Bordelet, G., Beaucaire, C., Phrommavanh, V., Descostes, M. (2018) Chemical reactivity of natural peat towards U and Ra. *Chemosphere*, 202, 651–660.
- Borůvka, L., Drábek, O. (2004) Heavy metal distribution between fractions of humic substances in heavily polluted soils. *Plant, Soil and Environment*, 50(8), 339–345.
- Bratskaya, S., Golikov, A., Lutsenko, T., Nesterova, O., Dudarchik, V. (2008) Charge characteristics of humic and fulvic acids: Comparative analysis by colloid titration and potentiometric titration with continuous pK-distribution function model. *Chemosphere*, 73(4), 557–563.
- Coggins, A.M., Jennings, S.G., Ebinghaus, R. (2006) Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. *Atmospheric Environment*, 40(2), 260–278.
- Covelo, E.F., Vega, F.A., Andrade, M.L. (2008) Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction. *Journal of Hazardous Materials*, 159(2–3), 342–347.
- Dai, L., Zhao, W., Wang, G., Wei, B., Zhang, K., Han, T., Ma, G. (2021). Competitive adsorption of Cd (II) and Pb (II) in aqueous solution onto humic acid derived from sewage sludge. *Desalination and Water Treatment*, 235, 221–230.
- De la Rosa, G., Peralta-Videa, J.R., Gardea-Torresdey, J.L. (2003) Utilization of ICP/OES for the determination of trace metal binding to different humic fractions. *Journal of Hazardous Materials*, 97(1–3), 207–218.
- Donner, M.W., Bicalho, B., Noernberg, T., Shoty, W. (2019) Contemporary and historical atmospheric deposition of arsenic and selenium in the Athabasca Bituminous Sands region. *Environmental Science & Technology*, 53(23), 14020–14028.



- Du Rietz, G.E. (1954) Die Mineralbodenwasserzeigergrenze als Grundlage einer natürlichen Zweigliederung der nord-und mitteleuropäischen Moore (The mineral soil water indicator limit as the basis of a natural division of the northern and central European moors). *Vegetatio*, 5(1), 571–585.
- Feng, Z.G., Yu, J.Y., Zhang, H.L., Kuang, D.L., Xue, L.H. (2013) Effect of ultraviolet aging on rheology, chemistry and morphology of ultraviolet absorber modified bitumen. *Materials and Structures*, 46(7), 1123–1132.
- Fiałkiewicz-Kozieł, B., Smieja-Król, B., Palowski, B. (2011) Heavy metal accumulation in two peat bogs from southern Poland. *Studia Quaternaria*, 28, 17–24.
- Frontasyeva, M.V., Steinnes, E. (2005) Distribution of 35 elements in peat cores from ombrotrophic bogs studied by epithermal neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 265(1), 11–15.
- Gao, K., Pearce, J., Jones, J., Taylor, C. (1999) Interaction between peat, humic acid and aqueous metal ions. *Environmental Geochemistry and Health*, 21(1), 13–26.
- Giovanela, M., Parlanti, E., Soriano-Sierra, E.J., Soldi, M.S., Sierra, M.M.D. (2004) Elemental compositions, FT-IR spectra and thermal behavior of sedimentary fulvic and humic acids from aquatic and terrestrial environments. *Geochemical Journal*, 38(3), 255–264.
- Gogmachadze, G.D. (2010) Гогмачадзе, Г.Д. *Агроэкологический мониторинг почв и земельных ресурсов Российской Федерации (Agroecological Monitoring of Soils and Land Resources of the Russian Federation)*. Moscow University Press, Moscow, 592 pp. (in Russian).
- Golubina, O.A., Tsybukova, T.N., Tveryakova, E.N., Perederina, I.A., Zholobova, G.A., Knyazeva, E.P., Zyкова, M.V. (2019) Голубина, О.А., Цыбукова, Т.Н., Тверякова, Е.Н., Передерина, И.А., Жолобова, Г.А., Князева, Е.П., Зыкова, М.В. Содержание биогенных элементов (Zn, Co, Cr), щелочных (Rb, Cs), щелочноземельных (SR, Ba) металлов и лантана в эвтрофной торфяно-болотной экосистеме (The content of biogenic elements (Zn, Co, Cr), alkaline (Rb, Cs), alkaline earth (SR, Ba) metals and lanthanum in the eutrophic peat-bog ecosystem). *Chemistry of Plant Raw Materials*, 4, 337–347 (in Russian).
- Gondar, D., Lopez, R., Fiol, S., Antelo, J.M., Arce, F. (2005) Characterization and acid-base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. *Geoderma*, 126(3–4), 367–374.
- Hayes, M.H.B., Clapp, C.E. (2001) Humic substances: considerations of compositions, aspects of structure, and environmental influences. *Soil Science*, 166(11), 723–737.
- Helal, A.A., Murad, G.A., Helal, A.A. (2011) Characterization of different humic materials by various analytical techniques. *Arabian Journal of Chemistry*, 4(1), 51–54.
- Inisheva, L.I. (2005) Инишева, Л.И. *Концепция охраны и рационального использования торфяных болот России (The Concept of Protection and Rational Use of Peat Bogs in Russia)*. CSTI, Tomsk, 76 pp. (in Russian).
- IUSS Working Group WRB (2015) *World Reference Base for Soil Resources 2014: International Soil Classification System for Naming Soils and Creating Legends for Soil Maps: Update 2015*. World Soil Resources Reports 106, FAO, Rome, 182 pp.
- Joosten, H., Clarke, D. (2002) *Wise Use of Mires and Peatlands - Background and Principles Including a Framework for Decision-Making*. International Mire Conservation Group and International Peat Society, Saarijärvi, 304 pp.
- Kalmykova, Y., Strömvall, A.M., Steenari, B.M. (2008) Adsorption of Cd, Cu, Ni, Pb and Zn on *Sphagnum* peat from solutions with low metal concentrations. *Journal of Hazardous Materials*, 152(2), 885–891.
- Kim, J.I., Buckau, G., Li, G.H., Duschner, H., Psarros, N. (1990) Characterization of humic and fulvic acids from Gorleben groundwater. *Fresenius' Journal of Analytical Chemistry*, 338(3), 245–252.
- Kozioł, K., Korzeniowska, J., Okupny, D., Bezak-Mazur, E., Żurek, S. (2020) Trace elements content of surface peat deposits in the Solovetsky Islands (White Sea). *Mires and Peat*, 26, 05, 13 pp.
- Krajnc, M., Štupar, J., Miličev, S. (1995) Characterization of chromium and copper complexes with fulvic acids isolated from soils in Slovenia. *Science of The Total Environment*, 159(1), 23–31.
- Kuznetsova, I., Bogolitsyn, K., Larionov, N., Boytsova, T., Palamarchuk, I., Aksenov, A. (2014) Structure and physical-chemical properties of humic acids of oligotrophic peat bog of Arkhangelsk region. *Ekologia (Bratislava)*, 33(1), 1–8.
- Kyzioł, J. (2002) Effect of physical properties and cation exchange capacity on sorption of heavy metals onto peats. *Polish Journal of Environmental Studies*, 11(6), 713–718.

- Le Roux, G., Weiss, D., Grattan, J.P., Givelet, N., Krachler, M., Cheburkin, A., Rausch, N., Kober, B., Shoty, W. (2004) Identifying the sources and timing of ancient and medieval atmospheric lead pollution in England using a peat profile from Lindow Bog. *Journal of Environmental Monitoring*, 6, 502–510.
- Levshina, S.I., Matyushkina, L.A. (2021) The distribution of dissolved forms of metals and metal–humus complexes in Zeya Reservoir water. *Water Resources*, 48(6), 967–976.
- Martyniuk, H., Więckowska, J. (2003) Adsorption of metal ions on humic acids extracted from brown coals. *Fuel Processing Technology*, 84(1–3), 23–36.
- Miszczak, E., Stefaniak, S., Michczyński, A., Steinnes, E., Twardowska, I. (2020) A novel approach to peatlands as archives of total cumulative spatial pollution loads from atmospheric deposition of airborne elements complementary to EMEP data: priority pollutants (Pb, Cd, Hg). *Science of The Total Environment*, 705, 135776, 15 pp.
- Mursito, A.T., Hirajima, T., Sasaki, K. (2010) The effect of hydrothermal dewatering of Pontianak tropical peat on organics in wastewater and gaseous products. *Fuel*, 89(12), 3934–3942.
- Niemeyer, J., Chen, Y., Bollag, J.M. (1992) Characterization of humic acids, composts, and peat by diffuse reflectance Fourier-transform infrared spectroscopy. *Soil Science Society of America Journal*, 56(1), 135–140.
- Orlov, D.S. (1997) Орлов, Д.С. Гуминовые вещества в биосфере (Humic substances in the biosphere). *Soros Educational Journal*, 2, 56–63 (in Russian).
- Orru, H., Orru, M. (2006) Sources and distribution of trace elements in Estonian peat. *Global and Planetary Change*, 53(4), 249–258.
- Попов, А.И. (2004) Попов, А.И. Гуминовые вещества: свойства, строение, образование (Humic Substances: Properties, Structure, Formation). Publishing House of St. Petersburg University, 248 pp. (in Russian).
- Попова, Л.Ф. (2014) Попова, Л.Ф. Химическое загрязнение урбоэкосистемы Архангельска: монография. Архангельск (Chemical Pollution of the Urban Ecosystem of Arkhangelsk: a Monograph. Arkhangelsk). Publishing House of NArFU, Arkhangelsk, 231 pp. (in Russian).
- Potapova, T.M., Markov, M.L., Zadonskaya, O.V. (2020) Потапова, Т.М., Марков, М.Л., Задонская, О.В. Установление гидрохимического фона верховых болот различных регионов России для обоснования нормативов допустимого воздействия на болота (The establishment of the background of raised bogs in various regions of Russia for justification of permissible impact standards). *Vestnik of Saint Petersburg University: Earth Sciences*, 65(3), 455–467 (in Russian).
- Rice, J.A., MacCarthy, P. (1991) Statistical evaluation of the elemental composition of humic substances. *Organic Geochemistry*, 17(5), 635–648.
- Ringqvist, L., Öborn, I. (2002) Copper and zinc adsorption onto poorly humified *Sphagnum* and *Carex* peat. *Water Research*, 36(9), 2233–2242.
- Ruggiero, P., Interesse, F.S., Cassidei, L., Sciacovelli, O. (1980) ¹H NMR spectra of humic and fulvic acids and their peracetic oxidation products. *Geochimica et Cosmochimica Acta*, 44(4), 603–609.
- Shoty, W. (1996) Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environmental Reviews*, 4(2), 149–183.
- Shoty, W., Weiss, D., Appleby, P.C., Cheburkin, A.K., Frei, R., Cloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O. (1998) History of atmospheric lead deposition since 12,370 ¹⁴C yr BP from a peat bog, Jura Mountains, Switzerland. *Science*, 281(5383), 1635–1640.
- Silamikele, I., Klavins, M., Nikodemus, O. (2011) Major and trace element distribution in the peat from ombrotrophic bogs in Latvia. *Journal of Environmental Science and Health, Part A*, 46(7), 805–812.
- Sypalov, S.A., Kozhevnikov, A.Y., Ivanchenko, N.L., Popova, Y.A., Sobolev, N.A. (2020) Assessment of peat pollution by heavy metals depending on the depth of occurrence. *Solid Fuel Chemistry*, 54(1), 32–36.
- Syrovetnik, K., Malmstrom, M.E., Neretnieks, I. (2007) Accumulation of heavy metals in the Oostriku peat bog, Estonia: Determination of binding processes by means of sequential leaching. *Environmental Pollution*, 147(1), 291–300.
- Tao, Z.Y., Zhang, J., Zhai, J.J. (1999) Characterization and differentiation of humic acids and fulvic acids in soils from various regions of China by nuclear magnetic resonance spectroscopy. *Analytica Chimica Acta*, 395(1–2), 199–203.
- The List of MAC and TAC № 6229-91 (1994) перечень предельно-допустимых концентраций (ПДК) и ориентировочно-допустимых количеств (ОДК) химических веществ в почве (List of

- Maximum Allowable Concentrations (MAC) and Tentative Allowable Concentrations (TAC) of heavy metals and arsenic in soils with different physical and chemical properties*). Designed by Research Institute of General and Communal Hygiene, A.N. Sysina All-Russian Research Institute of Hygiene and Toxicology of Pesticides, Polymers and Plastics of the Ministry of Health of the USSR, for Goskomsanepidnadzor (State Committee for Sanitary and Epidemiological Surveillance) of Russia (in Russian).
- Twardowska, I., Kyziol, J. (1996) Binding and chemical fractionation of heavy metals in typical peat matter. *Fresenius' Journal of Analytical Chemistry*, 354(5), 580–586.
- Ukonmaanaho, L., Nieminen, T.M., Rausch, N., Shotyk, W. (2004) Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland. *Water, Air, & Soil Pollution*, 158(1), 277–294.
- Van Reeuwijk, L.P. (2002) *Procedures for Soil Analysis*. Sixth edition, International Soil Reference and Information Centre, Wageningen, 130 pp.
- Wällstedt, T., Björkvald, L., Gustafsson, J.P. (2010) Increasing concentrations of arsenic and vanadium in (southern) Swedish streams. *Applied Geochemistry*, 25(8), 1162–1175.
- Xiaohu, L., Isacsson, U. (2002) Effect of ageing on bitumen chemistry and rheology. *Construction and Building Materials*, 16(1), 15–22.
- Zaccone, C., Cocozza, C., Cheburkin, A.K., Shotyk, W., Miano, T.M. (2007) Enrichment and depletion of major and trace elements, and radionuclides in ombrotrophic raw peat and corresponding humic acids. *Geoderma*, 141(3–4), 235–246.
- Zhao, Q., Qiu, Y., Lan, T., Li, J., Li, B., Wu, Z., Chen, L., Liu, R., Zhou, Y., Wu, W. (2021) Comparison of lead adsorption characteristics onto soil-derived particulate organic matter versus humic acid. *Journal of Soils and Sediments*, 21(7), 2589–2603.
- Zherebtsov, S.I., Klimovich, M.Yu., Moiseev, A.I. (2008) Distribution of toxic elements in the products of the extraction of bitumens from coal and peat. *Solid Fuel Chemistry*, 42, 171–176.

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Appendix

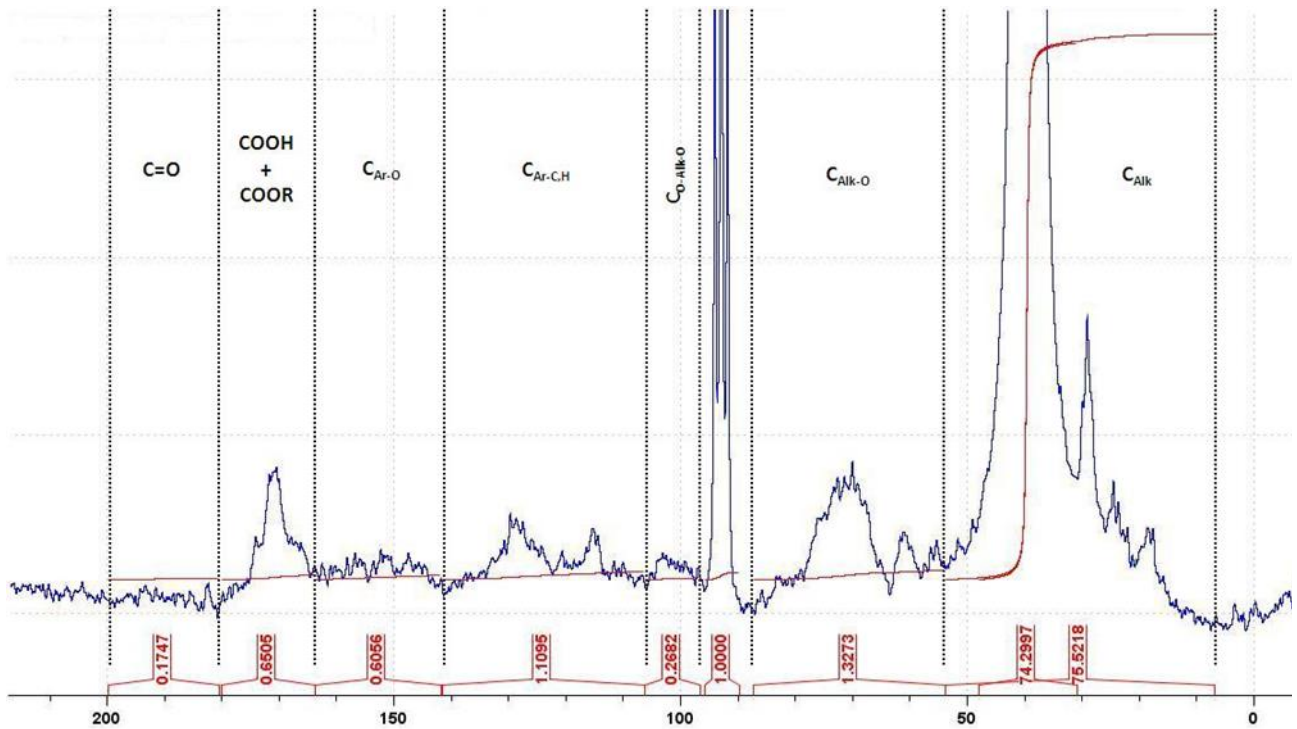


Figure A1. ^{13}C -NMR spectrum of humic acids in DMSO.

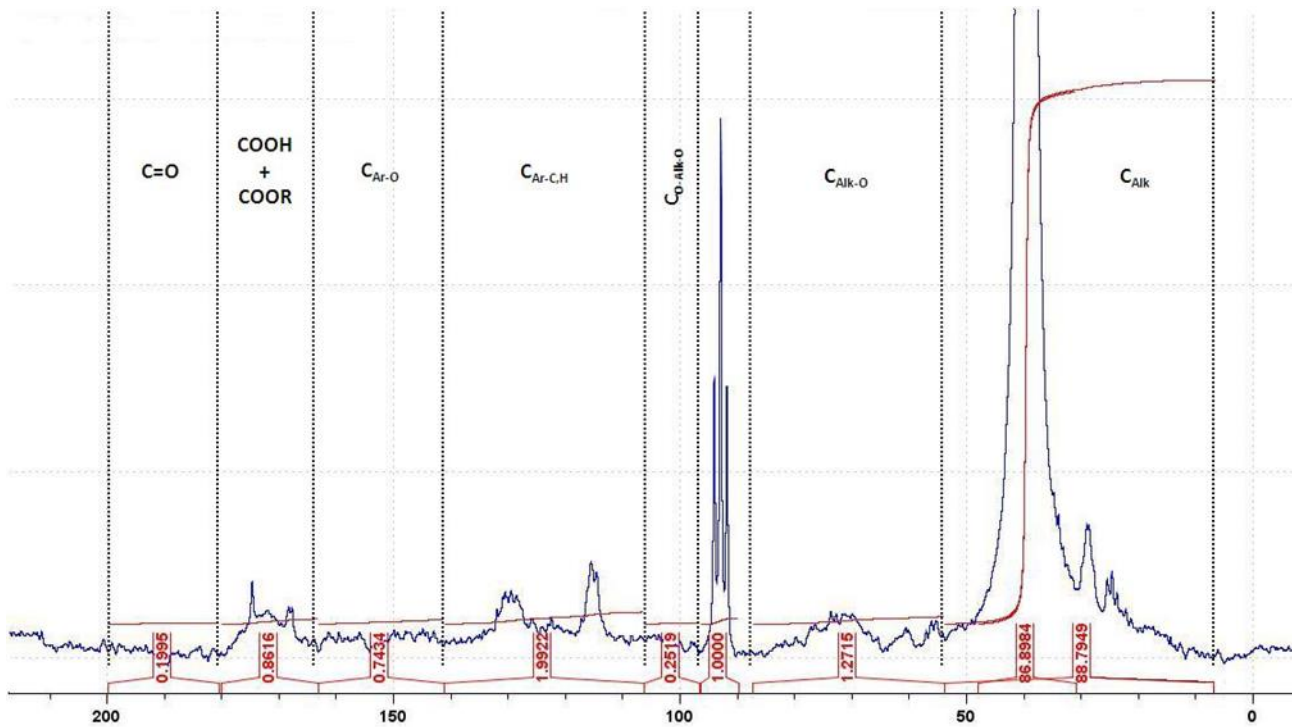


Figure A2. ^{13}C -NMR spectrum of fulvic acids in DMSO.

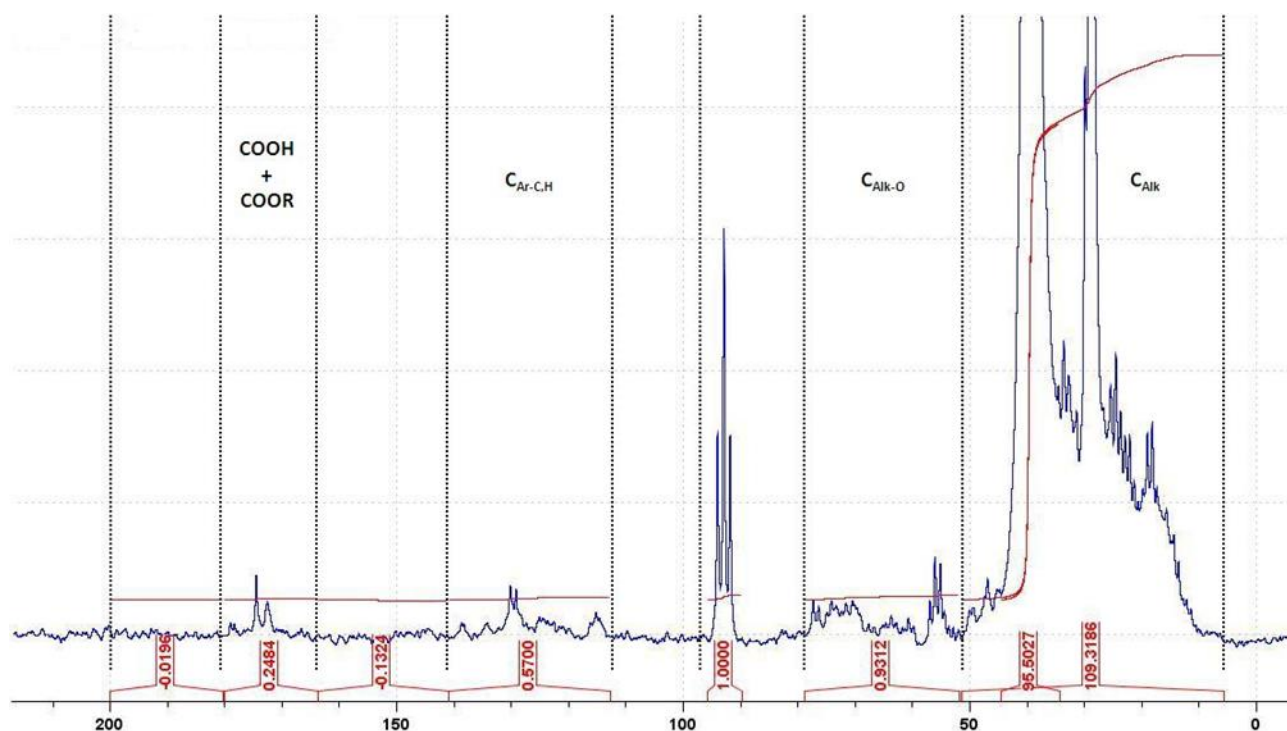


Figure A3. ^{13}C -NMR spectrum of bitumen in DMSO.

Table A1. The average concentrations of all elements (mg kg^{-1}), median concentrations (mg kg^{-1}) and coefficients of variation (CV) in the studied peat samples. Maximum permissible concentration (MPC) values (mg kg^{-1}) for these metals in Russian soils from The List of MAC and TAC № 6229-91 (1994) are also shown.

Elements	Velsk	Yemetsk	Severodvinsk-Onega	Arkhangelsk	Median	CV (%)	MPC
U	0.02	0.02	≤ 0.01	0.09	0.02	105	-
Pb	9.74	9.87	28.0	10.2	10.0	63	32
Hg	0.02	0.03	0.10	≤ 0.01	0.03	108	2.1
Cd	0.26	0.06	≤ 0.01	0.11	0.08	104	1.0
Ag	≤ 0.01	≤ 0.01	0.02	0.03	0.01	70	-
As	0.65	0.78	1.17	0.37	0.71	45	2.0
Zn	15.1	11.6	420	23.8	19.4	171	110
Cu	1.16	22.0	103	1.77	11.9	151	66
Ni	1.92	6.06	4.53	1.90	3.23	57	40
Co	0.36	0.27	0.69	0.70	0.53	44	-
Fe	979	557	3351	1061	1020	85	-
Mn	12.9	22.7	64.3	59.9	41.3	65	1500
Cr	2.21	2.27	4.26	1.89	2.24	41	-
V	2.23	1.38	2.69	10.2	2.46	99	150

Table A2. Median concentrations of all elements (mg kg^{-1}) and CV (%) values determined in this study (see Table A1) in comparison with average concentrations of elements reported in the literature for soils in Arkhangelsk region (Popova 2014). and for peat in the Russian Solovetsky Islands (Kozioł *et al.* 2020) as well as in other European countries: Estonia (Oru & Oru 2006); Hietajarvi, Finland (Ukonmaanaho *et al.* 2004); and Kistrand, Norway (Frontasyeva & Steinnes 2005).

Elements	Soil	Peat				
	Arkhangelsk	Arkhangelsk (this study)	Solovetsky Islands	Estonia	Hietajarvi	Kistrand
U	-	0.02 (105 %)	-	1.3	-	0.235
Pb	2.8	10.0 (63 %)	6.87	3.3	11.3	-
Hg	<0.1	0.03 (108 %)	-	0.05	-	-
Cd	<1.0	0.08 (104 %)	0.8	0.12	-	-
Ag	-	0.01 (70 %)	-	-	-	0.041
As	0.5	0.71 (45 %)	-	2.4	2.6	0.23
Zn	35.2	19.4 (171 %)	-	10.0	32.4	11
Cu	7.4	11.9 (151 %)	-	4.4	3.3	<5
Ni	14.7	3.23 (57 %)	4.01	3.7	2.5	1.07
Co	6.3	0.53 (44 %)	-	0.50	-	0.59
Fe	-	1020 (85 %)	-	-	-	1130
Mn	399	41.3 (65 %)	-	35.1	-	3.6
Cr	-	2.24 (41 %)	1.27	3.1	-	1.60
V	-	2.46 (99 %)	-	3.8	-	0.61

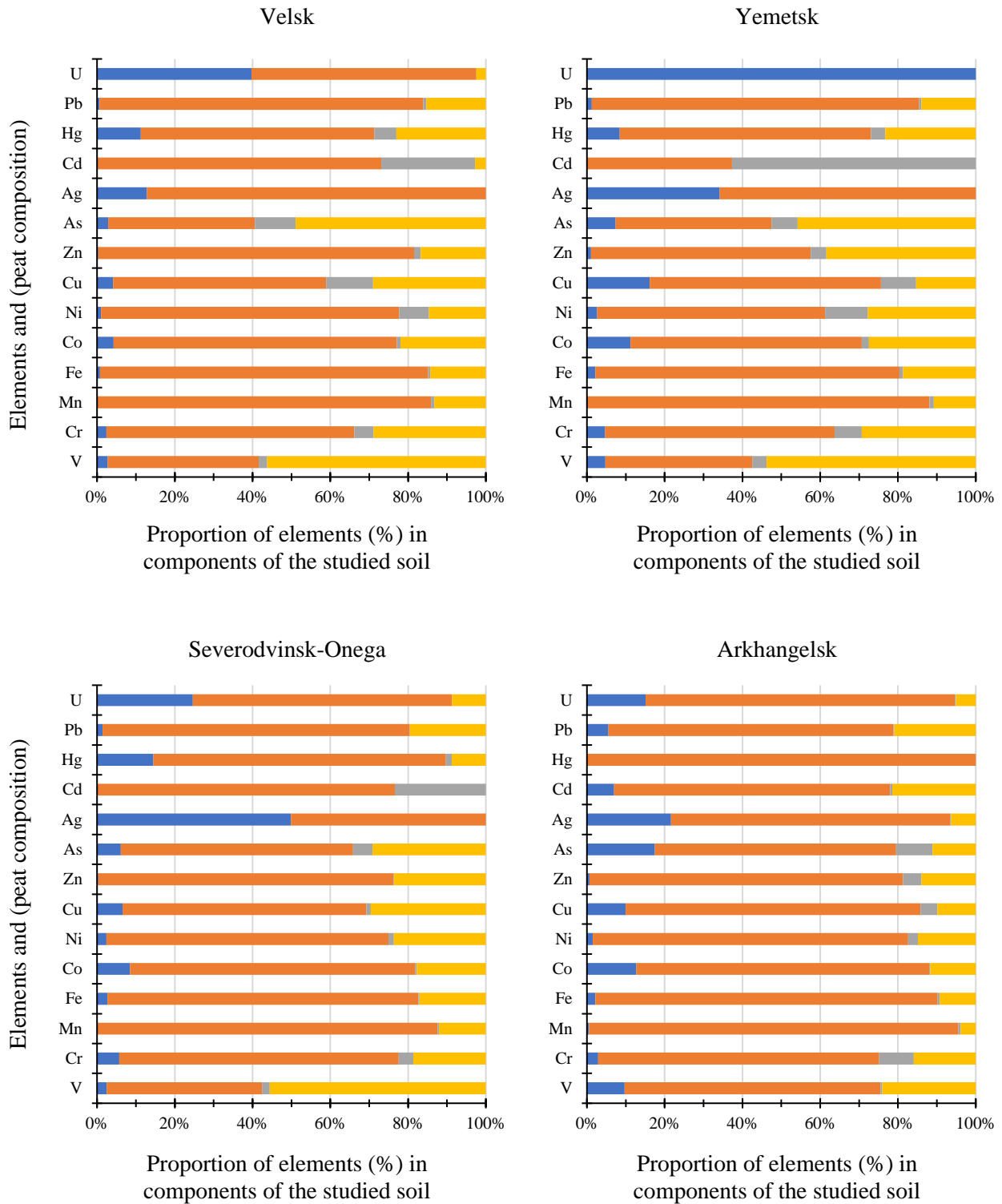


Figure A4. Distribution of elements between the components of peat at the four sampling locations: Velsk (top left), Yemetsk (top right), Severodvinsk-Onega (bottom left) and Arkhanelsk (bottom right). The components are, from left to right: humic acids (HA; blue), humin (orange), bitumen (grey) and fulvic acids (FA; yellow).



Table A3. The average concentrations of elements (mg kg⁻¹) in the components of the peat.

Velsk					Yemetsk				
Elements	Humic acids	Humin	Bitumen	Fulvic acids	Elements	Humic acids	Humin	Bitumen	Fulvic acids
U	< 0.01	< 0.01	< 0.01	< 0.01	U	< 0.01	< 0.01	< 0.01	< 0.01
Pb	0.05	6.1	0.06	1.1	Pb	0.07	5.0	0.04	0.84
Hg	< 0.01	0.02	< 0.01	< 0.01	Hg	< 0.01	0.02	< 0.01	< 0.01
Cd	< 0.01	0.17	0.05	< 0.01	Cd	< 0.01	< 0.01	< 0.01	< 0.01
Ag	< 0.01	0.05	< 0.01	< 0.01	Ag	< 0.01	< 0.01	< 0.01	< 0.01
As	0.02	0.25	0.07	0.32	As	0.04	0.24	0.04	0.28
Zn	0.04	12	0.25	2.46	Zn	0.05	2.6	0.19	1.8
Cu	0.06	0.85	0.19	0.45	Cu	0.39	1.4	0.22	0.37
Ni	0.03	2.41	0.24	0.46	Ni	0.04	0.92	0.17	0.44
Co	< 0.01	0.23	< 0.01	0.07	Co	0.03	0.13	< 0.01	0.06
Fe	6.4	690	4.2	120	Fe	9.4	340	3.9	82
Mn	0.02	9.9	0.10	1.5	Mn	0.04	14	0.18	1.7
Cr	0.06	1.6	0.13	0.74	Cr	0.11	1.4	0.17	0.71
V	0.05	0.77	0.04	1.1	V	0.06	0.52	0.05	0.74
Concentrations of elements (mg kg ⁻¹) in components of the studied soil					Concentrations of elements (mg kg ⁻¹) in components of the studied soil				
Severodvinsk-Onega					Arkhangelsk				
Elements	Humic acids	Humin	Bitumen	Fulvic acids	Elements	Humic acids	Humin	Bitumen	Fulvic acids
U	< 0.01	< 0.01	< 0.01	< 0.01	U	< 0.01	0.07	< 0.01	< 0.01
Pb	0.31	18	0.02	4.3	Pb	0.48	6.4	< 0.01	1.8
Hg	< 0.01	0.07	< 0.01	< 0.01	Hg	< 0.01	< 0.01	< 0.01	< 0.01
Cd	< 0.01	0.02	< 0.01	< 0.01	Cd	< 0.01	0.06	< 0.01	0.02
Ag	< 0.01	< 0.01	< 0.01	< 0.01	Ag	0.02	0.06	< 0.01	< 0.01
As	0.07	0.72	0.06	0.35	As	0.07	0.23	0.04	0.04
Zn	1.1	275	0.52	85	Zn	0.18	23	1.3	4.0
Cu	5.0	47	0.82	22	Cu	0.16	1.20	0.07	0.16
Ni	0.09	2.8	0.06	0.91	Ni	0.02	1.34	0.04	0.25
Co	0.05	0.43	< 0.01	0.10	Co	0.10	0.62	< 0.01	0.10
Fe	76	2200	7.1	480	Fe	19	780	4.8	82
Mn	0.05	46	0.16	6.3	Mn	0.30	52	0.30	2.1
Cr	0.24	3.0	0.16	0.79	Cr	0.07	1.6	0.20	0.36
V	0.07	1.0	0.05	1.5	V	0.74	5.0	0.03	1.8
Concentrations of elements (mg kg ⁻¹) in components of the studied soil					Concentrations of elements (mg kg ⁻¹) in components of the studied soil				