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# DIANA DUDARE, MARIS KLAVINS\* RAISED BOG PEAT HUMIC ACID ELEMENTAL COMPOSITION: TRENDS OF CHANGES AND RELATED FACTORS

*Abstract.* Peat deposits can be considered as archives of environmental changes and indicators of anthropogenic pollution. The character of element accumulation, the potential of metal ions to bind functional groups in the peat structure, the pH reaction, the presence of oxygen, the complexing compounds and inorganic ions are the main factors governing peat ability to accumulate major and trace elements. The aim of this paper has been to study the major and trace element accumulation in humic acids (HAs) in two well-characterized ombrotrophic peat profiles of Eipurs Bog and Dzelve Bog in Latvia and analyse factors affecting the element concentrations in HAs with reference to peat properties. The analysis of major elements (e.g., Ca, Fe, K, Mg, Na) and trace elements (e.g., As, Cd, Co, Cr, Cu, Ni, Pb, Se, Zn) was performed by total reflection X-ray fluorescence spectrometry. Thise c paper demonstrates that HAs are significant for several elements, however, they are not the dominant factor affecting the element accumulation. The concentration of trace elements in peat and in peat HAs depend not only on human-induced pollution (determining elevated concentrations of trace elements in upper layers of the bog). The study has revealed that for the accumulation of several toxic trace elements in peat (for instance, As, Pb and others) natural processes are of key importance.

Peat lands play a significant role in the global carbon biogeochemical cycle, thus reinforcing their impact on global climate, due to their ability to store and release large amount of carbon [1, 2]. Nowadays great attention is paid to studies about metals in peat with the aim to examine peat sorption abilities, as well as pollution history, where a great deal of research on metals in peat is focused on historical records of the deposition of trace metals [3, 4]. Similarly, the profile of complex formation between humic acids and major and trace elements has been the object of intensive studies during last decades [5-8].

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The pattern of major and trace element accumulation depends on the balance between natural and human-induced processes, whereas the accumulation of natural elements prevails at low pollution levels. The accumulation pattern of metals in peat profiles can serve as valuable archives of natural and human-induced changes [9].

The surface peat layers of ombrotrophic bogs receive elements only from the atmosphere, thereby reflecting the presence of these elements in the air [10]. The ability of peat to store major and trace elements depends on the profile of element supply (whether in particulate or ionic form), the potency of metal ions to bind to functional groups in the peat structure, pH reaction, oxygen presence, the presence of complexing compounds, inorganic ions and many other factors [11, 12]. Many studies have stressed that the main factor affecting the accumulation of metals in peat profile is a humic substance [13–16].

Humic acids (HA), organic macromolecules found in soils, sediments and waters play an important role in interaction processes with metal ions. They are soluble in the pH range of natural waters and possess the ability to support complex and colloid formation [17], therefore, HA can influence the oxidation state of metal ions and thus, their speciation and mobility [18]. Humic acids also are dominant in the composition of peat organic matter [13] and play a major role in the biogeochemical cycling of many trace elements due to the significant complex-forming ability [19].

The quantitative analysis of trace and major elements in peat humic substances might help to understand the character of their binding with natural organic matter and the processes affecting their cycling in the environment. The knowledge of the concentrations of trace elements in humic substances is also important because of their growing use in industry and agriculture. The content of trace and major elements has been characterized in humic acids of different origins such as peat humic acids [14, 15], sedimentary humic acids [20], aquatic humic substances [21].

The aim of this study hhas been to analyse the nature of element distribution between peat and peat humic acids in two well-characterized ombrotrophic bog profiles (Latvia). The studied peat profiles have been characterised using multi-proxy analysis, including radiocarbon dating, analysis of botanical composition, decomposition degrees, and other methods.

### MATERIALS AND METHODS

### Materials

Analytical quality reagents (Merk Co., Sigma – Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without purification. For the preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10–15 M $\Omega$ cm was used throughout the study. All the reagents used in the procedures were of analytical grade.

#### Description of Study Sites, Peat Sampling and Isolation of Humic Acids

Peat profiles were obtained from well-characterized [22, 23] ombrotrophic bogs – Eipurs and Dzelve. The studied bogs are located in the lowland. The location and hypsometry of Eipurs and Dzelve bogs are also relatively close (57°14'53"N, 24°37'00"E, 40 m a.s.l. and 57°13'58"N, 24°30'12"E, 20 m a.s.l.). Both bogs are located in Middle Latvia Lowland, Central Latvia. The most part of Eipurs Bog is surrounded by glacigenic deposits of the last Great Ice Age; however, there are also remnants of ancient dunes situated on the west side of the bog. Nowadays, Dzelve Bog is surrounded by glaciolimnic deposits of Weichselian Glaciation in the territory of Latvia [24]. Eipurs Bog has formed as fen by accumulation of grass - moss peat on sandy clay deposits 8700 cal. years BP. The accumulation of well-decomposed (58–40 %) transitional and raised bog wood peat reflects strong drainage and dry conditions in the research area during the development of the respective layers. The botanical composition of the upper deposit layer of peat in the research area reflects stable raised bog development with negligible surface drainage where bog vegetation receives nutrients from atmospheric precipitation.



Fig. 1. Peat stratigraphy and peat decomposition degree in Eipurs (A) and Dzelve (B) bogs.

Dzelve Bog has developed on sand deposits but, unlike Eipurs Bog, it was a raised bog from the beginning. The lowermost peat layer from 3.50–3.30 m started to form 4800 cal. years BP. The homogeneous botanical composition of peat and decomposition degree (9–24 %) in Dzelve Bog reflect constant wet conditions during the development of the *Sphagnum* moss peat layer, which is similar to nearby Eipurs Bog.

Peat sampling procedure has been done with a peat sampler in the cupola area of each bog, where samples were put in a cartridge and wrapped in polyethylene film for keeping the natural moisture.

For the isolation of humic acids, the obtained peat profiles were separated into 10 cm layers and humic acids were extracted using the procedures recommended by the International Humic Substances Society (IHSS) [25].

Metal concentrations in a 1-cm slice of peat profile were determined after nitric acid digestion by graphite furnace atomic absorption spectrometry (GFAAS, Perkin-Elmer AAnalyst 200) with background correction [26]. The concentrations of trace elements (Ti, Sr, Se) were measured with total-reflection X-ray fluorescence spectrometry (TXRF) [27]. The samples of humic acid were prepared: 25 mg HA was treated with 1 ml conc. HNO<sub>3</sub> and boiled until the solution completely evaporated. Afterwards, 1 ml 50 % HNO<sub>3</sub> was added. The samples were cooled. 10 mg  $l^{-1}$  of Ga internal standard (Sigma-Aldrich Co.) was added to each sample. To obtain complete results of X-ray fluorescence spectrometry, the samples were applied three times on each quartz glass and dried using the liophylizator (Labconco FreeZone). The analyzed samples were placed into the total-reflection X-ray fluorescence spectrometer (Röntec PicoTAX TXRF, Röntec GmbH) with a 1000-second measurement period. AThe accuracy was between 1–10 % for major elements and 1–2 % for trace elements.

## The Analysis of Botanical Composition and Decomposition of the Peat

The analysis of botanical composition was done using light microscope (Axiostar, Carl-Zeiss) with magnification 100–400 times. At the same time, the decomposition degree is a very important property of peat for the determination of element accumulation, which was measured using the centrifugation method [28] according to Standard GOST 10650–71.

The peat decomposition degree was evaluated by von Post pressing method [29] and then corrected by centrifugation method [30].

The dating of peat deposits was performed by <sup>14</sup>C dating method, which was done at the Institute of Geology of Tallin Technical University (Estonia).

### Characterization of Peat Humic Acids

Elemental analysis (C, H, N, S, O) was carried out using an Elemental Analyzer Model EA – 1108 (Carlo Erba Instruments) with the combustion-gas chromatography technique. The instrument was calibrated using cystine (Sigma – Aldrich Inc.), and all peat samples were analysed twice. UV/Vis spectra were recorded on a Thermospectronic Helios  $\gamma$  UV (Thermo Electron Co.) spectrophotometer in a 1-cm quartz cuvette. An automatic titrator titroLine easy (Schott – Gerate GmbH) was used to measure carboxylic and total acidity of each humic acid. Ba hydroxide method [31, 32] was used to estimate the total concentration of carboxylic groups and total acidity. 20.0 mg of humic acid was weighed out and dispensed in a 125-mL ground-stoppered Erlenmeyer flask, after that adding 10 ml of 0.1 *N* Ba(OH)<sub>2</sub> solution. The air in the flask was replaced by bubbling N<sub>2</sub> gas mixture, closed airtight and shaken for 24 hours with a wrist-action shaker at room temperature. The mixed solution was titrated potentiometrically with a standardized (0.1 *N*) HCl to pH 8.4. A microbiret for dispensing the standard acid was used.

### Data Treatment

The relationships between different characteristics were assessed with Spearman rank correlation coefficients. In all cases the significance level between values was p = 0.05 and p = 0.01. The obtained data revealed methodological distinctions, namely, performance in respect to the analytical recovery of TXRF was in range 65–105 %. All measurements of element detection were repeated three times. The calculated lower limits of detection (LLDs) for most elements (e.g., Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Ba) are distinctly below 1 mg l<sup>-1</sup>, whereas the lower limits of detection for other heavy elements are significantly higher.

#### RESULTS AND DISCUSSION

The studied bogs – Eipurs and Dzelve – have a very much different botanical composition and varying decomposition degrees of the peat (Fig. 1) and the current paper, which involves the study of the accumulation of metals as well as peat properties, the character of metal accumulation in humic acids isolated from the peat, can reveal not only the metal-binding character over the time of bog development, but also the factors controlling it. The binding of major and trace elements in peat humic acids is largely dependent on their elemental (CHN) and functional (COOH) composition (Fig. 2, 3).





The variable elemental composition of the studied humic acids reflects their original material and is characterized by increasing values of carbon (C) in humic acids from peat with higher decomposition degree, while the concentrations of hydrogen (H) and nitrogen (N) are fluctuating within the limits of values common for peat humic acids and, thus, does not show any well-expressed trends of changes within the peat profiles. The content of carboxyl groups is lower in the humic acids from the uppermost peat layers and it can even reach the values > 6 mEq g<sup>-1</sup> in the humic acids isolated from the peat with a higher decomposition degree (Fig. 3).



Fig. 3. The content of COOH (mEq g<sup>-1</sup>) in humic acids of Eipurs and Dzelve bogs.

The distribution pattern of the total amount of major and trace elements in peat and their humic acids considerably differs depending on the element (Fig. 4), respectively, while the metal content of presumably natural origin (e.g., K, Ca, Fe, Mn) is higher in peat than in humic acids, the values of other elements, presumably of anthropogenic origin (e.g., Cu, Ni, Cr, Pb, As) are higher in humic acids than in peat. The obtained concentrations of major and trace elements in peat, compared with the values found in other countries [14–16, 21], cannot be considered as high and indicate a low level of anthropogenic pollution, considering the possibilities of using peat and isolated humic acids in the agriculture.

In peat from Eipurs Bog, the highest amount of Ca was in raised bog wood peat, while in peat from Dzelve Bog it was in pine - cotton-grass peat. Although depth range of the highest accumulation rate of calcium differs between research sites, still, it is more characteristic for peats with a high amount of wood residues. The average concentration of Fe (the third most common element) is rather variable between research sites. The smallest average content of Fe (0.30  $\mu$ g g<sup>-1</sup>) was detected in Dzelve Bog. In peat from Eipurs Bog the highest amount of iron was represented in the bottom part of the peat profile where grass - moss peat was located. In the peat profile from Dzelve Bog the distribution of Fe was similar to calcium and the highest amount was represented in raised bog pine – cotton-grass peat. The results show that the distribution of this natural element was definitely



affected by various contributors specific to each site at different periods of time, whereas botanical composition was of secondary importance.

Fig. 4. Concentrations (µg g<sup>-1</sup>) of major and trace elements in peat and in humic acids from Eipurs and Dzelve bogs.

The average amount of Zn in both raised bogs is considerably high. The average concentration of zinc is around 9  $\mu$ g g<sup>-1</sup> in peat from Dzelve and Eipurs bogs. In peat from Eipurs Bog the highest amount of Zn was in Sphagnum peat in the upper part of the peat profile. In the peat profile from Dzelve Bog the highest concentration of zinc was in Sphagnum peat, like in the peat profile from Eipurs Bog – only in this case, the most saturated was peat in the middle part of the profile. In contrast to that, the situation with manganese was just the opposite. On average, the highest awerage concentration of manganese was detected in peat from Dzelve Bog (3.2  $\mu$ g g<sup>-1</sup>).

The average concentrations of other detected metals are various and site-specific, not directly dependent on the respective peat type. The distribution of Na in the peat profile from Eipurs is rather unstable. The highest amount of Na was detected in the upper part of the profile, where Sphagnum peat was located. In the peat profile from Dzelve the highest concentration of sodium was in same Sphagnum peat, only in this case in the middle part of the layer. It can be presumed that accumulation of this alkali metal has been affected by current geodynamical processes in the area. As Dzelve and Eipurs Bogs are closer to the sea, the elevated amount of Na can also be explained by the impact of salty air flow from the Baltic Sea.

In peat profiles from all four research sites, it is possible to define several element pairs that are specific to certain peat types.

It is possible to observe that a definite type of peat affects the distribution of elements along bog profile, for instance, elements of anthropogenic origin form most of relations between metals in Sphagnum peat of Eipurs Bog. However, Cr does not form any significant correlation. Almost all trace metals correlate with Ca, Fe, Mn, Ni and K. In cotton-grass - sphagnum peat, relations between elements emerge, including new correlations between elements of natural origin. The average concentrations of metals in this peat layer are lower in comparison with Sphagnum peat. If there were no negative correlations between elements in the sphagnum peat layer, then in this layer there were several: Ca with Cr and Ni, Na with Mn, Pb with K, Cu with Co and Cr with Mg. Beneath that, where Sphagnum peat is located, the situation again was rather different than in the same peat type above. The average concentration of calcium was about 2 times higher, whereas that of zinc was 9 times lower and that of Pb - 10 times lower, etc. In addition, the quantity of significant correlations was also reduced, and there were also some negative relations that were not identified in the layer above. In wood peat of the underneath layer, the concentration of calcium significantly increased with the average amount of 12.73  $\mu$ g g<sup>-1</sup> of dry peat weight. The quantities of lead, copper, chromium and cobalt (forming only negative correlations) also were increased. In the wood peat layer, both natural and anthropogenic metals are related. The last statistically significant peat layer in the peat profile is grass - moss peat, which is fen peat. The quantity of natural metals in the peat layer is about the same as in wood raised bog peat; however, the total amount of trace elements, such as lead, copper and chromium, is decreased. The most of significant correlations are made of trace elements, and there are even more relations than in the surface sphagnum peat layer. Most of these correlations are negative (precursors are Pb, Cu, Cr and Co).

The found chemical elements and their concentrations in our study were compared with the results obtained in other studies, including the reference samples (Table 1). Since the formation of bogs is affected by local and regional environmental conditions, it was interesting to find out what exactly affects the accumulation of elements in bogs of Latvia (namely, Dzelve and Eipurs), compared with bogs of other regions. The concentrations of chemical elements of the studied bogs are relatively low compared with other regions, where the intense human activity has affected the accumulation of chemical elements in the upper layers of the peat. The average values of the elements in humic acids in this study are quite similar to those found in the Swiss region obtained by the Italian research group [15, 16], for instance, the average value of chromium (Cr) reaches 1.62  $\mu$ g g<sup>-1</sup>. The relatively small difference between values can be related to similar conditions of the formation of the bogs, as according to the classification

both compared bogs are high – type bogs. The average values of chemical elements in HA of Dzelve and Eipurs bogs are considerably lower than those found in the North region [20] where the precipitation containing sea salt aerosols leads to the increase in the concentrations of definite elements. Different mean values were observed by the Norwegian research group [21], where the reference humic samples isolated from Suwannee River (USA) were analyzed.

# TABLE 1. CONCENTRATION OF TRACE AND MAJOR ELEMENTS (μg g<sup>-1</sup>) IN THE SAMPLES OF HUMIC ACIDS FROM EIPURS AND DZELVE BOGS AND FROM OTHER SITES

Element	Eipurs Bog <sup>1</sup>	Dzelve Bog <sup>1</sup>	Switzerland <sup>2</sup>	North Sea <sup>3</sup>	North Sea <sup>3</sup> USA <sup>3</sup>		IHSS Waskish HA reference <sup>4</sup>	
Fe	191.07	76.78	57.62	_	0.54	1813.65	308.64	
Pb	0.33	0.40	1.15	_	_	1.83	0.78	
As	1.57	1.49	9.10	_	_	1.75	0.54	
Cu	3.59	2.44	13.85	447.17	_	13.83	28.26	
Ca	102.18	95.04	776.96	-	_	333.73	630.64	
Mn	0.75	0.37	2.57	157.60	_	_	2.38	
Cr	2.16	1.21	1.62	482.17	11.7	2.48	29.66	
Ni	1.21	0.73	6.12	_	_	8.35	2.72	
K	51.01	40.77	-	_	_	1856.03	121.60	
Zn	3.99	6.85	17.50	435.67	2.98	95.01	33.32	
Ti	10.17	4.10	16.8	1030.00	_	2.80	18.86	
Se	0.42	0.22	_	_	1.10	1.44	0.64	
V	0.61	0.67	_	305.67	_	_	_	
Sr	0.30	0.31	2.53	_	_	7.24	1.36	
Со	1.76	0.44	_	_	_	1.2	-	
Rb	0.44	0.29	2.20	_	_	0.16	_	
Br	2.70	11.91	_	_	196.00	9.24	4.68	

 $^{1}$  – average values for the studied bog profiles;  $^{2}$  – [15];  $^{3}$  – [6];  $^{4}$  – estimated analysed reference samples.

The differences between average concentrations of the studied HA affect processes of element accumulation, based on physico-chemical interaction between chemical element ions or their compounds in which form they are and certain functional groups or structures in the HA molecule. As the composition of humic acids isolated from river sediments differs from HA isolated from bogs the character of element accumulation and the total amount of concentrations changes considerably.

Significantly higher average concentrations of metals were observed with Waskish (IHSS reference sample, isolated from the Pine Island Bog, USA) and Pahokee (IHSS reference sample, isolated from Pahokee peat, USA), with a higher concentration of carboxyl groups and a lower amount of aliphatic structures in the HA molecule, affecting the intensity of element accumulation in HA, which determines the difference between the average values of the studied bogs and the reference samples. Variable mean values of the studied HA and HA in other regions may also affect the selected method for element analysis – the energy-dispersion miniprobe X-ray fluorescence spectrometry (EMMA – XRF) was used for element analysis in the Swiss region; the instrumental neutron activation analysis (INAA) was used in the USA; the proton-excited X-ray emission analysis (PIXE) was used for element determination in the North Sea.

Despite the use of the multiple methods in other studies, it is evident that with total reflection X-ray fluorescence spectrometry (TXRF) it is possible to detect very low concentrations of chemical elements.

The changes of concentrations of major and trace elements in HA (Fig. 5) from the studied bog profiles correspond to general pattern: to) elements of elevated concentrations in HA from the upper layers of the bog (Cr, Ni, Pb, Zn, Cu), b) elements of elevated concentrations in HA from the bottom layers of the bog (Mn, Mg, Ca, Fe) and c) elements of increased concentrations in HA from the bottom and upper layers of the bog in comparison with their concentrations in the middle layers of the bog (As, K). A similar accumulation pattern of major and trace elements was previously found to be common in raised bogs and can be interpreted as the accumulation of metals due to anthropogenic pollution in the upper layers or due to supply in groundwater from the bottom of the bog. The concentrations of Cr and Pb in HAs of Eipurs Bog form some peaks at different layers of depth. This fact can be related to the impact of soil organic matter on Cr mobility due to the formation of high molecular weight insoluble complexes with HAs. The tendency of Cr concentration increase with depth can be related to the increase in the degree of humification.

The nature of arsenic values, both in peat and peat HA of Eipurs Bog, has a tendency to decrease in the middle layers, while As values in the upper layers of Eipurs Bog are relatively high. The obtained data can be explained by the fact that As has a similar chemistry to that of P and can, thus, be taken up by plants. The tendency of As could reflect the changing rate of anthropogenic atmospheric



inputs during the past few centuries, for example, due to the increased coal burning during the industrial revolution and the use of Pb arsenates as pesticides.

Fig. 5. Concentrations of As, Zn and Fe in peat and HA along the Eipurs Bog profile.

The concentrations of As in HAs range between 0.37 and 3.13  $\mu$ g g<sup>-1</sup>. In the first 30 cm, in particular, the average value of the total As is recovered into HA molecules, while below this depth this metalloid becomes almost undetectable. This behaviour could be explained by the ability of As to bound indirectly to organic functional groups through bridge metal such as Fe<sup>3+</sup>. The Zn<sub>HA</sub>/Zn<sub>peat</sub> ratio ranges between 0.2 and 1.26, with an average of 0.62, showing that this element seems to be recovered into the peat mass. The Fe<sub>HA</sub>/Fe<sub>peat</sub> ratio ranges between 0.05 and 0.59, with an average of 0.25, showing that Fe is not bound to HAs.

The nature of the major trace elements of anthropogenic origin (e.g., Cu, Ni, Cr, Mn, As) and their increase in the deeper layers of both bog peat profiles can be explained by the supply from groundwater. The elevated values of the studied trace elements, such as Ni, Cr and Cu, in the upper layers of the peat core of Eipurs Bog can be attributed to air pollution due to industrial production (Fig. 6). The detected elements are immobile in peat, thus, they can be used as the indicators of anthropogenic activity.

The analysis of correlations between the concentrations of dominant elements in the peat of Eipurs and Dzelve bogs and humic acids, isolated from the corresponding peat layers, shows that there are elements for which the noticed correlations are significant (Fig. 7, Table 2). The correlation between the values of copper and iron, both in peat and humic acids, isolated from the corresponding peat layers are statistically significant, indicating that the above-mentioned metals in the composition of peat are bound in the form of complexes with HS. At the same time, in the case of such elements as As and K, the correlations between their values in peat and HAs are weak, indicating that HS play a minor role in the binding of these elements in peat, while the dominant factor could be their binding either in the form of mineral phases or other forms.



Fig. 6. Concentrations (µg g<sup>-1</sup>) of Cr, Ni and Cu in HA along the profile of Eipurs Bog.

The differences in the binding of major and trace elements in peat and peat HAs increasingly highlight the correlation between the concentrations of metals in peat and peat HAs as well as among different metals (Table 2). Strong and statistically significant correlations between elements in peat and HAs have been found only for Fe, Zn and Cu. Simultaneously, there are evident correlations between elements depending on their origin, as follows, that the element pairs can be identified according to their dominant natural sources such as Fe-Mn, Fe-Cu, Mn-Cu, Ca-Mn, Ca-Fe. Nevertheless, the pairwise correlation between the concentrations of elements can also indicate their joint complexes, for example, there is a close correlation in the pair As-Fe similar to that in the pair As-Mn. Close correlations are also common for the elements of evidently anthropogenic origin.



Fig. 7. Correlations between Fe and Cu concentrations in peat and peat humic acids in the studied bogs.

														0.42	As - P
													0.09	0.09	Ni - HA
												-0.04	0.93	0.18	Ni - P
											-0.19	-0.12	-0.21	0.35	Pb - HA
										0.15	-0.08	-0.18	0.05	0.62	Pb - P
									-0.19	-0.03	0.67	-0.39	0.49	-0.13	Ca - HA
								0.64	-0.36	-0.27	0.93 (**)	-0.09	0.87	-0.02	Ca - P
							0.67	0.73	0.03	-0.14	0.78	-0.18	0.56	-0.03	Cu – HA
						0.85	0.79	0.68	-0.02	-0.15	0.89	-0.19	0.72	-0.02	Cu - P
					-0.21	-0.17	-0.46	-0.17	0.74	0.17	-0.24	-0.06	-0.09	0.63	Zn - HA
				0.88	-0.15	-0.12	-0.43	-0.23	0.75	0.19	-0.19	-0.06	-0.05	0.59	Zn - P
			0.67	0.65	-0.08	-0.09	-0.23	-0.32	0.91	0.17	-0.02	-0.08	0.16	0.69	Mn -HA
		0.21	0.08	-0.01	0.77	0.66	0.85	0.51	0.08	-0.15	0.93	-0.05	0.96	0.40	Mn - P
	0.72	0.08	0.02	0.03	0.63	0.82	0.63	0.71	0.08	-0.17	0.77	0.01	0.69	0.29	Fe - HA
•69.0	0.92	-0.09**	-0.30	-0.32	0.75	0.62	0.97	0.59	-0.23	-0.26	0.95	-0.01	0.95	0.19	Fe - P
Fe - HA	Mn - P	Mn -HA	Zn - P	Zn - HA	Cu - P	Cu - HA	Ca - P	Ca - HA	Pb - P	Pb - HA	Ni - P	Ni - HA	As - P	As - HA	

#### CONCLUSIONS

1. Trace and major element concentrations in peat and humic acids isolated from two raised bogs – Eipurs and Dzelve (Latvia) – of similar origin and mainly differing lithology points out the impact of human-induced pollution on element concentrations in the upper layers of the studied bogs, both in humic substances and in peat.

2. Simultaneously, increased concentrations of elements, such as Zn, Fe, Mn, As, Cu, etc., have been determined in the deeper layers of the bog and their main source is the natural weathering of bedrock and supply in groundwater.

3. On the other hand, the total concentration levels of major and trace elements in the studied peat and humic acid samples can be considered as comparatively low.

4. The correlation analysis between major and trace element concentrations in peat and humic acids demonstrate that several elements in peat are bound in the form of humic substances, but other forms of binding dominate for other elements.

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# KIERUNKI ORAZ CZYNNIKI REGULUJĄCE SKŁAD PIERWIASTKOWY KWASU HUMUSOWEGO TORFOWISKA WYSOKIEGO

Złoża torfu mogą być uważane za archiwa zmian środowiskowych, jak również za wskaźniki zanieczyszczenia antropogenicznego. Głównymi czynnikami regulującymi zdolność torfu do akumulowania pierwiastków głównych i śladowych są: stężenie pierwiastków, zdolność jonów metali do wiązania/łączenia w grupy funkcyjne w strukturze torfu, odczyn - pH, obecność tlenu, związki kompleksujące oraz jony nieorganiczne. Celem niniejszej pracy było zbadanie stopnia kumulacji / koncentracji pierwiastków głównych i śladowych w kwasach humusowych (HAs) w dwóch dobrze scharakteryzowanych torfowiskach ombrotroficznych – bagnach Eipurs Bog oraz Dzelve Bog na Litwie oraz analiza czynników wpływających na stężenie pierwiastków w kwasach humusowych w odniesieniu do właściwości torfu. Analiza pierwiastków głównych (np. Ca, Fe, K, Mg, Na) oraz pieriwastków śladowych (np. As, Cd, Co, Cr, Cu, Ni, Pb, Se, Zn) przeprowadzona została przy użyciu spektrometru fluorescencji rentgenowskiej całkowitej absorpcji. W niniejszej pracy wykazane zostało, że kwas humusowy jest czynnikiem znaczącym, jednak dla niektórych pierwiastków siladowych w trofie, a także w kwasach humusowych torfu, zależy nie tylko od zanieczyszczenia wywołanego działalnością człowieka (oznaczenie podwyższonego stężenia pieriwastków śladowych w górnych warstwach bagna). Badania wykazały, że procesy naturalne mają kluczowe znaczenie przy akumulacji niektórych toksycznych pierwiastków śladowych w trofie (na przykład As, Pb, oraz innych).