ELEMENTAL COMPOSITION OF HUMIC ACIDS FROM RAISED BOG PEAT PROFILES

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Annotation. Peat profiles serve as archives for environmental change and soil composition research, and the recent, as well as historic, accumulation of elements in peat profiles depending on the intensity of anthropogenic pollution has been widely studied. The ability of peat to accumulate major and trace elements depends on the character of element supply, functionalities in the peat structure conducive to metallic ion binding, pH reactions, the presence of oxygen, complex compounds, inorganic ions and many other factors. The aim of this study was to determine the major and trace element distribution 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 concentration in humic acids with respect to peat. The study demonstrates that humic acids are an important – but, for many elements, non-major – factor affecting the accumulation of elements. Trace element concentrations in peat and in peat humic acids depend not only on human-induced pollution (causing the accumulation of elements in upper bog layers). For several toxic trace elements (for example, arsenic, lead and others), natural processes are of key importance.
Keywords: humic acids, peat, trace and major elements, X-ray fluorescence spectroscopy.

Introduction

The presence of major and trace elements in peat is an essential indicator of peat genesis and organic matter humification processes, and it is also important for the industrial use of peat (Fuchsman 1980). The upper peat layer of ombrotrophic bogs receives chemical elements only from the atmosphere, thus reflecting the presence of these elements in the air (Shotyk *et al.* 1998). Trace element accumulation in peat profiles has been used for reconstructing changes in human pollution and for tracking the sources of anthropogenic pollution and characterizing its intensity. The recent as well as historic accumulation of many trace elements in peat profiles depending on the

intensity of anthropogenic pollution has been widely studied (Shotyk 2002; Orru *et al.* 2006; de Vleeschouwer *et al.* 2007). The ability of peat to accumulate major and trace elements depends on the character of element supply (whether in particulate or ionic form), potency of metal ions to bind functionalities in the peat structure, pH reaction, oxygen presence, presence of complexing compounds, inorganic ions and many other factors (Shotyk 2002; Orru *et al.* 2006). Researchers have hypothesized that the main factor affecting the accumulation of metals in peat profile are humic substances (Gondar *et al.* 2005; Zaccone *et al.* 2007; Zaccone *et al.* 2008; Zaccone *et al.* 2009).

Humic substances (HSs) are a general category of naturally occurring, biogenic, heterogeneous organic substances that can be generally characterized as yellow to black in colour, of high molecular weight and refractory to degradation (Stevenson 1994). Depending on their solubility, humic substances can be grouped into humic acids (HAs) (the fraction insoluble in water under acidic conditions pH < 2, but is soluble at greater pH) and fulvic acids (the fraction soluble in water at all pH values (Aiken (ed.) 1985). Humic acids are dominant in the composition of peat organic matter. HSs form most of the organic component of peat, and they play a major role in the biogeochemical cycling of many trace elements (Falkowski *et al.* 2003) due to significant complex-forming ability. The character of complex formation between humic acids and major and trace elements has been an object of intensive studies during last decades (Davies *et al.* 1997; *Tipping* 2002; Zhou *et al.* 2005; Pourret *et al.* 2007).

The analysis of trace and major elements in humic substances might help to understand the character of their binding with natural organic matter and the processes affecting their cycling in the environment. Knowledge about trace element concentrations in humic substances is also important because of their growing use in industry and agriculture. Until now, trace and major element concentrations have been analysed in aquatic humic substances (Riise *et al.* 1989), sedimentary humic acids (Fengler *et al.* 1994) and peat humic acids (Zaccone *et al.* 2008; Zaccone *et al.* 2009).

The aim of this study was to determine the major and trace element distribution between peat and peat humic acids in two well-characterized ombrotrophic bog profiles and analyse factors affecting the element concentrations in peat humic acids.

Materials and methods

Materials. Analytical quality reagents (Merk Co., Sigma – Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without purification. For preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10–15 MΩcm was used throughout the study.

Peat sampling and characterization, isolation of humic acids. Peat profiles were obtained from well-characterized (Kuske *et al.* 2010; Silamikele *et al.* 2010) ombrotrophic bogs – Eipurs and Dzelve. Both bogs are located in lowlands, they are of similar origin (they have developed due to ground paludification), although their lithology is largely differing (Figure 1). Both bogs are typical raised bogs, and they have never been affected by direct pollution sources, either presently, or historically.
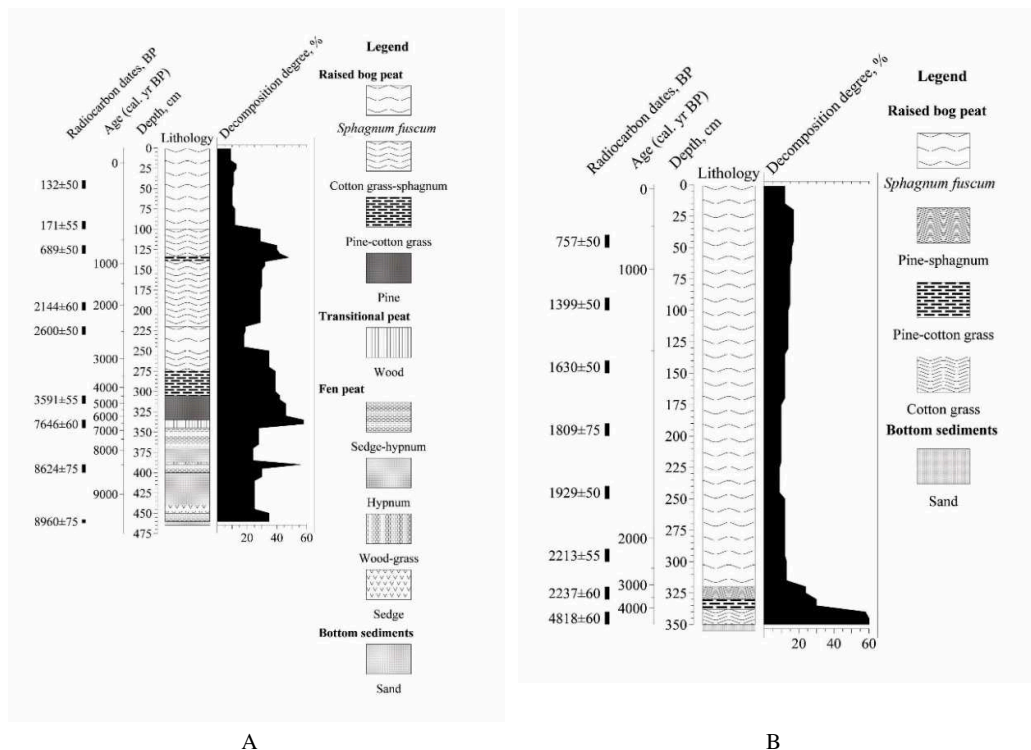
Figure 1. **Peat stratigraphy and peat decomposition degree in Eipurs (A) and Dzelve (B) bogs**

Trace elements in a 1-cm slice of peat profile were determined after nitric acid digestion by GFAAS (Krachler *et al.* 2001). For 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) (McCarthy 1976).

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). UV/Vis spectra were recorded on a Thermospectronic Helios γ 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 (Schnitzer 1982; Tan 1982) 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)$_2$ solution. The air in the flask was replaced by bubbling N$_2$ 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. Trace element (Ti, Sr, Se) concentrations were measured with total-reflection X-ray fluorescence spectrometry (TXRF) (Cabaniss 1992). The samples of humic acid were prepared: 25 mg HA was treated with 1 ml conc. HNO$_3$ and boiled until the

solution completely evaporated. Afterwards, 1 ml 50% HNO_3 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 Labconco liofilizator. The analyzed samples were placed into the total-reflection X-ray fluorescence spectrometer with a 1000-second measurement period.

Results and discussion

The two studied bogs have a very differing botanical composition and variable peat decomposition degrees (Figure 1), and the study of metal accumulation in their peat properties, and metal accumulation character in humic acids in isolation from peat, can reveal not only the metal-binding character over the time of bog development but also the factors controlling it. Major and trace element binding in peat humic acids is largely dependent on their elemental (C, H, N) and functional (COOH) composition (Table 1).

Table 1. **Elemental composition of humic acids and the content of COOH (mEq g^{-1}) in humic acids from Eipurs and Dzelve bogs**

Eipurs Bog					Dzelve Bog				
Depth, m	C, %	H, %	N, %	COOH, mEq/g	Depth, m	C, %	H, %	N, %	COOH, mEq/g
0.0 - 0.25	52.35	5.39	2.43	2.7	0.0 - 0.10	42.74	4.23	2.32	3.90
0.25 - 0.50	52.83	5.12	2.34	5.10	0.20 - 0.30	51.95	4.88	2.79	4.70
0.50 - 0.70	53.46	5.41	2.53	4.50	0.40 - 0.50	53.43	4.86	2.25	4.30
0.70 - 1.20	52.16	5.25	2.42	4.40	0.60 - 0.70	48.36	4.08	2.05	4.70
1.20 - 1.35	48.82	4.43	2.07	3.90	0.80 - 0.90	52.89	4.85	2.18	4.30
1.35 - 1.70	53.24	4.80	2.13	4.70	1.00 - 1.10	52.18	4.86	2.23	4.80
1.70 - 1.87	54.36	4.76	1.82	4.60	1.20 - 1.30	54.00	5.17	2.41	4.60
1.87 - 2.20	53.64	4.93	1.91	4.20	1.40 - 1.50	58.28	4.64	2.23	4.70
2.20 - 2.30	53.81	4.93	1.80	4.40	1.80 - 1.90	59.01	5.29	2.27	4.40
2.30 - 2.40	54.75	5.04	1.87	4.60	2.00 - 2.10	54.81	5.18	2.25	4.30
2.40 - 2.50	54.68	5.04	1.98	4.70	2.20 - 2.30	55.90	5.03	2.22	4.10
2.50 - 3.20	51.44	5.02	1.59	4.10	2.40 - 2.50	56.41	4.99	2.04	4.4
3.20 - 3.58	52.74	4.34	2.25	6.20	2.60 - 2.70	55.14	4.70	2.09	4.20
3.58 - 3.62	54.98	4.25	2.09	6.60	2.80 - 2.90	54.97	4.78	2.07	4.30
3.62 - 4.10	55.98	4.82	2.53	4.70	3.00 - 3.10	55.14	4.53	2.46	4.30
4.10 - 4.56	55.33	4.49	2.48	4.70	3.20 - 3.30	56.58	4.56	2.34	4.40
4.56 - 4.62	48.32	4.24	2.31	6.10	3.40 - 3.50	59.49	3.98	2.02	5.40

The elemental composition of the studied humic acids reflects their original material and is characterized by increasing values of C in humic acids from peat with higher decomposition degree, while the content of H and N is 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 carboxyl group concentration

is lower in the humic acids from the uppermost peat layers, and it can even reach the values >6 mEq g^{-1} in the humic acids isolated from the peat with higher decomposition degree (Table 1).

The concentration distribution of major and trace elements in peat and in humic acids isolated from peat significantly differs depending on the element (Figure 2): whereas the concentrations of some elements (supposedly of natural origin, such as Ca, Fe, K, Mn) are higher in peat than in humic acids, the concentrations of other elements (supposedly of anthropogenic origin, such as Pb, As, Cr, Ni, Cu) are higher in humic acids than in peat. Considering the possibilities of using peat and isolated humic acids in agriculture, the found values of major and trace elements in peat, especially if compared with the values found in other countries (Riise *et al.* 1989; Zaccone *et al.* 2007; Zaccone *et al.* 2008; Zaccone *et al.* 2009), cannot be considered as high and indicate a low level of anthropogenic pollution.
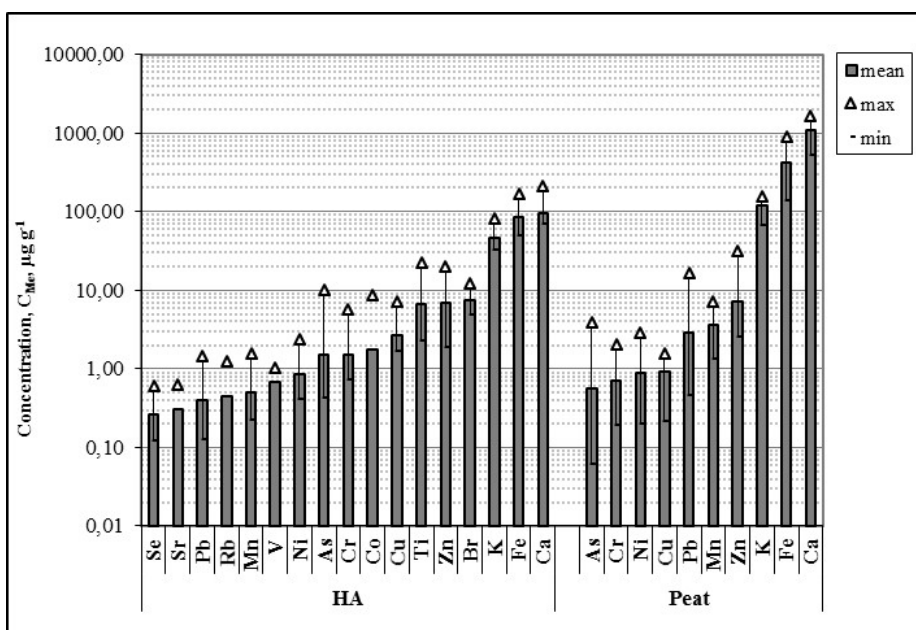

Figure 2. **Concentrations (μg g^{-1}) of major and trace elements in peat and in humic acids from Eipurs and Dzelve bogs**

A comparison of element concentrations found in the humic acids in our study with those in other samples of humic acids, including reference samples (Table 2), indicates the major importance of the source of the element for its presence in humic acids. The highest major and trace element concentrations were common for the humic acids isolated from sea sediments. In the humic acids isolated from peat, the major and trace element concentrations depend on their presence in natural bog environment (for example, a relatively high variability of Fe, Br, Zn, Ti). However, the concentrations of elements associated with recent human pollution are at a relatively similar level.

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Table 2. **Concentration of trace and major elements (µg g⁻¹) in the samples of humic acids from Eipurs and Dzelve bogs and from other sites**

Element	Eipurs Bog[1]	Dzelve Bog[1]	Switzerland[2]	North Sea[3]	USA[3]	IHSS Pahokee HA reference[4]	IHSS Waskish HA reference[4]
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
Co	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] – (Zaccone et al., 2009); [3] – (Riise et al., 1989); [4] – estimated analysed reference samples

Major and trace element concentration changes in humic acids from peat profiles from the studied bogs follow general patterns: a) elements of increased concentrations in the humic acids from the upper layers of bog (Zn, Pb, Ni, Cr, Cu), b) elements of increased concentrations in the humic acids from the bottom layers of bog (Fe, Ca, Mn, Mg) and c) elements of elevated concentrations in the humic acids from the bottom and upper layers of bog in comparison with their concentration in the middle layers of bog (K, As). A similar major and trace element accumulation pattern was previously found to be common in raised bogs and can be interpreted as accumulation of metals due to anthropogenic pollution in the upper layers or due to supply with groundwater from the bottom of bog. Cr and Pb concentrations 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, and it can be related to the increase in the degree of humification.

The As_{HA}/As_{peat} ratio ranges between 0.37 and 8, with an average of 2.49, showing that this trace element seems to be adsorbed on the humic material surfaces. The character of As concentration in the peat and HA of Eipurs Bog has a tendency to decrease in the middle layers, while As concentrations in the upper layers of Eipurs Bog are comparatively high. The observed data can be explained with the fact that As has a

similar chemistry to that of P, and can thus be taken up by plants. The arsenic trend 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.

The concentration of arsenic in HAs ranges between 0.37 and 3.13 mg·kg^{-1}. 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^{+3}. The Zn$_{HA}$/Zn$_{peat}$ 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$_{HA}$/Fe$_{peat}$ ratio ranges between 0.05 and 0.59, with an average of 0.25, showing that Fe is not bound to HAs.

The character of the dominant anthropogenic trace elements, such as Cr, Ni, Cu, Mn and As, and their accumulation in the deeper layers of both peat profiles can be explained by supply from groundwater. The increased levels of the studied trace elements, such as Cr, Ni and Cu in the upper layers of the peat core of Eipurs Bog can be ascribed to air pollution due to industrial production. The detected elements are immobile in peat; therefore, they can be used as the indicators of anthropogenic activity.

Table 3. **Correlation between major and trace element concentrations in peat (P) and peat humic acids (HAs) in Eipurs Bog**

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

The analysis of correlations between major and trace element concentrations in the peat of Eipurs and Dzelve bogs and the humic acids isolated from the corresponding peat layers indicates that there are elements for which the mentioned correlations are significant. At the same time, there are also elements for which the correlations are statistically insignificant (Table 3). For example, the correlations between Cu and Fe concentrations in peat and in humic acids isolated from the corresponding peat layers are statistically significant, indicating that the aforementioned elements in the composition of peat are bound in the form of complexes with humic substances. At the same time, in the case of such elements as As and K, the correlations between their concentrations in peat and humic acids are weak, indicating that humic substances play

a minor role in the binding of these elements in peat, while the major factor could be their binding either in the form of mineral phases or other forms.

The differences in the major and trace element binding to peat and peat humic acids increasingly highlight the correlation between metal concentrations in peat and peat humic acids as well as among different metals (Table 3). Strong and statistically significant correlations between elements in peat and humic acids has been found only for Fe, Zn and Cu. At the same time, there are evident correlations between elements depending on their origin. In this way, the element pairs can be identified according to their dominant natural sources. For example, Fe-Mn, Fe-Cu, Mn-Cu, Ca-Mn, Ca-Fe and others. However, the pairwise correlation between element concentrations 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.

Conclusions

The study of trace and major element concentrations in peat and humic acids isolated from two raised bogs – Eipurs and Dzelve (Latvia) – of similar origin and largely differing lithology indicates the impact of human-induced pollution on element concentrations in the upper layers of the studied bogs, both in humic substances and in peat. At the same time, elevated concentrations of many elements (Fe, Zn, As, Cu, Mn and others) have been found in the deeper layers of the bog, and their source is the natural weathering of bedrock and supply with groundwater. However, the total concentration levels of major and trace elements in the studied peat and humic acid samples can be considered as relatively low. Correlation between major and trace element concentrations in peat and humic acids demonstrate that many elements in peat are bound in the form of humic substances, whereas other forms of binding dominate for other elements.

Acknowledgements

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