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MAJOR AND TRACE ELEMENTS IN HUMIC ACIDS FROM RAISED BOG PEAT PROFILES IN LATVIA

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SUMMARY

Major and trace element concentrations in peat profiles support the concept of using element concentration records to track regional and global environmental pollution problems, owing to peat ability to accumulate elements. In our study we have selected two raised bogs with contrasting lithology, consequently, peat composition, as indicated by elemental composition. The aim of our study was to assign major and trace element distribution in humic acids (HA) for two well characterized raised bog peat profiles of Eipurs and Dzelve Bog and analyse factors affecting element concentration in peat humic acids, relating to element concentration in peat. The content of 17 elements was determined in humic acids of Dzelve and Eipurs Bogs. Our study 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.

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). 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 (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 (Orru and Orru, 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*., 2008).

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 and Salbu, 1989), sedimentary humic acids (Fengler *et al*., 1994) and peat humic acids (Zaccone *et al*., 2008). The objectives of this study were to determine the distribution of metal content in peat humic acids from two well-characterized ombrotrophic bog profiles, as well as factors affecting it and designate physical and chemical properties of 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 (Silamikele *et al*., 2010) ombrotrophic bogs – Eipurs and Dzelve. 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) (MacCarthy, 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. Trace element (Ti, Sr, Se) concentrations were measured with total-reflection X-ray fluorescence spectrometry (TXRF) (Cabaniss, 1992).

RESULTS AND DISCUSSION

The two studied bogs have a very differing botanical composition and variable peat decomposition degrees, 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 (CHN) and functional (COOH) composition.

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 concentration distribution of major and trace elements in peat and in humic acids isolated from peat significantly differs depending on the element (Fig. 1): 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 and Salbu, 1989), cannot be considered as high and indicate a low level of anthropogenic pollution.

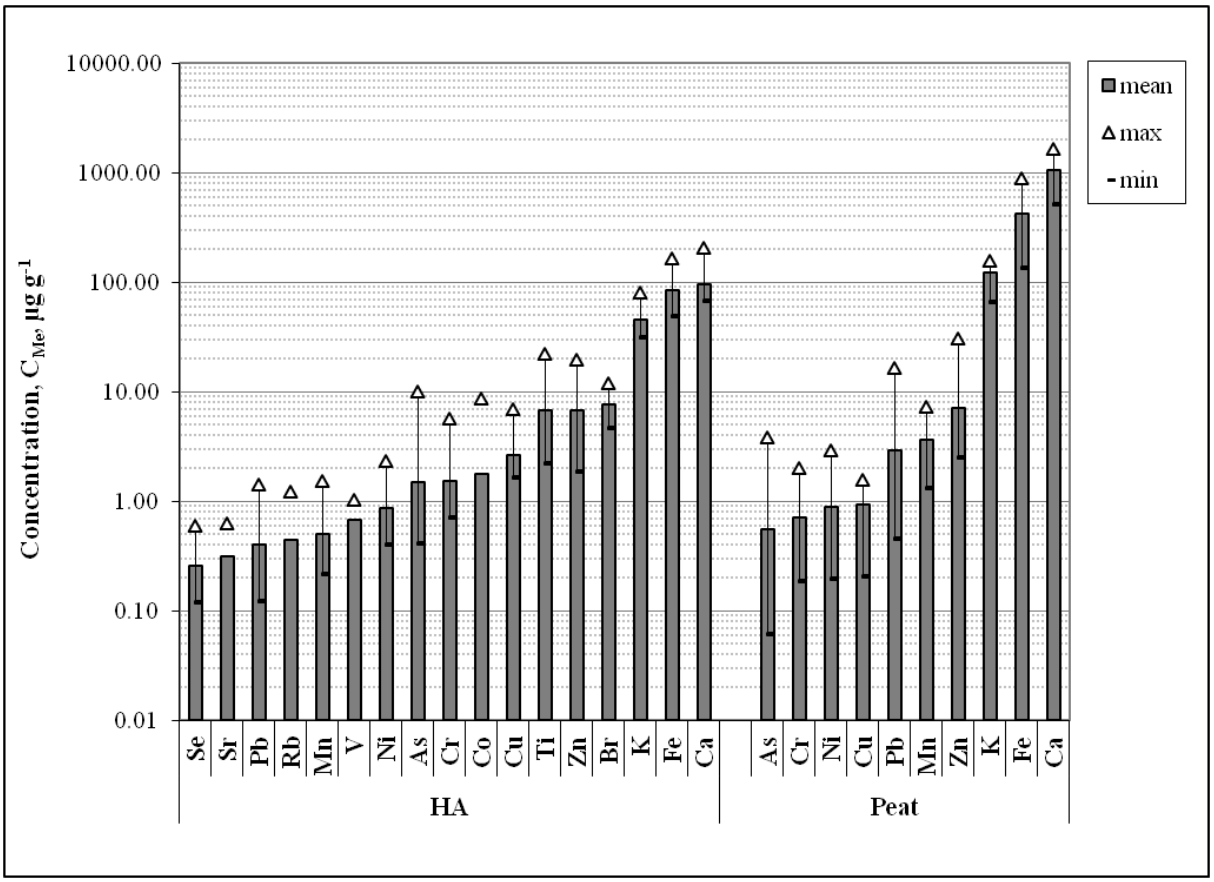

Fig. 1. Concentrations (µg g^{-1}) of major and trace elements in peat and humic acids from Eipurs and Dzelve bogs.

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.
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 1).

Table 1. Correlation between major and trace element concentrations in peat (P) and peat humic acids (HAs) in Eipurs Bog. Correlation is significant at the 0.01 level (2-tailed). Correlation is significant at the 0.05 level (2-tailed)

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
	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

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 1). Strong and statistically significant correlations between elements in peat and humic acids has been found only for Fe, Zn and Cu.

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. 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.

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