

Chemical Element Accumulation in Peat and Its Humic Substances

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Abstract — Peatland cores provide us with the potential to research aspects of atmospheric cycling of elements, such as metal pollutants, on timescales. Our study provides a better understanding of basic peat properties and their effects on trace and major element distributions in peat and its humic substances (HS). Humic substances isolated from an ombrotrophic bog peat profiles (Latvia) were used as study objects. Relations among peat depth, properties of peat and its HS (elemental composition), as well as element content, were studied.

Keywords — Component analysis, heavy metals, humic substances, peat.

I. INTRODUCTION

Several studies have been conducted to assess the behaviour of heavy metals in polluted or naturally contaminated soils and deposits [1]–[3]. Waste deposits, that contain a multiplex mixture of organic, as well as inorganic matter, pose a presumable risk to the environment in a long-time perspective via the disposal of heavy metals [4].

Geochemical studies in Latvia were launched in the 20th century at '50s and '60s and were carried out by different organizations. The geochemical studies within geological mapping work can be highlighted. In 1966 geochemical studies were included in geological mapping work programs in order to solve the correlation of geological cut, also to clarify the conditions of sedimentation [5].

In 2007 the regional geochemical mapping surveys were carried out in the territory of Latvia, taking into account the geological, pedological and land use properties. The content of 32 chemical elements was determined in topsoil and bedrock samples in order to characterize the distribution of element content and its regularities [5].

Peat bogs store authentic records of data on environmental and paleoenvironmental evolution and are exploited as references in studies of present patterns and past in global climatic change and also are used to determine the impact of historical human activity [1] that causes the contamination of heavy metals [6]. In general, these ecosystems are notable sources of data about carbon cycle and processes of acid deposition and heavy metal cumulation.

Organic matter is an integral and substantial part of peat, more than 80 %. Humic substances (HS) are some of the most important constituents of organic matter of soil, and, by definition, are macromolecular, negatively charged polyelectrolytes, mostly composed of carboxylic and phenolic functional groups [7]. Humic substances (HS) influence soil chemical properties, including buffer capacity, cation exchange capacity, acid-base reactions and metal complexation [8]. Most

of the data describes that peat contains large amount of humic acids [9]; also it has been stated that humic matter in peat constitutes mostly of fulvic acids [10]. It is believed that elemental composition and chemical properties of peat HS are equal to those of humic acids (HA) in mineral soils [11]. Nowadays it has not yet been explored whether the properties of HS may be different in various kinds of peat, since sphagnum peat is chemically dissimilar to peat of heath vegetation or peat formed from woody trees [12].

HS are significant agents for speciation and mobility of metals in soils and present an intense control on the behaviour of pollutant metals in the environment [13].

II. MATERIALS AND METHODS

Materials

Analytical quality reagents (*Merck Co.*, *Sigma-Aldrich Co.*, *Fluka Chemie AG*) were used without purification. High purity water *Millipore Elix 3* (*Millipore Co.*) 10–15 MΩ was used throughout the study for preparation of solutions [14].

Peat Sampling and Characterization, Isolation of Humic Acids

Peat profiles were obtained from well characterized ombrotrophic bogs — Eipurs, Dzelve and Dizpurvs. Bogs are located in lowlands; they are of similar origin (they have developed due to ground paludification) although their lithology is largely differing. Studied bogs are typical raised bogs and have never been affected by direct pollution sources, either presently, or historically [14].

Trace elements in a 1 cm slice of peat profile were determined after nitric acid digestion by GFAAS. To isolate humic acids the obtained peat profiles were separated into 10 cm layers and humic acids were extracted using procedures recommended by the International Humic Substances Society (IHSS) [15].

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 groups and total acidity of each humic acid. Barium hydroxide method [16] was used to estimate the total concentration of carboxylic groups and total acidity. The content of trace elements was measured with total-reflection X-ray fluorescence spectrometry (TXRF) and atomic absorption spectrometry (AAS).

Statistical Treatment of Data

Statistical and graphical data post-processing was performed by multivariate data analysis using *PC-ORD*, version 5 and *SPSS Inc.* statistical program *SPSS 17*, by using a correlation analysis. It was done between concentration of major (by distribution) element and trace element in peat and peat humic substances. Pearson correlation coefficients of chemical elements in the element pair correlations were calculated as well.

III. RESULTS AND DISCUSSION

Influencing Factors of Major and Trace Element Accumulation

The distribution and content of chemical elements in bog profiles are influenced by several factors, such as geographical location of studied bogs, the nature of formation and differences of possible element supply source. The compiled principal component matrix of studied chemical elements, taking into account a number of variables, gave a better understanding of which processes — natural or anthropogenic — influence the accumulation of elements in peat bog profiles and humic acids.

The component analysis showed that metal accumulation in peat formation processes depends on the depth of the bog, carbon content, sulfur and carboxylic groups, whereas a correlation between the content of S in humic substances and concentrations of Zn in peat and its HS was observed. The accumulation process of chemical elements, such as As, Ni, Ca, Fe, Cu, Cr, Mn, is characterized by a strong resemblance (see Fig. 1).

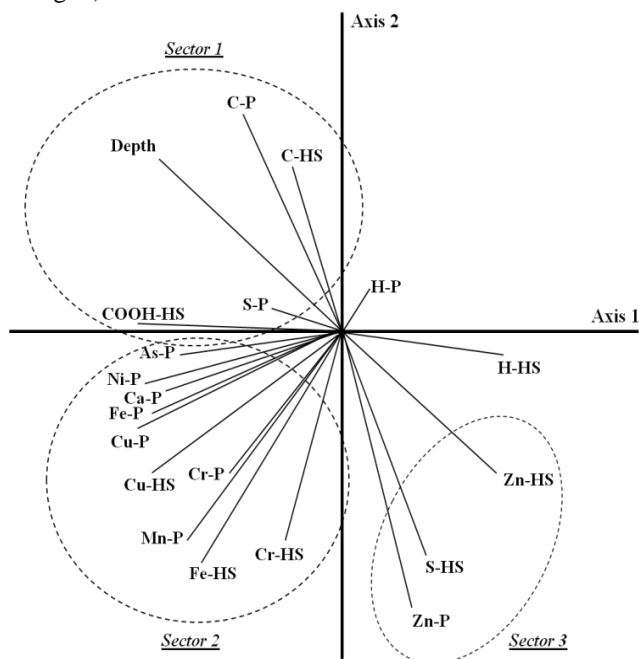


Fig. 1. Distribution of elemental composition (C, S, H, COOH), depth and concentrations of chemical elements ($\text{mg}\cdot\text{kg}^{-1}$) in bog peat (P) and humic substances (HS) of studied bogs in PCA axes.

Parameters that characterize composition and variability of peat and humic substances were grouped in sector 1, including the depth of peat (humic substances) in bog profiles, the content of carbon in peat and humic substances, the concentration of

COOH in HS, as well as the content of S in the peat. These data showed the importance of elemental composition of peat and humic substances that predominantly have the ability to bind metals.

The variability of metal concentration, including non-metallic As, in both peat and its HS was displayed in sector 2, moreover, the variability of both naturally occurring elements, such as Ca and Fe, and of anthropogenic origin, such as Ni and Cu, were displayed in peat and HS; nevertheless, the variability of elements in sector 2 was related to fluidity of elements of anthropogenic origin. The variability of Zn concentration in both peat and humic substances was situated in sector 3, which obviously affects the prevalence of sulfur concentration in the composition of HS.

In the component analysis of the elemental composition, depth and chemical elements in HS of studied bogs, two sectors were silhouetted. Mutually correlating chemical elements, such as Mn, S, As, Pb, Zn, were characterized in sector 1. The relationship between naturally occurring chemical elements, such as Cr, Ni, Fe, Cu, Ca, as well as depth, the concentration of carboxylic groups and oxygen was observed in the content of HS in sector 2.

The content variability of chemical elements, such as S, Zn, As, Mn, Pb, in peat humic substances was characterized by sector 1, and it was mainly attributed to the mutability of elements of anthropogenic origin. On the other hand, composition and basic properties of peat HS, such as depth, content of oxygen and amount of carboxyl groups, responsible for formation processes of HS structure, were grouped in sector 2 (see Fig. 2).

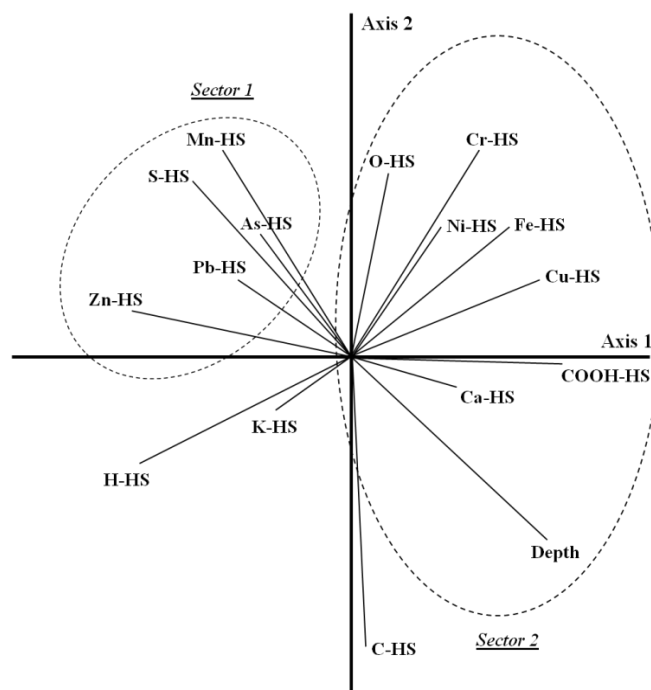


Fig. 2. Distribution of elemental composition (C, S, H, COOH), depth and concentrations of chemical elements ($\text{mg}\cdot\text{kg}^{-1}$) in peat humic substances (HS) of studied bogs in PCA axes.

As mentioned before, the decisive factor for accumulation of metals in HS was carboxylic groups. Thus in sector 2, without constituent elements in HS, the presence of accumulation

process of metals such as Cu, Cr, Ca, Ni, Fe was observed in HS. The relationship between the depth and dispersion of chemical elements in the studied bog peat can be explained by the form of metal distribution and mobility in the peat profile. Furthermore, any significant correlation between concentration of carbon and potassium in composition of HS in sector 1, as well as between carbon and content of hydrogen in sector 3, was not found.

Three sectors of descriptive parameters in component analysis of studied peat bogs are characterized, distinguishing between peat-forming basic elements and the presence of chemical element (Ni, Ca, Fe, Cu, Mn, Cr, As, K, Zn, Pb) accumulation process in the studied peat bogs.

The basic elements of peat, namely, C and N, depth, as well concentration of S are characterized by sector 1 (see Fig. 3). On the contrary, elements of natural origin, such as Ni, Ca, Fe, Cu, Mn, Cr, are grouped in sector 2 and also the accumulation of element As (anthropogenic origin) in peat is observed. The relevance between naturally occurring elements Zn and K and the content of anthropogenic element Pb in peat composition is observed in sector 3; moreover, any significant relation between two axis and concentration of H in the studied peat composition was not found.

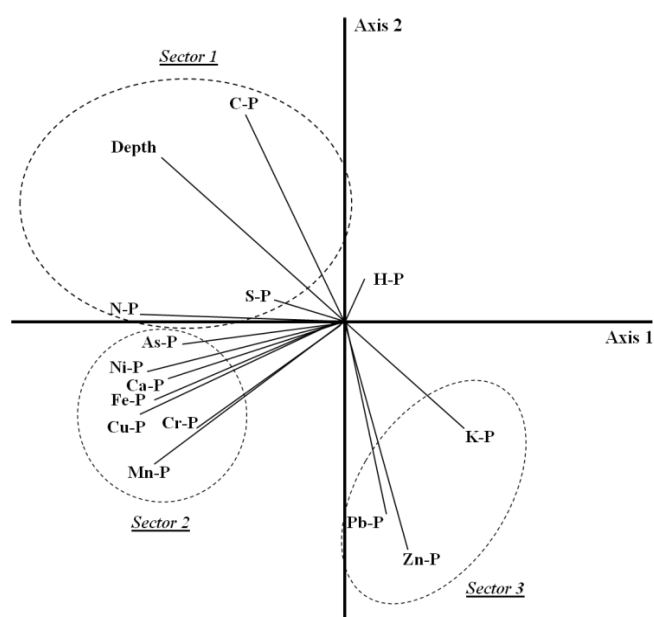


Fig. 3. Distribution of elemental composition (C, S, H, COOH), depth and concentrations of chemical elements ($\text{mg} \cdot \text{kg}^{-1}$) in peat (P) of studied bogs in PCA axes.

In pair correlation analysis of concentrations of chemical elements in HS of Eipurs, Dzelve and Dizpurvs bogs, isolated from different peat layers, groups of elements with significant pair correlation ($p > 0.05$), strong correlation ($p > 0.01$) and negative correlation can be divided (see Fig. 4).

As shown in Fig. 4, Pb forms a relatively close correlation with As ($p > 0.05$) in HS isolated from the upper layers of Eipurs bog peat; besides, this chemical element fairly well correlates with selenium and bromine, but copper with chromium. Close and statistically significant correlation ($p > 0.01$) in the upper layers of Eipurs HS was identified for

element pairs, such as Fe-As, Fe-Mn, Fe-Zn, Fe-Se, As-Mn, As-Zn, Cu-Mn, Mn-Zn, Mn-Se, Cr-Ni, Cr-Se.

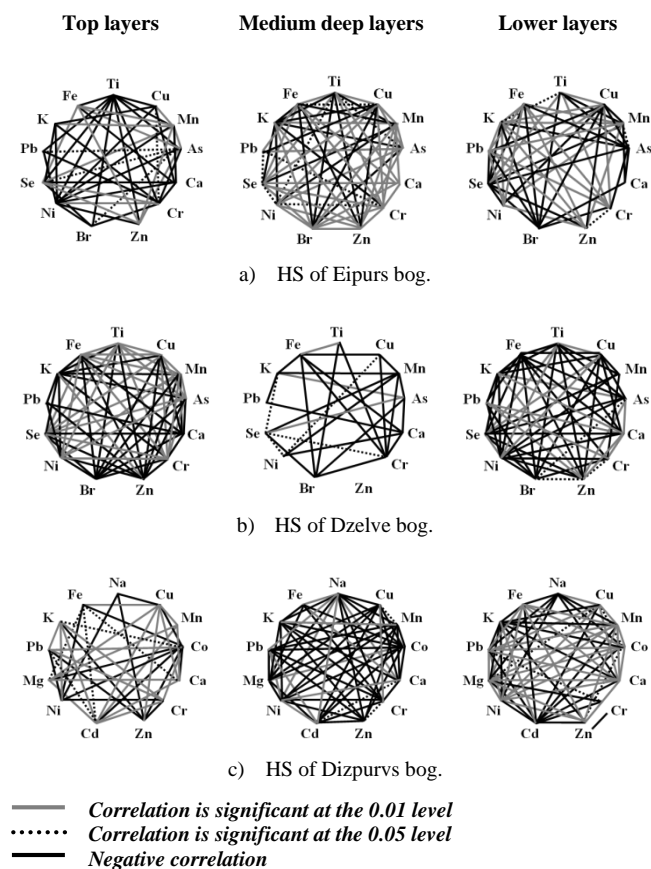


Fig. 4. Pair correlation between elements in HS of Eipurs, Dzelve and Dizpurvs bogs in peat layers of different depths.

The cross-correlation character of described elements in HS, isolated from the middle layers of Eipurs bog, showed a significant correlation ($p > 0.05$) between element pairs Fe-Cu, Pb-Cr, Pb-Se, As-Ti, Cr-Ni, Ni-Ti, Ni-Se. However, the strongest correlation ($p > 0.01$) was observed between naturally occurring element pairs Fe-Ca, K-Zn and anthropogenic element pairs As-Ni, Mn-Br, Cr-Ti, Cr-Se, Ti-Se. The source of some chemical elements in HS, isolated from medium deep layers of Eipurs bog peat, such as As, Cu, Cr, Ca, Ti, Zn, Br, can be both natural and anthropogenic, which is seen in mutual correlation of these elements.

A fairly close correlation ($p > 0.05$) between arsenic and manganese was observed in HS isolated from the lower peat layers of Eipurs bog, while chrome had a relatively close correlation with zinc, but potassium represented a significant correlation with titanium. Statistically significant correlation ($p > 0.01$) between chemical elements in HS, isolated from the lower layers of Eipurs bog peat, was observed for element pairs of natural origin, such as Fe-K, Fe-Zn, Cu-K, K-Zn, and element pairs of anthropogenic origin, such as Pb-Cr, Pb-Ni, Cr-Ti, Ti-Se, etc.

Element pairs, such as Cu-Cr and Mn-Zn, had a positive correlation in all characterized depth layers of Eipurs bog HS; furthermore, the element pairs Pb-As and As-Br in the upper peat layers had a positive correlation, which became negative

in average deep layers, while essential associations of elements in the lower peat layers were not found.

A positive relationship between Cr-Zn, K-Ti, Fe-Ni, Pb-Mn and Cu-K was observed only in the lower layers of peat, but in the upper and middle layers of peat HS a statistically significant correlation was not found.

Fe, As, Cu and Mn were dominant elements in Dzelve bog HS in different depth zones and formed a statistically significant correlation network with elements of both natural and anthropogenic origin in all investigated levels. Significant correlations ($p > 0.01$) between element pairs in HS isolated from the upper peat layers were observed for Fe-As, Fe-Cr, As-Mn, Ti-Se, Ni-Se.

Obvious pair correlations at correlation significance level $p > 0.01$ were observed between elements according to their origin, highlighting the naturally occurring element pairs, such as Fe-Cu, K-Zn, Ca-K, Ca-Zn, K-Zn. Tight correlation pairs were also established between 9 pairs of anthropogenic origin elements, such as As-Ti, As-Cr, Cr-Ni, Ti-Se, Cr-Se, As-Br, Pb-Cr, Cr-Ti, As-Se, thus linking the dispersion and cross-correlation of these elements with effects of industrial activity.

It should be noted that elements did not form a wide range of pair associations in the middle peat layers of Dzelve bog, as it was observed with HS of Eipurs bog, suggesting that various factors influence the accumulation of elements in the middle layers of Dzelve bog.

Elements, such as Fe, Cu, Cd, Mg and Cr, represented notable pair correlations in HS, isolated from the upper peat layers of Dizpurvs bog. Statistically significant pair correlations ($p > 0.05$) were determined between elements in HS isolated from the upper peat layers of Dizpurvs bog, respectively, Mg-Fe, K-Co, Ca-Fe, Fe-Cd, Cd-Pb. HS in the middle peat layers were characterized by a strong correlation ($p > 0.01$) between element pairs Na-Ca, Pb-Cd, Cr-Cu, Ni-Pb, K-Mn.

Apparent correlations ($p > 0.05$) in the medium depth layers of peat were found between element pairs Ca-Cd, Cr-Zn, Mn-Cu. The source of elements, such as nickel, manganese, zinc, copper, arsenic, in HS in the middle peat layers of Dizpurvs bog could be both natural and anthropogenic, marked by mutual interrelationship of these elements.

Mg quite closely correlated with copper ($p > 0.05$), while Cr was highly bounded to Pb, but Co had a significant correlation with Cu and Zn in HS, isolated from the lower peat layers of Dizpurvs bog. A statistically significant correlation ($p > 0.01$) was observed for naturally occurring element pairs Ca-Cu, Ca-Fe, Na-Cu, Cu-Zn and Fe-Zn and anthropogenic element pairs Co-Ni, Co-Pb and Ni-Pb in HS from lower peat layers of Dizpurvs bog.

Chemical element pairs, such as Mn-Cu and Ca-Fe, mutually formed a significant correlation in HS, isolated from different depth zones of Dizpurvs bog; at the same time it should be noted that relations of element pairs, such as Mg-Fe and K-Co, changed from positive in the upper layers to negatively correlating in the middle layers. A positive relation between element pairs of Co-Cu, Co-Zn and Na-Cu was found only in the lower layers of peat, but statistically significant correlation in the upper and middle layers was not detected.

In our study three associations between chemical elements could be found: 1) "pelitophile" (Fe, Co, Ni, Cr, Mg, K, Ti); 2) "phytophile" (Pb, Cd, S, Se); 3) "carbonate" (Mg, Ca) [5].

Similar associations are reflected in the studies of other countries, such as Lithuania, Germany, Sweden and Belgium.

IV. CONCLUSION

Correlation analysis between chemical elements in peat HS from different depth layers of Eipurs, Dzelve and Dizpurvs bogs marks an essential differences in natural and anthropogenic accumulation zones. The absolute values of chemical elements found in HS of studied bogs are similar to values obtained in other countries like Belgium and Sweden. This reflects the local distinctions, affecting the accumulation process of elements.

Accomplished correlation pair analysis allows assessing the mutability of interconnection between chemical elements in HS of studied bogs. Depending on the accumulation place of analyzed element, peat succession can be divided into the upper, medium deep and bottom layers. Factors, such as geographic location of studied bogs, peculiarities of bog formation character and differences of the possible element supply source, are substantial with respect to the content of chemical elements and their dispersion in peat HS of studied bogs.

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Diāna Dūdare, Māris Kļaviņš. Ķīmisko elementu akumulāciju kūdrā un tās humusvielās ietekmējošie faktori.

Pētījuma ietvaros tika sastādītas galveno komponentu matricas analizētajiem ķīmiskajiem elementiem, kas tika noteikti augstā tipa purvu — Dzelves, Eipura, Dižpurva — kūdrā un tās humusvielās (HV), ņemot vērā vairākus mainīgos, kas ļāva labāk izprast, kādi procesi (dabiski vai antropogēni) bija ietekmējuši elementu akumulāciju purvu profilos un kūdras humusvielās. Metālu satura analīzi pētīto humusvielu un kūdras paraugos veica, pielietojot tādas spektrālās analīzes metodes kā pilnīgās atstarošanas rentgenfluorescences spektrometrija, atomabsorbcijas spektrometrija. Noteikts pētīto HV un kūdras funkcionālais sastāvs un elementu sastāvs, kā arī aprēķināts kopējais skābums pētītajās HV, izmantojot titrēšanas metodi.

Pētījumā iegūtie rezultāti parādīja, ka metālu akumulācijā kūdras veidošanās procesos būtiska loma bija dziļumam, oglekļa, sēra un karboksilgrupu saturam; turpretī sēra daudzumam humusvielās novēroja sakarību ar cinka koncentrācijām kūdrā un humusvielās. Tādu ķīmisko elementu kā As, Ni, Ca, Cu, Cr, Mn, Fe akumulācijas procesu norisi raksturoja izteikta līdzība. Veiktā pāru korelācijas analīze ļāva novērtēt ķīmisko elementu savstarpējo attiecību mainību pētīto purvu HV un atkarībā no analizētā ķīmiskā elementa akumulācijas vietas varēja izdalīt virsējos, vidēji dziļos un apakšējos kūdras slāņus. Ķīmisko elementu satura absolūtās vērtības un to sadalījumu pētīto purvu — Dzelves, Eipura, Dižpurva — profilos bija ietekmējuši vairāki faktori: pētīto purvu ģeogrāfiskais izvietojums, to veidošanās raksturs un iespējamo elementu pieplūdes avotu atšķirības. Korelācijas analīze starp ķīmiskajiem elementiem pētīto purvu kūdras humusvielās atšķirīgā dziļumā iezīmēja būtiskas atšķirības dabiskās un antropogēnās akumulācijas zonās. Ķīmisko elementu absolūtās vērtības, kas noteiktas pētīto purvu HV, bija līdzīgas iegūtajām koncentrācijām citās valstīs, piemēram, Beļģijā, Zviedrijā. Tas parādīja elementu akumulācijas procesus ietekmējošās lokālās īpatnības.