

Chemical properties of peat in three peatlands with balneological potential in Estonia

Mall Orru^{a,b}, Monika Übner^c and Hans Orru^d

^a Geological Survey of Estonia, Kadaka tee 82, 12618 Tallinn, Estonia; orru@egk.ee

^b Department of Mining, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; Mall.Orru@hotmail.com

^c Pärnu College, University of Tartu, Ringi 35, 80010 Pärnu, Estonia; Monika.Ubner@ut.ee

^d Department of Public Health, University of Tartu, Ravila 19, 50411 Tartu, Estonia; Hans.Orru@ut.ee

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Abstract. Peat and various peat preparations have been successfully used in balneology. When considering the biological effects of peat, humic substances have been found to be of particular importance. The content of humic, hylatomelanic and fulvic acids as well as main characteristics of peat were measured in three areas with balneological potential, selected according to previous research and mapping of Estonian peatlands. It appeared that the content of bioactive substances in the sampled peat layers was relatively high. The concentrations were highest in the Parika peatland: humic acids 39.3%, hylatomelanic acids 19.3% and fulvic acids 1.3%. The main factors influencing the levels of bioactive substances were the degree of humification (more humified peat had higher concentrations) and peat type (forest(pine)–cottongrass composition increased the concentration levels). As lipids had high correlation with hylatomelanic acids and trace elements with fulvic acids, the mentioned components could be respectively bound to these humic substances.

Key words: peat, balneology, humic substances, trace elements.

INTRODUCTION

Peatland is the type of the landscape where in wet and oxygen-deficiency conditions part of organic matter will not degrade and accumulates as peat. Peat is an accumulation of partially decayed vegetation matter with a high water content. It is a mixture of plant parts at different decomposition stages. The transformation of peat organic matter by chemical, biochemical and biological decay leads to the formation of a number of chemical substances among which humic, and fulvic acids and their salts, cellulose, lignite, bitumens, peptides, enzymes and fats are the most common (Szajdak et al. 2007).

Peat and various peat preparations have been successfully used in the balneological practice of clinical medicine (Beer et al. 2007). Balneological peat as ecologically clean and natural substance is more human-friendly than synthetic substances. Several European countries (Germany, Austria, Czech Republic, Hungary) have long traditions of using balneological peat. In recent decades it has also been studied and used in Finland (Korhonen 1996).

It is important to consider the region and origin of the peat that is used for medicinal purposes. The quality, type and amount of the biologically active substances in peat make certain peat more medically useful (Groven 1999). However, it is well known that the composition of peat in general is very complex and varies according

to the source of peat. In addition, the quality and composition of peat depend on many different factors such as the place of origin, the primary types of the plants of origin and a whole spectrum of environmental factors (Beer et al. 2003a). Thus the mineralogical-geological setting as well as peat chemistry play a significant role in the development of peat.

According to Beer et al. (2003b), there are many indications that also a chemical component may contribute to the clinical success of cutaneous peat treatment because several pharmacological effects have been detected, which cannot be ascribed to the well-established physico-thermal effects. The physical effect influences through temperature and biochemical effect through bioactive substances (Lukanov et al. 2002). Balneology is largely used for the treatment of rheumatic diseases that are also common in Estonia (Saks et al. 2001). The biochemical effect of peat is related to the content of humic substances (HS) which participate in the peat healing effect (Klößing & Helbig 2005). Humic substances are natural products that develop during decomposition of organic matter in humus and constitute the most stable fraction of organic substances in soils (Wollina 2009). They form a dark brown non-soluble fraction of peat with an extremely high molecular weight, responsible for the capability to retain water, friability and electrostatic conductivity (Trckova et al. 2005). Humic substances from different sources (from different

types of peats and climate zones) have different compositions and biological effects, depending on their chemical structure and physico-chemical properties (Hayes 1997; Yamada et al. 2007). To understand the major processes and mechanisms that occur in peat, it is obligatory to know the components of HS (Hayes 1998) and compare their behaviour in aqueous solution in order to find out how their environmental interactions may differ from each other (Young & von Wandruszka 2001). The classical fractionation of HS is based on differences in solubility at different pH values. According to these differences, HS can be divided into four fractions: (1) humic acid (HA) – soluble in water at higher pH values; (2) hymatomelanolic acid (HMA) – soluble in ethanol; (3) fulvic acid (FA) – soluble in water under all pH conditions; (4) humin – not soluble in water at any pH value. Humic substances of peat have anti-inflammatory and pro-inflammatory (Junek et al. 2009), antiallergic (Yamada et al. 2007), and antibacterial, antifungal, immunomodulatory and photoprotective (Wollina 2009) effects. They sorb many biological molecules like peptides, sugars, nucleic acid residues and fats (Orlov 1990; Stevenson 1994; Hayes 1998). Biochemically active humic, fulvic and hymatomelanolic acids are successfully used against musculoskeletal, gynaecological and skin diseases (Klößing &

Helbig 2005). Fulvic, ulmic and humic acids, all of which have been isolated from peat, have been found to be of particular importance in the biological effects of peat (Beer et al. 2000).

According to experience of other countries, the peat suitable for balneology has to be well humified (40–50%). Its natural moisture content has to be at least 85% and the peat layer has to be under the peat water level (Uosukainen 2002). The content of HS should exceed 20% of dry weight. Balneological peat should not contain harmful bacteria and heavy metals (Orru & Orru 2006; Szajdak & Hladon 2009). Moreover, it should contain HA, HMA and FA, the ash content should be less than 12% and the thickness of the proper peat layer at least 0.7 m (Orru et al. 2008).

The aims of the current research were to find out the resources and chemical composition of balneologically suitable peat in Estonia and to identify the geological factors most influencing the properties of balneological peat.

MATERIALS AND METHODS

The study areas (Fig. 1) were chosen according to the research and mapping of Estonian peatlands by the

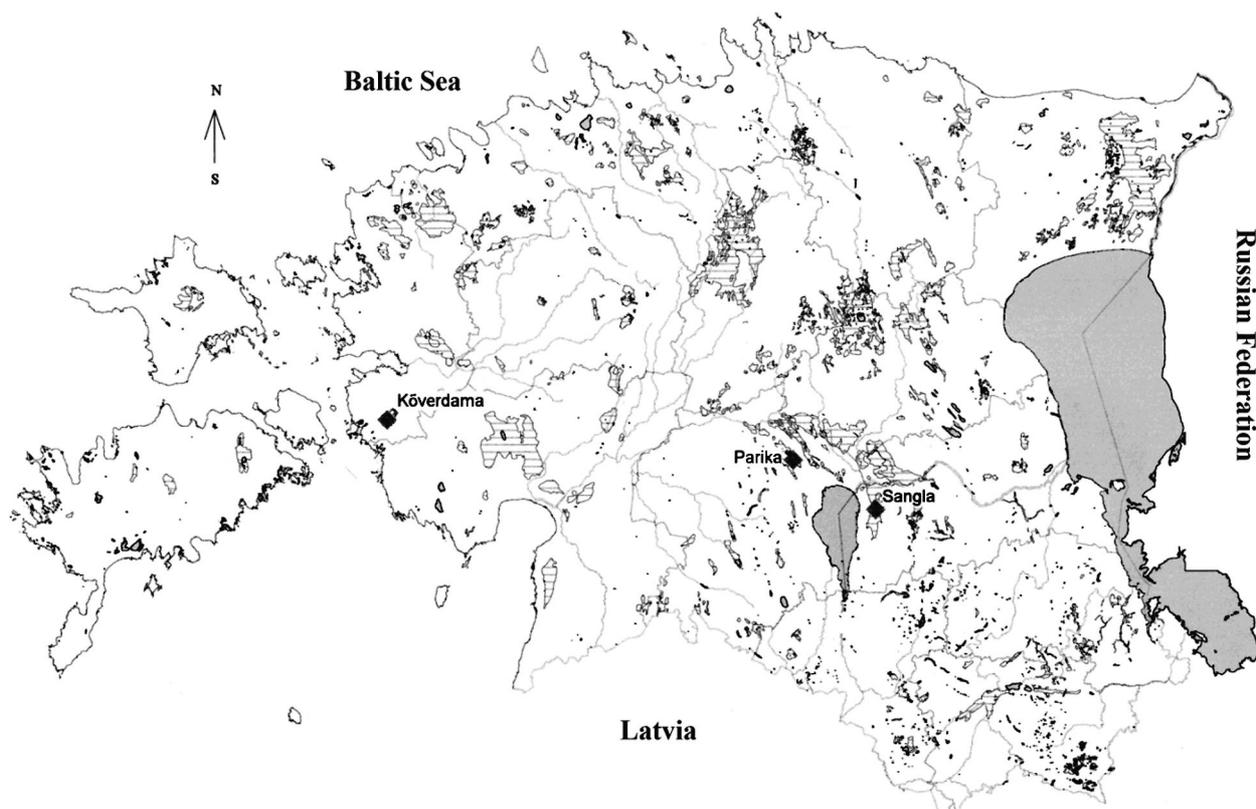


Fig. 1. Main peatlands in Estonia and the three study areas (Kõverdama, Parika, Sangla).

Geological Survey of Estonia (Orru et al. 1992). Through geological routes the natural conditions, especially vegetation and water regime were studied. At first the thickness of the proper layer, its position and the depth of the entire peat layer were sounded. To select a well-composed peat layer for laboratory analyses, the decomposition degree of peat in the horizon was determined in situ according to the von Post scale (von Post 1924). The samples were collected with a hand auger after every 0.5 m per one coring in the selected depth.

Two sets of analyses were made on natural peat: (1) characterization of the peat (ash content, pH, degree of humification and botanical composition) and (2) the yield of HS from natural peat. Ash content was determined after heating the sample at $450 \pm 10^\circ\text{C}$ up to constant weight. Loss on ignition represents the proportion of organic matter in the sample. Peat pH was determined in KCl extracts after 18 h, with a peat:solution volumetric ratio of 1:2.5. The degree of humification was found with the double-stage centrifuge method to separate the precipitate of coagulated humus from non-humified components of plants. The botanical composition (peat type) was determined with a microscope.

The procedure for assessing the yield of HA, HMA and FA has previously been described in detail by Übner et al. (2004). Natural peat (30 g) was stirred for 5 h with 100 mL of 0.2 M NaOH and then allowed to stand for 20 h at room temperature. The suspension was centrifuged at 5000 rpm for 30 min. The alkaline extract contained HS. The humin (insoluble part of peat) was separated as precipitate and was washed repeatedly with distilled water to separate soluble HS and dried. The alkaline extract was acidified to pH 2 by addition of 6 M HCl. After 20 h the soluble FA and insoluble HA, and HMA were separated. The precipitate was repeatedly washed with distilled water until Cl^- free (control with AgNO_3). The solid residue was many times treated with 96% ethanol to separate the soluble HMA and insoluble HA. Both fractions were dried. The FA solution was cleaned through the Amberlite XAD-7 resin column for desalination. After removal of salts with 0.01 M HCl, the pure FA fraction was recovered by elution with 0.1 M NaOH solution directly onto the strong cation exchanger Amberlite IR-120. The gathered fraction was dried. To determine the content of lipids, dry peat was repeatedly treated with mixture of chloroform and ethanol (2:1) to separate the soluble lipid fraction and dried. For statistical analyses, the Pearson correlation coefficients were calculated.

RESULTS AND DISCUSSION

Peat resources and main characteristics of peat

The depth of the balneologically usable peat layer in the studied peatlands is 1.1–1.5 m. If the depth is less than 0.7 m, peat is technically and economically difficult to use. In that case the layer can be separated by mining, thus one can be sure that the peat comes from the right depth interval. The resources of balneological peat in the studied peatlands were as follows:

- (1) Kõverdama, 226 000 t in 94 ha,
- (2) Parika, 113 000 t in 73 ha,
- (3) Sangla, 466 000 t in 151 ha.

However, together with the previously studied peatlands of Larvi, Hõreda and Oese the total resources of balneological peat would increase up to one million tonnes (Orru et al. 2008). The country most widely using peat for therapeutical purposes is Germany, where the annual consumption of balneological peat is around 0.4 million m^3 (~64 000 t) (Lüttig 1984). For Estonia, with its 1.35 million inhabitants, this amount would be sufficient for hundreds of years. However, according to Estonian peatland mapping (Orru et al. 1992), the suitable resources, where the content of HS is higher than the average, could be even much greater.

Mainly well-humified (40–50%, von Post 6–8) raised bog peat, represented by heath, *Sphagnum*, cottongrass and wood peat, suits for balneological purposes (Table 1). All areas in peatlands where balneological peat can be found are in natural condition. The water level is 0.3–0.6 m beneath the ground level, so the moisture content (87–88%) is higher than the minimum required value (85%) (Table 1). The ash content was relatively low, varying from 2.8 to 4.8%. In the countries where peat balneology is available (e.g. Germany, Austria, Finland), well-humified raised bog and fen peat is used, from raised bogs mainly *Sphagnum* (humification H6–H8) and from fens *Carex* peat (humification H8–H10) (Naucke 1981). While the ash content in raised bog peat in Germany and Finland is low like in Estonia, it is much higher in fen peat: ~15% in Germany (Naucke 1981), 6–12% in Finland (Uosukainen 2002) and 5–12% in Estonia (Orru et al. 1992).

Yield of humic fractions from peat

The analyses showed that HA, HMA and FA is found in all peat layers (Fig. 2). The abundance of HS was relatively high in the studied peatlands of Estonia. The concentration of HS was the highest (up to 60%) in the Parika peatland, exceeding the values from Finland: 20–40% for HA, and HMA and 4–12% for FA

Table 1. Characteristics of the research areas

Peatland	Genesis of the peat deposit	Mineral subsoil	Vegetation	Nutrition	Depth of the peat layer, m	Peat type	Degree of humification, %, von Post scale	Ash content, %	pH	Moisture content, %
Kõverdama	Paludification	Clay-sand	Pine forest, mosses	Precipitation	1.30–2.80	Heath- <i>Sphagnum</i> , heath-cottongrass peat	40–45, H7	4.5	4.55	88
Parika	Lake paludification	Sand	Pine forest	Precipitation	0.70–1.60	Pine- <i>Sphagnum</i> , forest-cottongrass peat	50, H8	2.8	4	87
Sangla	Basin paludification	Gyttja, sand-clay	Pine, birch forest	Precipitation	0.70–2.00	Heath- <i>Sphagnum</i> , heath-cottongrass peat	40–45, H7	4.8	4.8	88

(Uosukainen 2002). The highest concentrations could be found in well-humified (H9) *Sphagnum* peat and less in *Carex* and *Sphagnum-Carex* peat. Thus, both the degree of humification and peat type seem to be important factors affecting the concentration of HS in peat. However, according to Kleb et al. (1999), the content of HS in peat deposits near Lake Balaton was the highest in the 0.5–2 m zone, in the range of 43–68%, which is even more than in the Parika peatland. Compared to sea and lake sediments (that have historically been used in balneotherapy in Estonia), these levels of HS in peat are higher. Übner et al. (2004) have reported HA 0.15%, HMA 0.08% and FA 0.24% in Haapsalu Bay sediments and HA 2.81%, HMA 0.34% and FA 0.23% in Lake Ermistu sediments.

The content of HS somewhat depends also on the depth of peat layers. The smallest content (23.5%) was recorded in the Sangla peatland, at a depth of 0.50–1 m and highest (59.9%) at Parika, at a depth of 1.25–1.75 m. At Sangla the content of HS grew with the increase in depth, but decreased in the Kõverdama peatland. The main explanation for the higher content of HS could be the degree of humification that increases with depth, as the highest value of humification (50%) was found in the Parika peatland. Secondly, this could also be affected by the peat type and age, as Parika is one of the oldest peatlands in Estonia (Orru et al. 1992). In Orru et al. (1992) also the HA+HMA fraction was analysed in mixed samples from several peatlands, where the concentration was 16% in light humified (H1) *Sphagnum fuscum* peat, 20% in further humified (H2) peat, 32% in moderately humified (H4) cottongrass-*Sphagnum* peat and 41% in well-humified (H7) cottongrass peat.

The ratio of HA:HMA:FA varied as well, being 8:6:1 in the Kõverdama, 30:15:1 in the Parika and 16:4:1 in the Sangla peatland. Even more important, the ratios of HA to HMA were, respectively, 1.4:1, 2:1 and 3.9:1. Comparison of these data with sea and lake sediments (Übner et al. 2004) showed no big differences. Parika peat and sea sediments had almost the same HA:HMA ratio and lake sediment had the highest value. According to former research, HS occurring complexly in peat are good for human organisms due to their healing properties for arthritis, osteoporosis, rehabilitation problems after operations, degenerative joint-damages, skin problems, stress, etc. (Korhonen & Lüttig 1996).

In FA the amount of carboxyl and phenolic hydroxyl groups is usually higher than in HA (Stevenson 1994). Besides those major functional groups, HMA contains also different subunits from fatty acids, waxes, carbo-

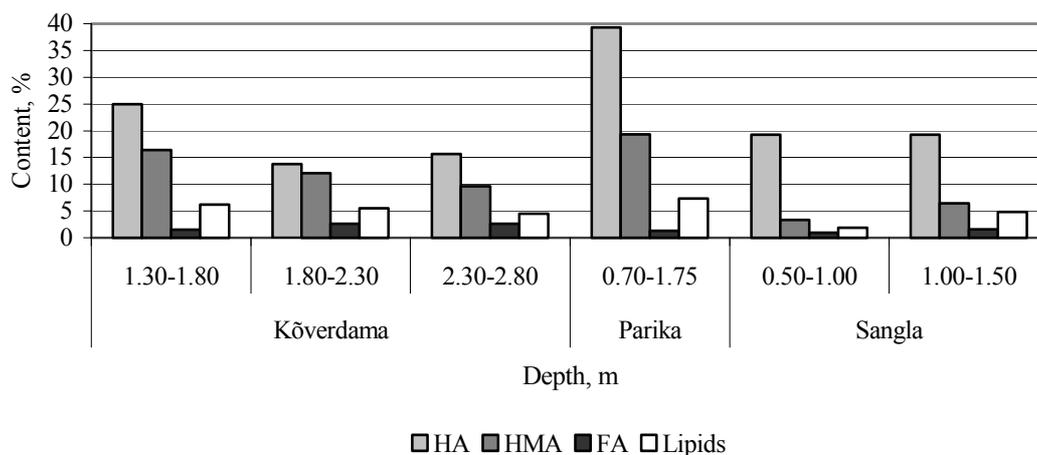


Fig. 2. The content of humic (HA), hyatomelanic (HMA), fulvic (FA) acids and lipids in peat dry weight.

hydrates, terpenes, and nitrogen-containing compounds (Glebova 1985). The content of lipids was the highest (7.3%) at Parika at a depth of 1.25–1.75 m and the smallest (1.9%) in Sangla at a depth of 0.50–1 m. The Pearson correlation coefficient calculated for the content of lipids and HS fractions was the highest ($r = 0.93$) for the HMA fraction, lower ($r = 0.57$) for HA and the lowest ($r = 0.22$) for FA. This confirms the previous findings by Glebova (1985) that HMA contain different lipids.

Trace elements and HS fractions

As mentioned above, the chemical composition of peat depends on a number of factors like feeding conditions of peatland, geomorphologic position, geological setting of the region, environmental conditions and anthropogenic impact. Feeding conditions have shown the main impact, especially on the concentrations of trace elements, as a negative factor limiting the usability of balneological peat (M. Orru & H. Orru 2008; Szajdak & Hladon 2009). The content of trace elements in the Köverdama, Parika and Sangla peatlands has been analysed by M. Orru & H. Orru (2003) and H. Orru & M. Orru (2006).

In general, the abundance of trace elements in these three peatlands was lower than on average in Estonian peatlands. However, the S content was slightly higher. Moreover, the small differences between peatlands could be related to HS. It is known that HS have an ability to react with cations because of strong association of HS with organic and inorganic compounds in soil and water, acting as both storage and transport agents for these

compounds (von Wandruszka 2000). If HS are acting as transport and storage agents, the content of metals and HS fractions must be correlated. For that purpose, the Pearson correlation coefficients were calculated for each HS fraction (Table 2). It appeared that FA had good correlation with most of the metals, especially with Cd, Th and Zn. For that reason concentrations of those metals were higher in the Köverdama peatland, where the concentration of FA was the highest. Furthermore, it is known that FA has higher affinity for Pb and Cd (Sekaly et al. 1999). The HA fraction showed good negative correlation with Th, Sr and Mn. Therefore, the concentration of Sr was probably lower in the Sangla peatland, where the concentration of HA was the highest. The HMA fraction which contains more lipids had good negative correlation with Mn. For that reason the concentration of the HMA fraction was the highest and the concentration on Mn was the lowest in the Parika peatland.

Table 2. Correlation coefficients for the contents of HS fractions and different metals. More important relations are in bold

	HA	HMA	FA
Cd	-0.50	0.14	0.91
Pb	-0.47	-0.15	0.67
U	-0.42	-0.21	0.61
Th	-0.76	-0.28	0.86
Sr	-0.82	-0.26	0.68
Cu	-0.48	-0.25	0.67
Zn	-0.47	-0.19	0.76
Mn	-0.75	-0.83	0.35

CONCLUSIONS

Balneologically usable peat was found in all three studied peatlands (Sangla, Parika and Kõverdama). The largest resources (0.47 million tonnes) were recorded in the Sangla peatland, but the content of humic substances (HS) was the highest at Parika (resources 0.11 million tonnes). The peat deposits were mainly formed by lake paludification, in the conditions of sand-clay mineral subsoil, vegetation pine forest, nutrition precipitation, degree of humification 40–50% (H6–H8) and moisture content 85–90%. Peat type varied, but cottongrass and *Sphagnum* were dominating.

The main factors influencing the levels of HS were the degree on humification and peat type. The concentration of HS was higher in more humified peat, however, it was also related to the age of peat layers as the formation of bioactive substances is a time-consuming process. The HS levels are the highest in the forest(pine)–cottongrass peat. The lipids in peat could be associated with hymatomelanin acids because of high correlation coefficients. Several trace elements well correlated with fulvic acids and some of them correlated negatively with humic acids.

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Kolme balneoloogilise potentsiaaliga Eesti turbaala turba keemilised omadused

Mall Orru, Monika Übner ja Hans Orru

Balneoloogias on muuhulgas edukalt kasutatud turvast ja mitmeid turbatooteid. Bioloogilise toime tõttu on erilise tähtsusega turbas leiduvad humiinained. Eesti soode revisjonist ja kaardistamisest johtuvalt valiti kolm balneoloogilise potentsiaaliga turbaala, kus analüüsiti humiin-, hümatomelaan- ning fulvohapete sisaldust ja turba üldtehnilisi näitajaid (mineraalainete sisaldus, niiskus, happesus, lagunemisaste ning turbaliik). Selgus, et bioaktiivsete ainete sisaldus kõikides uuritud turbakihtides oli suhteliselt kõrge. Suurimad sisaldused leiti Parika turbaalal, kus humiinhapete sisaldus turba kuivaines oli 39,3%, hümatomelaanhapete sisaldus 19,3% ja fulvohapete sisaldus 1,3%. Peamised faktorid, mis mõjutasid bioaktiivsete ainete sisaldust turbas, olid lagunemisaste (kõrgemad kontsentratsioonid olid enam lagunened turbas) ja turbaliik (metsa(männi)-villpeaturba leidumine suurendas sisaldusi). Kuna lipiididel oli kõrge korrelatsioon hümatomelaanhapetega ja mikroelementidel fulvohapetega, võivad need komponendid nimetatud humiinainetega vastavalt seotud olla.