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The stability of water molecular bridges in ombrotrophic peatland soil

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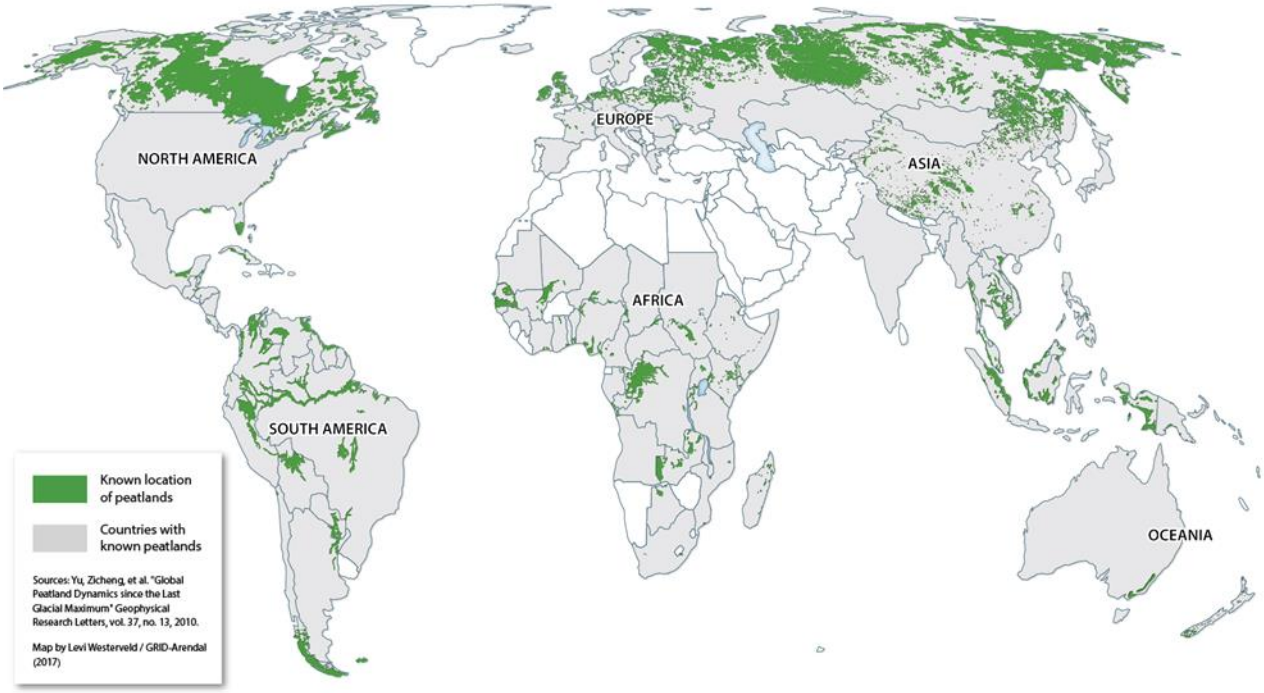
Abstract: *The stability of water molecular bridges (WaMB) is investigated on the ombrotrophic organic peatland type soil. The samples of the soil collected in the north part of Scotland (UK) near the city of Stornoway. The temperature dependence of the WaMB breaking point was measured through differential scanning calorimetry and shows how much are the organic structures inside the peat type soil susceptible to drying. The deeper peatland soil in this work shows much lower temperature values of WaMB breaking of around T* ~ 47 °C compared to the top layer where the middle temperature of WaMB breakage is T* ~ 58 °C, comparable to regular soil types. This temperature dependence shows higher susceptibility of the studied peal soil for drying and therefore higher sensitivity to changes in the water table levels and disturbance of the top layers of the soil system.*

Keywords: Peatland; Soil; Water; Water Molecular Bridges; Ombrotrophic.

1. INTRODUCTION

The latest estimates give peatland ground around 3 % of the globe's total land area[1] and according to the analysis of Yu et al.[2] the peat bogs across the world have accumulated approximately 530 – 694 Gt of carbon. However, some estimates believe that almost 50 % of the soil carbon deposits (soil carbon pool) are contained in the peatlands, which would be approximately around 1 600 – 1 700 Gt of carbon[3], in the northern regions only. That would be, technically, twice the amount of carbon in the atmosphere in a form of CO_2 (considering the concentration of 400 ppm). And truly, looking at the world map in Fig. 1, the majority of the peatland areas are located in the colder north climate region with a considerable amount of peatland stabilized in the permafrost of Russian's Siberia and North America[3]. Because of the amount of stored and relatively stabilized carbon, the peatland ecosystems are very important for sustaining and control of natural carbon cycle as disruption of those ecosystems can result in a significant release of CO_2 into the atmosphere.

The problematic of the rapid release of CO_2 from peatlands is often mentioned in connection to the underground peat fires in tropical regions[4]. However, the CO_2 and CH_4 release from peatland is a complicated process and can be also triggered by disruption of the water table and temperature changes as well. The release of CO_2 from a drained peatland in Southeast Asia was studied by Hooijer et al.[5] describing serious carbon emission due to the peatland decomposition in the magnitude of 355 Mt to 855 Mt p.a. Recently, the temperature effects on boreal fen were examined by Laine et al.[6] observing that temperature itself has only limited impact and concluding that water table levels are



Sources: Yu, Zicheng, et al. "Global Peatland Dynamics since the Last Glacial Maximum" Geophysical Research Letters, vol. 37, no. 13, 2010.

Map by Levi Westerveld / GRID-Arendal (2017)

Fig. 1. Global distribution of peatlands[12]

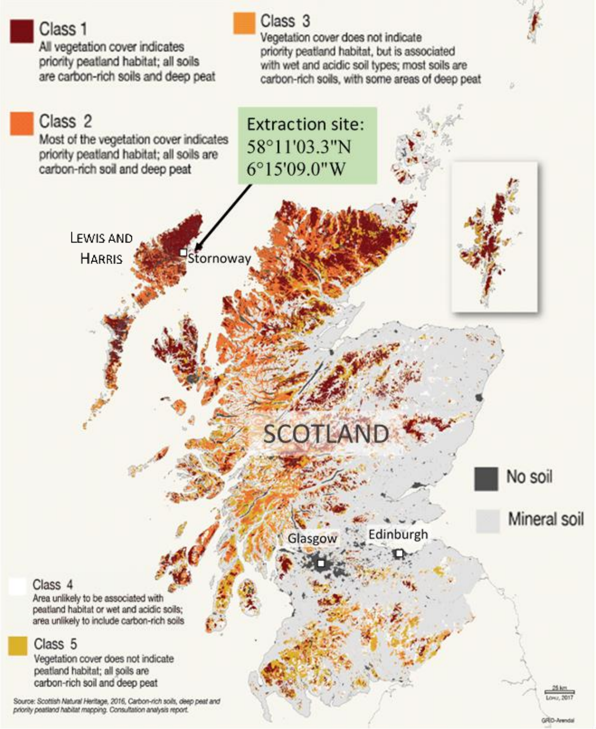


Fig. 2. Extraction location and peatland habitat coverage of Scotland, UK (original map from[13], adjusted)

a more serious matter for northern regions, thus similarly to the finding of Hooijer et al.[5] in case of hot regions of Southeast Asia. Accordingly, based on those findings we can assume that water levels and water retention capabilities of peat bogs and fens will play an important role in the future sustainability of the peatlands.

Sustainable water levels are naturally mostly connected to the prevalent water transportation mechanism at a given location, however, the water retention mechanisms of the particular soil type play an important role in its tolerance for sudden changes in the water level over short periods of time. One way how to describe the peat macromolecular stability is its dependence on temperature in polymer or polymer-like materials is the determination of water molecular bridges (WaMB). The water molecular bridges connect hydrophilic functional ends of the present macromolecular organic compounds thus stabilizing them inside the peat matrix. Consequently, the increased crosslinking of the structure better binds the water inside the organic matrix. Therefore, the presence of WaMBs is usually connected to the actual material stability and depending on the composition of the given peat soil type we can assume a correlation to the endurance against water shortage as well. Here, we study stability of the peat soil through the determination of the energy of WaMB as the temperature of the decomposition of water molecular bridges structures. The water molecular bridges were extensively studied by Shuman at el.[7, 8] trying to explain the effect of the WaMB on the biochemical and hydrological processes inside peat soil. In this work, the focus is given to the quality of the WaMB and its analytical importance on the water retention capabilities of examined peat samples.

2. EXPERIMENTAL

2.1 Location and sample treatment

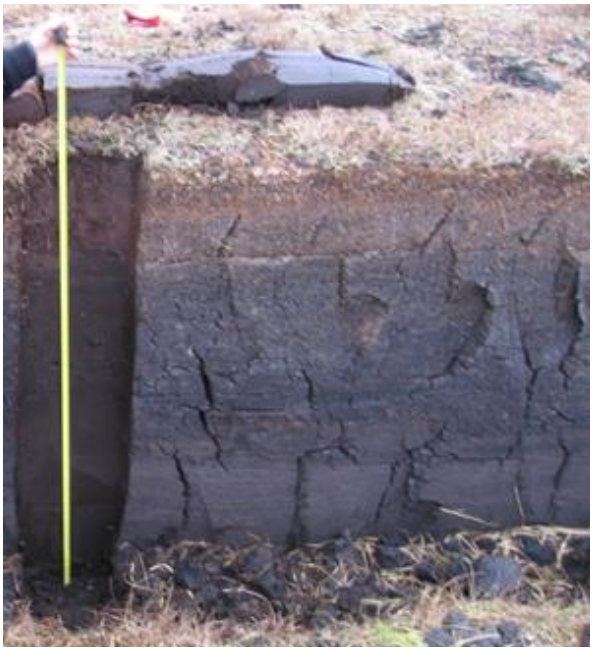


Fig. 3. Extraction site inside the peat bog – uncovering of the fresh layers of peat

Samples were collected on the Outer Hebrides' island Lewis and Hariss in Scotland, the United Kingdom near the harbour city Stornoway. The exact location is shown in Fig. 2 together with the peat classifications of the soil types associated with peat formation. The sampling was conducted in March before the start of a new vegetation period.

The sample was taken from inside an active peat bog area at the full depth from the top vegetation layer down to the solid bedrock as shown in Fig. 3. To obtain a fresh sample first 10 - 20 cm of the weathered peat was removed prior to the actual sampling to uncover undisturbed peat layers. The full length of the sample of 120 cm was vertically separated into 18 equally sized rectangular blocks of thickness around 3 cm and length of 6-7 cm. The individual blocks of the samples were then dried slowly inside an exicator at 20 °C and 43 % humidity until no weight loss was observed any more. After the drying, the samples were ground in a standard laboratory agate mortar to be homogenized and easier to analyse.

2.2 Methods

The main method to study the breaking point of the water molecular bridges was used the Differential Scanning Calorimetry (DSC). For the measurement was used instrument Discovery DSC 2500 (TA Instruments, US) equipped with an automatic handler and cooling system RSC90. The temperature program was set in the first phase to cooling from ambient temperature to -40 °C with the gradient of 10 °C/minute and then heating to 110 °C again at the rate of 10 °C/min. the amount of the sample was in the range 2-8 mg inside a standard aluminium pan. The purge gas was nitrogen with a flow of 50 ml/min. The DSC was acquired at least twice for each sample type.

The dry mass (water content) was measured for both treated and untreated samples by thermogravimetry (TG). The weight of the dry mass was acquired at the point where the mass change d*w* was equal to 0 °C in the temperature range from 100 °C to 150 °C. The temperature range was selected in respect to the thermally unstable component which started to influence the mass change typically beyond the 150 °C mark. The

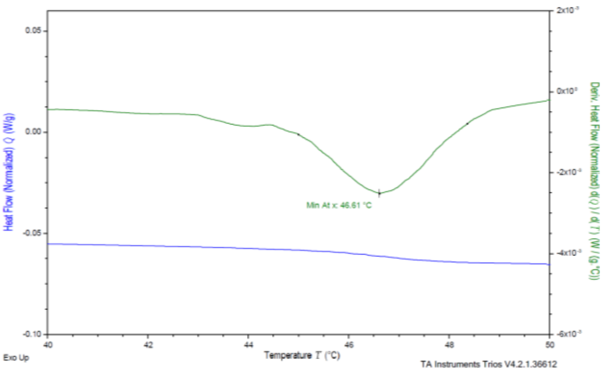


Fig. 4. Establishing of WaMB breakage point

measurement was repeated three times for each type of sample, always with a fresh sample.

Values of pH were established on the untreated samples due to the better wettability of the material and therefore better access and mobility of water and creation of hydronium cations as the basic measure for acidity. 130-200 mg of the raw peat was mixed with 60 ml of distilled and deionized water and after 15 minutes the pH was measured as a direct consumption of NaOH solution until neutral pH was achieved. The measurement was conducted on automatic titration stand Schott, TitroLine alpha plus (SI Analytics, Germany). The freshly prepared NaOH solution was calibrated by a standard solution of oxalic acid. The pH meter was calibrated as well by a precise laboratory buffer solution of pH = 7.00±0.05 (Sigma Aldrich, Germany). The measurement was repeated twice for each sample type.

3. RESULTS AND DISCUSSION

The amount of carboxylic acids contained in individual peat layers lowers the value of pH depending on the concentration and type, therefore the measured pH value gives us some basic information about the peat type and composition. The top layer of the extracted peat is only slightly acidic (pH ~6) allowing the existence of more diverse botanical environment rather than predominant *Sphagnum* moss as in case of more acidic peat bogs [9]. The pH then drops with the depth reaching the minimum of pH = 5.1 at the utmost bottom. Although the actual composition of the organic acid composition was not analysed typical humic substances such as humic and fulvic acids can be expected. The increase in acidity is apparently connected to the dominant transport mechanism of nutrients in the observed peat column (rainfall) when the smaller and better soluble fulvic acids are transported to the lower layers. From the results shown in Fig. 5 are apparent two zones, one with a rapid change of acidity down to around 50 cm of depth and slow a change zone all the way down to the bedrock. This boundary may suggest a change in the transport process and water permeation. Once we compare the actual peat layers, as can be seen in Fig. 3, we can see that around the 50 cm mark the soil colour and consistency start to change rapidly turning into much more compact and highly decomposed peat. Even though that the actual water content stays almost constant through the peat layers as they are listed in the Table 1., the consistency changes significantly from the top with roots and many herbal residues to the bottom layers which behave more like a paste-type material without any traces of original organic material. This stratification is, of course, typical for peat bogs, although the ratio of individual layers is dependent on the stage of ageing of the peat. The pH measurement was also attempted on treated and homogenized samples (dried) as well, however, the results showed no change of pH over the whole depth of the peat samples. The reasons for this measurement fail can be several, however, one of the more probable ones is the hydrophobic change of dried peat described in the literature on several occasions [10], as well as showed by our direct observation.

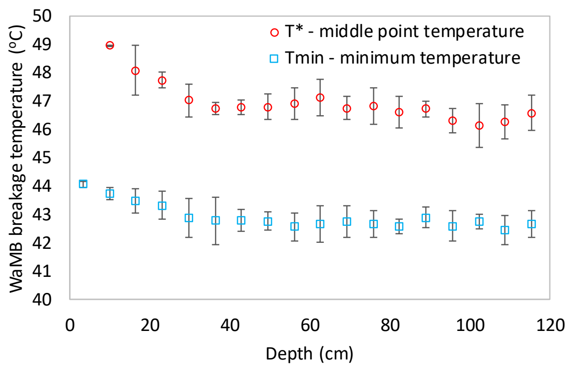


Fig. 6. Temperature of the collapse of the WaMB

Fig. 5. pH dependence of the peat on the depth

Table 1. pH, dry mass share and separation temperature of the WaMB (the numerical part of the sample's names represents median of its depth range in centimeters from the top)

Sample	pH	Dry mass (fresh) w_F/(%)	Dry mass (prepared) w_P/(%)	WaMB break temp. T_{WaMB}/(°C)
D3	6.3	23.1	86.5	58.5
D10	6.1	15.8	87.9	49.0
D17	6.0	15.8	87.5	48.1
D23	5.8	13.2	88.1	47.7
D30	5.7	14.0	89.9	47.0
D36	5.6	15.4	89.3	46.7
D43	5.5	13.9	88.4	46.8
D50	5.4	15.7	88.7	46.8
D56	5.3	17.0	88.1	46.9
D63	5.4	18.0	88.9	47.1
D69	5.3	18.2	90.4	46.8
D76	5.4	16.2	88.3	46.8
D83	5.3	15.4	89.2	46.6
D89	5.3	14.4	87.5	46.7
D96	5.2	16.5	88.0	46.3
D102	5.3	15.9	88.3	46.1
D109	5.3	17.4	88.2	46.3
D116	5.1	35.0	87.4	46.6

The temperatures at which the water molecular bridges break apart are shown in Fig. 6 where the middle pint temperature of the process is signed as T^* and the starting or minimum temperature for the bridges to start collapsing is marked as T_{min}. If we compare the utmost top layer with the lower layers we can see that the difference is not dramatic but, similarly to the pH, two zones can be distinguished this time around the 40 cm mark. This time the visual change is more apparent in Fig. 3. The change in colour and consistency is mostly caused by the presence of active root system of the herbs living on the surface together with the *Sphagnum* moss. If we compare the values of the peat from this work with other soil types we can see that the regular soil has much higher values for the breaking of the water molecular bridges 50 - 70 °C[11], and that it stabilizes with depth as the peat becomes more compact and regular. This means that the water is actually connected to the peat structures only poorly and peat type of soil is more endangered by lack of water and the process of drying can be much faster than usually expected.

4. CONCLUSION

The breaking temperature of the water molecular bridges is highest in the top layers of the examined peat column at T_{WaMB} = 58.5 °C and drops with the increasing depth. This shows higher susceptibility to drying when the top layers are removed or damaged.

Significant complications are brought by the problematic of the low rewetting ability of once dried peat which requires a long time for regeneration.

The temperature of the WaMB collapse is significantly smaller for peat than for regular soil, therefore the synergic effect of the drying process and reduced rewetting ability makes the peatland more sensitive to sudden changes in the water cycle.

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