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HETEROGENEITY IN PEAT DECOMPOSITION EVALUATED BY FOURIER TRANSFORM INFRARED MICRO-SPECTROSCOPY

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SUMMARY

Peat decomposition is locally processed at the micro scale, owing mainly to the diversity of redox condition because of the heterogeneous distribution of micro-pores in peat. In this study, we evaluated this heterogeneity in peat decomposition in order to obtain useful data on the peat decomposition process. To this end, we differentiated types of peat micro-fragments to describe the diversity of decomposed states in peat. The differentiation was based on their chemical structural analysis using Fourier transform infrared (FTIR) micro-spectroscopy and multivariate analysis. Based on the results of this analysis, the observed peat fragments were classified into five types. The transition of the frequency of each classified fragment type indicated heterogeneity in peat decomposition. Conversely, the bulk analysis was unable to estimate such parameter.

Keywords: Peat decomposition; FTIR micro-spectroscopy; organic matter

INTRODUCTION

Peat decomposition is caused by aeration processes mainly due to human impacts, such as drainage for cultivation or afforestation (Moore, 2002; Kroetsch *et al.*, 2011). Peat decomposition has been involved in agricultural activities for over a century (Lohila *et al.*, 2014); this peat degradation changes wetlands from carbon sinks to sources of CO_2 leading to alterations in wetland ecosystems. The study of the peat decomposition process represents a key to understanding the mechanisms of decrease in sequestered soil carbon and past environmental change in wetland systems. In this respect, the evaluation of the degradation state of peat is an effective means to understand the process of peat decomposition. Spectroscopic methods have been used to study the decomposed state of peat. Fourier transform infrared (FTIR) spectroscopy is a useful method to assess the state of decomposition or humification of organic materials (Prasad *et al.*, 2000; Biester *et al.*, 2014). However, these methods have considerable limitations when applied to decomposed peat. This is because decomposed organic substances (humic substances) are composed of ill-defined mixtures and their spectra represent the summation of responses of many different organic components (MacCarthy and Rice, 1985). For this reason, spectroscopic analyses using bulk samples might be inappropriate for detailed evaluations of the properties of decomposed peat.

Additionally, peat has diverse redox conditions in micro-scale, and peat decomposition is therefore considered to be processed locally. This is mainly due to the considerable heterogeneity in the distribution of micro-pores, which renders the surrounding environment oxidative after water drainage. This heterogeneity would also be the key to understand the state of peat decomposition. However, it is difficult to detect such heterogeneity using spectroscopic analysis, because of the limitation of bulk sample methodology, as mentioned earlier.

Hence, we applied Fourier transform infrared (FTIR) micro-spectroscopy as a screening tool to examine the heterogeneous properties of peat. FTIR micro-spectroscopy has been achieved by coupling a microscope with an FTIR spectrometer. This method allows us to analyze the chemical structure of peat micro-fragments by selecting them individually at the microscopic level. By using this technique and multivariate analysis, we tried to classify the state of decomposition of peat micro-fragments based on the chemical structural properties of each peat fragment. In addition, we intended to characterize the composition of peat micro-fragments based on the frequency of each cluster. By comparing these compositional patterns between peat samples at different degrees of decomposition, we proposed to evaluate heterogeneity in peat decomposition.

The aim of this study is to evaluate heterogeneity in peat decomposition, which provides new aspects for studies on the peat decomposition process and improves the limitations of current spectroscopic methods using bulk samples. To this end, we proposed (1) to represent the diversity of the state of decomposition of peat micro-fragments and (2) to characterize the heterogeneity in peat decomposition.

MATERIALS AND METHODS

Soil samples and analysis

Soil samples were taken from buried peat horizons distributed on Sagami Plain, Japan (35°23′31″N; 139°10′04″E). Field observations revealed the presence of large amounts of undecomposed plant tissues, known as fibric peat, in the deeper organic horizon (70–80cm). The soil color of this horizon was brownish black (5YR 2/2). In contrast, the upper peat horizon (50-60cm) was composed of well-decomposed sapric peat with a blacker color (10Y2/1). To investigate the transition of decomposed state between these horizons, intermediate peat soil samples were collected from depths of 60 and 70 cm, together with sapric peat from depths of 50 and 60 cm and fibric peat from depths of 70 and 80 cm. Peat samples were air-dried followed by sieving through 2-mm screen. Peat samples were characterized using the humification index (Kaila, 1956), C/N ratio, bulk density, and ash content as indicators of decomposition.

FTIR micro-spectroscopy

Peat fragments were fixed in a KBr pellet to obtain the fine FTIR spectra from a peat fragment in the microscope's field of view. FTIR absorbance was recorded from each peat fragment in a 70×70 μm aperture in a fixed range of wavenumber from 700 cm^{-1} to 4000 cm^{-1} with 2-cm^{-1} intervals using IR Prestige-21 and AIM-8800 (Shimazu, Kyoto). Scans were repeated 100 times to enhance the signal-to-noise ratio. Approximately 50 fragments were measured using five pellets at each sampling depth. Differences in relative absorption intensities between the measurements were corrected by normalizing each spectrum as described by Artz *et al.* (2008). Normalization of the spectrum enables comparison of each measurement via the correction of differences in Infrared (IR) transmittance due to sample thickness. The normalized intensities at all wavenumbers of the spectra of peat samples were averaged to obtain the mean IR spectra of samples from each horizon. The specific absorption bands were assigned based on previous reports, mainly those of Niemeyer *et al.* (1992), Artz *et al.* (2008), and Biester *et al.* (2014).

Statistical classification of fragments

The classification of peat fragments was performed by using Ward's method of cluster analysis in the IBM SPSS Statistics program version 21 (IBM, New York). Characteristic absorption intensities, which were observed at around 832, 915, 1040, 1125, 1160, 1227, 1266, 1331, 1375, 1424, 1463, 1510, 1600, 1636, 2852, 2922, and 3400 cm^{-1}, were extracted from the normalized spectra as variation for clustering analysis. After clustering, the mean IR spectra of each cluster were gained.

RESULTS AND DISCUSSION

Averaged spectra of peat fragments at each depth

The mean IR spectra were obtained by averaging all spectra from peat fragments at each horizon (Figure1). Some absorption bands were assigned as functional groups of organic compounds, such as lignin (832, 1227, 1227, 1266, 1375, 1463, 1510, and 1600cm^{-1}), polysaccharides (1040, 1125, and 1160 cm^{-1}), and silicate ion (915 cm^{-1}). They were weakened and broadened in the spectrum of peat from 50 to 60 cm in depth compared to those of organic compounds in the deeper horizon. The decreasing intensity of specific absorption suggested that degradation of peat in the upper horizon was greater than that in the deeper horizon. However, differences in spectra between the horizons appeared to be small. Similar small differences between depths were also observed in the range of the C/N ratio (19.2– 21.1) and in the humification index (18.4–21.6). These small differences among peat horizons can be attributable to evaluation using the averaged data without accounting for the heterogeneous structure of peat.
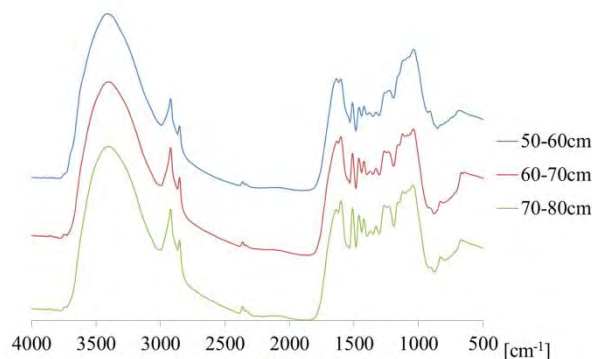

Figure 1: Mean IR spectra of peat fragments in each depth

Classification of peat by cluster analysis

Cluster analysis divided the studied samples into five groups (Figure2). Averaged IR spectra in each cluster group are shown in Figure3. The spectrum of the Group I was characterized by many sharp peaks corresponding to the structure of polysaccharides (1040, 1125, and 1160 cm^{-1}) and lignin (832, 1227, 1227, 1266, 1375, 1463, 1510, and 1600cm^{-1}). Group I was mainly composed of low-decomposed plant materials. Group II was characterized by weaker peaks than those of Group I. Group III was distinguished from the previous two clusters by the broadening of three small peaks corresponding to polysaccharides (1040, 1125, and 1160 cm^{-1}) into a single peak. These

polysaccharide bands were almost indistinguishable in Group IV due to the presence of broader of peaks than those in Groups I, II, and III. The spectrum of Group V showed broad absorption of peaks. Additionally, Group V was characterized by a shoulder band at 915 cm^{-1}, identified as a silicate ion-specific feature (Asapo and Coles, 2012). These results suggested that FTIR micro-spectroscopy can differentiate five types of peat micro-fragments based on their chemical structural properties. Furthermore, the difference in peak intensities between the spectra of each cluster was more obvious than in the averaged spectra of peat at each depth (Figure1). This indicates that peat intrinsically has a wide range of structural heterogeneity, which is difficult to understand by any spectral analyses using bulk samples.
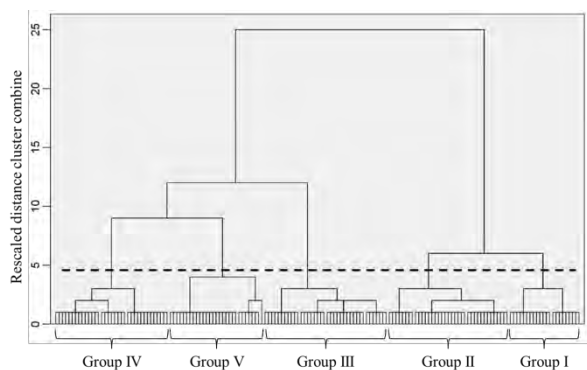

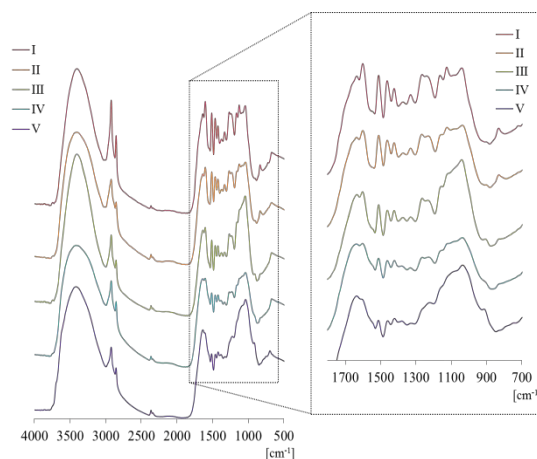Figure 2: The dendrogram given by a cluster analysis.

Figure 3: Mean IR spectra of peat on each group.

Cluster composition of decomposed peats

Cluster composition for each sampled depth is shown in Figure 4. At 70–80 cm depth, over 80% of the fragments belonged to cluster Groups I, II and III. Similarly, around 70% of the fragments 60 -70 cm in depth were classified into the Groups I to III, while less than 40% of peat at 50-60 cm depth was classified in these groups. On the other hand, Groups IV and V occupied over 60% of the peat in the horizon 50-60 cm depth. The proportions in each Group proved that peat is a mixture of micro peat fragments existing in a variety of chemical structural degradations. Additionally, given the degree of decomposition of each depth (see Figure4), vertical compositional differences between horizons represented the heterogeneous progress of peat decomposition in each horizon.
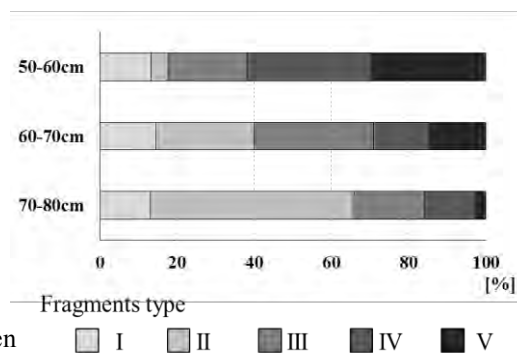

Figure 4: Chemical structural diversities of peat depending on classified types at each depth.

CONCLUSION

The microscopic and chemical structural differentiation of peat fragments clearly revealed the diversity of peat micro-structure, as shown in the spectra (Figure3 and Figure4). In addition, heterogeneity in peat decomposition was indicated by the compositional differences in peat fragment types at each depth (Figure4). These results are novel in that they quantitatively represent the heterogeneity in peat characteristics. A further advantage of the classification of heterogeneous properties is that it can evaluate decomposition state better than bulk analysis can.

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