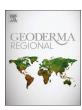
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# Heterogeneity of peat decomposition under rice cultivation on the Pacific coast, Japan



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#### ABSTRACT

Peat decomposition has micro-scale heterogeneity because the rate of decomposition differs between micro-local conditions related to pore distribution, botanical composition, and differences in plant parts. Therefore, the heterogeneity of peat decomposition degree in micro-scale can be a good indicator for further understanding of peat decomposition process. However, previous studies using "bulk analysis" have denoted peat heterogeneity as merely chemical structural diversity, and did not examine the heterogeneity of peat constituents at a microscopic level. This study aimed to obtain peat heterogeneity in the micro-scale as a new indicator of peat decomposition and conducted "heterogeneity analysis" as follows: (1) analyzing a decomposition index of individual peat micro-fragments using spectral data from Fourier transform infrared (FTIR) micro-spectroscopy and principal component analysis (PCA) for specific absorption intensities, and (2) determining the distribution of peat decomposition index as an indicator of the heterogeneity of peaty soils. Twelve peaty horizons were sampled from three sites on coastal or alluvial plains. These horizons were buried under mineral soils used for rice cultivation. We applied PCA to 775 infrared (IR) spectra obtained from observed peat micro-fragments and calculated the micro-fragment decomposition degree (MDD) which was the first principal component score explained by a decrease in C-H single bonds and a relative increase in polymerized aromatic C-C double bonds. The distribution range of MDD demonstrated that heterogeneity of decomposition degree tends to be large in middecomposed peat. Moreover, the bimodal distribution pattern of MDD represented heterogeneous state formed by mineral inter-bedding in peat. Therefore, "heterogeneity analysis" could effectively represent the intrinsic heterogeneity of peat decomposition degree without losing the microscopic diversity.

#### 1. Introduction

Peatlands store one-third of the world's soil carbon and 10% of global freshwater resources (Joosten and Clarke, 2002). However, these precious ecosystems face the threat of disappearance, mainly because of ground-water drainage resulting from afforestation and cultivation (Chapman et al., 2003; Kroetsch et al., 2011). Lowering of water level due to such activities induces peat decomposition because of an increase in decomposer fungi activities under oxidative conditions (Moore, 2002). Chimner and Cooper (2003) detected the emission of extremely high levels of  ${\rm CO}_2$  from peatlands with a decrease in the level of ground-water. In other cases, liming of peatland for its agricultural use also promoted high microbial activity, resulting in oxidative decomposition of peat (Ivarson, 1977). Lohila et al. (2004) predicted that a high rate of cultivation-induced peat decomposition would continue for more than a century. Therefore, the study of peat decomposition is critical to predict the deterioration of peatland ecosystems and the global terrestrial carbon cycle.

Many spectroscopic studies have provided information on heterogeneous peat properties related to their decomposition processes.

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The heterogeneous property of peat decomposition degree has often been discussed to understand the peat decomposition process. Peat constituents have diversity of decomposability because peat is a complex mixture with respect to botanical composition and different parts of plants (Freschet et al., 2012). Moreover, non-random variation occurs in the microbial community structure at the micro-pore scale in the soil, and the rate of organic-carbon decomposition is location-specific in pore network (Strong et al., 2004; Ruamps et al., 2011). Therefore, the rate of peat decomposition differs at the micro-scale as a result of this substantial and/or micro-environmental diversity. Decomposition model studies also indicate that it is important to consider the substrate heterogeneity derived from the diversity of decomposability and accessibility for microorganisms when assessing heterogeneous decomposition processes (Carpenter, 1981; Sierra et al., 2011). Therefore, the heterogeneous properties of peat can be a good indicator for further understanding of peat decomposition processes at the micro-scale.

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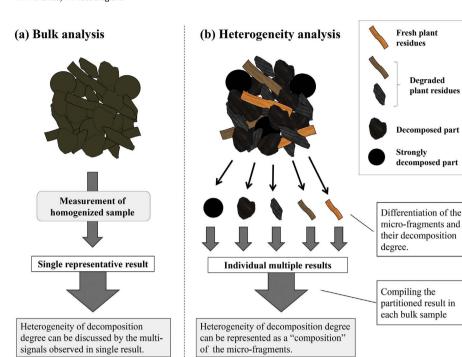


Fig. 1. The concept of "heterogeneity analysis" in peat decomposition studies.

Cocozza et al. (2003) distinguished differences in peat heterogeneity following decomposition stages in terms of chemical structural composition in solid peat samples using Fourier transform infrared (FTIR) spectroscopy and electron spin resonance (ESR) spectroscopy, and in peat-pore water samples using molecular fluorescence spectroscopy. Pyrolysis gas chromatography-mass spectrometry (Py-GCMS) can also represent the heterogeneity of peat by indicating the relative abundance of easily degradable and more resistant compounds, which can be used as an indicator of decomposition degree of peat (Biester et al., 2014). These studies have contributed to improving our understanding of heterogeneous changes in peat following decomposition. However, these studies have focused only on peat heterogeneity in chemical structural moieties, and excluded the heterogeneity of peat constituents with different decomposition degrees at a microscopic level. As schematically shown in Fig. 1, there is heterogeneity of decomposition degree even in a bulk sample. "Bulk analysis" including the above spectroscopic methods indicates the result as a single representative value from a specific amount of the sample (Fig. 1a). Therefore, previous discussions about heterogeneity in peat using the "bulk analysis" were based on only multi-signals originating from different chemical components observed in a single homogenized spectrum, which is insufficient to reveal the heterogeneity of the degree of peat decomposition at a microscopic level. Furthermore, destructive procedures such as combustion (pyrolysis mass spectrometry) and extraction (ultraviolet-visible [UV-vis] spectroscopy and liquid state nuclear magnetic resonance spectrometry) are often applied in "bulk analysis" which completely homogenizes diverse constituents of peat. Thus, results obtained from such procedures should lose heterogeneous information due to the mixing of signals from diverse components. Although FTIR is a non-destructive method to identify the chemical structural characteristics of peat and to analyze its decomposition (Chapman et al., 2001), even IR spectra (generally obtained from 2 mg of solid samples) generate complicated results because signals are averaged from homogenized constituents. On these points, Falconer et al. (2015) stated that the bulk analysis might not sufficiently predict the rate of the microbial decomposition of soil organic matter. Ruamps et al. (2011) also suggested that a homogenized bulk sample analysis is not preferred because its preparation precludes the analysis of pore-

scale variations in microbial activity. Therefore, we hypothesized that "heterogeneity analysis," which separates the micro-fragments in a bulk sample and individually analyzes the decomposition degree at a microscopic scale (Fig. 1 b), can enable us to examine the intrinsic heterogeneity of decomposition degree in a bulk peat sample without a "bulk analysis."

Fourier transform infrared micro-spectroscopy is an excellent tool to conduct above-mentioned "heterogeneity analysis." This spectroscopic tool denotes the infrared (IR) spectra of a small peat fragment by restricting the micro-area irradiated by the infrared beam with an aperture of a pre-defined size (Bhargava et al., 2003). This combination of microscopic analysis and FTIR presents a considerable advantage to represent heterogeneity in peat. Microscopic analysis is known as a good evaluation for heterogeneity of soil constituents at the micro-scale (Kooistra and van Noordwijk, 1996). Moreover, IR spectra provide sufficient signals to characterize principal chemical classes such as carbohydrates, lignins, and cellulose in soil organic matter (e.g. Artz et al., 2008; Biester et al., 2014) and compositional changes occurring in a peat decomposition process (Prasad et al., 2000; Zaccone et al., 2007; Biester et al., 2014). Therefore, FTIR micro-spectroscopy can distinguish decomposition degree at the microscopic level in bulk samples based on objective chemical structural data. To integrate individual chemical characteristic information from micro peat fragments, the principal component analysis (PCA) is a useful method to handle spectral datasets without any preliminary assumptions (Philippe et al., 2006) and to distinguish very subtle spectral differences (McCann et al., 1997). Therefore, we hypothesized that a combination of FTIR micro-spectroscopy with PCA could suggest peat heterogeneity as a new and highly-resolved peat decomposition index that has been overlooked in bulk analyses. Previous studies have not used FTIR micro-spectroscopy to examine peat decomposition. Hence, our "heterogeneity analysis" is an innovative approach because peat constituents at the microscopic level can now be differentiated by chemical structural information.

In this study, we aimed to represent the heterogeneous properties of peat as a composition of micro-constituents in a range of decomposition degrees using FTIR micro-spectroscopy. Therefore, we conducted "heterogeneity analysis," which differentiates the micro-fragments

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