



Title	Effect of peat fire on chemical characteristics of humic acid and fulvic acid in soil and water of peatland of Central Kalimantan, Indonesia [an abstract of dissertation and a summary of dissertation review]
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# 学位論文内容の要旨

博士 (環境科学)

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## 学位論文題名

Effect of peat fire on chemical characteristics of humic acid and fulvic acid in soil and water of peatland of Central Kalimantan, Indonesia

(インドネシア中央カリマンタン泥炭地の土壌及び水中のフミン酸とフルボ酸の化学的特性への泥炭火災の影響)

Peatlands are areas of land with a thick water-logged organic soil layer called peat soil, which was formed from dead and decaying plant materials. Peatlands accumulate huge amount of organic matters in soil and play the role as a carbon sink. Indonesia has the largest area of peatlands in South East Asia, which are distributed in Sumatra, Kalimantan and Papua islands. However, the peatlands in Indonesia have been degraded rapidly by deforestation due to logging and agriculture, construction of drainages and forest fires. Since early 1990s, forest fires have become one of severe disasters in the peatland area, especially in the year when El Nino phenomena happened in Indonesia. In the forest fires, not only the surface vegetation of the peatlands burns, but the peat in soil also burns. Once ignited, peat soil could be burnt and smoldered under the ground slowly for many weeks as called the peat fire (Siegert et al., 2004). The forest fires happened most frequently during 2002-2011 in Indonesia, especially in Mega Rice Project (MRP) area of Central Kalimantan. MRP was initiated in 1996 by Indonesian Government to open the peatland in Palangka Raya of Central Kalimantan for paddy fields and then irrigation canals as long as 4400 km were constructed to support the new paddy field. However, the MRP was discontinued and the long irrigation canals were left. The existence of canals lowers the water level of peatland to lead to dryness of peat and peat fires. Consequently, organic matters accumulated in the peatland are released to river as dissolved organic matters(DOM) and to atmosphere as carbon dioxide.

Peat soil contains at least 65 % organic matters and less than 35 % mineral content. Most parts of organic matters in peat soil consist of humic substances including humic acid, fulvic acid and humin. Therefore, humic substances play important roles in soil environment and the degradation of soils starts from the destruction of humic substances. In Central Kalimantan, the river is important for daily activities of local people such as for transportation, washing, fishing and bathing. The water quality of river water affects directly the life and health of people around the river. On the other hand, since peat fires often happen around the river and canal, the water quality of river water may be affected with DOM released by a peat fire.

Based on the above backgrounds, the objective of study is to investigate the chemical changes in peat soil as an impact of peat fire through the chemical characteristics of extracted humic acid(HA) from peat soil and water from burnt sites and unburnt sites in Central Kalimantan. The study was conducted in a peatland of Central Kalimantan, Indonesia. Soil samples were collected from Mega Rice Project (MRP) area in Kalamangan village, Sebangau National Park and a burnt area in Kereng. Water samples were collected from the Sebangau River and the canal in MRP area. HAs were extracted from dried soil samples and purified according to the method recommended by International Humic Substances Society (IHSS) and Stevenson (1994). HA and fulvic acid(FA) were also extracted from water samples and purified according to Thurman's method (1982). Water quality including pH, temperature, TDS, DO, EC were measured by Horiba multi checker 51 U. Dissolved organic carbon(DOC) concentration in water samples are measured by TOC Analyzer 5000 A, Shimadzu, Co. Japan. The characterization of HA and FA was performed by elemental analysis, a size exclusion chromatography, TG-DTA, three-dimensional spectrofluorometry, pyrolysis gas chromatography/mass spectrometry(GC/MS).

The water quality of the Sebangau River and canal was quite similar and pH values of both sites were in

the range of 3 to 4.5. This acidic condition is a specific property of water in peatlands. The DOC concentration of the Sebangau River was in the range 32-58 mg/L. The trend of DOC concentration in the Sebangau River was quite similar to that of the precipitation data. In rainy season, the organic matters must be eluted from peat soil in the surrounding areas of the river to the river by runoff. The DOC concentration of the canal water varied depending on the sampling site. The characteristics of HA and FA from the Sebangau River and the canal were also investigated using purified HA and FA from the Sebangau River and the canal waters. The molecular weight of HA and FA from the canal water was lower than that from the unburnt site. It seems the humic substances of burnt sites have been degraded partially. The fluorescence intensity of HA from burnt sites by three-dimensional spectrofluorometry was higher than that from unburnt site.

The chemical characteristics of HAs from burnt sites and unburnt sites were investigated using extracted HAs from four sampling sites as well as heated HAs. From the elemental analysis data, the ratio of hydrogen to carbon (H/C) and the ratio of oxygen to carbon (O/C) were calculated and then plotted to the Van Krevelen Diagram. The higher value of the H/C indicates the higher aliphaticity and the lower H/C indicates the higher aromaticity. The ratio of the O/C is related to the amount of the functional groups containing oxygen of humic acid. The decrease in the O/C value means the loss of the functional groups containing oxygen. After heating of HA at 200, 300 and 400 °C, the values of the O/C decreased gradually with increasing the heating temperature. The H/C value of HAs also showed similar behavior to the O/C value. This indicated that the heating process released the functional groups containing oxygen and consequently increased the aromaticity of HA. The evidence that the molecular weight of humic acid decreased with increasing the heating temperature suggested the release of some functional groups and moieties from the HA structure. <sup>13</sup>C-NMR spectra data also confirmed the increase in the aromatic carbon after the heating process. It is well known that HA contains some fluorophores and then the three-dimensional spectrofluorometry has been used to investigate the characteristic of HA from different origins. HA from burnt sites showed the higher intensity of fluorophores than that of HA from unburnt sites. It means the HA from burnt sites contained more fluorophores such as phenolic moiety.

The changes in the chemical composition of HA due to the effect of heating were considered on the basis of pyrolysate compounds detected by a pyrolysis-GC/MS. The pyrolysate compounds of HA from an unburnt site were dominated with alkanes, alkenes and alkynes, saturated fatty acids, unsaturated fatty acids. These compounds are pyrolysis products originated from lignin and soil organic matters. The relative peak areas for the alkanes, alkenes and alkynes in HA from an unburnt site were larger than those of HA from a burnt site. Contrary, the relative peak area for the phenolic compounds in HA from a burnt site was larger than that of HA from an unburnt site. HA from the burnt sites contained more aromatic compounds, on the other hand, HA from the unburnt site contained more aliphatic compounds. This data had a strong correlation with the elemental analysis data that indicated the H/C and O/C values of HA from the burnt sites were lower than from the unburnt sites.

The present study provided the information concerning the structural change in HA affected by peat fire. Peat fire and heating process induced the releasing of the functional groups containing oxygen in humic acid such as carboxylic group and also increased the aromaticity of HA. The conclusion from the data obtained in this study is important for the evaluation of peatlands and the conservation in tropical area.