Title	Effect of peat fire on chemical characteristics of humic acid and fulvic acid in soil and water of peatland of Central Kalimantan,Indonesia
Author(s)	Syawal, Yustiawati
Citation	北海道大学. 博士(環境科学) 乙第6933号
Issue Date	2014-09-25
DOI	10.14943/doctoral.r6933
Doc URL	http://hdl.handle.net/2115/57141
Type	theses (doctoral)
File Information	Yustiawati_Syawal.pdf

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)

Yustiawati Syawal

Division of Environmental Science Development
Graduate School of Environmental Science
Hokkaido University
September, 2014

Acknowledgement

I would like to acknowledge the support and assistance of many people who have contributed to the completion of this study.

First of all, I would like to express my deepest thank to my supervisor, Professor Shunitz Tanaka for his valuable advice, guidance, encouragement and patience throughout my study in Japan. I learn much from him how to be a good and tough researcher, I am grateful to have had opportunity to do research with him.

I also express my gratitude to Professor Noriyuki Tanaka, Professor Shiro Tsuyuzaki, Professor Bunshi Fugetsu and Professor Masami Fukushima for their valuable and useful suggestions and comments.

I sincerely thank to Professor Hideki Kuramitz for his support, valuable discussion and encourage me in accomplishing this study.

I also thank to Dr. Kazuto Sazawa for helping and teaching me, during my laboratory work in Toyama University.

I sincerely thank to all members of Tanaka's laboratory for their friendship, support and encouragement during my study in Japan. Special thanks to Dr. Takahiro Sasaki, Mr. Yusuke Kihara, Mr. Yasuhisa Ohkawa, Dr. Yoshihiro Mihara, they for training me use some instruments in our laboratory to, Mr. Eko Siswoyo, Mr. Satya Candra Wibawa Sakti, Mr. Yasuhiro Akemoto, Miss Aoi Nasu, for their support, friendship, kindness, and encouragement both in research activities and daily life. I also sincerely thank to my best friend, Dr. Nina Yulianti for her help and awesome friendship in hard times of my study. I also thank to all my friends from Indonesia and other countries for their kindness and friendship during my study in Japan.

My sincerely thank also to the staffs of fisheries laboratory, University of Palangka Raya, Central Kalimantan, Indonesia for their collaboration in the field investigation. Special thanks to Prof. Sulmin Gumiri, Dr. Ardianor, Linda Wulandari, M.Si, Dr.Rossana Elvince, Mr. Hendri and Mr. Agus.

I also thank to the Research Center for Limnology, Indonesian Institute of Sciences (LIPI) on behalf the Government of Indonesia who gave me the opportunity to join the JST-JICA Project and study in Graduate School of Environmental Science, Hokkaido University, Japan.

I also thank to JST-JICA (Wild Fire and Carbon Management in Peat-Forest in Indonesia) for providing the scholarship and supporting my research.

I deeply thank to my beloved mother and father for their love, support, encouragement and prayer throughout my study in Japan. Their hope and prayer have been my strength to accomplish my study. My deeply gratitude also to my lovely daughter Mutiara Saraswati, my husband M.Suhaemi Syawal, my sisters Farida Indriawati, Dini Triaswati, Mulia Ibeti, Marina Asti, my brother Imanuel Akbar, my auntie Mariati, and all my family for their love, many kinds of support, prayer and continuous encouragement.

Finally, I owe it all to Almighty Allah SWT for granting me the wisdom, health and strength to undertake this research task and enabling me to its completion.

Contents

List of Figures

List of Tables

Summary

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 with a thick water-logged organic soil layer called peat, which is generated from dead and decaying plant materials. Peatlands store huge amount of organic matters in the soil and play the important 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. The peatlands in Indonesia have been degraded rapidly by deforestation/logging, agriculture, constructing drainage, peat drying 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 happen in Indonesia. In the forest fires of peatlands, not only the surface vegetation of the peatland burns, but also the underlying peat in soil burns. Once ignited, peat soil could be burnt and smoldered under the ground slowly for many weeks as called a peat fire (Siegert et al., 2004). The hotspots of forest fire happened most frequently in Indonesia during 2002-2011 were detected in Mega Rice Project (MRP) area of Central Kalimantan. In 1996, MRP was initiated 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 maintain the new paddy fields. However, the MRP was discontinued and the long irrigation canals have been left. The

presence of canals lowers the water level of peatland to occur peat drying and peat fires. Consequently, organic matters stored in the ground are released to atmosphere as carbon dioxide and to river as dissolved organic matters (DOM).

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 role in soil environment. The degradation of soils starts with the destruction of humic substances, and it brings with many kinds of environmental disasters. In Central Kalimantan, Indonesia, the rivers are 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. In the other hand, peat fires happen around the river and canal, probably the water quality of river water get and canals has been affected by peat fires.

Based on the above background, the objective of study is to investigate the chemical changes in peat soil as the impacts of peat fire through the characteristics of extracted humic substances from peat soil and water from burnt sites and unburnt sites in Central Kalimantan, Indonesia. The study was conducted in peatland area of Central Kalimantan, Indonesia. Soil samples were collected from Mega Rice Project (MRP) area in Kalampangan Village, Sebangau National Park and a burnt area in Kereng. Water samples were collected from the Sebangau River and Canal water in the MRP area. Humic acids were extracted from dried soil samples and purified according to the method recommended by International Humic Substances Society (IHSS) and Stevenson (1994). Humic acid and fulvic acid 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 a Horiba multi checker 51 U. Dissolved organic carbon(DOC) concentration in water samples was measured by a TOC Analyzer 5000 A, Shimadzu, Co.Japan. The characterization of humic acid and fulvic acid was performed by elemental analysis, a size exclusion chromatography, TG-DTA, three-dimensional fluorometry and Pyrolisis GC/MS.

The water quality of the Sebangau River and Canal was quite similar. The pH of both sites were in the range of 3 to 4.5. The acidic condition is a specific property of water in peatland area. The DOC of the Sebangau river was in the range of 32 to 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 run off. The DOC concentration of canal water varied depending on the sampling site. The characteristics of humic acid and fulvic acid from water were also investigated using purified humic acid and fulvic acid from the Sebangau river and canal water. The molecular weight of humic acid and fulvic acid from the canal in the burnt area was lower than those from the unburnt site. The humic substances of the burnt sites seem to have been degraded partially. The fluorescence index of humic acid from the burnt site by a three-dimensional fluorometry spectra was higher than that from the unburnt site. The canal water contained more fluorophores such as phenolic compounds that might be originated from the burnt soil.

The chemical characteristics of humic acid from the burnt sites and unburnt sites were investigated using humic acids extracted from four sampling sites. From the elemental analysis data, the ratio of hydrogen to carbon (H/C) and the ratio of oxygen to carbon(O/C) value were calculated and then plotted into 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 humic acid at 200, 300 and 400 ^{o}C, the value of the O/C decreased gradually with increasing the heating temperature. The H/C value of HAs also showed the 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 increase of heating temperature suggested us the release of some functional groups. ^{13}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 fluorescence spectra has been used to investigate the characteristics of HA from different origins. HA from burnt sites showed the high intensity of fluorophores of HA from the burnt sides, it means the HA contained more fluorophore compound such as phenolic moiety.

The changes of the chemical composition of HA due to the effect of heating were considered on the basis of pyrolysate compounds detected by a pyrolysis-gas chromatography. The pyrolysate compounds of HA from an unburnt site were dominated with alkanes, alkenes and alkynes, saturated fatty acids and unsaturated fatty acids. These compounds are the pyrolysis products originated from lignin and soil organic matters. The relative peak area for the alkanes, alkenes and alkynes in HA from an unburnt site was larger than that in 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, in the other hand, HA from the unburnt site contained more aliphatic compounds. This data of pyrolysates had a strong correlation with the elemental analysis data, which

indicated that 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 molecular and structural change in humic acid affected by peat fire. Peat fire or heating process induced the release of the functional group containing oxygen in humic acid such as carboxylic groups. On the other hand, fire or heating also increased the aromaticity of humic acid. These structural changes in humic acid consequently will decrease the ability of humic acid to bind with metal ions, destroy the crumb structure, and decrease the water holder capacity of soil, furthermore it will reduce the soil fertility and cause the environment damages. The conclusion from the data obtained in this study is important for the evaluation of the peat land and the conservation in tropical area.

CHAPTER 1

General Introduction

1.1. Peat Formation and humic substances

Peat is formed chemically and biologically from decayed plant materials such as leaves, wood that falled to the forest floor, usually in wet area and under the acidic and anaerob condition. As repeating the decomposition and formation, the peat is accumulated gradually in soil for long period. The formation and preservation of peat depend on the positive climatic moisture, high-relative humidity, topographic and geological conditions (Page et al. 2006). The accumulation of peat into soil is a result of the higher rate of supply of organic material in soil compared to the rate of decomposition. Peat contains many kinds of organic matters, and most parts of organic consist of humic substances including humic acid, fulvic acid and humin. The peatland is an area where a layer of peat has been formed in soil naturally over thousand of years. This peatland area is called “Carbon Sink” that stores large amount of carbon. The tropical peatlands play an important contribution in the global carbon cycle. However, the function of tropical peatland has now become uncertain because some pristine peatlands are likely a net carbon sink, whereas in steady state, it is found that formerly accumulated carbon resources are loosing under the dried condition. The large areas of tropical peatland are undergoing degradation, which shifts the ecosystem’s carbon balance from a net carbon sink to a source (Hirano et al, 2009).

Humic substances (HSs) are amorphous, brown or black, hydrophilic, acidic, polydisperse substances, whose molecular weights are in the range from several hundred to tens of thousands Daltons. Humic substances are usually divided into three main fractions, based on their solubility in alkali and acid. The fractions are as follows (Schnitzer and Khan 1972):

1. Humic acid (HA): It is soluble in dilute alkaline solution but is precipitated by acidification of the alkaline extract.

2. Fulvic acid (FA): It remains soluble even in aqueous acidified solution and then is soluble in both acid and base.
3. Humin: It is not soluble in dilute base and acid.

The three humic fractions are similar structurally, but they differ in molecular weight, elemental composition, and functional group content, FA has a lower molecular weight but contains more oxygen-containing functional group per an unit weight than HA and humin fraction.

All humic fractions have important characteristics such as the resistance to microbial degradation, the ability to form stable salts and complexes with metal ions and hydrous oxides, and the surface activity. They also can bind with clay minerals and anthropogenic organic chemicals (organic pollutants) on the basis of the electro statistic and hydrophobic interaction. These reactions of humic substances in soil and water play the important functions in biogeochemical processes in environment (Schnitzer and Khan 1972).

The structure of humic acid and fulvic acid are shown in Fig.1.1 and Fig.1.2.

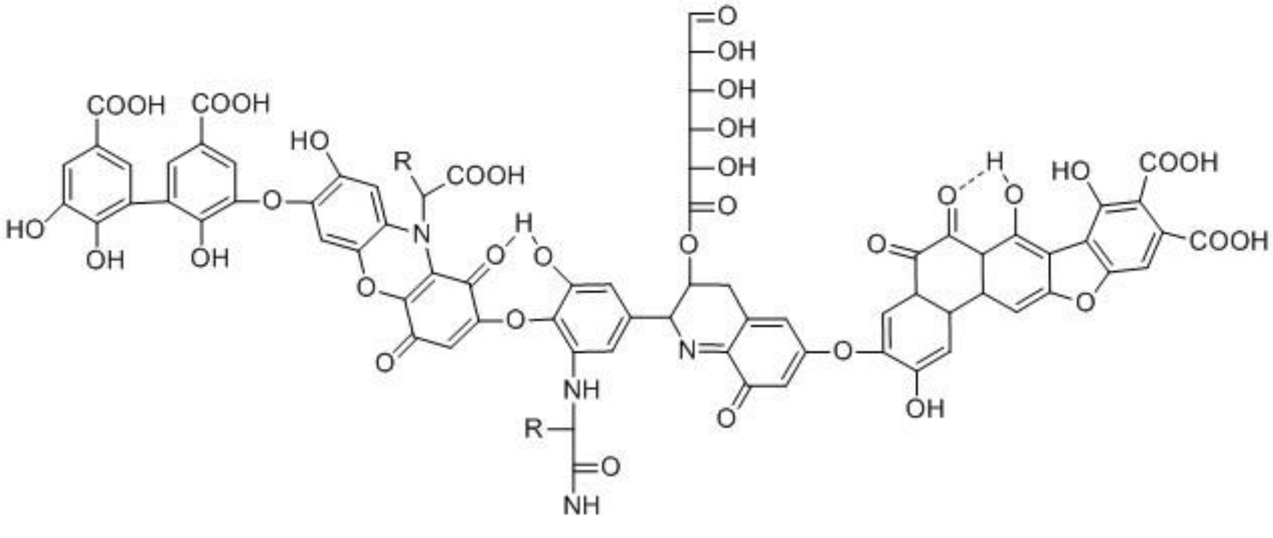


Fig.1.1. The structure of humic acid (Stevenson (1982).

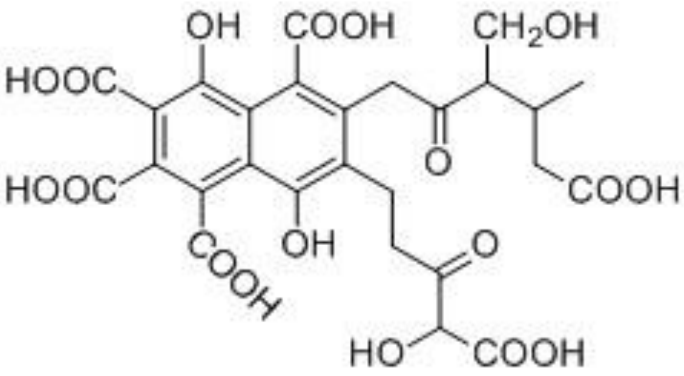


Fig. 1.2. The structure of fulvic acid

1.2. Peatland area in Indonesia

Tropical peatlands are widely distributed at the mainlands of East Asia, Southeast Asia, the Caribbean and Central America, South America and Southern Africa. The tropical peatlands are mostly located in Southeast Asia and the total area is about 26 million ha, that is 57 % of the whole peatlands. In Southeast Asia, Indonesia has the largest peatland area about 20 million ha, 80 % of the total peatlands in this area. The distribution of the peatlands area in Kalimantan and Sumatra island are 6 million ha and 7 million ha, respectively (Page, 2010). However, the peatlands in Kalimantan and Sumatra islands are now under the severe degradation and rapid deforestation. The conversion of the peatlands to other land uses, especially to plantation of oil palm and pulpwood trees has been proceeding rapidly. The conversion of the peatland will lead to the oxidation of organic matter and consequently increase the emission of greenhouse gases, carbon dioxide (Jaenicke et al. 2008). Recently, peat forest fires have caused the worst effect to the environments.

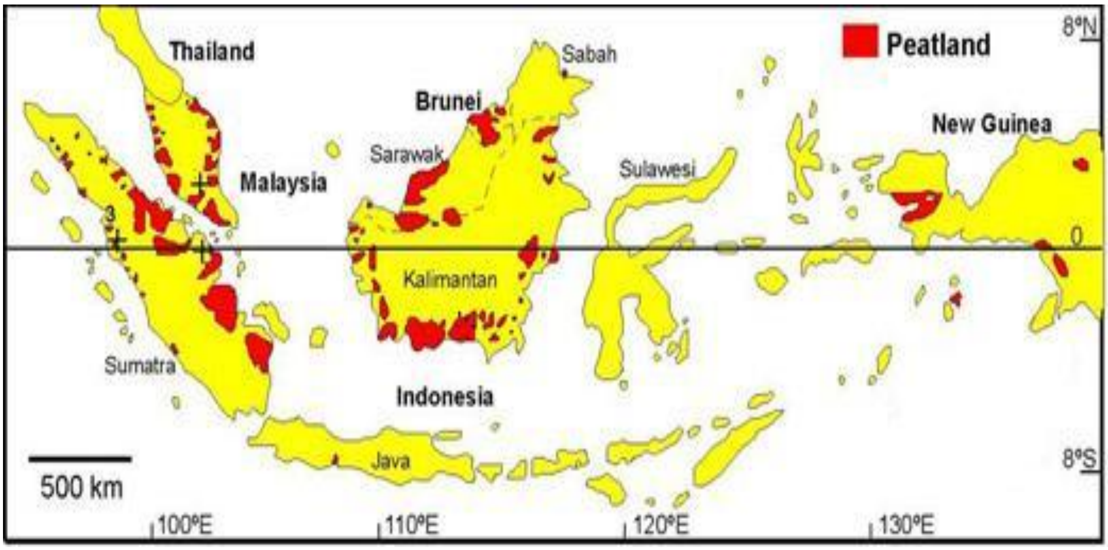
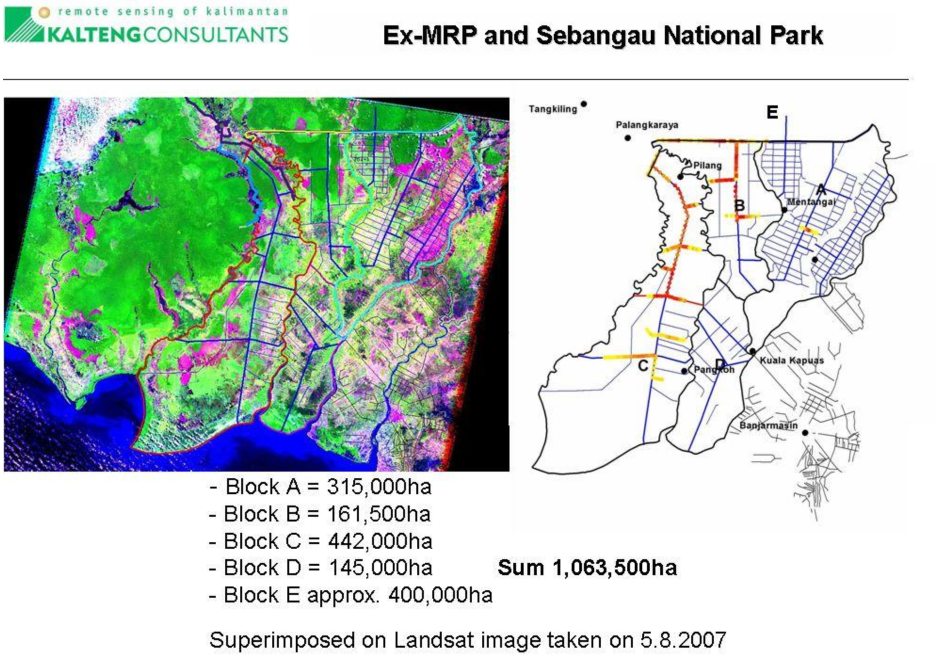


Fig. 1.3. Distribution of peatland in Southeast Asia (Page et al., PAGES News 18 No.1:25-27, 2010).

1.3. Distribution of peat fires in Indonesia and its impacts

According to Yulianti et al. (2012), in Southeast Asia, the worse air pollution due to smoke from fires occurred in *El Nino* event 1997-1998. The dense smoke came from the forest and peat fires that happened in Indonesia. The peat fire is the fire where peat in soil burnt, usually occur in relative low temperature, spreads slowly and flameless like a smoldering coal. The peat fire can go into the soil and travel underground (below the surface). Peat fire does not destroy only forest land but also cause destruction of the peat wetland habitat in where many plants and animal live. The smoke released to the atmosphere also cause air pollution not only Indonesia but also to the neighbors countries such as Malaysia and Singapore. This dense haze causes health problems due to large amount of smoke and deterioration in air quality (Page 2002). The green house gases, especially carbon dioxide was detected in high concentration when peat fire happened. The method of one-degree cell has been used to detect hotspots of the peat-forest fire. The preliminary analysis using one-degree cells, has noticed the eleven cells with the highest hotspot, and the number of the hot spots is greater than 1,000. These highest hotspots cells were distributed in South Kalimantan, South Sumatra, and North Sumatra. The highest hotspots area is mostly located in peatland areas. The most fire-pore in Indonesia (H1) is located in one of Mega Rice Project areas in Kalimantan. In 1996, Indonesian Government initiated Mega Rice Project to open the peat forest in Palangka Raya of Central Kalimantan. Through this project, one million ha of peat forest area was opened to make paddy fields, and then the long irrigation canals were constructed for new paddy fields as shown in Fig 1.4. Unfortunately, this project was discontinued and remained the long irrigation canals. The presence of canals led to the decrease of the water level and dryness of peat. Consequently the degradation of peat has progressed rapidly in this area. Once peat fire is ignited, not only the surface vegetation on the peatland but also peat in soil can be burned up to 100 cm below the surface. These peat fires release plenty amount of carbon dioxide and other pollutant gasses to the atmosphere, also some parts of pyrolisate organic matters may be released to the aquatic environment, the illustration is presented in Fig. 1.5. Thus, Indonesia is one of carbon emitter countries due to very high amount of carbon emission release from forest and peat fire in Indonesia.

Certini (2005) reported that the fires on soil influenced physical, chemical, mineralogical and biological properties of soil. The fires removed organic matters, deteriorated of both structure and porosity of soil, lost nutrient through volatilization, leaching and erosion of soil, changed the composition and quantities of microbial and invertebrate communities in soil.



Ex-MRP and Sebangau National Park

- Block A = 315,000ha
- Block B = 161,500ha
- Block C = 442,000ha
- Block D = 145,000ha
- Block E approx. 400,000ha

Sum 1,063,500ha

Superimposed on Landsat image taken on 5.8.2007

Fig.1.4. Landsat image of Mega Rice Project area in Central Kalimantan, Indonesia.

(Source: http://www.kalteng.org/start.php?katlD=3).

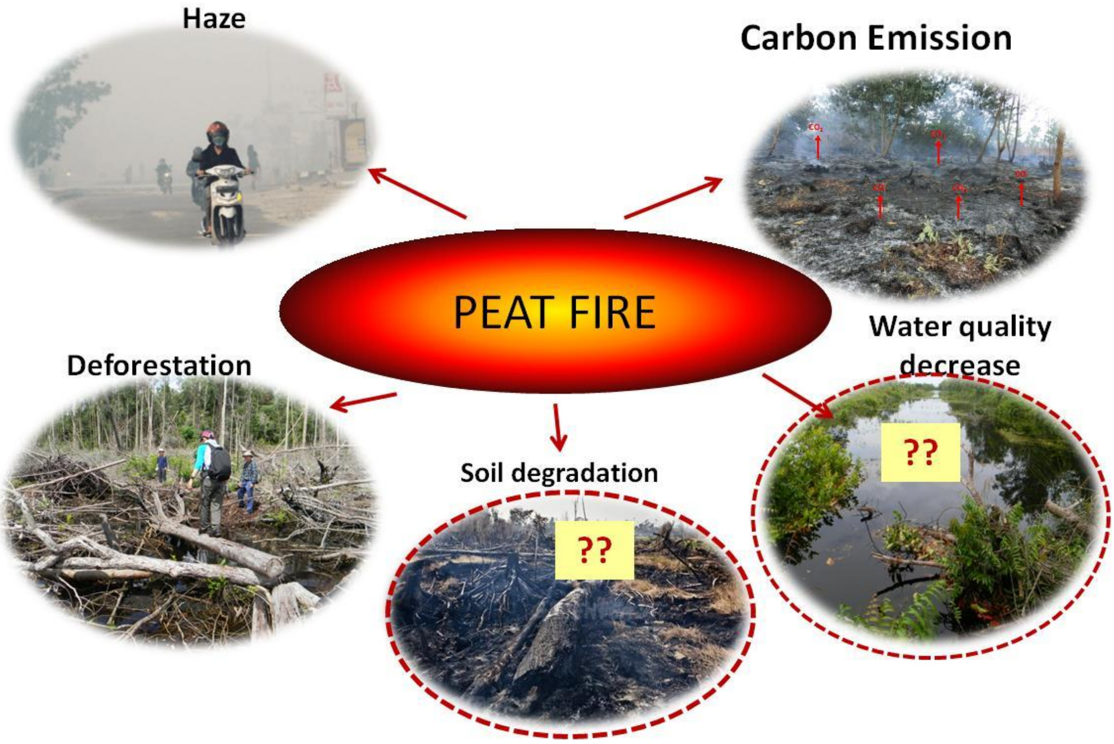


Fig. 1.5. Impacts of peat fire to the environment.

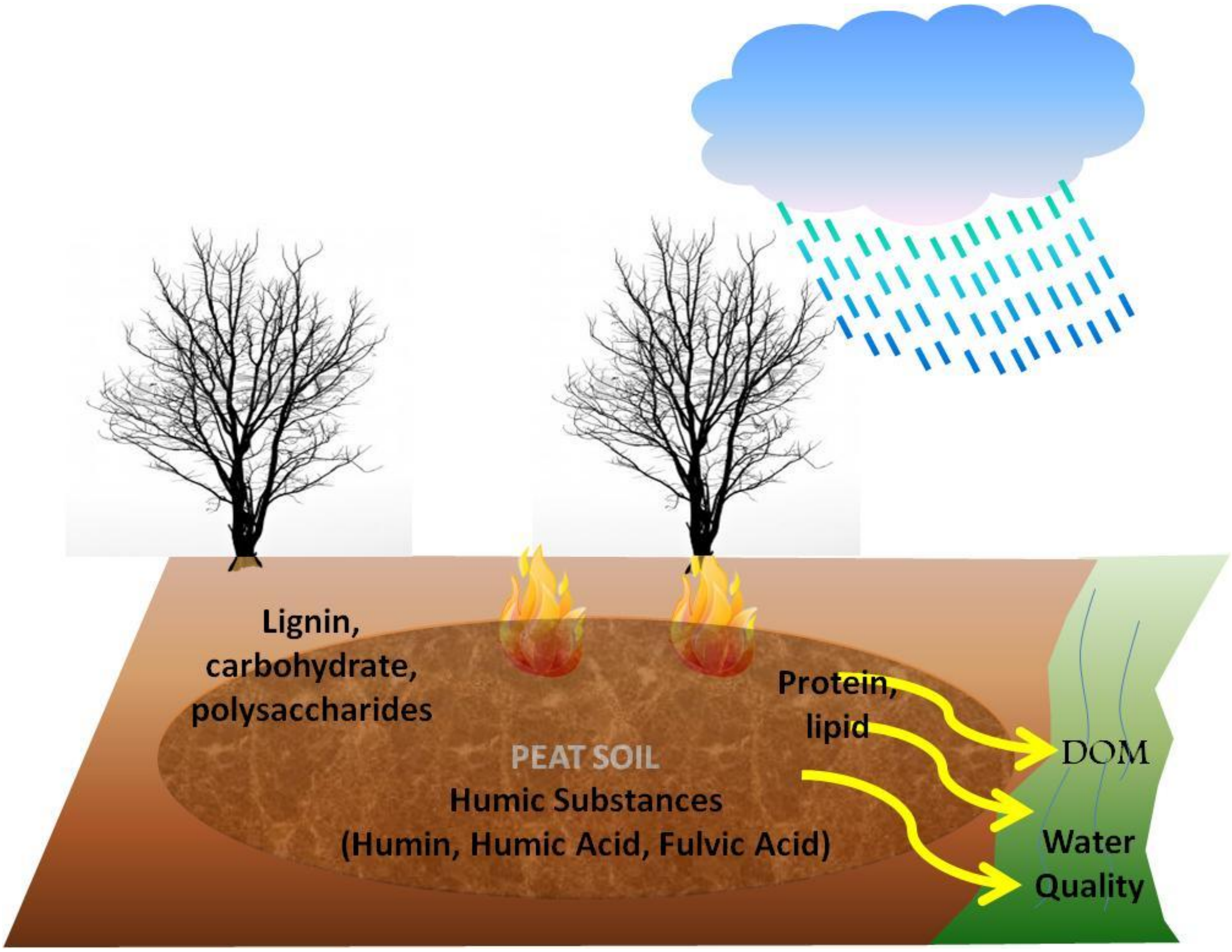


Fig. 1.6. The illustration of the impact of peat fires to soil and water.

1.4.Objectives

Peatlands in Central Kalimantan are the important carbon sink in regional and globally. Deforestation, peat drying and peat fire have threatened the preservation of the carbon sink in this peatland area. When peat-forest fires happen, the release of carbon dioxide to the atmosphere, carbon and elution of carbon in soil to the aquatic environment cannot be avoided as shown in Fig.1.6. The major components of organic matters in peat soil are humic matters. Humic acid (HA) is a dominant component of humic substances. The element composition, molecular size, structure, functional groups of HAs are different depending on the origin and their genesis way. It is said that the degradation of soils starts with the destruction of humic matter, and it brings many kinds of environmental disasters (Tan 2003). When rain fall, the degraded compounds in soil will be eluted to the aquatic environment.

Therefore, the objective of this study is to investigate the chemical changes in peat soil as an impact of peat fire, through the characteristics of extracted humic acid and fulvic acid from peat soil and water from burnt sites and unburnt sites in Central Kalimantan, Indonesia.

In details:

1. To investigate the effect of peat fire on the characteristics of humic acid from soil in Central Kalimantan.
2. To compare the characteristics of aquatic humic substances from Sebangau and Canal Kalampangan.
3. To measure the physico-chemical properties of the Sebangau River and Canal Kalampangan.

References

Certini G (2005), Effect of fire on properties of forest soil: a review. *Oecologia* 143: 1-10.

Hirano T, Jauhiainen J, Inoue T, Takahashi H (2009), Controls on the carbon balance of tropical peatlands. *Ecosystem* 12: 873-887.

Jaenicke J, Rieley JO, Mott C, Kimman P and Siegert F (2008), Determination of the amount of carbon stored in Indonesian peatlands. *Geoderma* 147: 151-158.

Page SE, Siegert F, Rieley JO, Boehm HV, Jaya A, Limin S (2002), The amount of carbon released from peat and forest fires in Indonesia during 1997. *Nature* 420: 61- 65.

Page SE, Rieley JO, Wust R (2006), Lowland tropical peatlands of South East Asia. In: Peatlands: Evolution and Records of Environmental and climate changes. Martini, I.P, Cortizas, A.M, Chesworth, W (Eds). Elsivier.

Page S, Wust R and Banks C (2010), Past and present carbon accumulation and loss in Southeat Asian peatlands. *PAGES News* 18 No.1: 25-27.

Schnitzer M and Khan SU (1972), Humic substances in the environment. Marcel dekker, Inc. USA. pp 323.

Stevenson FJ (1994), Humus Chemistry: genesis, composition, reaction. 2nd edition. John Wiley & Sons, Inc. USA.

Tan KH (2003), Humic Matter in Soil and Environment. Principles and Controversies. Marcel Dekker, Inc. USA. page 292.

Yulianti N, Hayasaka H and Usup A (2012), Recent forest and peat fire trends in Indonesia, The latest decade by MODIS Hotspot data. *Global Environmental Research* 16: 105-116.

CHAPTER 2

Physico-chemical properties of water of the Sebangau River and Canal at Kalampangan in Central Kalimantan, Indonesia

2.1. Introduction

In Central Kalimantan, Indonesia, the rivers are important for daily activities of local people such as for transportation, washing, fishing and bathing. The rivers in Central Kalimantan flows through the peatland area. Peatland area has an unique ecosystem that mostly consists of organic matter in soil. The properties of the river water are influenced by natural and anthropogenic allochthonous sources from the catchment area and from autochthonous sources. The river water in Central Kalimantan also have an unique property that is called black water river. Naiman et al.(1987) reported that the dark colour of the black water river originated from humic acids and particulate organic carbon (POC) consisted of plant litter and soil organic matters. Meybeck (1993) explained more detail of the carbon sources in the river water. Dissolved Inorganic Carbon (DIC) in the river water originates from weathering of carbonate mineral, atmospheric and soil CO_2, whereas Dissolved Organic Carbon (DOC) originates from leaching of organic matters in soil. Human activities also produce some organic pollutants. Particulate Carbon consists of Particulate Organic Carbon (POC) and Particulate Inorganic Carbon (PIC). POC particularly originates from soil erosion, and small amount of sedimentary rock and autochthonous, while PIC originates from autochthonous and sedimentary rock such as carbonate mineral.

In peatland area, the fluctuation of water level of the river is significantly different between rainy and dry season. However, the water quality did not differ greatly between rainy and dry season as observed in the Sebangau River (Central Kalimantan) by Tachibana et al. (2006). Generally, in peat swamp area, the pH of river water, conductivity, dissolved oxygen (DO) were relatively low whereas pH was in the range 3.5- 4.5, conductivity 0.056 - 0.062 mS/cm, and dissolved oxygen (DO) 0.54-1.76 mg/L as reported by Gasim et al (2007). According to Moore et al. (2011), DOC concentrations of Sebangau River were higher in the rainy season compared to the dry season, differently, POC concentrations were lower in rainy season compared to the dry season.

In 1996, Mega Rice Project (MRP) had started in Palangka Raya of Central Kalimantan, Indonesia. The peat forests were opened and the irrigation canals were constructed to support this project. Canal construction might give the large impacts to the environments such as deforestation, destroying animal habitat and degraded peat area. The decrease of the water level in peat area is one of the most severe impact because it, causes the dryness of peat soil and consequently peat fires.

In recent years, many peat fires happened in peatland areas, especially in MRP area in Central Kalimantan. These peat areas have a function as the watershed of some rivers and streams. The disturbances of watershed will influence the water quality of the river. The chemical, physical and biological parameters should be determined to reveal the impacts of peat fires to the river water. In the present study, we investigated the water quality of the Sebangau River and canal in Kalampangan where flows through the peatland area where have different conditions.

In order to investigate the effect of peat-forest fire on the river water in Central Kalimantan, we compared the physico-chemical parameters of the Sebangau River and Canal Kalampangan.

2.2. Materials and methods

2.2.1. Sampling Area.

The measurements were conducted in the Sebangau River and Canal Kalampangan from 2009 to 2012. Water samples were collected in the rainy, dry and moonson season. The Sebangau River flows through the Sebangau National Park, surrounding with peat swamp forests. Peat swamp forests are tropical moist forests where waterlogged soil prevents dead leaves and wood from fully decomposing. In this study, the Sebangau River is representative of the river with less disturbances. The water samples of the Sebangau River were collected from four sampling points (S1, S2, S3 and S4). Other water samples were collected from Canal water in Kalampangan village. The catchment area of the canal is surrounding by the peat area, where peat fires have happened several times. Canal Kalampangan was chosen as a representative of water with many disturbances such as deforestation and peat-forest fire. In the canal, water samples were collected from eight sampling points (C1, C2, C3, C4, C5, C6, C7 and C8). The sampling points of both river and canal are shown in Figure. 2.1.

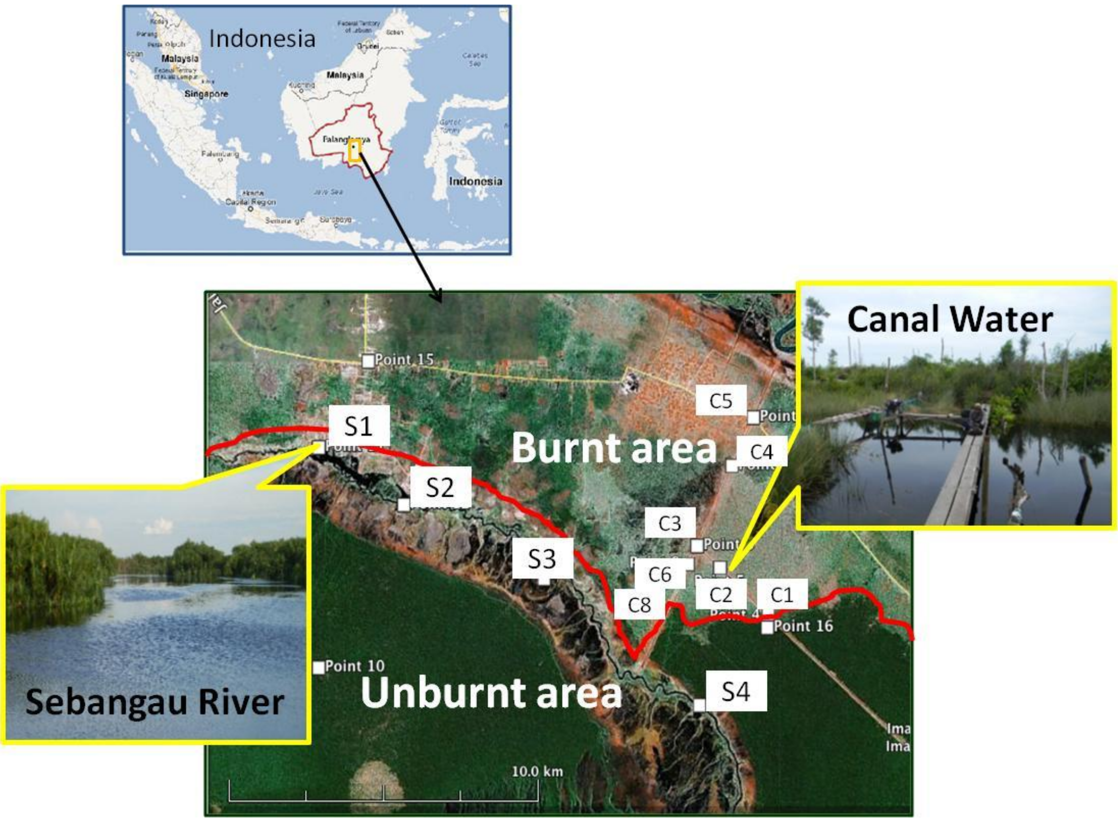


Fig.2.1. Sampling points of water samples in the Sebangau River and Canal Kalampangan.

2.2.2. Sample collection and analytical methods.

Water samples were collected from the surface water of the Sebangau River and Canal Kalampangan. The samples were stored at 4 ^{o}C, and filtered through 0.45 µm membrane filter. Some parameters such as Temperature, pH, Electro Conductivity (EC), ORP, Dissolved Oxygen (DO), Total Dissolved Solid (TDS) were measured *in situ* by using Horiba Multi checker U-51. Dissolved Organic Carbon (DOC) was measured by TOC analyzer 5000 A, Shimadzu Co. Japan, after filtration of the water samples with 0.45 µm membrane filter.

Preparation of Standard solutions for measurement of Dissolved Organic Carbon

Total Carbon (TC):

Phthalic hydrogen Potassium ($HOOCC_6H_4COOK$) solution (1000 mg C/l) was made by dissolving 1.06 g of $HOOCC_6H_4COOK$ with mili-Q in 500 ml volumetric flask. From this solution, 5, 20 and 50 ppm of TC standard solutions were prepared.

Inorganic Carbon (IC):

For making 1000 ppm IC standard solution, 2.205 g of Na_2CO_3 and 1.750 g $NaHCO_3$ were dissolved with 100 ml mili-Q, and then adjusted at 500 ml of volumetric flask. From this solution, 5 and 10 ppm of IC standard solutions were prepared.

Pretreatment of water samples: Water samples were filtered by 0.45 µm of membrane filter. Ten ml of filtered water were put into a TOC test tube. Two ml of 0.1 M HCl were added into water samples, then the solution was mixed well, and the TOC test tubes containing sample water were set to the auto sampler of TOC analyzer. DOC concentration in water sample was calculated by subtraction of IC value from TC value.

2.3. Results and Discussion

2.3.1. Temperature

The temperature of water has a large impact on the biological activity of aquatic organisms. Generally the rate of chemical reaction in the water increases at higher temperature, which also affects the biological activity. In tropical peatland, the water temperature in the Sebangau River and canal were relatively high because of the strong radiation of sunlight along the year. The high temperature often makes a problem whereas the metabolic rate of heterothrophs is greater and the solubility of oxygen (O_2) is lower in warmer water (Dodds 2002). Warm water contains less dissolved oxygen, and then the aquatics organism will be hard to be survived. The changes in temperature of the Sebangau and canal are shown in Fig.2.2 and 2.3. Water temperature in canal water was in the range of 28-35 ^{o}C, while the water temperature in the Sebangau River was in the range of 26-31 ^{o}C. The temperature of the canal water was slightly higher than in the Sebangau River because the water was not flowing and trapped by a dam, especially in dry season. The higher temperature of water in Sebangau River and Canal supposed to be correlated with DO concentration in these river and canal.

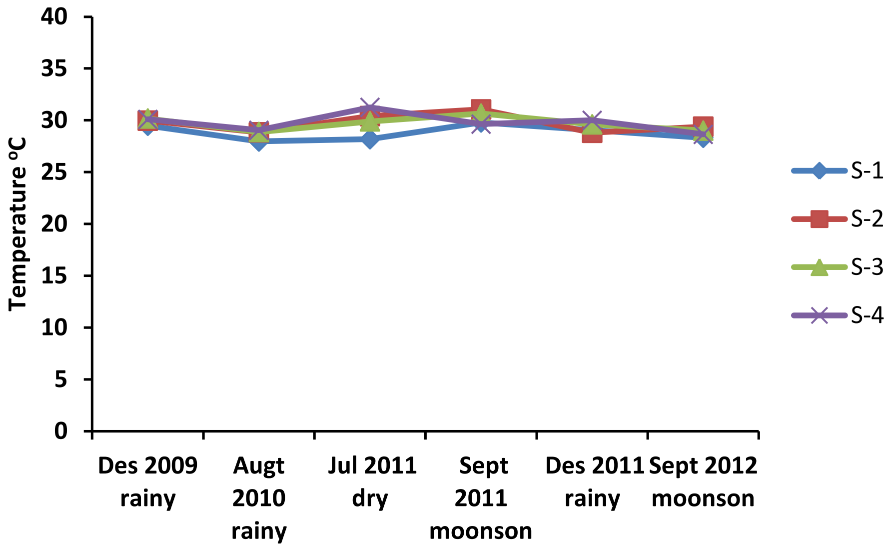


Fig. 2.2. Temperature of water in the Sebangau River

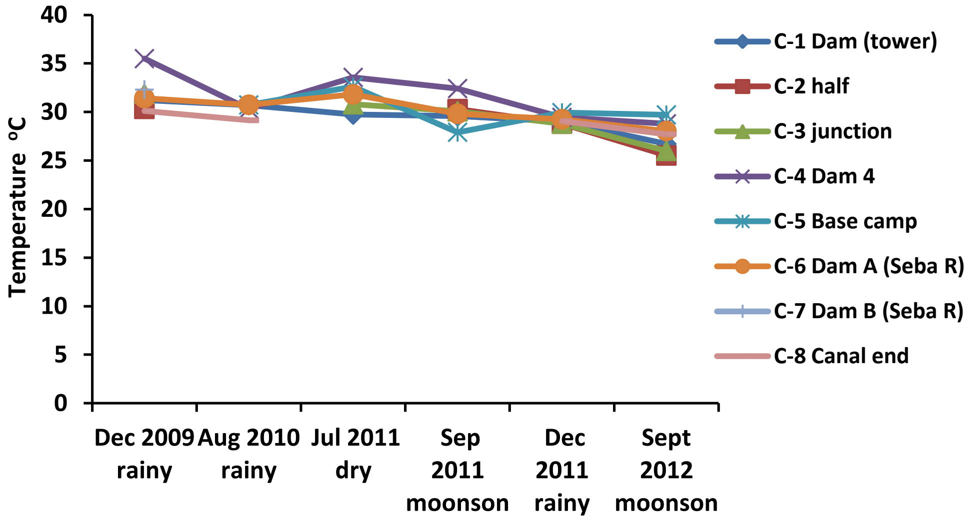
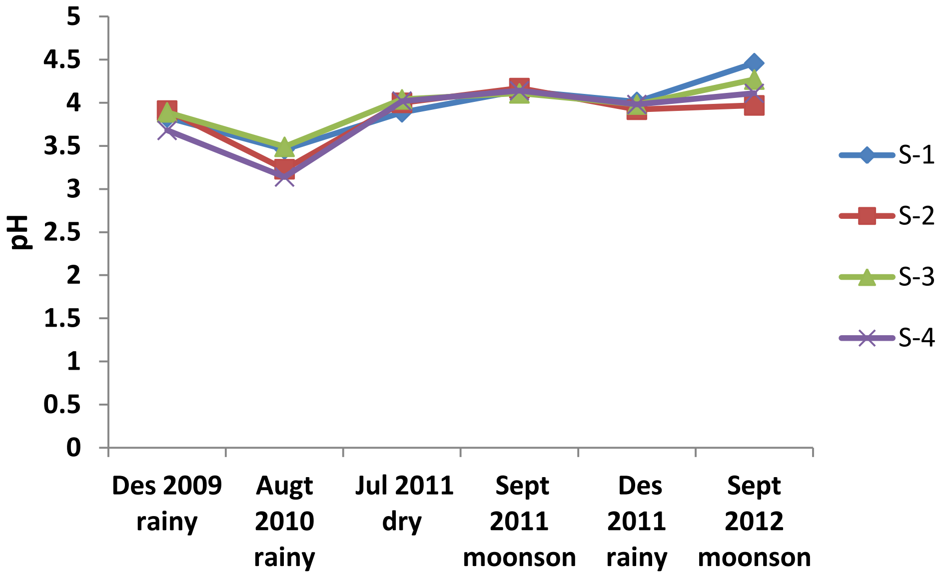


Fig. 2.3. Temperature of Canal water

2.3.2. pH

Generally the river water in peat area has a low pH, because of a large amount of organic matters including humic substances, as shown in the Sebangau River and Canal Kalampangan. The pH values in the Sebangau River and Canal Kalampangan were in the range of 3.0 to 4.5, there was no significant difference between both sites. During this study, the pH value in the Sebangau River was not so fluctuated. It means the seasonal change did not influence the pH value of the Sebangau River water. The water in Canal Kalampangan also showed low pH, especially in December 2009. This condition seemed to be related to the peat fire that happened in October 2009 in Palangka Raya city and MRP area (Kihara et al.2011). After peat fires, the burnt materials were eluted by rain fall from terrestrial to the canal. The data in Fig.2.9 showed the high precipitation in December 2009. According to Hemond (1980), dissolved humic substances and other organic acids can contribute to the acid-base status of natural water. Kurasaki et al (1999) reported the acidic condition of canal water was estimated to be caused by the presence of sulfonic ions.

(a) Sebangau River



(b) Canal

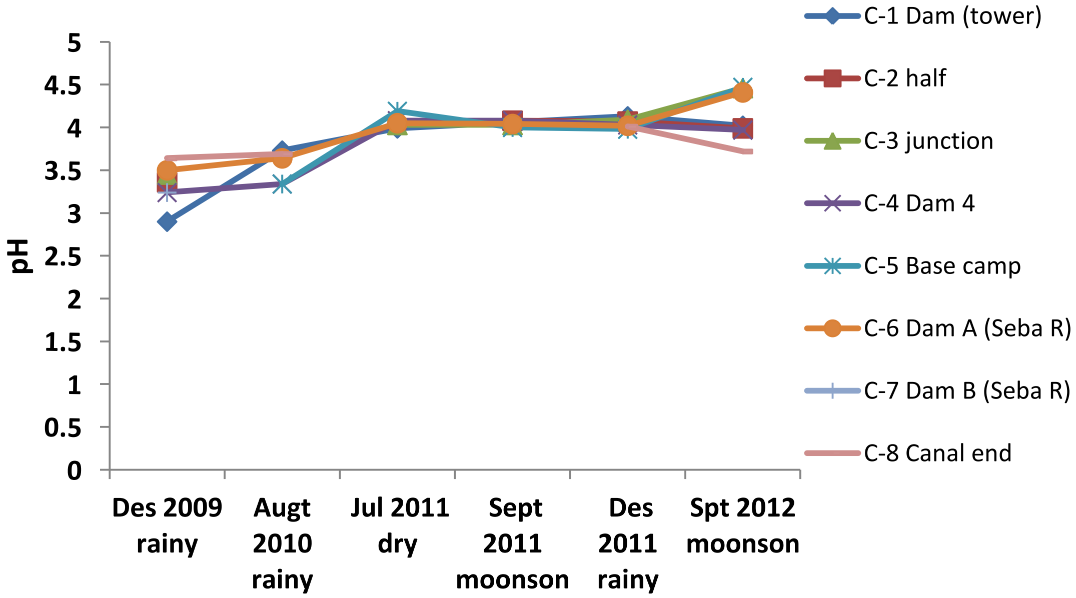


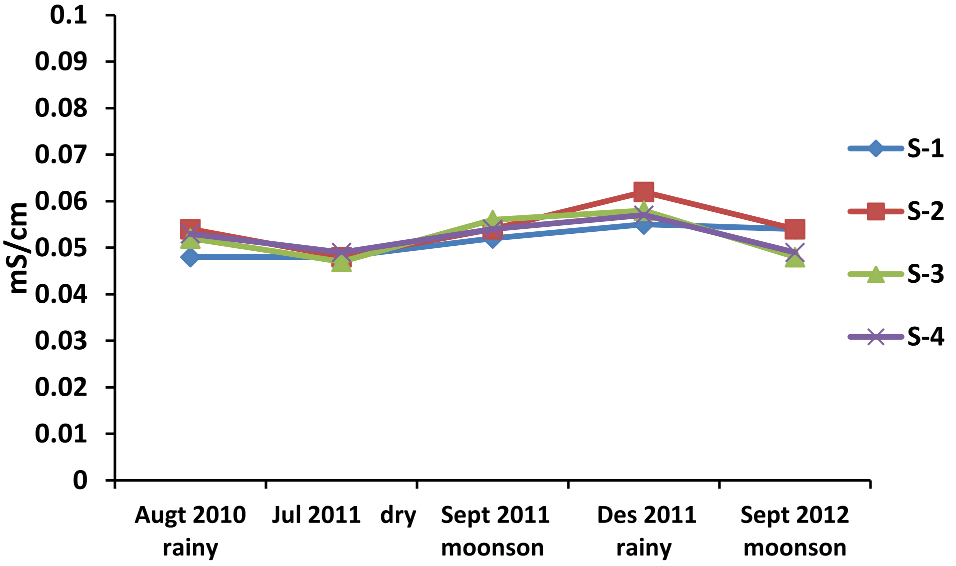
Fig. 2.4. pH in the Sebangau River (a) and Canal (b) water.

2.3.3. Electro Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, the mobility and valence and the temperature. The solutions of inorganic compounds shows relatively high conductivity. Conversely, organic compounds that do not dissociate in aqueous solution have a poor conductivity (Eaton et al.1995).

The conductivity of water in the Sebangau River and Canal were relatively low. This low value is because the water contained only organic matter but not inorganic electrolytes. In canal sampling point 5 (C5), where much disturbances from human activities, Electro Conductivity increased in monsoon and rainy season, and in dry season it was very low because no input to the canal.

a). Sebangau River



b). Canal

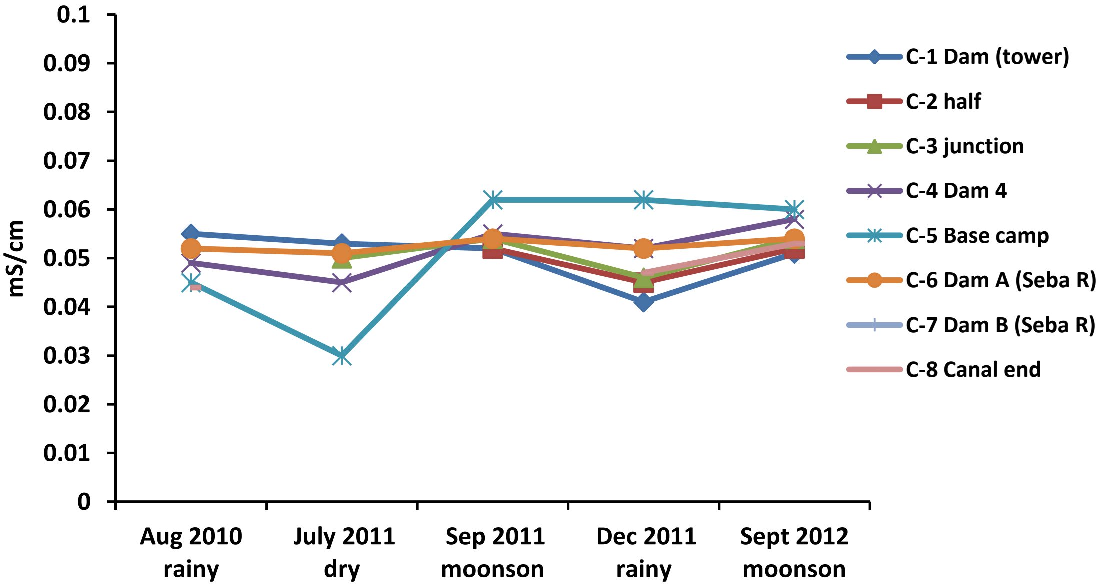


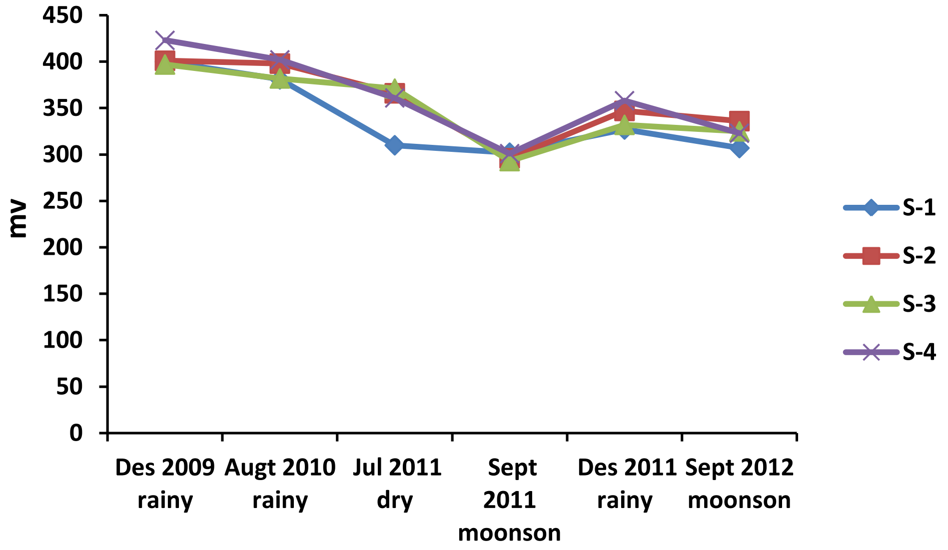
Fig. 2.5. Electro Conductivity in Sebangau River (a) and Canal (b)

2.3.4. Oxidation- Reduction Potential (ORP)

ORP is the potential of a chemical species to acquire (reduction) or lose (oxidation) electrons, in the simple words, the relative availability of electrons for chemical reactions in solution (Dodds 2002). The presence of an oxidizing substance, such as chlorine, will show a positive value, while a reducing agent, such as hydrogen sulfide, will have a negative ORP value. The higher the ORP level, the water has more ability to destroy the contaminants such as microbes or carbon based contaminants. The black river water contains mostly aquatic humic substances. Humic substances are oxidation-reduction species that may be significant as reducing species in chemical and biochemical processes that occur in natural water and wastewater system. The capability of humic substances to act as reductants is primarily due to the presence of quione/hydroquinone group that acts as an oxidation-reduction couple (Manahan 2010).

ORP value in the Sebangau River was in the range of 293-423 mV, with the average 352 mV, while in the Canal was in the range of 294-415 mV, with the average value of 361 mV. The ORP values of Sebangau River and Canal were still in the common value of black water in Central Kalimantan according to Hartoto (2000). Therefore, the impact of peat fire was not recognized by the ORP value of the river water.

(a) Sebangau River



(b) Canal

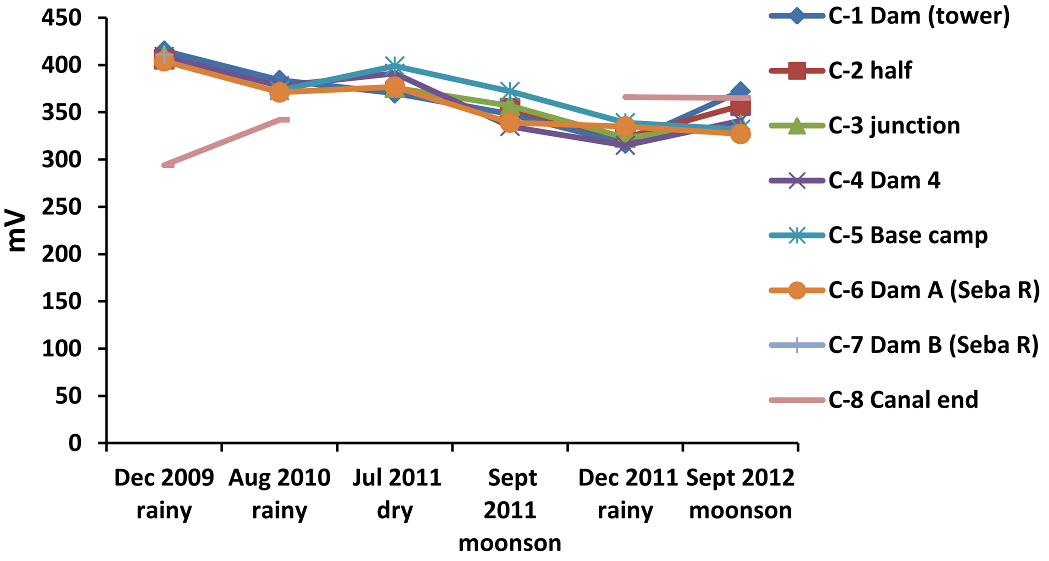


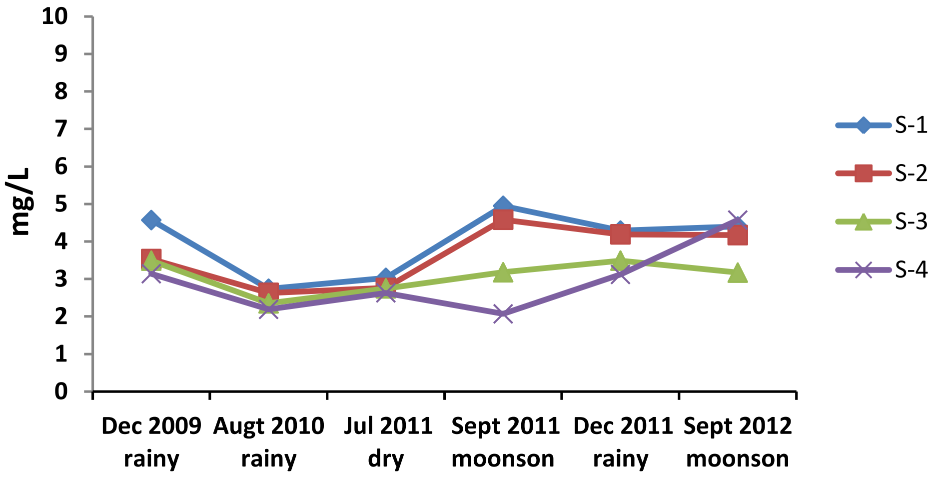
Fig. 2.6. ORP of the Sebangau River (a) and Canal water (b).

2.3.5. Dissolved Oxygen

The amount of dissolved oxygen (DO) in water is affected by many factors including metabolic activity rates, diffusion of oxygen, temperature and proximity to the atmosphere (Dodds 2002). Dissolved oxygen refers to the oxygen (O_2) dissolved in the water. The DO value in the Sebangau River were in the range of 2-5 mg/L (Fig.2.7.a). According to Indonesian Government Regulation No 82, 2001, the minimum level of DO for class 2 (for fishery, irrigation, animal farm) is 4 mg/L, therefore DO concentration in the Sebangau River is relatively low. Water temperature, the number of phytoplankton and the concentration of DOC were supposed to influence the DO level. The low DO concentration might be caused by the oxygen consumption for decomposing organic matter containing in river water by heterotrophs. In Canal Kalampangan, a large fluctuation in dissolved oxygen was observed, in the range of 2 to 9 mg/L (Fig. 2.7.b). The values depended on the sampling site condition. In September of 2011, the DO concentration was higher than that in other sampling time. It was due to high production of oxygen by aquatic vegetations which were growing abundant in canal, as shown in Fig. 2.8.

In common black water river, DO concentration is low as reported by Hartoto (2000). In canal water, the variation in DO concentration among the sampling points was relatively large, it indicates canal water had received some disturbances. One of the disturbances to the water property of canal is peat fire, which give an influence to the water indirectly. After peat fires happened, the plants growing in peat soil and also aquatic plants growing in the canal, enhanced DO production in canal water.

a. Sebangau River



b. Canal

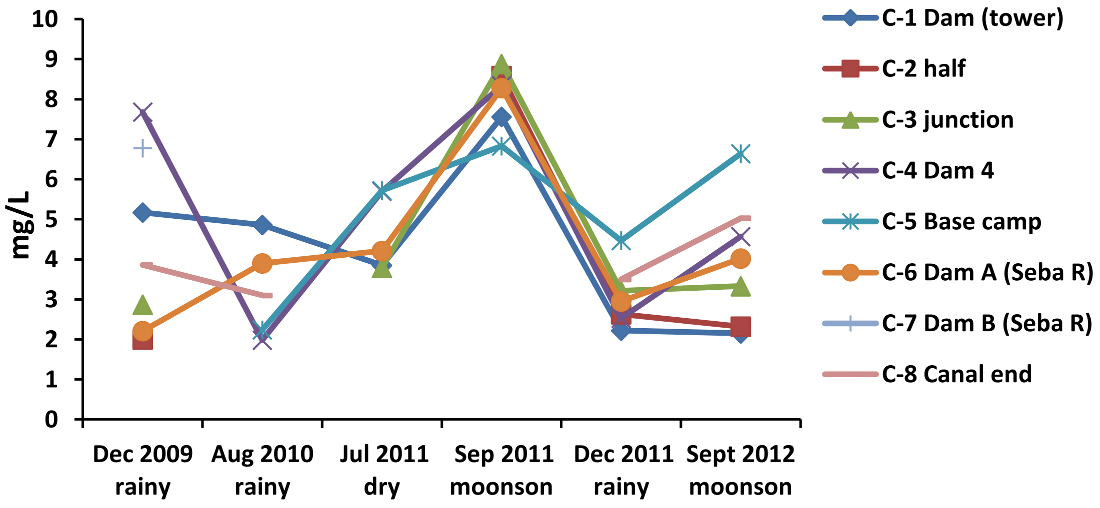


Fig.2.7. DO of the Sebangau River and Canal water

Fig. 2.8. Aquatic vegetations grown densely in Canal Kalampangan in September, 2011.

2.3.7. Dissolved Organic Carbon

Dissolved Organic Carbon (DOC) is a dominant form of carbon species in aquatic ecosystem, especially for the river located in peatland area. According to Sachse et al. (2005), DOC in surface water receives influences largely from natural and anthropogenic allochtonous sources in the catchment area, autochtonous production and degradation process. The DOC concentrations of the Sebangau River were in the range of 33.6 – 57.1 mg/L with the average concentration of 43.8 mg/L (Fig.2.10.a.). The trend of DOC concentration was quite similar to precipitation data (Fig.2.9) that was observed from 2009 to 2012. In rainy season the organic matters from peat soil in surrounding area of the river will be eluted to the Sebangau River by run off, and then slightly increased the DOC concentration. The similar phenomena was also observed in other rivers by Pearce et al. (1986) and Hornberger et al. (1994), that is when water level rised concurrently DOC concentration increased by the flushing effect .

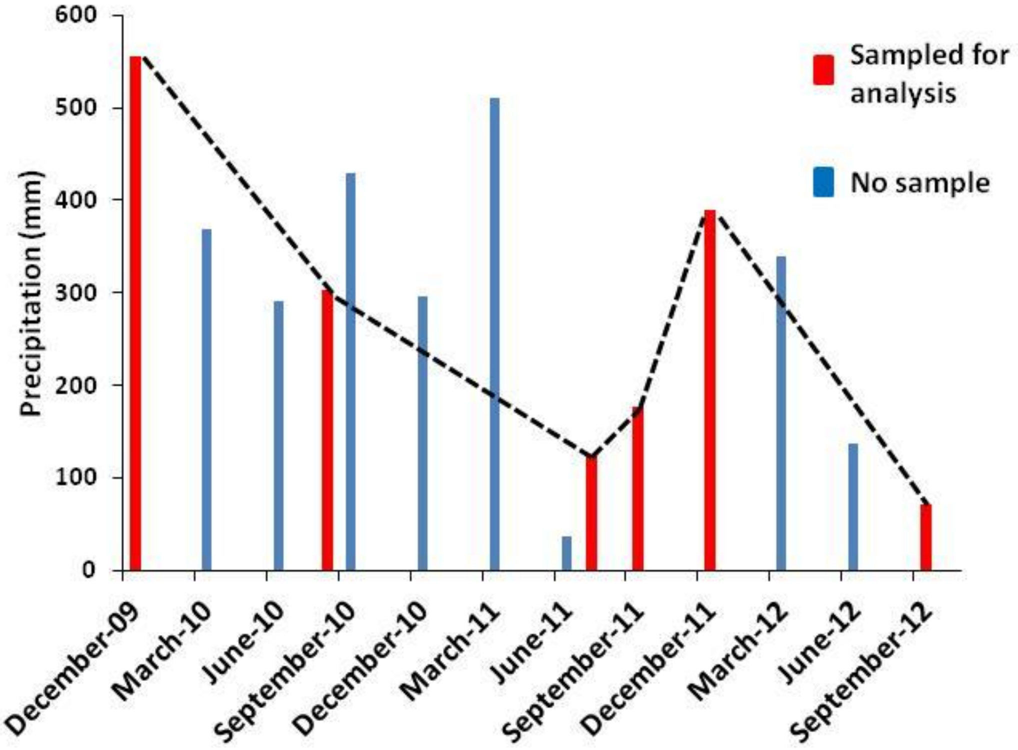
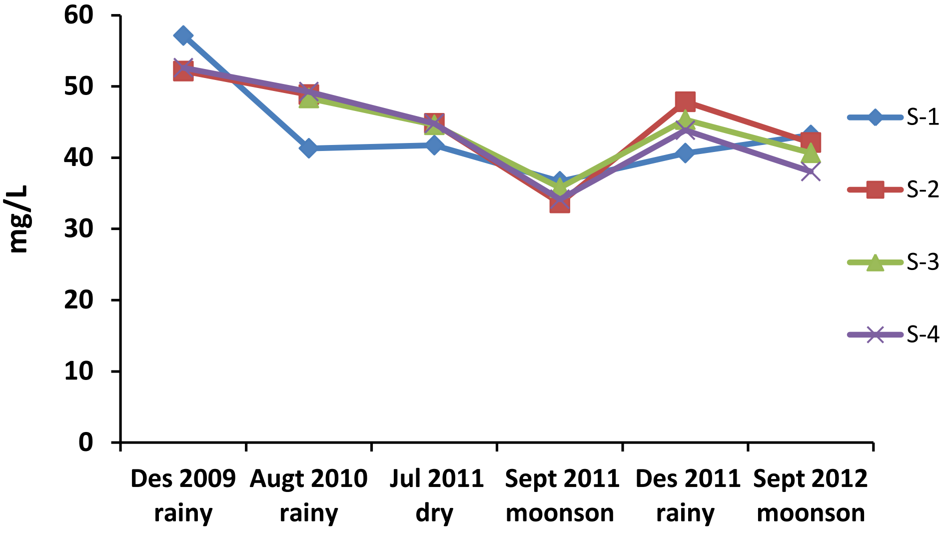


Fig. 2.9. Precipitation data of Palangka Raya , Central Kalimantan from Dec 2009 to September 2012, 3 months interval.

DOC concentrations at the eight sampling sites in Canal Kalampangan were observed in dry and rainy seasons, as shown in Fig. 2.10.b. The concentrations of DOC of those sampling sites fluctuated largely, that was in the range of 20.4 – 46.9 mg/L with the average concentration of 37.2 mg/L. Eight sampling sites in canal were separated by the dams, especially in dry season. Therefore, water quality in each sites were influenced by autochtonous and allochtonous from each surrounded area of the sampling points .

The DOC concentration in Canal was lower than that in Sebangau River. It was supposed that peat soil in surrounding of canal have been burnt, therefore the supply of dissolved organic carbon to the canal water decreased. As reported by Fernandez et al.(1997), the that the water soluble organic matters in the soil decreased after heating of the soil.

a. Sebangau River



b. Canal

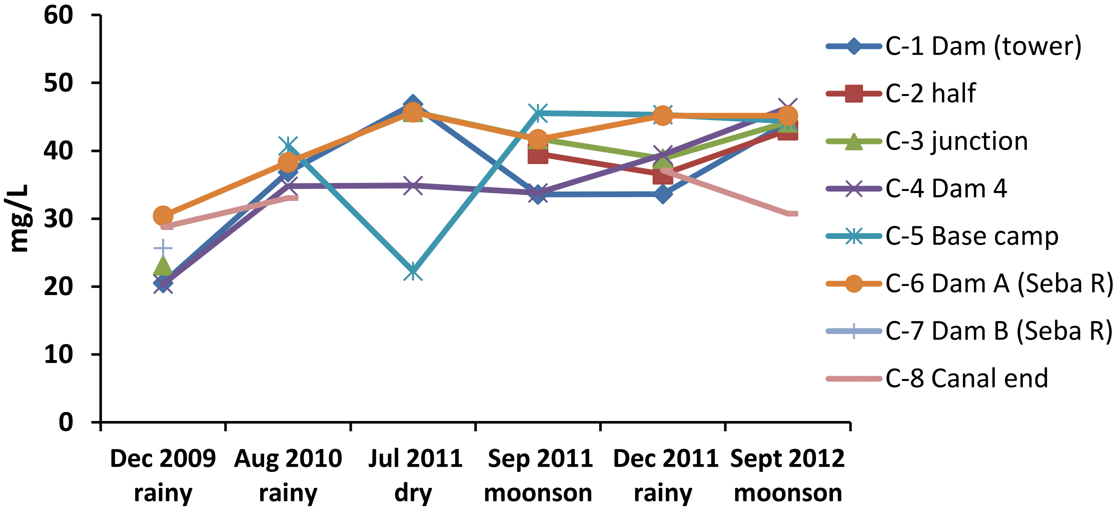


Fig. 2.10. DOC concentration in Sebangau River (a) and Canal water (b).

2.4. Conclusion

Some parameters of water quality could be used to indicate the impacts of peat fire to the aquatic environment. The Sebangau River as representative of the river with less disturbances showed that among the sampling points with the water quality is quite similar in dry, and also in rainy season. The quality of canal water with more disturbances was significantly different in some parameters, depending on the surrounding condition of the sampling points. However, impact of peat fire to the water quality could not be observed directly, but could be evaluated indirectly after the process of the elution, chemical transformation from peat soil into the river, by using some parameters such as pH, DO and DOC.

References

Dodds WK (2002), Aquatic chemistry controlling nutrient cycling: Redox and O_2. In: Freshwater Ecology, Concept and Environmental Application. Academic Press, USA.

Eaton AD, Clesceri LS, Greenberg AE (1995), Standard Methods for Examination of water and wastewater. 19th Edition. American Public Health Association, American Water Works Association, Water Environment Federation. Washington, DC-USA. Pp .

Gasim MB, Ismail BS, Toriman E, Mir SI, Chek TC (2007), A physico-chemical assessment of the Bebar River, Pahang, Malaysia. *Global Journal of Environmental Research,* 1 (I): 07-11, 2007.

Fernandez I, Cabaneiro A and Carballas A (1997), Organic matter changes immediately after a wildfire in an atlantic forest soil and comparison with laboratory soil heating. *Soil Biology & Biochemistry* 29, No 1: 1-11.

Hartoto DI (2000), Relationship of water level to water quality in an oxbow lake of Central Kalimantan. Proceeding of the International symposium on TROPICAL PEATLANDS, Bogor, 22-23 November, 1999. Pp 375-386.

Homberger GM, Bencala KE, Mcknight DM (1994), Hydrological controls on dissolved organic-crbon during snowmelt in Snake River near Montezuma, Colorado. *Biogeochemistry* 25: 147-165.

Kihara Y, Yustiawati, Sun Y, Tanaka M, Hosokawa T, Gumiri S, Ardianor, Tanaka S, Saito T, Kurasaki M (2012), Proceeding of 3rd International Workshop on Wild Fire and Carbon Management in Peat-Forest in Indonesia, 2011. Pp 202-212.

Kurasaki M (2000), Surface water quality in Central Kalimantan, Indonesia. Proceeding of the International symposium on TROPICAL PEATLANDS, Bogor, 22-23 November, 1999. Pp 367-374.

Manahan SE (2010), Environmental Chemistry. 9th Edition. CRC Press, Taylor & Francis Group. Boca Raton,US. Pp 628.

Meybeck M (1993), Riverine transport of atmosheric carbon: source, global typology and budget. *Water, Air and Soil Pollution*, *70*, 443–463.

Moore S, Gauci V, Evans CD, Page SE (2011), Fluvial organic carbon losses from a Bornean blackwater river. *Biogeosciences, 8*(4), 901–909. doi:10.5194/bg-8-901-2011

Naiman RJ, Melillo JM, Lock MA, Ford TE, Reice SR (1987), Longitudinal Patterns of Ecosystem Processes and Community Structure in a Subarctic River Continuum Author (s): Robert J . Naiman , Jerry M . Melillo , Maurice A . Lock , Tim E . Ford and Seth R . Reice Published by : Ecological Society of America LONGI. *Ecology, 68*(5), 1139–1156.

Pearce AJ, Stewart MK, Sklash MG (1986), Storm runoff in humid headwater catctments. *Water Resources. Res.*, 22, 1263-1272.

Sachse A, Henrion R, Gelbrecht J, Steinberg CEW (2005), Classification of dissolved organic carbon (DOC) in river system: Influence of catchment characteristics and autochthonous processes. *Organic geochemistry*, 36, 923-935.

Tachibana H, Iqbal R, Akimoto S, Kobayashi M, Kanie S, Mori A, Limin S (2006), Chemical characteristics of water at the upper reaches of the Sebangau River , Central Kalimantan , Indonesia. *Tropics*, *15*(4), 411–415.

CHAPTER 3

Comparative study on the characteristic of aquatic humic substances from Sebangau River and Canal Kalampangan.

3.1. Introduction

Frimmel (1998) reported that humic substances contribute to the DOC in the range between 40 – 70 %. Humic substances in aquatic system can be attributed to two main sources, one is the terrestrial ecosystems derivated from plants and soil (allochthonous) and another is materials resulting from biological activities within the water body itself (autochthonous). Therefore, the characteristic of humic substances vary depending on chemical, physical, and biological processes in the soil and aquatic environments. In this study, we compared the characteristic of aquatic humic substances extracted from the Sebangau River and Canal Kalampangan. Both river have different characteristics in the catchment area. The catchment area of the Sebangau River is peat swamp forest without disturbances, while Canal Kalampangan is peatland area with many disturbances especially by peat fires. Some parameters were selected to characterize humic acid and fulvic acid from water of the Sebangau River and Canal Kalampangan such as elemental analysis, molecular weight and 3-DEEM Spectrum.

3.2. Materials and Methods

3.2.1. Extraction and purification of humic acid and fulvic acid from water.

Humic substances from the Sebangau River and Canal Kalampangan water were extracted and purified according to Thurman and Malcom’s report (1981). Water sample from Sebangau River was collected at the sampling point S1 and from Canal Kalampangan at the sampling point C5, as shown in Fig 2.2. From each sampling site, 25-40 L of water sample were filtered by 0.45 μm membrane filter, and acidified with HCl until the pH of the sample become pH 2.0. Then the sample solution passed through a column of DAX-8 resin. The humic substances (HSs) were adsorbed on the resin. The adsorbed HSs were eluted from the resin by adding 0.1 M NaOH, this procedure was repeated several times. The eluate of HSs was acidified by HCl, passed through to the column of DAX-8 resin again, and then desorbed with 0.1 N NaOH again, repeated this procedure two-three times. To the eluate of HSs was added HCl until pH 1, settled for 24 h, centrifuged to separate the precipitate and supernatant. The precipitate (humic acid) was dialyzed the precipitate using membrane tube (molecular weight cut off 1000 Da) against pure water until free of Cl^-. The acidified supernatant where FA contained was passed through a DAX-8 resin column to absord FA. The column was rinsed with pure water until the effluent became clear. The adsorbed FA was then eluted with aqueous 0.1 M NaOH. The eluent was then passed through a H^+-type cation-exchange resin column (Dowex^R HCR-W2). Finally, a powdered sample of the H^+-type FA was obtained by freeze-drying (Iwai 2013). The Scheme of the extraction and purification is presented in Fig. 3.1.

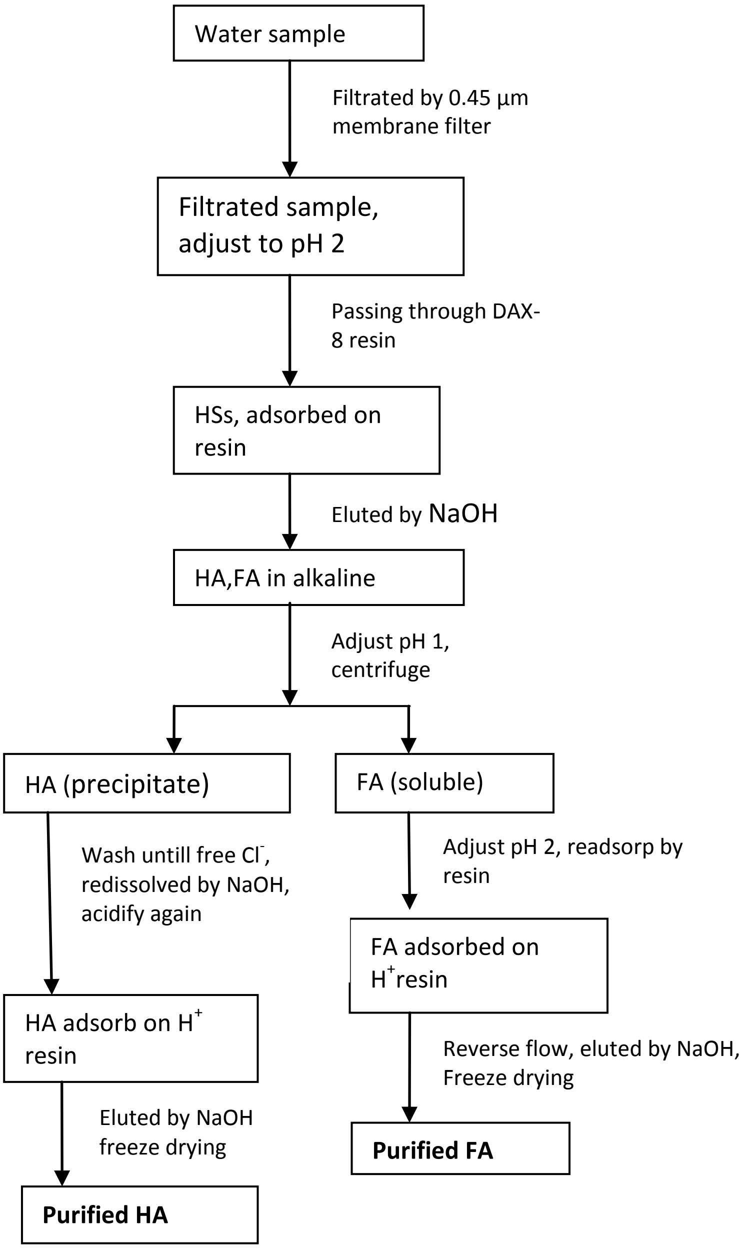


Fig. 3.1. Procedure for extraction and purification of humic acid and fulvic acid from water

3.2.2. Analytical methods

Elemental Analysis of humic acid and fulvic acid were carried out by JE. Science Micro Corder JM 10 at Instrumental Analysis Division, Equipment Management Center, Hokkaido University.

Molecular weights of humic substances were analyzed by HPSEC with TSK-Gel Colomn, at the oven temperature of 40 ^oC, and the flow rate of 0.5 ml/minute. A mixture of sodium phosphate buffer pH 7 and acetonitrile (7.5: 2.5) was used as the carrier eluent (Asakawa et al. 2008). The standards used for this analysis are poly(stryrenesulfonic acid sodium salt) 210, 4300, 6800, 17000 and Polystyrene 2000 Da.

3DEEM spectrum was measured using a fluorescence spectrophotometer (Model LS-55, Perkin Elmer). The scanning wave ranges were 200-600 nm for both of excitation and emission. The data was collected by reading at intervals of 10 nm excitation with 5 nm emission wavelengths using a scanning speed of 1,000 nm/ min and photomultiplier voltage of 775 V. Pure water (Mili-Q, Millipore Co. Ltd) was used as the blank for all fluorescencence analysis. Relative Fluorescence Intensity (RFI) was calibrated to be evaluated in quinine sulfate units (QSU); 1 QSU= 1 μg/L of quinine sulfate monohydrate in the solution of 0.05 M H_2SO_4 at excitation/emission (Ex./ Em) 350/455 nm. For all the fluorescence spectra were applied the inner-filter correction according to the method by McKnight et al. 2001. UV-Vis absorption spectrum was measured using a double beam spectrophotometer (U-2000A, Hitachi, Japan) equipped with a 1 cm quartz UV-Vis cell.(Sazawa et al. 2011).

3.3. Results and discussion

3.3.1. Yield of humic acid and fulvic acid

Amount of extracted humic acid and fulvic acid from Sebangau River and Canal Kalampangan are shown in Table 3.1. From Canal water, 6.07-19.72 mg/L of humic acid and 3.64-55.2 mg/L of fulvic acid were obtained. And from the Sebangau River 8.9- 24.65 mg/L of humic acid and 8.9-11.3 mg/L of fulvic acid were obtained.

The yield of humic acid and fulvic acid from the Sebangau River and canal water has large variation. Some factors influence the isolation process such as DOC concentration, disadvantages of isolation methods or technical error. The DOC concentration in canal water was 22-44 mg/L, and in the Sebangau River 41-43 mg/L. These values are relatively high to isolate humic substances from water. The acidification to pH 2 might be change the association metals ions with humic acid, otherwise the exposure to acid and base might cause chemical change of the orginal humic substance, as reported by Malcoms. It cannot be neglected that technical errors in some steps of isolation process led to the loss of some amount of humic substances.

Table 3.1. Extracted Humic Acid and Fulvic Acid from water in Central Kalimantan, Indonesia

No.	Sampling Sites	Humic Substances	Original weight/ volume	Amount (g)	Yield
1.	Canal (river water), 2010	Humic acid	40 L	0.6859 g	17.1 mg/L
2.	Canal (river water), 2011	Humic acid	20 L	0.1214 g	6.07 mg/L
3.	Canal (river water, 2012	Humic acid	20 L	0.3944 g	19.72 mg/L
4.	Sebangau R (water), 2011	Humic acid	40 L	0.3550 g	8.9 mg/L
5.	Sebangau R (water), 2012	Humic acid	25 L	0.6163 g	24.65 mg/L
6.	Canal (river water), 2010	Fulvic acid	40 L	2.2061 g	55.2 mg/L
7.	Canal (river water), 2011	Fulvic acid	20 L	0.0728 g	3.64 mg/L
8.	Canal (river water, 2012	Fulvic acid	20 L	0.1695 g	8.45 mg/L
9.	Sebangau R (water), 2010	Fulvic acid	40 L	0.3550 g	8.9 mg/L
10.	Sebangau R (water), 2011	Fulvic acid	40L	0.4058 g	10.1 mg/L
11.	Sebangau R (water), 2012	Fulvic acid	25L	0.2820 g	11.3 mg/L

3.3.2. Elemental Analysis

The elemental compositions (C,H,N,O) of aquatic humic acid and fulvic acid from the Sebangau River and Canal Kalampangan are provided in Table 3.2. It was observed that C and O contents of humic acid and fulvic acid were different largely. The carbon content in humic acid was higher than fulvic acid, and contrary the oxygen content was higher in fulvic acid than in humic acid. It reflected that humic acid was more hydrophobic, while fulvic acid was more hydrophilic because fulvic acid contained oxygen rich functional groups. The characteristics in the structure of humic acid and fulvic acid can be observed by the ratio of H/C and O/C (atomic percentage). These value were plotted on Van Krevalen Diagram as shown in Fig. 3.2 and 3.3.

Table 3.2. Elemental composition of humic acid and fulvic acid from the Sebangau River and Canal Kalampangan (weight percentage).

Location	HSs	% C	% H	% N	% O	% ash
Canal 2010	HA	50.63	4.65	1.07	42.67	1.58
Canal 2011	HA	52.06	4.28	1.41	42.21	0.04
Canal2012	HA	51.72	4.11	0.92	43.25	ND
Sebangau R 2010	HA	53.25	3.94	1	41.81	ND
Sebangau R 2011	HA	44.61	3.58	0.66	50.91	0.24
Sebangau R 2012	HA	50.82	4.18	0.97	44.03	ND
Canal 2010	FA	35.85	3.69	0.55	59.91	ND
Canal 2011	FA	44.59	3.9	0.8	42.71	8
Canal 2012	FA	40.5	3.69	0.67	51.17	0.33
Sebangau R 2010	FA	42.86	3.83	0.4	52.76	0.15
Sebangau R 2011	FA	44.21	3.82	0.67	51.14	0.16
Sebangau R 2012	FA	44.23	3.97	0.65	51.17	0.15

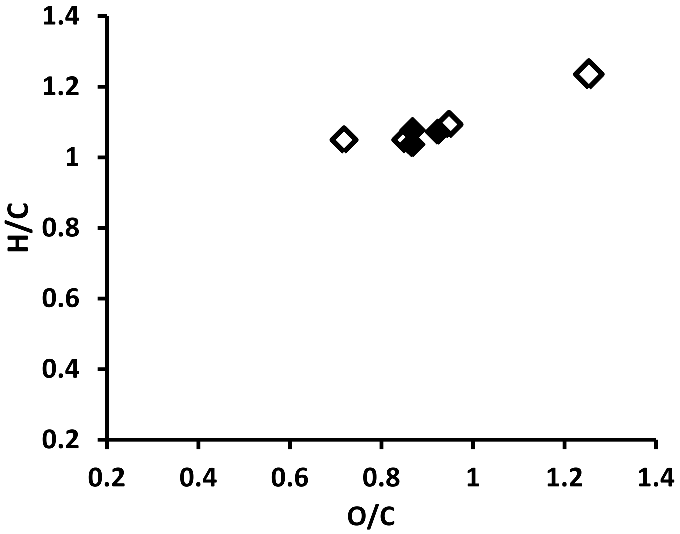


Fig.3.2. The Van Krevalen Plot (H/C and O/C ratio) of fulvic acid from Sebangau River water (♦) and Canal water (◊).

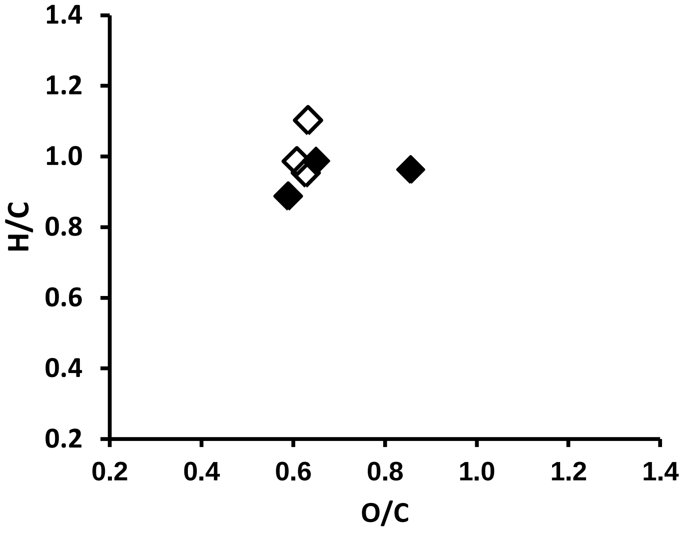


Fig.3.3. The Van Krevalen Plot (H/C and O/C ratio) of humic acids from the Sebangau River water (♦) and Canal water (◊).

The ratio of H/C and O/C of fulvic acid from Sebangau River water and Canal water are shown in Fig. 3.2. The higher value of H/C indicates the higher aliphaticity and the lower H/C indicates the aromaticity. The ratio of O/C is related to the amount of the functional groups containing oxygen. The Van Krevalen Plots of fulvic acids taken from the Sebangau river in the different sampling years were plotted in the narrow area, it indicated that the structure of aquatic fulvic acid from the Sebangau River was relatively stable compared to that of fulvic acids from canal water. However, the O/C value of fulvic acids from Canal water have a large variation.

Fig. 3.3. showed the ratio of H/C and O/C of humic acid from the Sebangau River water and Canal water. The O/C value indicates the oxygen content in functional groups that can be assumed the amount of carbohydrate content. The cluster of O/C value of humic acids from the Sebangau River and Canal is lower than that of fulvic acids, it indicates fulvic acid contains more COOH and/or carbohydrate than humic acid. The value of H/C of humic acids from the Sebangau River and canal were also plotted in narrow area. It indicates the characteristic of humic acid from the Sebangau River and Canal is not significantly different in the H/C and O/C values of humic acid.

3.3.3. Molecular Weight (MW)

Molecular weights of humic acids and fulvic acids from the Sebangau River and Canal are shown in Table 3.3. MW of humic acids from both sites was higher than MW from fulvic acids. The MW of humic acid and fulvic acids from Sebangau River were higher than from Canal water. It indicated that aquatic HA and FA had got large influences from the characteristic of its catchment area. Source of DOC from Canal water originated from peat soil and plantation which have been burnt by fires. Therefore, DOC of water flowing into the canal contained degraded humic acid and fulvic acid as a result of burning process in peat soil. by rain or run off.

Table 3.3. Molecular Weight of humic acid and fulvic acid from Sebangau River (unburnt site) and Canal Kalampangan (burnt site)

Unburnt Site				Burnt Site			
No.	Sample	HSs	MW (Da)	No.	Samples	HSs	MW (Da)
1.	Sebangau Water,2010	HA	4360	1.	Canal Water, 2010	HA	3738
2.	Sebangau Water,2011	HA	4242	2.	Canal Water, 2011	HA	3664
3.	Sebangau Water, 2010	FA	4348	3.	Canal Water, 2010	FA	3303
4.	Sebangau Water, 2011	FA	3883	4.	Canal Water, 2011	FA	3248

3.3.4. Three-Dimension Excitation Emission Matrix

Three-Dimension Excitation Emission Matrix (3-DEEM) spectrofluorometry is a useful method for analyzing organic substances containing the moieties with fluorophores. It is well known that humic acid and fulvic acid have fluorophores. According to Coble (1996), there are three commonly peaks which are characterized as humic-like peaks. Peak A, peak C and peak M are observed at λex/λem= 260/380-460 nm, λex/λem= 320-360/420-460 nm λex/λem= 290-310/370-410 nm. Peaks C and A are represented as humic-like component exported from the terrestrial sources (Birdwell and Engel, 2010).

Fig.3.4 shows the 3DEEM fluorescence spectra of humic acid from the Sebangau River (a) and Canal water (b). The bar chart next to the graph indicates the contour intervals of the relative fluorophore intensity (RFI) normalized with in the quinine sulfate. .Humic acid from Canal water had higher RFI value than that from the Sebangau River. It indicates canal water contained more fluorophores such as phenolic compounds that might be originated from peat burnt soil.

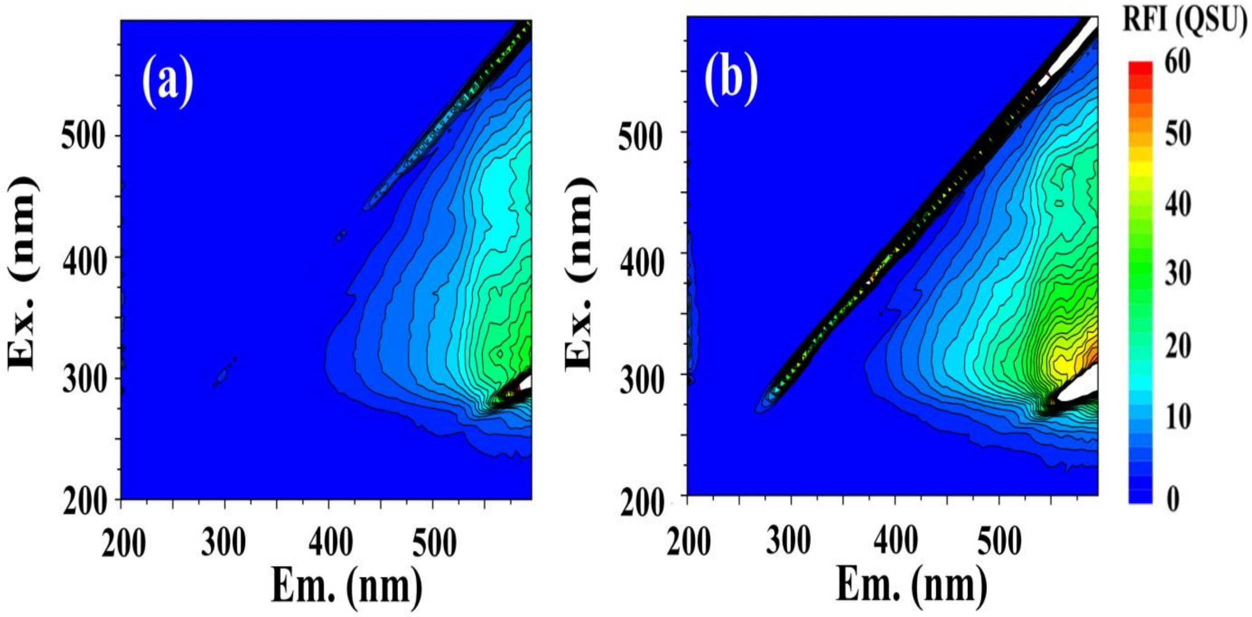


Fig.3.4. 3-DEEM fluorescence spectra of humic acid from Sebangau River (a) and Canal water (b).

3.4. Conclusion

The impact of peat fires to the aquatic environment could be observed through the characteristics of aquatic humic and fulvic acid. Some methods could evaluate the alteration, but the other methods did not evaluate the alteration effectively. Using elemental analysis, the elemental compositions (C,H, N, O) of humic acid and fulvic acid from the Sebangau and canal water did not show significant difference. However, in the molecular weight, the alteration of humic and fulvic acid from the Sebangau River and Canal could be observed. The molecular weights of humic acid and fulvic acid from canal were lower than from Sebangau River, It indicates humic acid and fulvic acid from Canal have been degraded partially. The impact of peat fire to the characteristic of aquatic humic substances also could be observed using 3-DEEM spectrum. From the 3-DEEM analysis data showed that RFI of humic acid from canal was higher than from the Sebangau River, It was supposed that humic acid from canal contained more flourophores compound such as phenolic compounds.

References

Abbt-Braun G, Lankes U, Frimmel FH (2004), Structural characterization of aquatic humic substances- The need for a multiple method approach. *Aquatic Science* 66: 151-170.

Asakawa D, Kiyota T, Yanagi Y and Fujitake N (2008) Optimization of condition for high-performance size-exclusion chromatography of different soil humic acid. Analytical Sciences 24: 607-613.

Birdwell JE and Engel AS (2010), Characterization of dissolved organic matter in cave and spring waters using UV-Vis absorbance and fluorescence spectroscopy. Organic Geochemistry 41:270- 280

Coble PG (1996), Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51:325-346.

Iwai H, Fukushima M, Yamamoto M, Komai T, Kawabe Y (2013), Characterization of seawater extractable organic matter from bark compost by TMAH-py-GC/MS. *Journal of Analytical and Applied Pyrolysis* 99: 9-15.

Sazawa K, Tachi M, Wakimoto T, Kawakami T, Hata N, Taguchi S, Kuramitz H (2011), The evaluation for alteration od DOM component from upstream to downstream flow of rivers in Toyama (Japan) using Three-Dimentional Excitation-Emission Matrix Fluorescence Spectroscopy. *Int.J.Environ. Res. Public Health* 8: 1655-1670.

Thurman EM, Malcom RL (1981), Preparative isolation of aquatic humic substances. *Science and Technology* 14, No. 4: 463-466.

CHAPTER 4

Effect of peat fire on characteristics of humic acid extracted from peat soil in Central Kalimantan, Indonesia.

4.1. Introduction

Peatland area plays an important role in the biosphere as the carbon sinks that store huge amount of carbon in the earth. According to Page (2010), 57 % of total peatland areas in the world are located in South East Asia, and 65 % of those areas are distributed in Indonesia, in Sumatra, Kalimantan and Irian. Peatland areas are usually covered by vegetation and associated with tropical forest. In Indonesia, peatland areas have been degraded rapidly by deforestation/ logging, agriculture, constructing drainage, peat drying and peat forest fire. Since early 90-ies, peat-forest fires have become one of severe disasters in peatland area, especially when El Nino phenomena happen in Indonesia. Peat-forest fires not only burn the surface vegetation, but also continue to burn peat in the ground. Then once ignited, peat soil could be burnt and smoldered underground slowly for many weeks as called the peat fire (Siegert et al. 2004). Yulianti et al. (2012) reported during 2002 to 2011, eleven highest fire hotspots were detected in Sumatra and Kalimantan islands. The highest of those fire hotspots was located in Central Kalimantan known as Mega Rice Project area. In 1996, Mega Rice Project (MRP) was initiated by Indonesian Government to open the peat forest in Palangka Raya of Central Kalimantan for paddy field and then irrigation canals as long as 4400 km were also constructed to maintan the new paddy fields (Siegert et al. 2001). However, the MRP was discontinued and the long irrigation canals and some environmental problems as mentioned above are remained. When peat soil dried, it will lead to peat oxidation and peat fire easily. Those will release carbon dioxide to atmosphere and consequently increase the amount of greenhouse gases (Jaenicke et al. 2008). Besides releasing carbon dioxide to the atmosphere, Certini (2005) and Pietikainen et al. (2000) reported that forest fires caused a lot of damages in peat soil such as physical, chemical, mineralogical and biological properties of soil. According to Siegert et al. (2001), in 1997, the total carbon loss due to the peat fires of a 25,000 km^2 peat swamp forest in Central Kalimantan was estimated to be in the range from

0.218 to 0.491 Gt carbon. This value indicates that the peat fires release more CO_2 to the atmosphere compared to the forest combustion.

Many kinds of organic matters exist in soil such as non humic molecules (protein, amino acid, sugar & starch), carbohydrate, polysaccharides, lipid, N compounds and humic substances. However, most parts of organic matters in soil consist of humic substances (HSs) that include humic acid, fulvic acid and humin. Humic Substances play significant roles in the environment. HSs enhance the fertility of soil by improving their physical properties such as crumb structure, aeration, drainage, and movement of water and nutrients. The biochemical activities in soil will come to a standstill in the absence of humic matters. Otherwise, HSs have an ability to form stable complexes with metal ions (Schnitzer and Khan 1972). It is said that the degradation of soils starts with the destruction of humic matter, and it brings with many kinds of environmental disasters (Tan 2003). In soil, humic acid (HA) is a dominant component of humic substances. The chemical composition, molecular size, structure, functional groups of HAs are different depending on the origin and their genesis way.

Base on the above background of the peatland area, where peat fire happened in peatland area in Indonesia every year, especially in Central Kalimantan, it is important to investigate the effect of peat fire on humic acid in the tropical peat soil. Some previous studies have investigated the effect of heating on soil organic matter properties, such as elemental composition changes, pyrolysis compounds, FTIR spectra, weight loss, etc (Vergnoux et al. 2011; Almendros et al. 1990; Lu et al. 2001; De la Rosa et al. 2008; Gonzalez-Perez et al. 2008). However, there were no reports about the effect of heating on the properties of humic acid properties from tropical peat soil. In the present paper the chemical change in the properties of humic acids before and after peat fires were investigated. The aim of this study is to clarify the impact of peat fires through the characterization of the extracted HAs from soil collected from several sites of burnt and unburnt in Central Kalimantan, Indonesia.

Some parameters were selected to evaluate the characteristics of HAs such as elemental composition, molecular weight, thermogravimetry, pyrolysis chromatography and fluorometric spectra. Since the humification process can be observed by the elemental composition of C, H, N, O of HA, the degradation process could also be observed by this analysis. The Van Krevelen diagram was developed to illustrate how elemental composition changes during the formation of coal, the diagram plotted the hydrogen to carbon atomic ratio (H/C) and the oxygen to carbon atomic ratio (O/C) are plotted in this diagram, therefore, it shows the decarboxylation and dehydration process of organic matters in soil (Van Krevelen 1950). Furthermore, this diagram has been developed to observe the characteristics of HSs (Yonebayashi and Hattori 1988; Fujitake et al. 2009). In this study, The Van Krevalen diagram was used to observe the change of elemental composition in tropical HAs by an impact of peat fire and heating process. To clarify the differences in the characteristics of HA from burnt and unburnt sites, at first the effect of heating at 200, 300 and 400 ^{o}C for 2 hours on HAs was investigated experimentally in the laboratory, and these data was compared with those of HAs from burnt and unburnt sites.

4.2. Materials and Methods

4.2.1. Sampling sites and soil collection

Soil samples were collected during 2010 to 2011 from four sites. There are located in Mega Rice Project (MRP) area in Kalampangan village and Sebangau National Park in Central Kalimantan Province, Indonesia. Mega Rice Project area showed extremely high fire density (hotspot), 0.188 hotspots/km^2/year as reported by Yulianti et al. (2012). Therefore, in this study, MRP area was selected as a representative of the burnt site. The soil samples collected from this site was termed as the burnt soil 1 (B1). In this site, peat fires happened in 1997, 2002, 2009. However, after these fires happened, some plants have been growing in this area and some parts of burnt area have been recovered. The other soil samples from burn site were taken from just burnt soil in Kereng village, then termed as the burnt soil 2 (B2). Sebangau area that locates in conservation area of peat swamp forest was chosen as an unburnt area, and soil samples taken in this area were termed as unburnt soil 1 (UB1). Another soil sample taken from peat forest near MRP area was termed as unburnt soil 2 (UB2). All collected samples from those four sampling sites were mentioned as UB1, UB2, B1 and B2. The sampling sites are shown in Fig.4.1. The soil samples were taken from A horizon, the depth of sampling was within 0-30 cm from the surface, and then the soil samples were stored in plastic bags. Those soil samples were dried in room temperature, sieved to pass a 2.0 mm sieve, and ready to be used for extraction and purification process of humic acid.

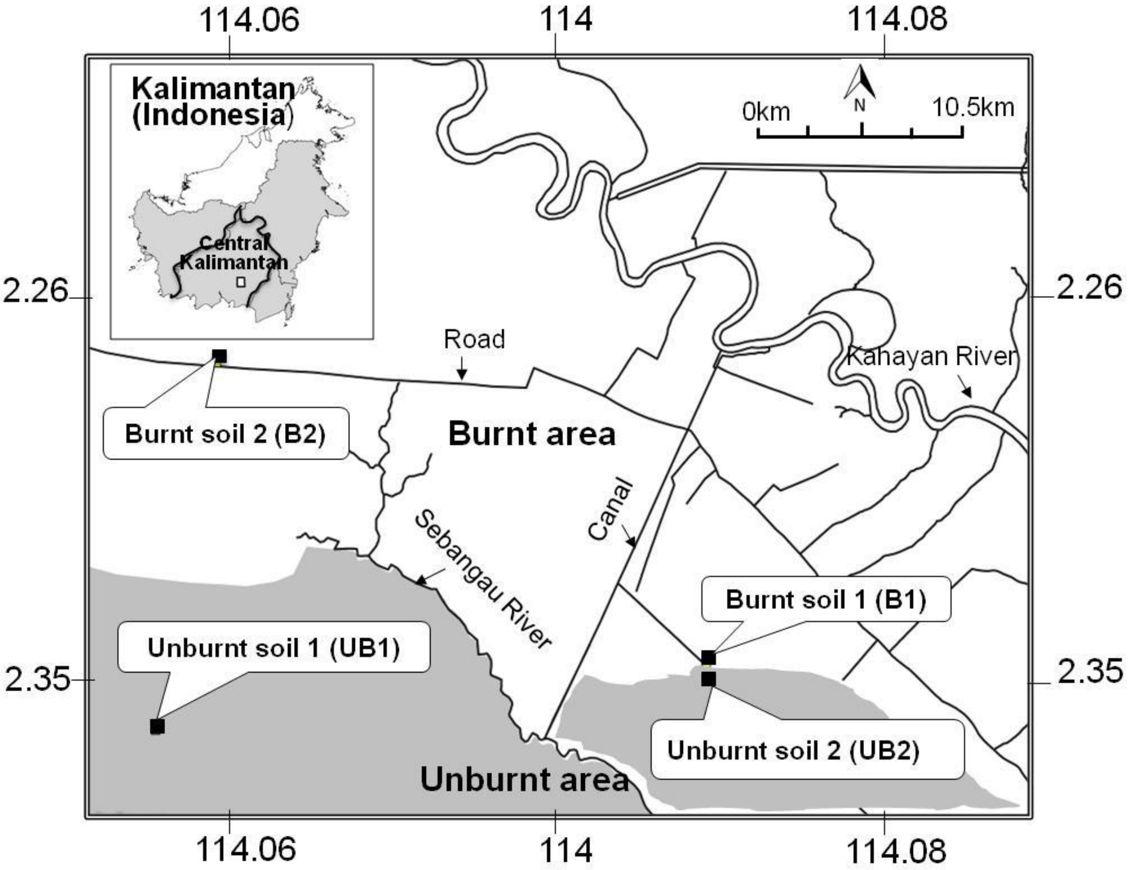


Fig.4.1. Sampling sites of soil samples in Central Kalimantan, Indonesia.

4.2.2. Extraction and purification of humic acids

Humic acids were extracted from dried soil samples and purified according to the method recommended by International Humic Substances Society (IHSS) and Stevenson (1994). 1 M HCl were added into 100-200 g dried soil and pH value was adjusted about 1 to 2. The suspension was made with the ratio of 10 ml: 1 g (0.1 M HCl solution: soil), then shaken for 1 hour, and then the supernatant was separated from the residue. The residue was neutralized with 1 M NaOH until pH 7, then redissolved with adding 0.1 M NaOH more, the ratio of solution and soil was 10 ml: 1 g, the extraction process was continued under N_2 for 24 hours. The suspension was acidified again with 6 M HCl until pH 1. This alkaline-acid treatment was repeated twice. In the last treatment, the precipitate of humic acid was redissolved with 0.1 M HCl/0.3 M HF solution in a plastic container and shaken for 24 hours, and repeated twice. The HA suspension was dialyzed in distilled water using a dialysis tube with a cut-off 1000 Da. The dialysis was continued until it became free of chloride ion. The purified HA solution was dried by freeze dryer, and then this prepared humic acids were used for the characterization.

4.2.3. Analytical methods

The humic acids were characterized by the measurement of elemental analysis, molecular weight by high performance size exclusion chromatography (HPSEC), thermogravimetry, three-dimentional excitation emission (3DEEM) spectrofluorometry and pyrolysis GC/MS. The elemental compositions of HAs were measured by JE.Science Micro Corder JM 10 at Instrumental Analysis Division, Equipment Management Center, Hokkaido University. The effect of heating on HAs was investigated by evaluating the H/C and O/C value after heating process at 200, 300 and 400 ^{o}C.

^{13}C-NMR analysis was carried out by ^{13}C-NMR Bruker MSL-300 (Germany) with a 4 mm CP-MAS probe; contact time 1 ms; pulse delay 6 s; scanning times 8000, line broadening width 30 Hz. An approximately 20 mg of HA was packed to 5-mm zirconium rotor (Tanaka et al. 2005).

The molecular weight of HAs was analyzed by HPSEC with TSK-Gel Colomn, at the oven temperature of 40 ^{o}C, and the flow rate of 0.5 ml/minute. A mixture of sodium phosphate buffer pH 7 and acetonitrile (7.5: 2.5) was used as the carrier eluent (Asakawa et al. 2008). A set of standards of poly(stryrenesulfonic acid sodium salt) with 0.21, 4.3, 6.8, 17 kDa (Fluka, Switzerland) was used for calibration standards.

Thermogravimetric (TG) and Differential Thermal Analysis (DTA) analysis were carried out by Thermo plus TG 8120, Rigaku, Japan. The combustion characteristics of HAs were determined by heating 10 mg of HA sample, from 25 to 500 °C with heating rate of 3 °C min^{-1}. Alumina was used as a reference standard (Sazawa et al. 2013).

3DEEM spectrum was measured using a fluorescence spectrophotometer (Model LS-55, Perkin Elmer). The scanning wave ranges was 200-600 nm for both of excitation and emission (Sazawa et al. 2011). The data was collected by reading at intervals of 10 nm excitation with 5 nm emission wavelengths using a scanning speed of 1,000 nm/ min and photomultiplier voltage of 775 V. Pure water (Mili-Q, Millipore Co. Ltd) was used as the blank for all fluorescencence analysis. The relative Fluorescence Intensity (RFI) was calibrated to be evaluated in quinine sulfate units (QSU); 1 QSU= 1 μg/L of quinine sulfate monohydrate in the solution of 0.05 M H_2SO_4 at excitation/emission (Ex./ Em) 350/455 nm. For all the fluorescence spectra were applied the inner-filter correction according to the method by McKnight et al. 2001. UV-Vis absorption spectrum was measured using a double beam spectrophotometer (U-2000A, Hitachi, Japan) equipped with a 1 cm quartz UV-Vis cell.

Pyrolysate compounds of HA were determined by pyrolysis-GCMS (Shimadzu GC-17A/QP5050 type GC/MS system, Japan. 0.5 mg HA was prepared in a deactivated stainless steel cup. After addition of 25 μl of TMAH (tetramethylammonium hydroxide) in methanol (40 mg/ml) into the cup, it was put in the vacum for 5 minutes until the aliquot was evaporated, and the procedure was repeated for 3 times. Five μl of internal standard solution (0.06 mg nonadecanoic acid in 1 ml of methanol-acetone (1:1)) was added into the cup and the cup was put into the vacuum for 5 minutes to evaporate the solvent, and then the prepared sample was ready to be analyzed by GC/MS-pyr. The operating temperature for this analysis was as follows: 50 ^{o}C for 1.0 min; 50-300 ^{o}C at a heating rate of 5 ^{o}C min^{-1}; 300 ^{o}C for 5 min. pyrolysis temperature 550^{o}C for 4 minutes. To compare the peak areas for each sample, the relative peak areas were calculated by the peak area for each pyrolysate compound by that of internal standard (ISTD), nonadecanoic acid methylester, the retention time at 34.6 minutes (Fukushima et al. 2009; Fukushima et al., 2011).

Heating experiments of extracted HA from burnt and unburnt sites were done in the laboratory. The constants amount of HA were put into a container with a cap and heated by a muffle furnace. The variation of heating temperature was 200, 300 and 400 ^{o}C, the heating processes were conducted for 2 hours with timer and heating rate program. After the heating process completed, the HAs were characterized by the measurement of elemental analysis, molecular weight by high performance size exclusion Chromatography (HPSEC), pyrolysis data by GCMS-pyr.

4.3. Results and Discussion

4.3.1. Elemental composition in humic acid

The Van Krevelen diagram has been used to illustrate the change in elemental composition that occurred during the alteration of organic geochemicals in a geological environment; e.g., the H/C and O/C ratios have been used to investigate the effects of diagenesis on humic substances (Schitzer and Hoffman, 1965; Yonebayashi and Hattori, 1998; Almendros et al. 1990). In this study, the impact of heating process on tropical HAs was clarified by observing the change in the value of the H/C and O/C. The elemental compositions of extracted humic acids after heating at various temperatures are shown in the weight percentage (Table 4.1) and atomic percentage (Table 4.2). The carbon contents of HAs after heating process increased relatively. This behavior of HAs seems to be different with that when soil was heated (Fernandez et al. 1997). The decrease in hydrogen and oxygen contents after heating process suggested that the heating process would release hydrogen and oxygen from the HA structure, then the composition of carbon in HA became relatively higher. 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 ^{o}C, the value of the O/C decreased gradually corresponding to the different heating temperature as shown in Fig.4.2. 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 such as carboxylic groups, and then consequently increased the aromaticity of HA.

The values of the H/C and O/C of humic acids extracted from burnt soil (B1 and B2) and unburnt soil (UB1 and UB2) are also plotted in Fig. 4.2, whereas the value of H/C and O/C of HAs from B1 and B2 are lower than that from UB1 and UB2. The diagram showed that the plots of HAs extracted from burnt soil (B1 and B2) were close to those of HAs heated at 200 ^{o}C. That means that HA from burnt sites in Central Kalimantan was affected by heating during peat fire and increased in the aromaticity. This behavior was a similar tendency to the research reported by Gonzales-Perez et al. (2004).

Table 4.1. Elemental composition of humic acid after heating at various temperatures (^{o}C). (in weight percentage).

Humic acids	%C	%H	%N	%O	% ash
HA UB1, before heating	48.5	5.2	1.7	43.6	1.0
HA UB2, before heating	52.4	4.7	1.8	41.1	0
HA B1, before heating	54.6	4.3	0.9	39.8	0.4
HA B2, before heating	56.7	4.0	0.5	38.9	ND
HA UB1, 200	60.5	4.5	2.1	32.8	ND
HA UB2, 200	57.0	4.3	2.0	36.7	ND
HA B1, 200	60.1	3.9	1.0	35.1	0.2
HA B2, 200	58.9	3.8	0.9	36.4	ND
HA UB1, 300	67.3	4.3	2.5	25.9	ND
HA UB2, 300	65.9	3.8	2.6	27.2	0.5
HA B1, 300	65.1	3.7	1.2	30.0	ND
HA B2, 300	66.5	3.6	1.1	28.6	0.2
HA UB1, 400	75.1	4.0	2.7	18.2	ND
HA UB2, 400	72.3	3.7	2.7	21.0	0.4
HA B1, 400	73.9	3.6	1.3	21.2	ND
HA B2, 400	75.0	3.3	1.4	20.3	ND

Table 4.2. Elemental composition of humic acid after heating at various temperatures (^{o}C). (in atomic percentage).

Humic acids	%C	%H	%N	%O	H/C	O/C
HA UB1, before heating	33.5	42.8	1.0	22.6	1.28	0.68
HA UB2, before heating	37.0	40.1	1.1	21.8	1.08	0.59
HA B1, before heating	39.9	37.6	0.6	21.9	0.94	0.55
HA B2, before heating	42.4	35.5	0.3	21.8	0.84	0.51
HA UB1, 200	42.8	38.5	1.3	17.4	0.90	0.41
HA UB2, 200	41.5	37.3	1.2	20.0	0.90	0.48
HA B1, 200	45.0	34.6	0.6	19.7	0.77	0.44
HA B2, 200	44.3	34.6	0.6	20.5	0.78	0.46
HA UB1, 300	47.8	36.9	1.5	13.8	0.77	0.29
HA UB2, 300	49.0	34.2	1.7	15.1	0.70	0.31
HA B1, 300	49.1	33.2	0.8	17.0	0.68	0.35
HA B2, 300	50.2	32.9	0.7	16.2	0.66	0.32
HA UB1, 400	54.0	34.6	1.7	9.8	0.64	0.18
HA UB2, 400	53.7	32.9	1.7	11.7	0.61	0.22
HA B1, 400	55.3	32.0	0.9	11.9	0.58	0.21
HA B2, 400	57.1	30.4	0.9	11.6	0.53	0.20

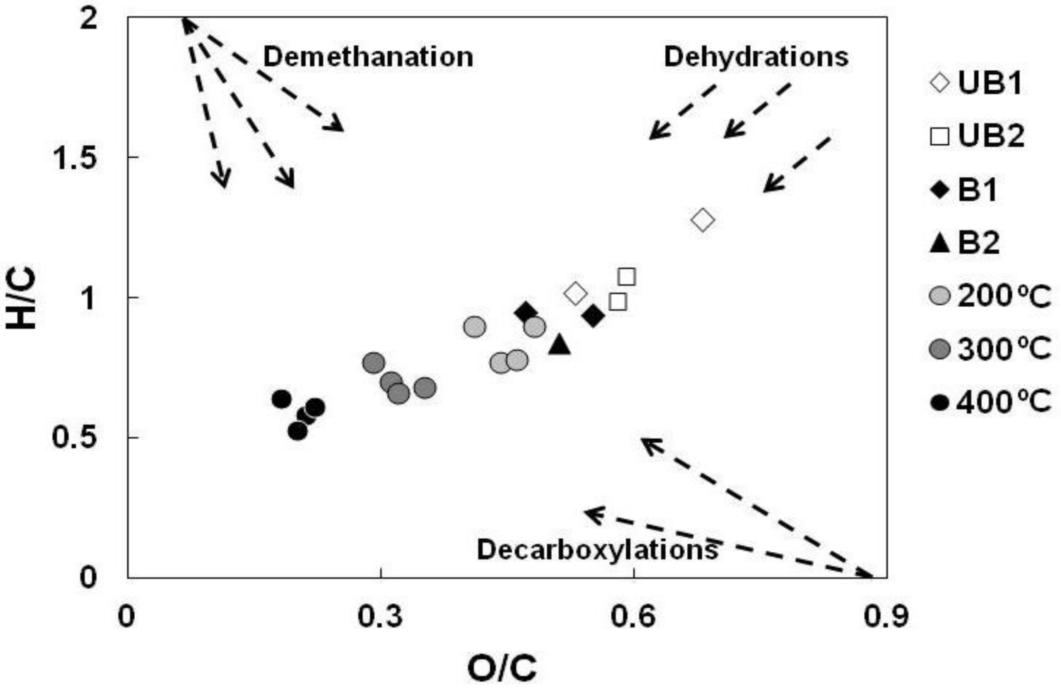


Fig. 4.2. The Van Krevelen plot (H/C vs O/C ratios) of humic acids collected from Sebangau soil (UB1), Forest soil (UB2), Deforest soil (B1), Burnt soil in Kereng (B2) and thermally treated samples (200, 300, 400 °C).

4.3.2. ^{13}C-NMR Spectroscopy

^{13}C-NMR spectroscopy has been used to analyze the composition of carbon in various structural groups. According to some previous reports (Gonzales-Vila et al. 1983; Tanaka et al. 2005), the spectra was devided into five chemical regions, long chain aliphatic C (0-55 ppm), substituted aliphatic C (55-90 ppm), anomeric carbon polysaccharide (90-110 ppm), aromatic C (110-160 ppm) and C-carbonyl, carboxyl, amide, ester (160-190 ppm). The ^{13}C-NMR spectra of HAs from unburnt site (UB1), burnt site (B2), and after heating process are presented in Fig.4.3.

The relative contents of carbon in various structure were calculated according to five regions spectra as described above, and HAs from peat soil in Central Kalimantan contained those various carbon. HAs from burnt sites (B2) contained more aromatic carbon than HA from unburnt site (UB1). After heating process until 300 ^{o}C, the aromaticity of HA UB1 increased from 23.3 % to 40.2 %, while HA B2 increased from 42.0 to 56.7 % (Table 4.3). It indicated that the heating process changed the structure and composition of carbon in humic acid to increase the aromaticity. This behavior also was observed, in the elemental analysis data.

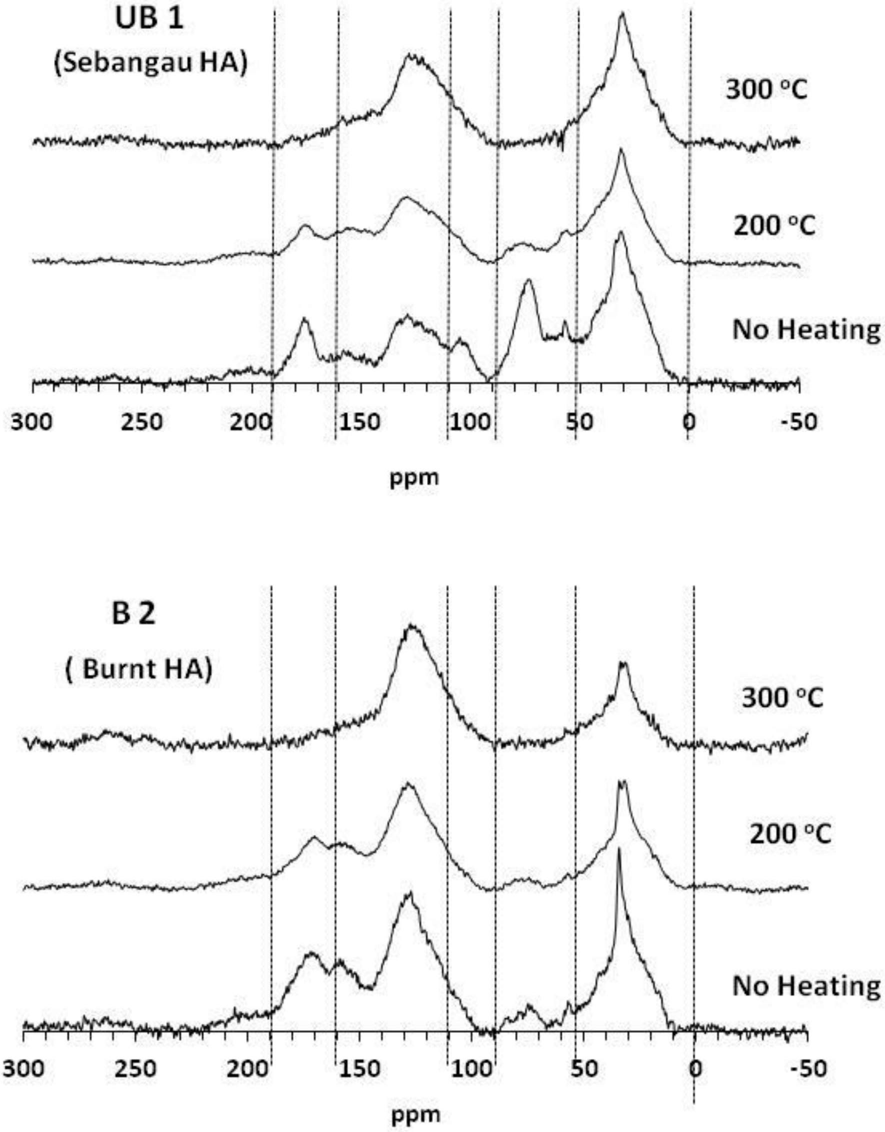


Fig.4.3. CP/MAS 13C-NMR spectra of humic acids from unburnt site (UB1), burnt site (B2) and thermally treated samples (200, 300 ^{o}C)

Table 4.3. Relative content (%) of various C atoms in humic acids from ^{13}C-NMR spectra

No.	Samples	Shift range (ppm)				
		0-50	50-90	90-110	110-160	160-190
		Long chain aliphatic C	Substituted aliphatic C	Anomeric carbon of polyssacharide	Aromatic Carbon	Carbonyl, carboxyl, amide, ester carbon
1.	HA UB1 no heating	37.9	21.7	5.8	23.3	11.3
2.	HA UB1 200 ^{o}C	35.5	12.5	4.4	34.8	12.7
3.	HA UB1 300 ^{o}C	44.4	6.1	7.2	40.2	5.1
4.	HA UB2 no heating	31.9	28.6	7.7	22.9	8.9
5.	HA B1 no heating	43.0	9.4	3.3	33.6	10.7
6.	HA B2 no heating	28.5	7.6	3.7	42.0	18.2
7.	HA B2 200 ^{o}C	29.1	5.2	3.4	45.9	16.4
8.	HA B2 300 ^{o}C	26.1	4.8	7.0	56.7	4.9

4.3.3. Molecular weight

Humic acid has a wide variety of molecular weight depending on their origin, environment and age. The shape and molecular size of humic substances are still unresolved issue. Piccolo (2001) revealed the important point on the structure and molecular size of humic substances, that is described the humic substances as a supramolecule associated with heterogenic small molecule and it is not polymer. High performance size exclusion chromatography (HPSEC) is a popular method that is used to evaluate the molecular size of humic acid. However, it is still lack of compounds that have the similarity on the structure and charge density to HA. Some researchers used polystyrene sulfonate (PSS) for calibration standard, because PSS has the charge density that is most similar to natural organic matters (NOM) including HA, while the structural similarity is debatable (Zhou et al. 2000, Asakawa et al, 2008). In this study, we also considered to use sodium salt of polystyrene Sulfonate acid due to the above reason. Using the method above, the relative molecular weight (MW) of the humic acid extracted from several sites in peat area in Central Kalimantan was determined, it was in the range of 3380 to 4550 Da (Table 4.4). The relative molecular weights of HAs in Central Kalimantan were lower compared to the HAs from temperate areas (Fong and Mohamed, 2007 ; Asakawa et al (2008); Conte and Piccollo, 1999). The effect of burning process on the molecular weight of HA was investigated by using heated HAs collected from four sites containing unburnt and burnt area as shown in Fig.4.4. A tendency that the Relative MWs of HA extracted from burnt soil (B1 and B2) was smaller than that of HAs extracted from unburnt soil (UB1 and UB2). When these HAs were heated at 200 ^{o}C for 2 hours, the molecular weight of each HA decreased about 10 to 40 %. And after heating at 300-400 ^{o}C the molecular weight of HA decreased until 43-55 %. These results showed that the molecular weight of HA decreased gradually with increasing the heating temperatures. The decrease in the molecular weight of HAs from UB1 and UB2 soil by heating process was larger than that of HAs from B1 and B2. That is, HAs extracted from Sebangau soil (UB1) and forest soil near MRP (UB2) were degraded in this heating process more than HA from B1 and B2 soil, since HA from B1 and B2 had been already degraded some parts of HAs structure which could be degraded by this heating process have not remained. Finally, after heating at 300 and 400 ^{o}C, the molecular weight of HA showed a similar size among each other, around 2000 Da. The value of 2000 Da is the lowest range of HA molecular weight as reported previously. The heating process might degrade the chemically unstable parts of HA such as carboxylic group, and remaining the chemically persistent moiety of HA. During heating at 300-400 ^{o}C, dehydration and decarboxylation process will be going on the structure of humic acid, it will be described in the latter section. The difference in molecular weight of HAs between burnt sites and unburnt sites was not so large, about 15 %. It corresponded with the temperature when HAs in soil burnt seemed to be not so high.

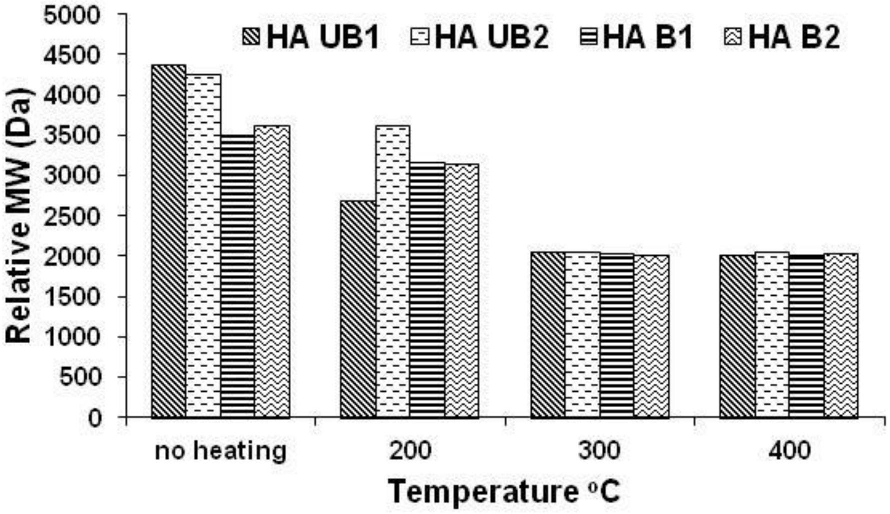


Fig.4.4. Changes in the relative molecular weight (MW) of humic acids by heating at various temperatures.

Table 4.4. The relative molecular weight of humic acids , extracted from unburnt sites and burnt sites in Central Kalimantan, Indonesia.

No.	Unburnt sites	MW (Da)	No.	Burnt sites	MW (Da)
1	HA UB1 (Sebangau 1, 2010)	4368±39	1	HA B1 (Deforest canal 1, 2010)	3495±68
2	HA UB2 (Sebangau 2, 2010)	4550	2	HA B1 (Deforest canal 2, 2010)	3380
3	HA UB1(Sebangau, 2011)	4100±50	3	HA B1 (Deforest canal, 2011)	3562±61
4	HA UB2 (Forest canal, 2010)	4254±80	4	HA B2 (Kereng, 2011)	3612±103
5	HA UB2 (Forest canal, 2011)	3934±10			

4.3.4. Thermal Analysis

The TG-DTA data of HA from unburnt soil (HA UB1) and burnt soil (HA B1) are shown in Fig. 4.5. TG curve shows the weight loss of HA, while DTA curve shows the heat release rate of HA during pyrolysis process. There are endothermic and exothermic reactions occur during pyrolysis process. The moisture (H_2O) will be released in endothermic reaction, and then dehydration, decarboxylation and decomposition of HA occur in exothermic reaction. Some researchers (Francioso et al. 2005, Marcos et al. 2007, Francioso et al. 2009) observed two exothermic reactions on humic acid. First exothermic reaction was attributed to decarboxylation reaction of acidic groups, protein, carbohydrate and fatty acid decomposition, and the second exothermic reaction related to the breakdown of aromatic structure and cleavage of C-C bond, was mentioned to Peak A.

The different thermal profiles between HA UB1 and HA B1 were observed in Fig.4.5. Two exothermic peaks raised at the DTA curve of HA UB1, the peaks of exothermic 1 and 2 were observed at 318.3 and 458.5 ^{o}C (Peak A). It indicated HA UB1 contained polysaccharides, carboxylic groups, hydroxyl aliphatic groups that combusted in exothermic reaction 1, and therefore the aromatic structures were combusted in exothermic 2. The similar pattern of DTA curve was shown for HA UB2, the peak of exothermic 2 was observed at 451.6 ^{o}C. The thermal behavior of humic acids from UB1 and UB 2 indicated that humic acids from UB1 and UB 2 contained polysaccharides, carboxylic acid, protein and fatty acid.

As compared with HA UB1, the Peak A of HA B1 significantly increase, and the combustion temperature of aromatic structure and cleavage of C-C bond was shifted become higher. The peaks of second exothermic for HA B1 and B2 were observed at about 487.3 and 482.5 ^{o}C. These values indicated HA from B1 and B2 contained aromatic compounds that were resistant from high temperature. These resistant aromatic compounds raise as corresponding to degradation process of HAs caused by peat fire. It was appropriate to the elemental analysis data as shown previously, whereas the aromaticity increased correspond to increasing heating temperature.

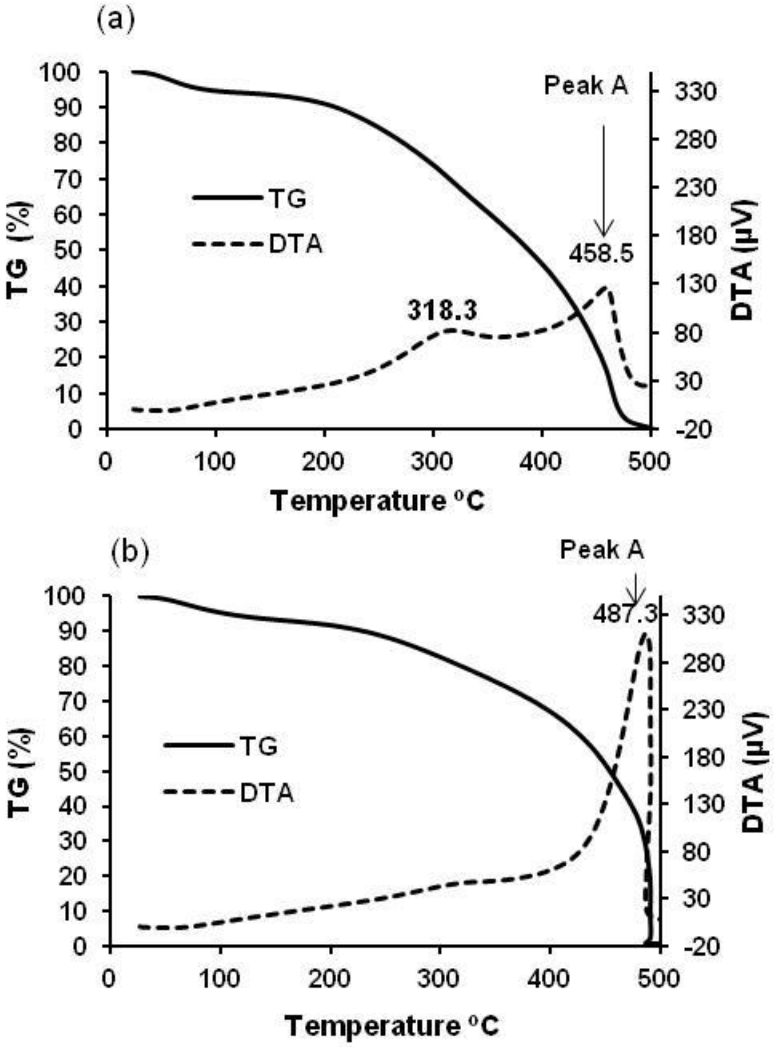


Fig.4.5. TG-DTA Curve of humic acids. (a) HA extracted from unburnt soil (UB1). (b)) HA extracted from burnt soil (B1). Peak A: combution of carbide.

4.3.5. Three-dimensional excitation-emission fluorescence matrix

It is well known that HA contains some fluorophores, and then the fluorescence spectra has been used to investigate the characteristics of HA from different origins as reported by Matthew et al. (1996). In this study, the effect of peat fires on characteristics of HA was evaluated from the alteration of fluorescence spectra of HAs from unburnt site and burnt site. Coble (1996) characterized the humic-like component by fluorescence properties as peak C (λex/λem= 320-360/420-460 nm), peak A (λex/λem = 260/380-460 nm) and peak M (λex/λem = 290-310/370-410). The peak C and peak A which are represented as humic-like components exported from terrestrial sources (Birdwell and Engel 2010).

The 3DEEM fluorescence spectra of humic acid from unburnt soil and burnt soil are shown in Fig.4.6. There are two prominent peaks in fluorescence spectra observed at λex/λem=300/595 and λex/λem=450/595. Theses peaks seem to be peak A and peak C, however if we compare them with the peaks reported by Coble (1996), the wavelength of these maximum peaks has been shifted. The fluorescence indices were calculated with the term FIX and BIX, as shown in Table 4.5. FIX was calculated from the ratio of emission intensity at 450 nm to that at 500 nm, following excitation at 370 nm, and provides a metric for disguising DOM derived from terrestrial and microbial source. Terrestrial organic compounds, particularly lignin, are expected to contain more conjugated aromatic structures than microbially-derived substances. The FIX value of 1.4 or less indicates DOM of terrestrial origin and the values of 1.9 or higher corresponds to microbial-derived material. The data showed that the FIX values of HA from both sampling sites were less than 1.4, it is means all humic acid origin from terrestrial, however the FIX value of HA from unburnt site (UB1 and UB2) was slightly higher than that from burnt site (B1and B2). It suggested HA from unburnt site might contain more lignin like structure. The peak C showed that HA from burnt sites have higher value of RFI, it indicated HA from burnt soil contained more fluorophores. The BIX value was calculated from the ratio of the emission intensities at the shorter (λem 380 nm) and the longer (λem 430 nm) wavelength using a fixed excitation (λem 310 nm). This value indicates the relative contribution of biological or autochthonous DOM. Formulation of BIX was influenced by presence of two common peaks in fluorescence spectra attributed to terrestrial and microbial components. The BIX values of both sites were about 0.31- 0.39 that indicated the microbe activities were less at both sites (Birdwell and Engel 2010). Therefore, HAs from both sites originated from autochthonous. Beside the fluorescence spectra, UV-Vis properties of HAs also were observed. The ratio of absorbances at 465 and 665 nm, as mentioned the E_4/E_6 ratio of HAs were determined in this study. The high value of E_4/E_6 indicates the prominence of aliphatic structure, otherwise the low value of E_4/E_6 indicates much of aromatic constituents were contained (Fong and Mohamed 2007, Stevenson 1982). The E_4/E_6 ratio of humic acids from temperate climate area usually less than 5 while in this study the humic acid from unburnt sites in Central Kalimantan are 8. It indicated humic acid from tropical peatland relatively contained more aliphatic structures than humic acid from temperate climate area.

The E_4/E_6 value of HA from unburnt sites (UB1 and UB2) were higher than that from burnt sites, it suggested HA from unburnt sites contained more aliphatic structure, while HA from burnt sites contained more aromatic moiety. HA from burnt soil contained more fluorophores such as benzoic acid and phenol as shown in the latter section on pyrolysate compounds. Richard et al. (2004) reported that most of fluorophores are contained in the low molecular size of HA, similar behavior is shown by HAs from burnt site which have lower molecular weight than that from unburnt site, evidently the 3DEEM spectra of HA from burnt site showed higher intensity of fluorescence than from unburnt site.

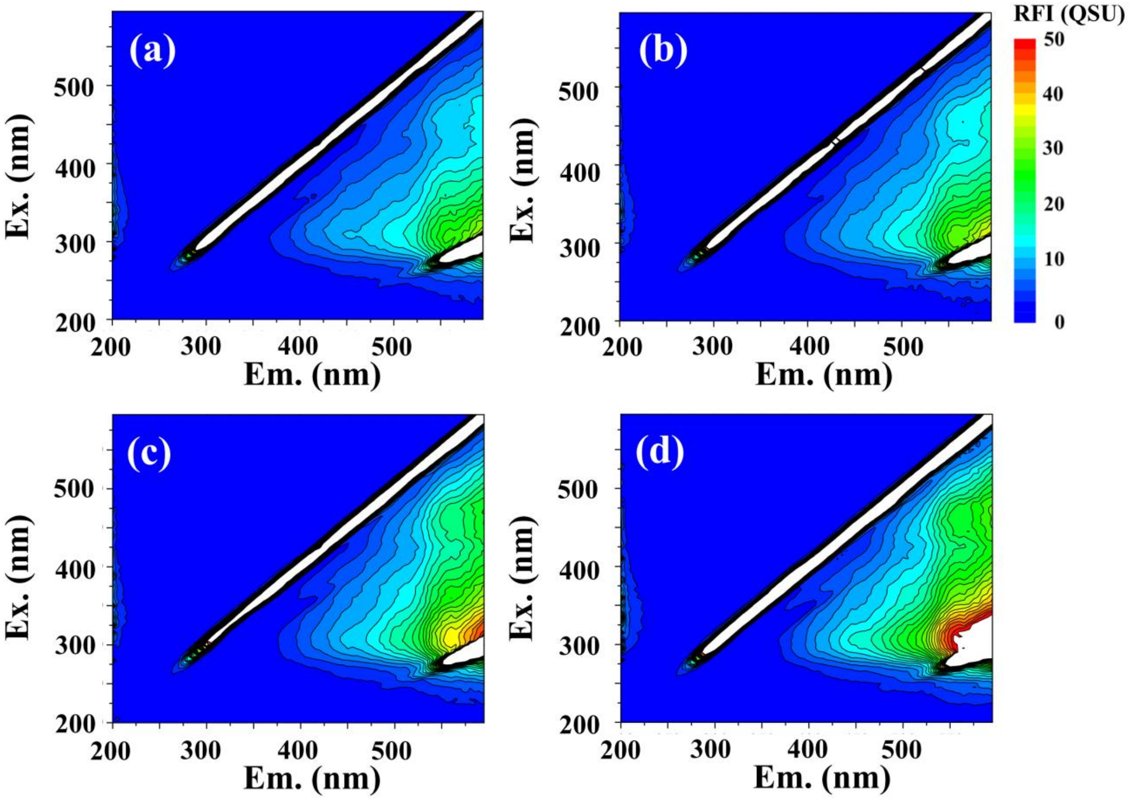


Fig 4.6. The 3DEEM fluorescence spectrum of humic acids from unburnt soil (a and b), and from burnt soil (c and d). The bar chart next to the graph indicates contour intervals of the relative fluorescence intensity (RFI) in the quinine sulfate normalization.

Table 4.5. Spectrophotometric parameter and Fluorescence indices.
UB: Unburnt, B: Burnt

Humic acids	UV-Vis Spectra	Fluorescence indices			
	E4/E6	FIX	BIX	Peak A (λex 300/em595) RFI (QSU)	Peak C (λex 450/em595) RFI (QSU)
HA from Sebangau (UB 1)	8.22	0.67	0.39	443.72	12.92
HA from Forest (UB 2)	8.00	0.63	0.35	394.94	14.68
HA from Deforest (B1)	5.53	0.62	0.32	310.83	23.61
HA from Kereng (B2)	5.84	0.61	0.33	504.89	28.19

4.3.6. Pyrolysis-gas chromatogram/mass spectrometry

The change of the chemical composition of HA due to the effect of heating was observed by pyrolysate compounds. The pyrolisate compounds are classified into some groups according to a report by Fukushima et al. (2011) with some modification, those are nitrogen-containing pyrolysate compounds (A), phenolic compounds (B), aromatic aldehydes and ketones (C), aliphatic and aromatic alcohols (D), saturated fatty acids (E), unsaturated fatty acids (F), aliphatic alkanes, alkenes and alkynes (G) and benzene derivatives (H). These compounds were originated from carbohydrate, lignin, lipids and protein as well as from the soil organics reported by Gonzalez-Perez et al. (2004). HA extracted from Sebangau soil was (HA UB1) representative of HA unburnt sites and HA extracted from the burnt soil of Kereng (HA B2) was representative of HA from burnt sites.

The distributions of pyrolysate compound in HA from UB1, B2, UB2 and B1 are interpreted using the relative peak area as shown in Fig.4.7 and Fig.4.8. The pyrolysate compounds of HA UB1 (before heating) were dominated with alkanes, alkenes and alkynes (G), saturated fatty acids (E), unsaturated fatty acids (F). These compounds are the pyrolysis products originated from lignin and soil organic matter. The relative peak area for the alkanes, alkenes and alkynes in HA UB1 was larger than in HA B2. Contrary, the relative peak area for the phenolic compounds in HA from B2 was larger than that of HA from UB1. It indicated HA B2 have been oxidized and then produced benzenecarboxylic and phenolic acid from degradation process of humic acid (Almendros et al. 1988). These data had a strong correlation with the elemental analysis data that indicated the H/C and O/C values of HA from burnt sites were lower than from unburnt sites, It means HA from burnt sites contained more aromatic compounds, in the other hand, HA from unburnt site contained more aliphatic compounds. In burnt sites, humic acids which have the long chain aliphatic groups had been broken down by burning process to become short chain.

When HA UB1 was heated at 200 ^{o}C, the composition of pyrolysate compounds was changed, whereas alkanes, alkenes and alkynes (G) were released by heating, however the fatty acids were still as a main compounds. Fatty acids are a stable component which is remaining in soil after heating (Almendros 1988). The increase of heating temperature leads the dehydration and the decarboxylation process in humic acid structure between 200 and 500 ^{o}C, then further heating would lead to the dehydrogenation process between 500-650 ^{o}C, then the aromaticity increased more (Schitzer and Hoffman 1965). In this study, after heating process at 300 ^{o}C, the relative peak area of both HAs decreased significantly.

The total ion chromatograms (TIC) of HAs from Sebangau soil (UB1) and from burnt soil Kereng (B2) were shown in Fig. 4.9 and 4.10. The detail of pyrolysate compounds of humic acids that consist of eight groups (A, B, C, D, E, F, G, H) from Sebangau soil (UB1) and Kereng (B2) are presented in Table 4.6 and 4.7. The effect of heating on the pyrolysis chromatogram of HA from unburnt sites and burnt sites was observed using the HA samples heated experimentally in laboratory. Increasing the heating temperatures has decreased the relative abundant of pyrolysate compounds. HA from Sebangau soil (before heating) released the pyrolisate compounds that consist of phenolic compounds (B), aldehydes and ketones (C) and aliphatic alkanes, alkenes and alkynes (G), saturated fatty acids (E). Heating process at 200 ^{o}C have released more kinds of pyrolysate compounds that consist of pyrolysate compounds (A), phenolic compounds (B), aromatic aldehydes and ketones (C), aliphatic and aromatic alcohols (D), saturated fatty acids (E), unsaturated fatty acids (F), aliphatic alkanes, alkenes and alkynes (G) and benzene derivatives (H). It indicated that humic acid molecule have been degraded partially, and then distributed as those of pyrolysate compounds. After heating at 300 ^{o}C, the pyrolysate compounds were dominated by phenolic compounds (B), saturated fatty acids (E), aliphatic alkanes, alkenes and alkynes (G), benzene derivatives (H). According to Lu (2001), heating temperature at 300 ^{o}C will remove some aliphatic compounds such as octane, nonane and undecane, however in HA from UB1, these aliphatic compounds were still detected (Fig. 7). It indicated HA from tropical peat soil contained more aliphatic structures. In the other hand, benzene derivatives have been observed after heating at 300 ^{o}C, whereas in Mediterranean soil were observed after heating at 520 ^{o}C as reported by De la Rosa (2008). It seem dehydration and decarboxylation are easier to proceed in humic acid from tropical peatland. Heating process at 400 ^{o}C has released most compounds, and then remained nitrogen-containing pyrolysate compounds (A), saturated fatty acids (E), benzene derivatives (H). The elemental analysis data also showed this behavior whereas nitrogen content increased as increasing the heating temperature (Table 1). The increase in N content of HA after heating process was explained by some factors such as increase of ammoniacal N that caused by the chemical mineralization of soil organic matters and the deposition of ashes on soil surface, reduction of the N absorption by vegetation, the loss of significant amount of C, H, O by heating process (Prieto-Fernandez et al. 2004). The nitrogen in HA can be attributed to the lignoprotein and/or phenolprotein (Fukushima et al. 2009). The results of H/C and O/C value from elemental analysis data and the pyrolisis data, suggested that heating process let to the increase in the aromaticity and the loss of oxygen-containing functional groups of HAs, as reported by Gonzales (2004).

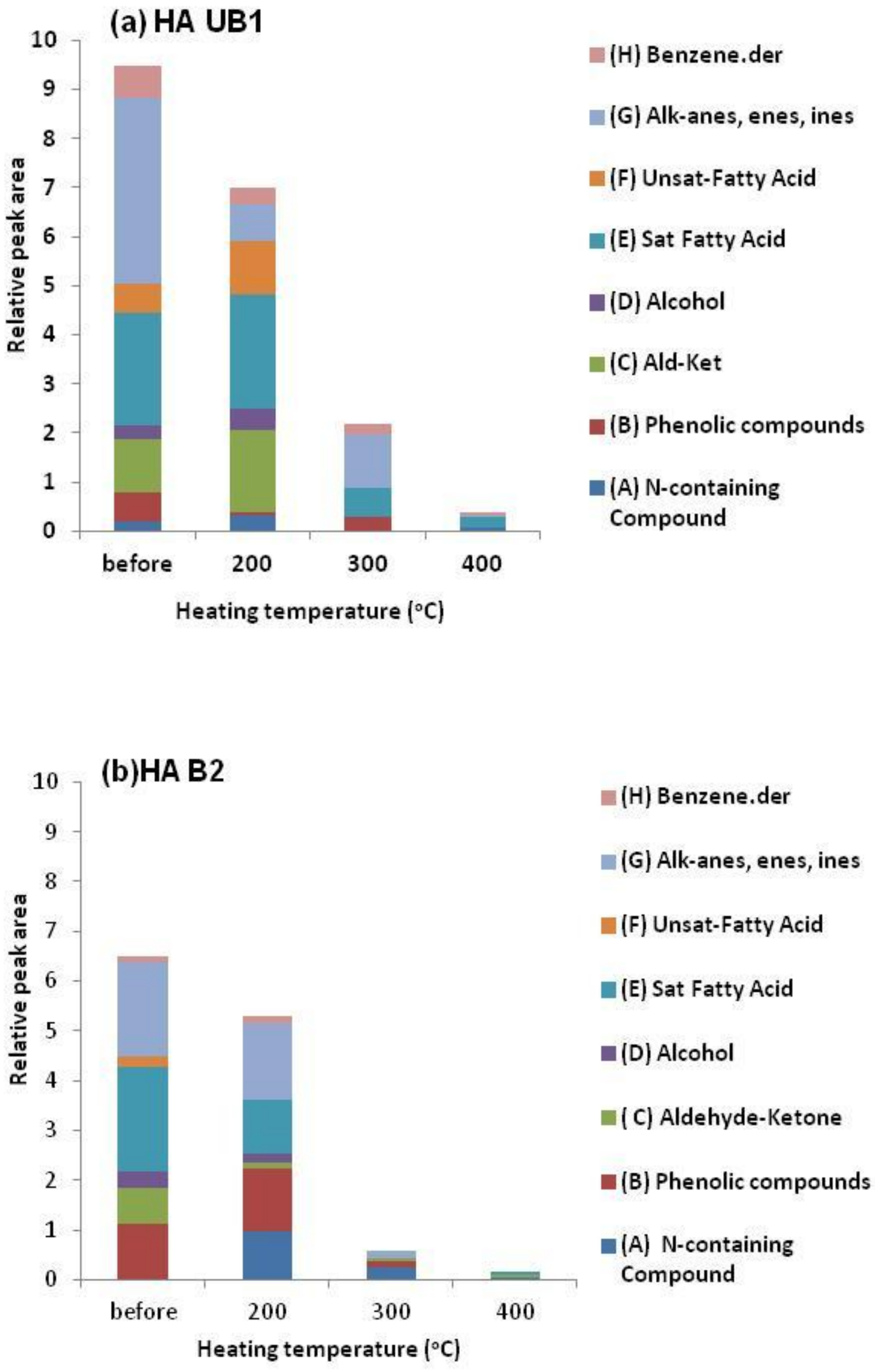
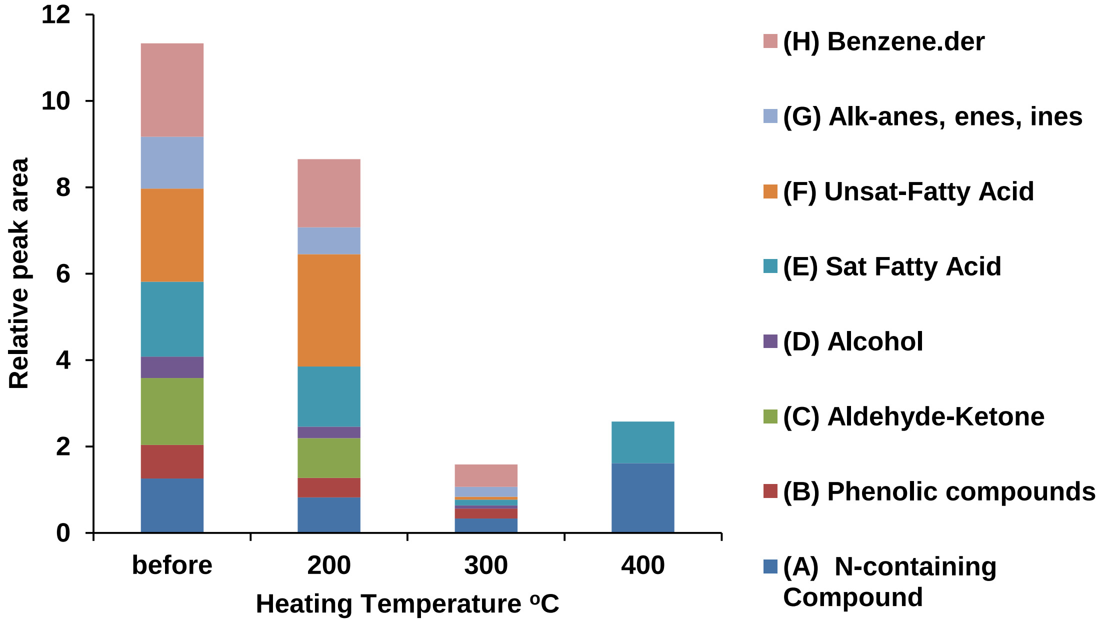


Fig.4.7. Pyrolisate compounds of humic acids from unburnt site (a) and burnt site (b), divided to A: Nitrogen containing compound, B: Phenolic compound, C: Aldehide, ketones, D: Alcohol compounds, E: Saturated fatty acid, F: Unsaturated fatty acid, G:Alkanes-alkenes-alkynes, H: Benzene derivatives.

(a). UB2



(b) B1

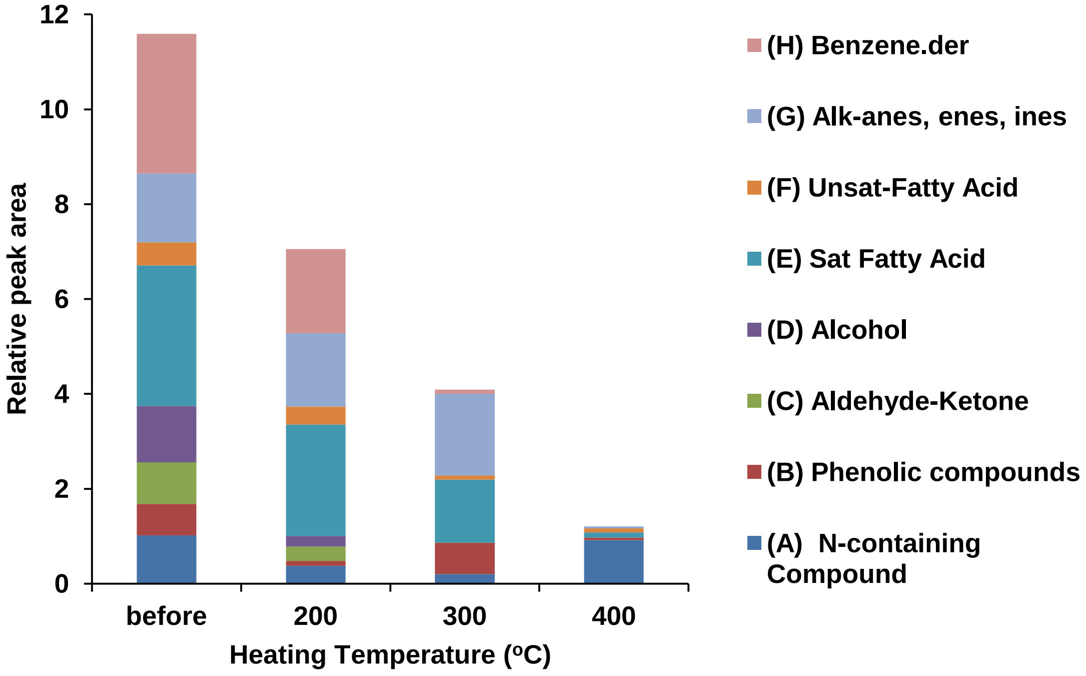


Fig.4.8. Pyrolisate compounds of humic acids from unburnt site, UB2 (a) and burnt site B1 (b).

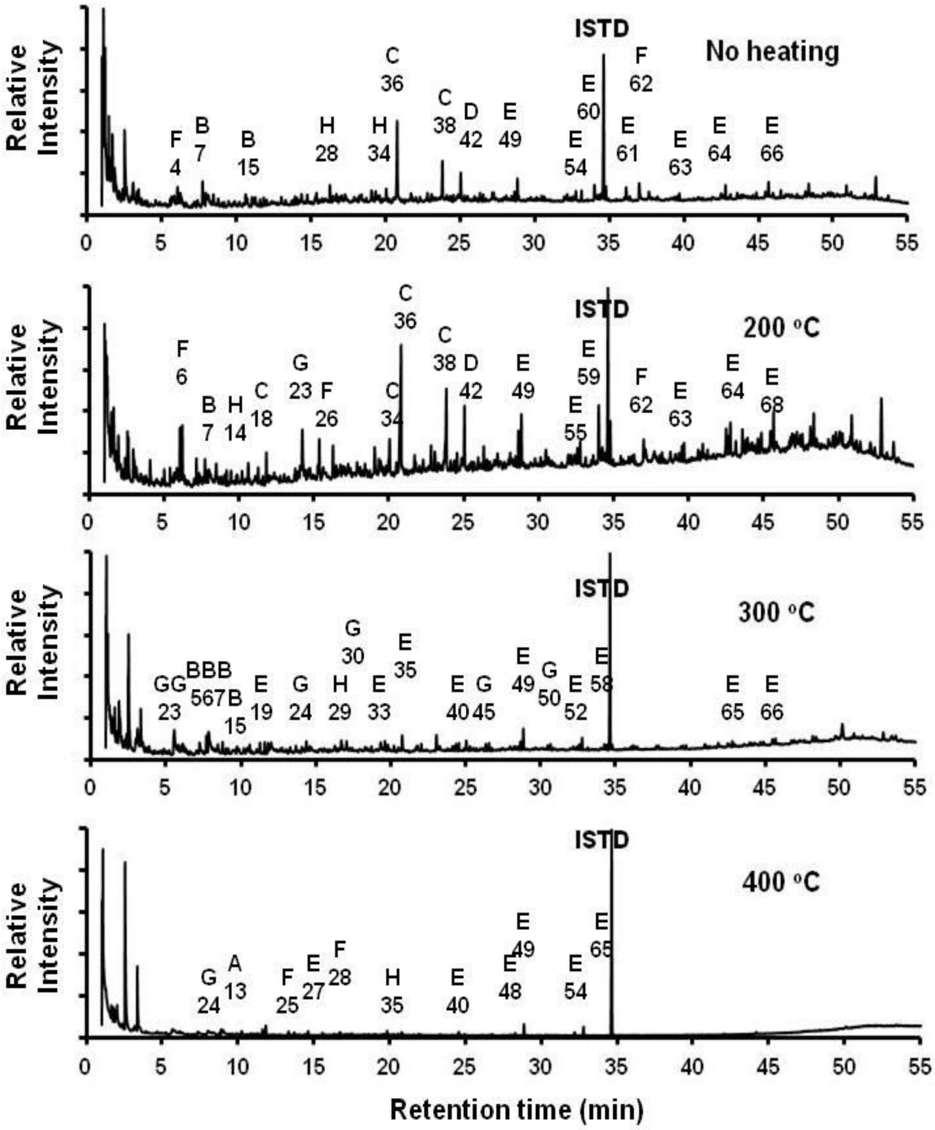


Fig.4.9. Py-GC/MS total ion chromatogram of humic acids from unburnt soil in Sebangau (UB1) after heating process at variation temperature.

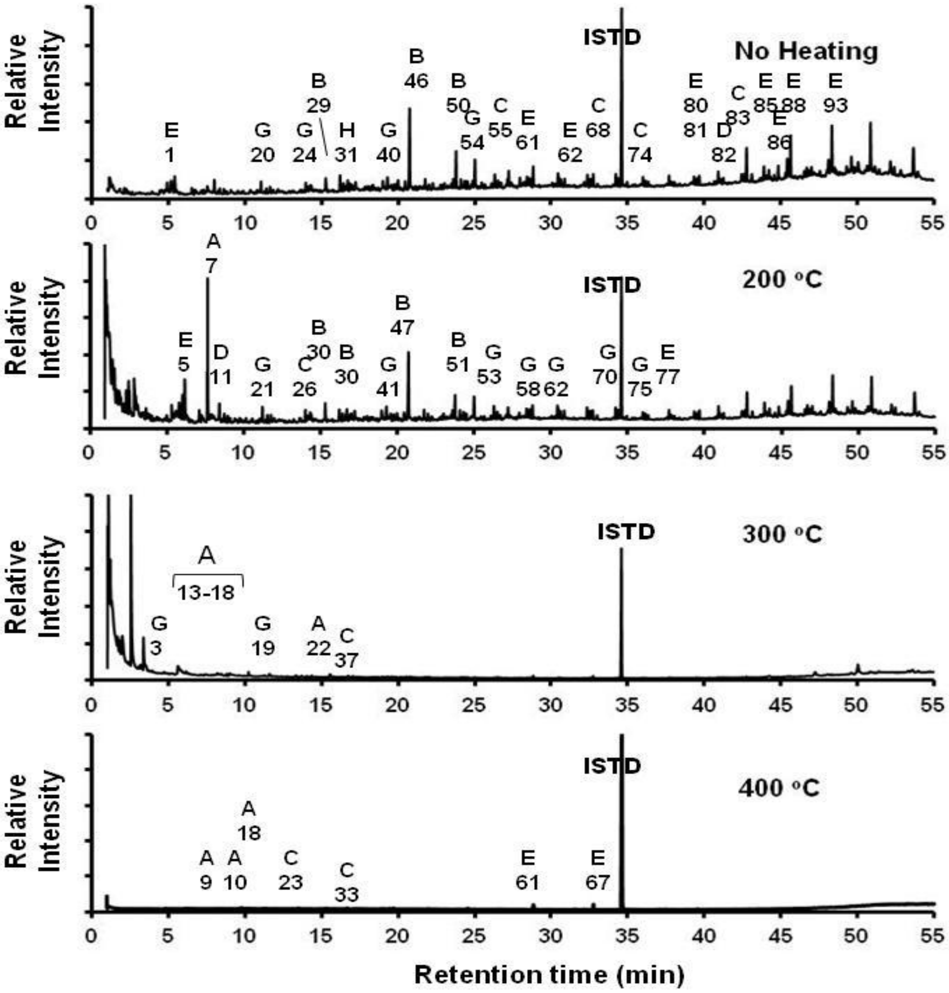


Fig.4.10. Py-GC/MS total ion chromatogram of humic acids from burnt soil in Kereng (B2) after heating process at variation temperature.

Table .4.6. Pyrolysate compounds of humic acid from unburnt soil in Sebangau (UB1)

Peak No.	RT	assignment	Group Code	Before heating	After heating 200 ^{o}C	After heating 300 ^{o}C	After heating 400 ^{o}C
1	5.825	cyclopropane	G		x		
2	5.833	1-Decene	G			x	
3	6.125	Decane	G			x	
4	6.192	Butanedioc acid, methyl ester	F		x		
5	7.250	Phenol, 2-methyl	B			x	
6	7.700	Mequinol	B			x	
7	7.742	Phenol, 2-methoxy	B	x	x	x	
8	8.475	2-Trifluoroacetoxydodecane	G	x		x	
9	8.783	Nonane, 2-methyl	G			x	
10	8.792	Decane, 2-methyl	G	x			
11	8.867	1,2-ethanediamine, N-ethyl-N'-methyl-	A				x
12	9.000	1-Propanaminium, 3-carboxy-2-hydroxy-N,N,N,-trimethyl-,chloride	A				x
13	9.150	Benzene, 1,2-dimethoxy	H		x		
14	9.750	Phenol, 2,5-dimethyl	B			x	
15	11.275	2-Trifluoroacetoxydodecane	G	x	x		
16	11.592	Decane, 2-methyl-	G	x			
17	11.808	Benzene, 1,2-dimethoxy-4-methyl	H		x		
18	11.817	Cyclopentaneundecanoic acid	E			x	
19	13.292	Napthalene, 2-methyl	H			x	
20	14.058	Cyclononanone	C		x		
21	14.208	Pyrrolin-2-one-5-methanol-, N-methyl	A		x		
22	14.358	Octadecane	G	x	x		
23	14.367	Isooctane	G			x	
24	14.583	Undecanoic acid, 2-methyl-	E				x
25	15.342	Benzoic acid, 4-methoxy-, methyl ester	F		x		
26	15.542	Biphenyl	H				x
27	16.625	Napthalene, 1,7-dimethyl-	H				x
28	16.700	Napthalene, 1, 5- dimethyl	H			x	
29	17.050	Tridecane	G			x	
30	19.042	Benzoic acid, 4-hydroxy-3-methoxy, methyl ester	F		x		
31	19.333	2-Trifluoroacetoxydodecane	G	x	x		
32	19.608	Tridecane	G			x	
33	19.800	Dodecanoic acid, methyl ester	E			x	
34	20.042	Ethanone1- (dimethoxyphenyl)	C	x	x		
35	20.200	Napthalene	H			x	x
36	20.775	Benzoic acid,	C	x	x		
37	22.808	Ethanone	C	x	x		
38	23.817	Benzoic acid	C	x	x		
39	24.342	Undecane, 2, 10-dimethyl	G			x	
40	24.542	Methyl tetradecanoate	E			x	x
41	24.550	Tetradecanoic acid, 12-methyl-, methylester	E	x			
42	25.042	1-nonanol, 4,8-dimethyl	D	x	x		
43	25.275	2-Trifluoroacetoxydodecane	G				
44	26.325	1-Hexadecene	G				

Peak No.	RT	assignment	Group Code	Before heating	After heating 200 ^{o}C	After heating 300 ^{o}C	After heating 400 ^{o}C
45	26.542	Pentadecane	G			x	
46	28.242	7-Hexadecenoic acid	F				x
47	28.633	Oxirane	G			x	
48	28.450	2-Trifluoroacetoxydodecane	G	x			
49	28.842	Hexadecanoic, methyl ester	E	x	x	x	x
50	30.650	Eicosane	G			x	
51	32.558	Heptadecane	G			x	
52	32.750	Octadecanoic acid, methylester	E			x	
53	32.758	Tetradecanoic acid, 12-methyl-methyl ester	E		x		
54	32.158	10-Octadecenoic acid, methyl ester	E				x
55	32.750	Octadecanoic acid, methyl ester	E				x
56	34.000	Cyclopropaneoctanoic acid, 2	E	x			
	34.000	17-Octadecenoic	E		x		
57	34.242	2-Trifluoroacetoxypentadecane	G		x	x	x
58	34.392	Hexatriacontane	G			x	
59	34.775	Dodecanedioc acid, di methyl ester	E		x		
60	34.775	Undecanenoic dioic	E	x			
61	36.125	Cyclopropaneoctanoic acid, 2	E	x			
62	37.000	Linoleic acid	F	x	x		
63	39.692	Tetradecanoic acid, 12-methyl-	E	x	x		
64	42.783	Heptacosanoic acid	E	x	x		
65	42.783	Heptadecanoic, 10-methyl,-methyl ester	E			x	
66	45.658	Hexacosanoic acid	E			x	
67	45.658	Heptacosanoic acid	E	x			
68	45.683	Tetradecanoic acid, 12-methyl-	E		x		

Table.4.7. Pyrolysate of humic acid from burnt soil in Kereng (B2).

Peak No.	RT	Assignment	Group Code	Before heating	After heating 200 ^{o}C	After heating 300 ^{o}C	After heating 400 ^{o}C
1	5.400	Butanedioic acid, dimethyl ester	E	x			
2	5.625	Phenol	B		x	x	
3	5.825	7-tetradecene	G			x	
4	5.833	cyclopropane	G		x		
5	6.208	Butanedioic acid, dimethylester	E		x		
6	7.142	Butanedioic acid, methyl-, dimethylester	E		x		
7	7.692	Methylamine, N, N-dimethyl	A		x		
8	7.983	E-11.13-tetradecadien-1-ol	D				
9	8.242	2-propanamine	A				x
10	8.408	2-propanamine	A				x
11	8.450	E-11.13-tetradecadien-1-ol	D		x		
12	8.767	Pentanal	C			x	
13	8.958	Ethamine, 2-(3,6-dimethylphenoxy)-N-methyl	A			x	
14	8.958	Ethamine, 2-(3,6-dimethylphenoxy)-N-methyl	A			x	
15	8.967	Ethamine, 2-(3,6-dimethylphenoxy)-N-methyl	A			x	
16	9.108	Ethamine, 2-(3,6-dimethylphenoxy)-N-methyl	A			x	
17	9.233	Ethamine, 2-(3,6-dimethylphenoxy)-N-methyl	A			x	
18	10.175	2-Butamine,(S)	A				x
19	10.208	azulene	G			x	
20	11.042	2-tridecene	G	x			
21	11.258	2-tridecene	G		x		
22	11.258	N’-Isopropylureidoacetic acid	A			x	
23	13.525	Pentanal	C				x
24	13.950	3-trifluoroacetoxypentadecane	G	x			
25	14.042	2-heptanamine, 5-methyl-	A			x	
26	14.050	2-Tridecene	C		x		
27	14.092	3-trifluoroacetoxypentadecane	G	x			
28	14.342	Tridecene	G		x		
29	15.267	Benzoic acid, 4-methoxy, methylester	B	x			
30	15.342	Benzoic acid, 4-methoxy, methylester	B		x		
31	16.200	Benzene, 1,3,5-trimethoxy	H	x			
32	16.750	Benzene, 1,3,5-trimethoxy	H		x		
33	16.683	pentanal	C				x
34	16.700	1-Hexadecene	G	x			
35	16.750	1-Hexadecene	G		x		
36	16.883	Methyl 3-methoxy-4-methylbenzoate	F	x			
37	17.033	Pentanal	C			x	
38	19.008	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	B	x			
39	19.017	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	B		x		
40	19.300	1-Hexadecene	G	X			

Peak No.	RT	Assignment	Group Code	Before heating	After heating 200 ^oC	After heating 300 ^oC	After heating 400 ^oC
41	19.325	1-Hexadecene	G		x		
42	19.800	Dodecanoic acid, methylester	E		x		
43	20.000	3’,5’-dimethoxyacetophenone	C	x			
44	20.458	Benzoic acid, 3, 5-dimethoxy, methylester	B	x			
45	20.475	Benzoic acid, 3,5-dimethoxy-, methyl ester	B		x		
46	20.742	Benzoic acid, 3, 4-dimethoxy, methylester	B	x			
47	20.758	Benzoic acid, 3, 5-dimethoxy-,methylester	B		x		
48	21.767	1-Hexadecene	G	x			
49	21.775	1-Hexadecene	G		x		
50	23.783	Benzoic acid, 3,4,5-trimethoxy-, methyl ester	B	x			
51	23.792	Benzoic acid, 3,4,5-trimethoxy-, methyl ester	B		x		
52	24.100	1-Hexadecene	G	x			
53	26.533	Undecane, 2,10-dimethyl	G		x		
54	26.533	Eicosane	G	x			
55	27.142	2-undecanone, 6,10-dimethyl	C	x			
56	28.433	E-14-Hexadecenal	C	x			
57	28.433	Trifluoroacetic acid, n-heptadecyl ester	E		x		
58	28.633	nonadecane	G		x		
59	28.633	2-hexy-1-octanol	D	x			
60	28.833	Hexadecanoic acid, methylester	E	x	x		
61	28.842	Hexadecanoic acid, methylester	E				x
62	30.450	Cyclooctadecane, ethyl	G	x	x		
63	30.642	2-Hexyl-1-octanol	D	x			
64	30.642	Heptadecane, 9-hexyl	G		x		
65	32.558	Hexadecane	G		x		
66	32.750	Octadecanoic acid, methyl ester	E		x		
67	32.767	Heptadecanoic acid, 9-methyl-,methylester	E				x
68	34.233	E-15-Heptadecenal	C	x			
69	34.233	Trifluoroacetic acid, n-octadecyl	E		x		
70	34.408	Docosane, 5-butyl-	G		x		
71	34.600	Nonadecanoic acid, methylester				x	
72	34.608	Nonadecanoic acid, methylester					x
73	34.617	Nonadecanoic acid, methylester		x			
74	36.008	E-15-Heptadecenal	C	x			
75	36.158	Heptadecane, 2,6,14 ,20-tetramethyl	G		x		
76	36.167	Hexatriacontane	G	x			
77	37.708	Trifluaroacetic acid, n-octadecyl ester	E		x		
78	39.358	E-15-Heptadecenal	C	x			
79	39.483	Eicosane, 10-methyl-	G	x			
80	39.558	9-octadecenoic acid (z)-, methyl ester	F	x			

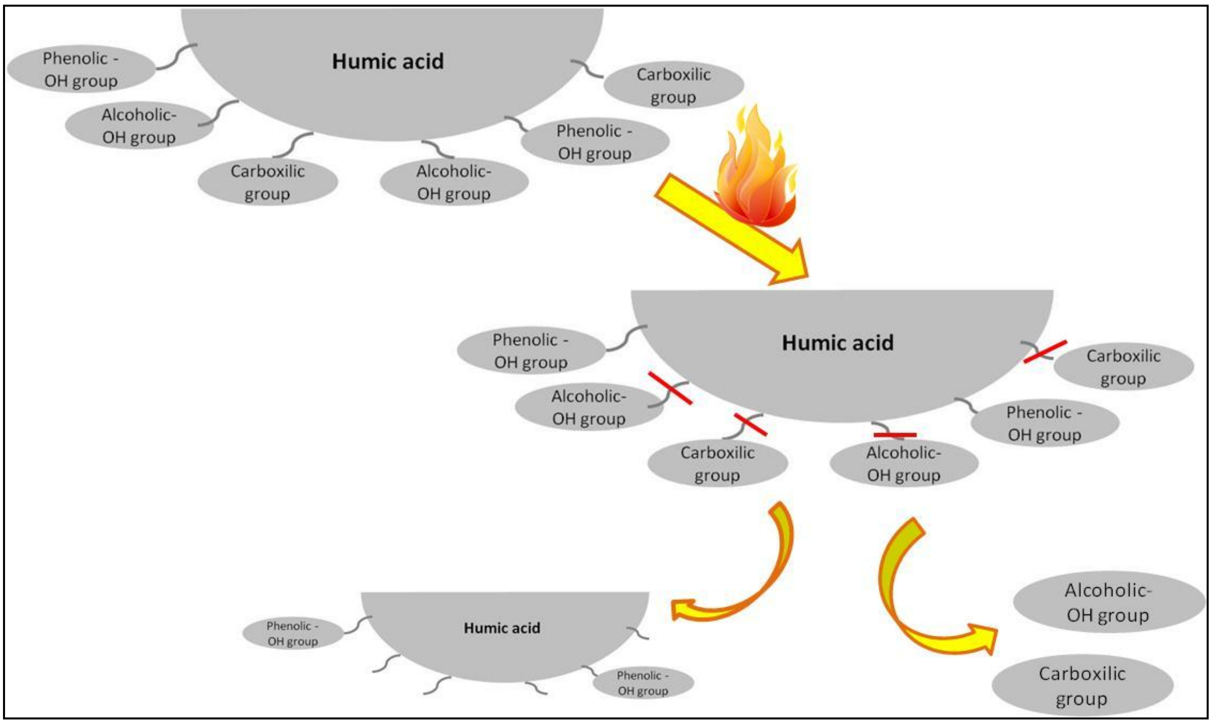


Fig. 5.1. Effect of peat fires to the characteristic of humic substances in soil.

4.4. Conclusion

The present study provided the information concerning the molecular and structural change in humic acid affected by peat fire. The impacts of fire to peat soil or humic acid can vary depending on several factors such as characteristics of soil, environmental condition and vegetation types. Humic acids extracted from Central Kalimantan have low molecular weight relatively and contained more aliphatic structures such as carboxylic and fatty acid. Base on H/C and O/C values, it indicated humic acid from burnt sites in Central Kalimantan had affected by fire, whereas the values of H/C and O/C were closed to those of HAs heated at 200 ^{o}C. Peat fire or heating process induced the release of the functional group containing oxygen in humic acid such as carboxylic groups as illustrated in Fig. 4.11. Other than that, fire or heating also increased the aromaticity of humic acid and degraded the humic acid molecule that was observed by decreasing the molecular weight of humic acid. From pyr-

GC/MS data, the composition of HA from burnt site was dominated with phenolic compounds, fatty acid and benzene derivatives. These structural changes in humic acid consequently will decrease the ability of humic acid to make binding with metal ions, destroy the crumb structure and decrease water holder capacity of soil, furthermore it will reduce the soil fertility and cause the environment damages.

References

Almendros G, Martin F and Gonzalez-Vila F.J (1988), Effect of fire on humic and lipid fraction in a Distric Xerochrept in Spain. Geoderma 42: 115-127.

Almendros G, Gonzalez-Vila FJ and Martin F (1990), Fire Induced Transformation of soil organic matter from an Oak Forest: an experimental approach to the effects of fire on humic substances. Soil Science 149 No.3:158-168.

Asakawa D, Kiyota T, Yanagi Y and Fujitake N (2008), Optimization of condition for high-performance size-exclusion chromatography of different soil humic acid. Analytical Sciences 24: 607-613.

Birdwell JE and Engel AS (2010), Characterization of dissolved organic matter in cave and spring waters using UV-Vis absorbance and fluorescence spectroscopy. Organic Geochemistry 41:270- 280.

Certini G (2005), Effect of fire on properties of forest soil: a review. Oecologia 143: 1-10.

Coble PG (1996), Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51:325-346.

Conte P, Piccolo A (1999), High pressure size exclusion chromatography (HPSEC) of humic substances: Molecular sizes, analytical parameters, and column performance. Chemosphere 38 No.3: 517-528.

De la Rosa JM, Gonzalez-Perez JA, Gonzalez-Vazquez R, Knicker H, Lopez-Capel E, Manning DAC and Gonzalez-Vila FJ (2008), Use of pyrolysis/GC-MS combined with thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest. Catena 74: 296-303.

Fernandez I, Cabaneiro A and Carballas A (1997), Organic matter changes immediately after a wildfire in an atlantic forest soil and comparison with laboratory soil heating. Soil Biology & Biochemistry 29, No 1: 1-11.

Fong SS and Mohamed M (2007), Chemical characterization of humic substances occuring in the peats of Sarawak, Malaysia. Organic geochemistry 38: 967- 976.

Francioso O, Montecchio D, Gioacchini, Claudio C (2005), Thermal analysis (TG-DTA) and isotopic characterization (13C-15N) of humic acids from different origins. Applied Geochemistry 20: 537-544.

Francioso O, Montecchio D, Gioacchini P, Cavani L, Ciavatta C, Trubetskoj O, Trubetskaya O (2009), Structural differences of Chernozem soil humic acids SEC-PAGE fractions revealed by thermal (TG-DTA) and spectroscopic (DRIFT) analyses. Geoderma 152: 264-268.

Fujitake N, Kodama H, Nagao S, Tsuda K and Yonebayashi K (2009), Chemical properties of aquatic fulvic acids isolated from Lake Biwa, a clear water system in Japan. Humic Substances Research vol.5/6.

Fukushima M, Yamamoto M, Komai T and Yamamoto K (2009), Studies of structural alterations of humic acids from conifer bark residue during composting by pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide (TMAH-py-GC/MS). Journal of Analytical and applied Pyrolysis 86: 200-206.

Fukushima M, Furubayashi K, Fujisawa N, Takeuchi M, Komai T, Otsuka K, Yamamoto M, Kawabe Y, Horiya S (2011), Characterization of humic acid in sediments from dam reservoirs by pyrolysis-gas chromatography/ mass spectrometry using tetramethylammonium hydraxide: Influence of the structural features of humic acid on iron (II) binding capacity. Journal of Analytical and Applied Pyrolysis 91: 323-331.

Gaffney JS, Nancy AM and Sue BC (1996), Humic and fulvic acids and organic colloidal material in the environment. In: Humic and fulvic acids; isolation, structuture and environmental role. Gaffney, J.S; N.A. Marley; S.B. Clark. Eds. American Chemical Society, Washinton, DC.

Gonzales-Perez JA, Gonzalez-Vila FJ, Almendros G and Knicker H (2004), The effect of fire on soil organic matter-a review. Environmental International 30: 855-870.

Gonzales-Perez JA, Gonzalez-Vila FJ, Gonzalez-Vazquez R, Arias ME, Rodriguez J, and Knicker H (2008), Use of multiple biogeochemical parameters to monitor the recovery of soil after fires. Organic Geochemistry 39: 940-944.

Gonzales-Vila FJ, Ludemann HD, Martin F (1982), 13C-NMR structural peatures if soil humic acids and their methylated, hydrolyzed and extracted derivates. Geoderma 31: 3-15.

Jaenicke J, Rieley JO, Mott C, Kimman P and Siegert F (2008), Determination of the amount of carbon stored in Indonesian peatlands. Geoderma 147: 151-158.

Kiersch K, Kruse J, Eckhardt K, Fendt A, Streibel T, Zimmermann R, Broll G and Leinweber P (2012), Impact of grassland burning on soil organic matter as revealed by a synchroton- and pyrolysis-mass spectrometry-based multi-methodological approuch. Organic Geochemistry 44: 8-20.

Lu XQ, Hanna JV and Johnson WD (2001), Evidence of chemical pathways of humification: a study of aquatic humic substances heated at various temperatures. Chemical Geology 177: 249-264.

Marcos E, Tarrega R, Luis E (2007), Changes in humic cambisol heated (100-500 ^{o}C) under laboratory condition: The significance of heating time. Geoderma 138: 237-243.

Matthew BJH, Jones AC, Theodorou NK and Tudhope AW (1996), Excitation-emission-matrix fluorescence spectroscopy applied to humic bands coral reefs. Marine Chemistry 55: 317-332.

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kule T, Andersen DT (2001), Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanography 46: 38-48

Page S, Wust R and Banks C (2010), Past and present carbon accumulation and loss in Southeat Asian peatlands. PAGES News 18 No.1: 25-27.

Picolo A (2001), The supramolecular structure of humic substances. Soil Sience 166, 11: 810-832

Pietikainen J, Hiukka R and Fritze H (2000), Does short-term heating of forest humus change its properties as a substrate for microbes?. Soil biology & Biochemistry 32: 277-288.

Prieto-Fernandez A, Carballas M and Carballas T (2004), Inorganic and organic N pools in soils burned or heated: immediate alterations and evolution after forest wildfires. Geoderma 121: 291-306.

Richard C, Trubetskaya O, Trubetskoj O, Reznikova O, Afanas’eva G, Aguer JP, and Guyot G (2004), Key role of the low molecular size fraction of soil humic acids for fluorescence and photoinductive activity. Environ. Sci. Technol 38: 2052-2057.

Sazawa K, Tachi M, Wakimoto T, Kawakami T, Hata N, Taguchi S, Kuramitz H (2011), The evaluation for alteration od DOM component from upstream to downstream flow of rivers in Toyama (Japan) using Three-Dimentional Excitation-Emission Matrix Fluorescence Spectroscopy. Int.J.Environ. Res. Public Health 8: 1655-1670.

Sazawa K, Wakimoto T, Hata N, Taguchi S, Tanaka S, Tafu M, Kuramitz H (2013), The evaluation of forest fire severity and effect on soil organic matter based on the *L**, *a**, *b** color reading system. Anal.Methods 5: 2660-2665.

Schnitzer M and Hoffman I (1965), Thermogravimetry of soil humic compounds. Geochimica et Cosmochimica Acta, Vol 29: 859-870

Schnitzer M and Khan SU (1972), Humic substances in the environment. Marcel dekker, Inc. USA. pp 323.

Siegert F, Boehm HDV, Rieley JO, Page SE, Jauhiainen J, Vasander H, Jaya A (2001), Peat fires in Central Kalimantan, Indonesia: Fire impacts and carbon release. Proceeding of International Symposium on Tropical Peatland, 22-23 August 2001, Jakarta, Indonesia.

Siegert F, Zhukov B, Oertel D, Limin S, Page SE and Rieley JO (2004), Peat fires detected by the BIRD satellite. International Journal of Remote Sensing, 25,16 : 3221-3230.

Stevenson FJ (1994), Humus Chemistry: genesis, composition, reaction. 2nd edition. John Wiley & Sons, Inc. USA.

Tan KH (2003), Humic Matter in Soil and Environment. Principles and Controversies. Marcel Dekker, Inc. USA. page 292.

Tanaka F, Fukushima M, Kikuchi A, Yabuta H, Ichikawa H, Tatsumi K (2005), Influence of chemical characteristics of humic substances on the partition coefficient of a chlorinated dioxin. Chemosphere 58: 1319-1326).

Van Krevelen DW (1950), Graphical-statistical method for the study of structure and reaction processes of coal. Fuel 20: 269-284.

Vergnoux A, Guliano M, Di Rocco R, Domeizel M, Theraulaz F, Doumenq P (2011), Quantitative and mid-infrared changes of humic substances from burned soils. Environmental Research 111: 205-2014.

Yonebayashi K and Hattori T (1998), Chemical and biological studies on environmental humic acids: I. Composition of elemental and functional groups of humic acid. Soil Sci. Plant Nutr. 34 (4): 571-584.

Yulianti N, Hayasaka H and Usup A (2012), Recent forest and peat fire trends in Indonesia, The latest decade by MODIS Hotspot data. Global Environmental Research 16: 105-116.

Zhou Q, Cabaniss SE, Maurice PA (2000), Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weight of aquatic humic substances. Water Research 34 No.14: 3505-3514.

CHAPTER 5

General Conclusion

The present study described the effect of peat fires to the soil and aquatic environments through the changes of chemical properties of humic substances in soil and water in peat area of Central Kalimantan, Indonesia. This chapter is to conclude the results that have been presented in the earlier chapters. The alteration of the water quality of samples and the properties of humic substances and humic properties between soil and water which were collected from water and soil at the unburnt sites and burnt sites were evaluated to reveal the effect of peat fire on these environments.

This study has been conducted in peatland areas in Central Kalimantan that included the Sebangau River, Canal Kalampangan, peat swamp forest in Sebangau National Park and Mega Rice Project area. Those areas have a connectivity one and others, therefore it is important to investigate the effect of peat fire on the whole environment, which has received directly the impact like peat soil in Mega Rice Project area, and also which has received indirectly the impact like canal water. Peat swamp forest of Sebangau National Park and the Sebangau River are considered as a representative standard to detect the effect of fire on peat soil and aquatic environment.

Because the Sebangau River and Canal water are located in peatland area, these rivers have the specific water quality such as low pH, low DO and high concentration of DOC. During my sampling period from 2009 to 2012, the water quality of the Sebangau River did not change significantly. Seasonal changes of dry and rainy seasons also did not influence the water quality of the river water, except DOC. The pattern of DOC fluctuation of the Sebangau River from 2009 to 2012 was quite similar to the pattern of precipitation data in that area.

The canal is an artificial river that was constructed to support paddy field. There was no significant difference in the water qualities between the Sebangau River and the canal water. However, the water quality of canal depended largely on the condition of each sampling site. Several small dams were constructed along the canal, and the water level of the area interposed with the dams was low in the dry season, and the water could not flow by being blocked by the dam. Under this condition, the water quality in each sampling site was influenced by the vegetation and ecosystem in the water and catchment areas around the sampling points. Furthermore, degraded peat soil as the result of peat fires cannot retain much water inside.

Major components which compose DOC in river water are humic substances including humic acid and fulvic acid. Therefore, these compounds are important indicators to reveal the change of water quality in river water in peatland area. In this study, the characteristics of humic acid and fulvic acid from the Sebangau River and Canal water were also investigated. Elemental compositions (C,H, N,O) of humic acid and fulvic acid between unburnt and burnt sites did not show the significant difference. However, the molecular weight (MW) of humic acid and fulvic acid from Sebangau River and Canal water showed the difference clearly. The MW of humic acid and fulvic acid extracted from the canal water was lower than from the Sebangau River. It indicated the degradation of humic substances occurred around the canal. 3-DEEM data suggested that humic acid from canal contained more phenolic compound as the result of degradation.

The effect of peat fire to the soil was investigated through the characterization of humic acids extracted from unburnt sites (Sebangau peat swamp forest and forest near MRP area) and from burnt sites (deforest soil in MRP area and burnt soil in Kereng. The structure and chemical characteristics in humic acid from the burnt sites have been changed by burning process. On the basis of analysis of elemental composition and H/C and O/C values, molecular weight, composition of functional groups, 3-DEEM fluorometry data, GC/MS-Pyr data of humic acid, it was indicated that peat fires have degraded humic acid in the structure and composition and then formed lower molecular weight compounds which are more aromatic. These degraded compounds would contain like poly aromatic hydrocarbons, the effects on the environments and living organisms in water and soil, furthermore human being, are threatened.

As the results of this study, it could be illustrated in Figure 5.1. Peat fires had degraded humic substances in soil whereas the oxygen containing in functional groups of humic substances such as carboxyl and hydroxyl was released, and then the aromaticity increased. Releasing of carboxyl from humic substances will be decreasing the ability of humic substances to make binding with metal ions. The decreasing of the molecular weight of humic substances, it supposed to destruct the crumb structure of humic substances, and then it will reduce the soil fertility. The degraded humic substances in peat soil will be eluted to the aquatic environment by rain fall as dissolved organic matter. Therefore, when peat fires happened in peatland, carbon loss not only released to the atmosphere, it also will release to the aquatic environment. Continuous measurement of water quality in canal and river should be implemented to investigate the impact of peat fires to aquatic environment more accurately. Conservation of peatland area in Central Kalimantan should be implemented to avoid the global and local environmental damage in the future.