Chemical and spectroscopy of peat from West and Central Kalimantan, Indonesia in relation to peat properties

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Abstract— *Improving peat soil is difficult but not impossible. Managed correctly, peat can be a highly productive medium for agriculture, but drainage and cultivation can lead to irreversible peat shrinkage. Vegetational changes during the restoration of cutover peatlands leave a legacy in terms of the organic matter quality of the newly formed peat. Current efforts to restore peatlands at a large scale therefore require low cost and high throughput techniques to monitor the evolution of organic matter. In this study, we assessed the merits of using Fourier transform infrared (FTIR) spectra to predict the organic matter composition in peat samples in relation with soil peat properties, tends to to be hydrophobic, flammable.*

Keywords— chemical properties, FT-IR spectroscopy, peat, West and Central Kalimantan.

I. INTRODUCTION

Reclamation of peat requires knowledge of different properties, including those that put emphasis on the nature of the peatswamps rather than the peat material itself. Peat is derived from the remains of plants and animals and peatland occurs normally in flooded areas, such as tidal swamp, flat areas and leeves. Under these condition the populatin of aerobic microorganisms drop drastically and only anaerobic microorganism are able to survive in large numbers. Peatlands in Indonesia cover an area of appoximately 27 million hectares mostly in Sumatra, Kalimantan, and Irian Jaya (Radjagukguk, 1992). Most of this peatland is ombrogenous while topogenous peat only occurs in isolated locations. In Central Kalimantan, peat varies greatly in thickness and covers an area of 18,615 km^2 or 18.14% of the total area (153,660 km^2) (Hanudin and Rusmarkam, 2001). West Kalimantan reviewed in terms of the distribution of peat area is approximately 1.73 million hectares (8.49% of the peat bogs area in Indonesia), compared to the extent of West Kalimantan province of around 14.680.700 ha land area, means that the area of peat 11,79 %t of West Kalimantan areas (Noor and Heyde, 2007)

In their natural state peat bogs are saturated with water. One of the first steps in agricultural development is to drain the bog. Ditches and subsurface drains are used to enhance the movement of water from the peat, thereby lowering the water table and aerating the peat soil. Aeration of the soil is necessary for plant growth, aerobic microbial processes, and to ease the operation of farm machinery. Before vegetable production can begin, the peat soil must also have its pH and fertility adjusted. The drainage, liming, fertilization and tillage required for vegetable production radically alter the physical, chemical, and biological properties of the peat. Under vegetable production the growth and accumulation of peat stops and decomposition is accelerated. On peat soils, nutrient management is complicated by the soil's naturally low fertility, high carbon content, and very acid pH. Poor nutrient management can result in crop failure or make the cost of producing a good crop economically unsustainable.

For soil improvement, identifying the problems associated with peat soils is necessary. This can reduce the life of the peat soil – shrinkage can continue until there is no peat left – and compromise the status of adjacent peat lakes and wetlands. For peat farming to be successful and profitable in the long term, farmers must find a balance between maintaining the water table at levels low enough to optimize production, yet high enough to minimize shrinkage and the impact on adjacent wetlands and peat lakes. Current efforts to restore peatlands at a large scale therefore require low cost and high throughput techniques to monitor the evolution of organic matter. Methods to analyze SOM composition include FT-IR or nuclear magnetic resonance (NMR) spectroscopy. In FT-IR spectra, absorption bands at distinct wave numbers indicate the presence of functional groups with known chemical compositions and properties. The intensity of the aliphatic (CH) absorption band in DRIFT and FT-IR spectra was used to estimate the hydrophobic character of soil samples (Capriel *et al.*, 1995; Capriel, 1997; Hsu and Lo, 1999; McKissock *et al*., 2003). The composition of SOM may, in addition to the SOM content, be used for studying quantitative effects of different management practices or even land use changes on soil properties. A detailed analysis of the SOM-composition (Ellerbrock et al., 1997) using Fourier Transform infrared (FT-IR) spectroscopy showed that the content of the carboxyl-and hydroxyl-groups in the SOM pyrophosphate extracts was higher in the plots fertilized with cattle manure than in those that received straw+mineral nitrogen.

II. MATERIALS AND METHODS

The characterization of peat include: ash content, pH H_2O, pH KCl, EC, cation exchange capacity, organic C, total N (Tan, 1996). Subsamples of solid peat for spectroscopic analyses were freeze-dried, milled very finely (0.25 mm) and analyzed by means of Fourier transform infrared (FTIR). Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 5 PC FTIR Spectrometer on KBr pellets obtained by pressing under vacuum uniformly prepared mixtures of 1 mg sample and 400 mg KBr (spectrometry grade) and kept under a N_2 atmosphere during spectra recording. Spectral characterization of peat samples was performed by diamond attenuated total reflectance FTIR spectroscopy using a Nicolet Magna-IR 550 FTIR spectrometer (Thermo Electron, Warwick, U.K.) fitted with a potassium bromide beam splitter and a deutroglycine sulphate detector. A Diamond Attenuated Total Reflectance (DATR) accessory, with a single reflectance system, was used to produce transmission-like spectra. The samples were dehydrated by freeze drying and powdered by ball milling with zirconium balls. Samples were placed directly on a DATR/KRS-5 crystal and a flat tip powder press was used to achieve even distribution and contact. Spectra were acquired by averaging 200 scans at 4 cm^{-1} resolution over the range 4000 – 350 cm^{-1}. A correction was made to spectra for the ATR to allow for differences in depth of beam penetration at different wavelengths (Omnic software, version 7.2, Thermo Electron). All spectra were also corrected for attenuation by water vapour and CO2. Minor differences in the amplitude and baseline between runs were corrected by normalization of the data by subtraction of the sample minimum followed by division by the average of all data points per sample (Artz et al, 2008).

III. RESULTS AND DISCUSSION

SPT1, SPT3 had soil water depth shallower than SPT4, while G1 and G2 had soil water depth shallower than G3 and G4. Peat samples from West Kalimantan (SPT1, SPT3 and SPT4) had more ash content than peat samples from Central Kalimantan. Peat samples from Central Kalimantan were higher in CEC than peat samples from West kalimantan due to the higher organic C content.

TABLE 1
PEAT PROPERTIES OF SAMPLES

Parameter	SPT 1	SPT 3	SPT4	G1	G2	G3	G4
Peat maturity	hemist	saprist	saprist	saprist	saprist	saprist	saprist
Sulfidic material depth	>100 cm	>52 cm	>100 cm	>100 cm	>100 cm	>100 cm	>100 cm
Soil water depth	41-60 cm	36-60 cm	65-72 cm	50 cm	50 cm	100 cm	120 cm
organicC (%)	43,85	38,51	29,74	57,10	57,30	57,30	57,50
Ash content (%)	7,91	11,09	16,13	1,44	1,69	1,93	1,35
CEC cmol(+)kg^{-1}	88,57	78,29	57,37	94,42	98,56	101,97	184,89
Soil Great group	Typic Haplohemist	Typic Sulfisaprist	Typic Haplosaprist	Typic Haplosaprist	Typic Haplosaprist	Typic Haplosaprist	Typic Haplosaprist

Sample characterization using FTIR spectroscopy concerned the correct assignment of the observed spectral characteristics to the most likely origin of the absorption bands. A summary of the most characteristic bands observed in peat and their assignment is presented in Table 2 (Artz et al, 2008). Generally, FTIR analysis on the peat horizon samples showed a decline of the main polysaccharide markers (absorption bands around 3400 and 1040 cm^{-1}) and relative increase of the main bands assigned to lignin-like (1513, 1450, 1371, 1265 and 835 cm^{-1}) and aliphatic structures (2920 and 2850 cm^{-1}) with depth, as expected with increasing humification.

TABLE 2
ASSIGNMENT OF THE PRINCIPAL DESCRIPTIVE IR ABSORPTION BANDS IN PEAT SAMPLES

Wavenumber, cm^1	assignment	Characterisation	References
3340	(O-H) stretching	Cellulose, in samples with defned 3340 peak	Cocozza et al., 2003
2920	Antisymmetric CH2	Fats, wax, lipids	Niemeyer et al., 1992, Cocozza et al., 2003
2850	Symmetric CH2	Fats, wax, lipids	Niemeyer et al., 1992, Cocozza et al., 2003
1720	C=O strech of COOH or COOR	Carboxylic acids, aromatic esters	Niemeyer et al., 1992, Haberhauer et al, 1998, Cocozza et al., 2003, Gondar et al., 2005
1710-1707	C=O strech of COOH	Free organic acids	Gondar et al., 2005
1653	C=O of amide I	Proteinaceous origin	Ibarra et al., 1996, Zaccheo et al., 2002
1650=1600	Aromatic C=C stretching and/or asymmetric C-O strech in COO-	Lignin and other aromatics, or aromatic or aliphatic carboxylates	Niemeyer et al., 1992, Cocozza et al., 2003
1550	N-H in plane (amideII)	Proteinaceous origin	Ibarra et al., 1996, Zaccheo et al., 2002
1515-1513	Aromatic C=C stretching	Lignin/phenolic backbone	Cocozza et al., 2003
1426	Symmetric C=O stretch from COO- or stretch and OH deformatio (COOH)	Carboxlylate/carboxylic structures (humic acids)	Parker, 1971
1450, 1371	C-H deformation	Phenolic (lignin) and aliphatic structures	Parker, 1971
1265	C-O strecching of phenolic OH and/or arylmethylethers	Indicative of lignin backbone	Niemeyer et al., 1992, Ibarra et al., 1996,
1080-1030	Combination of C-O stretching and O-H deformation	Polysaccharides	Grube et al., 2006
900	Out of phase ring stretching (ring breathing)	Cellulose, corresponding band to sharpened 3340 peak	Zaccheo et al., 2002
720	CH_2 wag	Long chain > C4 alkanes	Ibarra et al., 1996,
835	Aromatic CH out of plane	lignin	Zaccheo et al., 2002

The FTIR spectrum displayed a number of characteristic absorbance peaks. Fig. 1 shows the mean absorbance of all the peat samples from West Kalimantan. Well-resolved peaks are seen for carbohydrate or polysaccharide (1061 cm^{-1}), `carboxylate' ($RCOO^-$; 1630 cm^{-1}) and wax (strictly, aliphatic CH_2 and CH_3; 2800±3000 cm^{-1}) as well as the broad hydroxyl band (centred at 3340 cm^{-1}). This finding is similar with Chapman et al., 2000, Utami et al., 2009.

Despite the overall similarity of the spectra for each of the peat samples, subtle differences could be seen between samples from the three zones. Fig. 1 shows the difference spectra between the mean absorbances for the three zones. Particularly marked are the decrease in the carbohydrate (1063 cm^{-1}) and the increases in the `carboxylate' (1601 $cm^{-1}$) and carboxylic acid (1710 $cm^{-1}$) peaks in saprist samples (SP3 and SP4) compared to SPT 1 (hemist). Differences between the hemist and saprist were less distinct with less wax (2924 $cm^{-1}$) and `carboxylate' (1624 cm^{-1}) in the former.

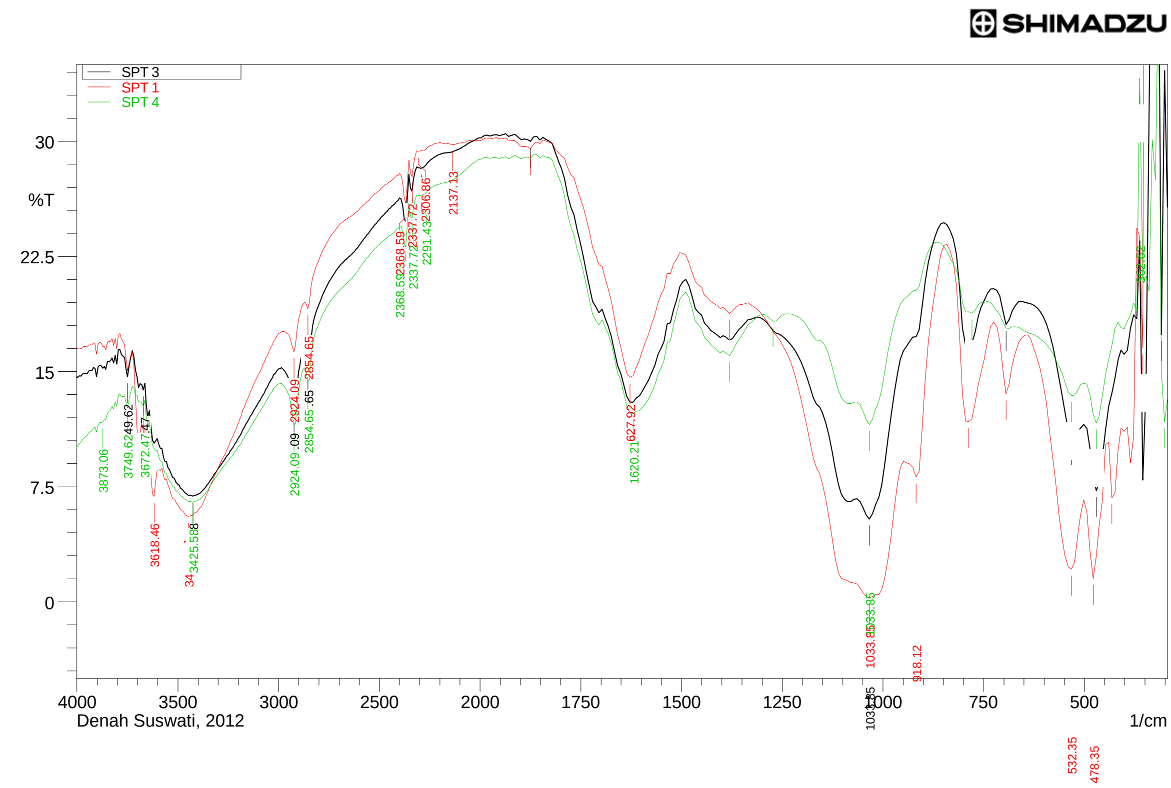

FIGURE 1: IR SPECTRA OF SPT1, SPT3 AND SPT4 OF PEAT SAMPLES FROM WEST KALIMANTAN

The relative absorbance of the band at 1630 cm-' (carboxylic and aromatic) slightly increased from the SPT4, SPT3 to SPT1. These observations can be explained by an increase of aromatic and carboxylic groups during litter degradation and are in general agreement with published NMR data of degradation of organic matter (Inbar et al., 1989). The slight decline of the relative absorbance of the band at 1630 cm^{-1} from SPT4 to SPT1 are due to the presence of inorganic materials, which leads to an increase of the band at 1050 cm^{-1} (Si-0 vibratitons) and influences all other relative absorbance values (relative absorbance = % of the sum of all selected peak heights). This is proven by the ash content of the three peat samples. SPT4 has highest ash content (16, 13%).

TABLE 3
THE IR SPECTRA OF PEAT SAMPLE FROM WEST KALIMANTAN

Wavenumber, cm^{-1}	SPT 1	SPT 3	SPT 4	Characterisation
3340	604,69	618,29	693,85	Cellulose
2920	75,48	90,41	94,26	Fats, wax, lipids
2850	285,14	306,863	321.15	Fats, wax, lipids
1650=1600	245,65	222,6	164,91	Lignin and other aromatics, or aromatic or aliphatic carboxylates
1450, 1371	108,2	57,61	70,26	Phenolic (lignin) and aliphatic structures
1265			39,55	Indicative of lignin backbone
1080-1030	511,08	186,87	148,02	Polysaccharides

From the point of view it can be seen that SPT1 (Typic Haplohemist) which has low ash content, less mature and less soil water holding capacity has less hydrophilic character of the SOM (mainly carboxyl and hydroxyl groups). This findings was supported by Inbar et al. (1989), Niemeyer et al. (1992), and Hempfling et al. (1987. They found differences between two woodland soils using FT-IR spectroscopy. They hypothesized that during litter decomposition, humification, and soil podzolization the content of cellulose and lignin in SOM decreases, whereas hemicellulose and protein fractions remain unchanged. The results of Ellerbrock et al. (1997) indicated that differences in crop yields may be explained by variations in the hydrophilic character of the SOM. The hydrophilic character organic substance depends on the composition (type and amount) of functional groups, mainly carboxyl and hydroxyl-groups (Autorenkollektiv, 1984) and may affect, e.g., the soil water storage capacity of the plough horizon.

3.1 Peat samples from Central Kalimantan

Generally, FTIR analysis on the peat horizon samples showed a decline of the main polysaccharide markers (absorption bands around 3400 and 1040 cm^{-1}) and relative increase of the main bands assigned to lignin-like (1513, 1450, 1371, 1265 and 835 cm^{-1}) and aliphatic structures (2920 and 203 2850 cm^{-1}) with the increase of water depth of peat samples, as expected with increasing humification (Berengbengkel4 and Berengbengkel3 have deeper water depth (100-120 m) than berengbengkel 1 and 2 (50 cm). Spectral bands indicative of 'carboxylates', which include contributions from vibrations of aromatic and aliphatic carboxylates ($R\text{-}COO^{-}$) and/or aromatic C=C structures also increased in relative terms with depth (1650-1600 and 1426 cm^{-1}).

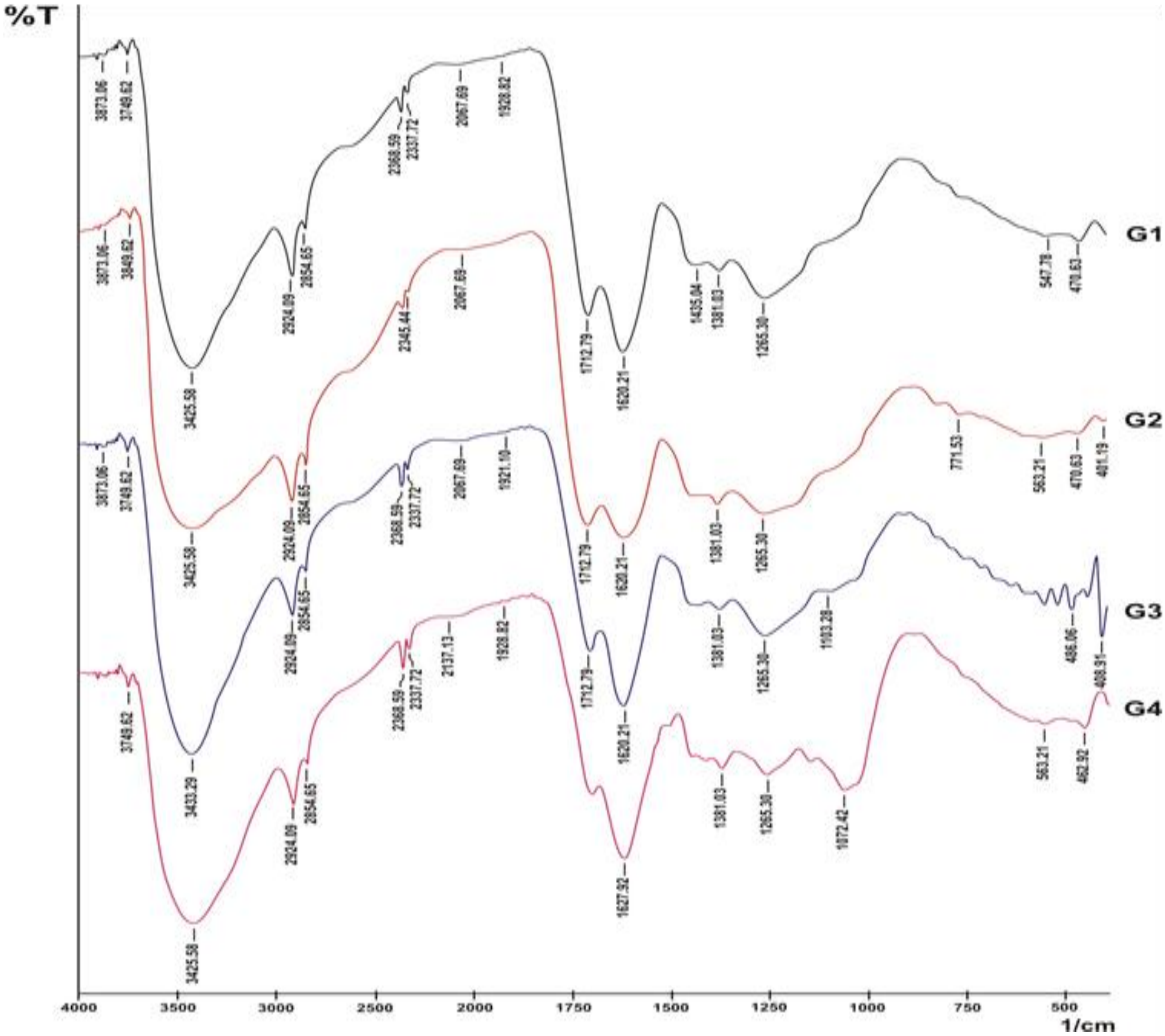

FIGURE 2. IR SPECTRA OF G1, G2, G3 AND G4 OF PEAT SAMPLES FROM CENTRAL KALIMANTAN

Peat samples from Berengbengkel3 and Berengbengkel4 had more hydrophobic fungsional group than Berengbengkel1 and Berengbengkel2. These areas had become hydrophobic due to mismanagement such as burning and draining and were then abandoned by farmers. In general, one may assume that the hydrophobicity of the soil organic matter is caused by methyl, methylene and methine groups present in aliphatic and aromatic (olefinic) compounds. The asymmetric and symmetric stretching vibrations of the aliphatic C-H bond in methyl, methylene and methine units typically absorb in the 3000-2800cm^{-1} IR region. The IR bands between 3000-3100 cm^{-1} result from aromatic and olefinic C-H stretching.

TABLE 4
THE IR SPECTRA FROM CENTRAL KALIMANTAN

Wavenumber, cm^{-1}	Berengbengkel1	Berengbengkel2	Berengbeng kel3	Berengbengkel4	Characterisation
3340	727	641,31	81,9	480,46	Cellulose
2920	145,62	139,86	170,23	212,15	Fats, wax, lipids
2850	331,82	272,09	320,59	300,5	Fats, wax, lipids
1650-1600	189,67	173,65	94,84	86,17	Lignin and other aromatics, or aromatic or aliphatic carboxylates
1450, 1371	64,59	158,53	99,9	140,35	Phenolic (lignin) and aliphatic structures
1265	263,68	130,55	64,1	123,83	Indicative of lignin backbone
1080-1030	338,71	188,12	154,77	227,61	Polysaccharides

Berengbengkel 1 and 2 are pristine peat, while Berengbengkel3 and Berengbengkel4 has been neglected thus become hydrophobic. Conditions reflected by the more hydrophobic area at least a representation of cellulose. While the content of fats, waxes and lipids increased.

Peat is characterized by colloidal behavior and irreversible loss of wettability produced by drying. Long-term cultivation and agricultural use of peatlands and their exploitation have revealed a number of effects including lowering of the water table, increased aeration, changes in plant communities, and release of carbon content. These processes show the disturbance of the thermodynamic balance in peat. Decline in peat soil moisture content resulting from drainage leads to shrinkage of peat. Change of volume due to shrinkage is the result of several forces acting at micro-scale, and its mechanism and magnitude differ from that in mineral (clay) soils. It was showed that drainage in particular results in a sharp change of biotic and abiotic conversions and consequent degradation of peat organic matter (Lüttig, 1986, Szajdak & Szatlylowicz, 2010).

In general, drainage of peat leads to progressive differentiation of hydrophobic peptides and total amino acid contents in organic matter. In proteins of peat, hydrophobic contacts exist between hydrophobic structural elements (between the side chains of the radicals of phenylalanine, leucine, isoleucine, valine, proline, methionine, and tryptophan). Hydrophobic forces stabilize the tertiary structure of proteins and determine the properties of lipids and biological membranes. The presence of amino acids, hydrocarbon chains, and other nonpolar fragments in their composition is related to the hydrophobic properties of humic substances (Sokołowska et al., 2005). Organic matter constitutes the major part of the soil phase of peat and moors and causes soil water repellency. The hydrophobicity of soil organic matter is essentially caused by aliphatic C-H units present in methyl, methylene and methine groups. Capriel *et al.* (1995) defined hydrophobicity index (HI) as the area of the aliphatic C-H infrared band in the 3000–2800 cm^{-1} region divided by organic C.

TABLE 5
ALIPHATIC C, C-ORG AND ALIPHATIC C-TO C-ORG OF PEAT TREATMENTS

Peat samples	Aliphatic C (% area)	C-org (%)	Aliphatic C-to C-org/hydrophobicity index
SPT1	360.62/4000	43.85	8.2
SPT3	397.27	38.51	10.3
SPT4	415.41	29.74	16
Berengbengkel1	477.44	57.10	8.3
Berengbengkel2	411.95	57.30	7.1
Berengbengkel3	490.82	57.30	8.5
Berengbengkel4	512.65	57.50	8.9

SPT3 and berengbengkel4 had higher hydrophobic index. SPT4 was peat samples which had soil water depth deeper than the other peatsamples form Pontianak, West Kalimantan. Berengbengkel4 also had soil water depth deeper than other peatsamples from Berengbengkel, Central kalimantan. The deeper soil water depth tends to result in hydrophobic peatsamples. Most aliphatic compounds are flammable. Dry peat becomes flammable. Therefore, maintenance of soil water depth is very important to keep the moisture of peat.

This finding was similar with Hribljan' finding (2012). Hribljan who studied about the effect of longterm water table manupulations on vegetation, pore water, substrate quality and carbon cycling reported that vegetation in both the raised and lowered water table treatments has different community structure, biomass, and productivity dynamics compared to the intermediate site. Peat substrate quality exhibited differences in chemical composition and lability across the water table treatments. Correlation scores of predominant soil chemical groups agreed with constituent concentrations apparent in the spectra graphs. Most pronounced associations were elevated polysaccharides in hummocks and elevated lignin, phenolics, and proteins in the lawns. Cellulose was most strongly correlated with hummocks in the raised WT treatment. Fats, lipids, and waxes were most abundant in the lawns of the lowered WT treatment and in high concentrations in the intermediate lawns. Long carbon chain alkanes strongly correlated with hummocks across the WT treatments and were most pronounced in the raised WT treatments.

IV. CONCLUSION

1. Peat samples from Central Kalimantan and West Kalimantan with deeper water table had higher aromatic percentage and the absorpsion area width of aromatic characterizing groups.
2. The depth of water table affects the properties of peat. The deeper groundwater peat tends to be hydrophobic, flammable.
3. There must find a balance between maintaining the water table at levels low enough to optimize production, yet high enough to minimize shrinkage and the impact on adjacent wetlands and peat lakes

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