

Cupric Oxide Oxidation Products of Tropical Peat Soils

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Cupric oxide oxidation was used in order to examine the composition of lignin-derived phenolic compounds and to estimate the degree of lignin alteration of tropical peat soils. Kaila's pyrophosphate index (PPI) was used to assess the degree of decomposition of peat soils. Tropical peat soil samples were collected from soil profiles in three areas of Indonesia including of 11 sites, located in reclaimed / cultivated areas and under forest stands. Oxidation of these samples produced vanillyl and syringyl phenols as major components while cinnamyl phenol as a minor component. Phenolic aldehydes almost always predominated, followed by phenolic acids. High correlations between the yield of the oxidation products and PPI suggested that lignin-derived oxidation products could be used to describe the alteration of lignin in tropical peat soils. Based on the samples studied, two groups of lignin alteration with depth were recognized, which could be best described by acid to aldehyde ratios. The first group was observed in inland peat soils associated with a relatively more anaerobic history of alteration in the lower layers and the second group in marginal peat soils. The pattern of lignin alteration with depth also revealed that reclamation / cultivation mostly affected the surface layers to a depth of about 40 cm.

Key Words: CuO oxidation, decomposition, lignin alteration, phenolic compounds, tropical peat soils.

Peat soil is primarily composed of a complex mixture of both vascular and nonvascular plant residues in different states of decomposition. Due to the natural anaerobic environment of peatland, organic matter composition of peat soil hardly changes with time, and, therefore, information on the past peatland environment throughout the duration of peat accumulation can be obtained. When the natural anaerobic environment of peatland changes or no longer prevails, naturally or artificially, decay of peat materials will, however, proceed and result in changes in the organic matter composition.

Lignin is one of the most abundant biopolymers in vascular plants and the most resistant to microbial degradation (Hedges et al. 1985). In organic matter decomposition on a long-term basis, the lignin content has been found to be the major regulating factor (Keenan et al. 1996). Compared to cellulose and other organic matter constituents, lignin decomposes slowly and represents a recalcitrant fraction in soil and litter (Guggenberger et al. 1995). However, lignin is known to be very sensitive to oxidation (Chang and Allan 1971), and hence mere exposure to more aerobic environment dur-

ing a prolonged period of time may cause structural changes in lignin within the organic materials.

Lignin structure (Chen 1991) is composed of phenolic and etherified units, with the phenolic unit being the reactive part. Since lignin in plants is closely associated with polysaccharides, its isolation is very difficult and the content of lignin is usually determined by proximate analysis (Ryan et al. 1990) as an acid-insoluble residue called Klason lignin. Nevertheless, proximate fractions do not correspond to specific chemical entities, and the acid-insoluble residues are likely to contain components other than lignin (Kögel 1986), leading to the over-estimation of the lignin content. Furthermore, this technique offers little insight into the subtle changes that occur in lignin among plant types and during degradation, even though conspicuous differences have been demonstrated (Johansson et al. 1986). No method enabling to isolate lignin in a high yield, as it actually occurs in organic materials is available (Johansson et al. 1986). However, a specific method is commonly used for the characterization of lignin at the molecular level, i.e. oxidation with alkaline CuO (Kögel-Knabner 1995).

Although it was assumed that lignin and its phenolic compounds are abundant in tropical peats (Driessen and Suhardjo 1976), few chemical studies of tropical peats have been conducted in relation to this organic component. Since the lignin polymer might be significant in tropical peats and may in part control the decomposition rate of peat materials, it might be interesting to apply the CuO oxidation method to analyze the decomposition dynamics of tropical peat soils. The objectives of this study were (1) to examine the composition of lignin-derived phenolic compounds, and (2) to estimate the degree of lignin alteration of tropical peat soils, based on the CuO oxidation products.

MATERIALS AND METHODS

Peat soil samples. The samples were collected from tropical peat soil profiles in three areas in Indonesia including 11 sites (Fig. 1) located at Air Sugihan (AS-1, AS-2, AS-3, and AS-4) in South Sumatra, Rupert Island (RP-1, RP-2, and RP-3) in the Malacca Strait, and Garung (GR-1 and GR-2), Lamunti (LAM), and Setia Alam Jaya (SAJ) in Central Kalimantan. The sampling profiles are described in Table 1. Air Sugihan peatland has been reclaimed and used for agriculture and transmigration settlement since 1982. However, AS-3

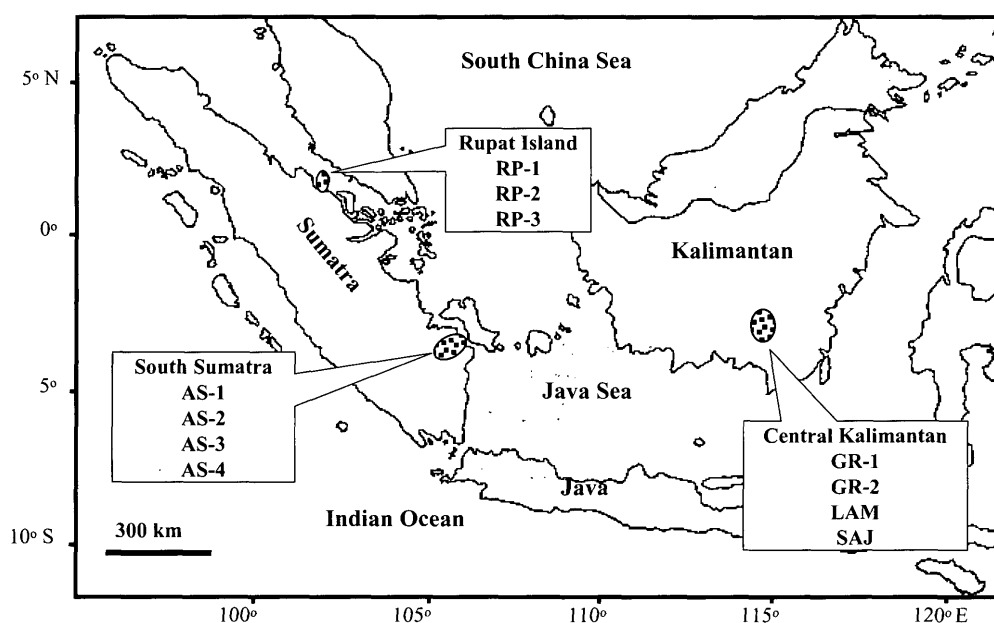


Fig. 1. Location of study sites in South Sumatra, Rupert Island, and Central Kalimantan, Indonesia.

Table 1. Average^a values of total organic carbon content, total nitrogen content, carbon to nitrogen ratio, ash content, and pyrophosphate index (PPI) in each profile.

Profile	Depth of peat layer (cm)	Number of depthwise sampling	Total carbon content (g kg ⁻¹)	Total nitrogen content (g kg ⁻¹)	Carbon to nitrogen ratio	Ash content (g kg ⁻¹)	PPI
Inland peats							
AS-2	82	4	552	16.7	33.5	63	151
AS-3	105	6	554	14.4	37.4	76	81
AS-4	145	6	528	14.3	38.8	60	120
RP-1	135	5	568	11.9	49.4	27	88
RP-3	155	7	567	12.1	50.1	38	87
SAJ ^b	>200	3	526	18.7	28.3	12	45
Average ^c			547	14.2	41.1	44	103
Marginal peats							
AS-1	37	3	469	13.4	35.5	209	135
RP-2	71	3	497	17.2	28.8	130	69
GR-1	77	4	451	19.1	23.7	237	125
GR-2	91	4	426	17.2	25.6	242	121
LAM	48	3	482	20.1	25.9	158	112
Average ^c			462	17.5	27.5	200	114

^aObtained from the number of depthwise samples in each profile. ^bSAJ profile only collected to 40 cm depth. ^cObtained from the total number of depthwise samples in each group.

and AS-4 were abandoned after 5 years and only occasionally cultivated thereafter. The other sites were located under forest stands, except for RP-1, which had been planted with rubber trees for about 5 years at the time of sampling. In this paper, at the AS-1, RP-2, GR-1, GR-2, and LAM sites that were located more or less near the edge or margin of peat deposits, bordered by mineral materials, in particular near rivers, the peat samples were referred to as marginal peats. On the other hand, at the remaining sites located near the center or in the central part of peat deposits, the samples were referred to as inland peats. Soil sampling was performed depthwise in soil profile pits in 10 to 20 cm increments, in accordance with our other study on soil micromorphology (Anwar et al. 2001). From these 11 sites, a total of 48 peat soil samples were collected.

Methods of analysis. Peat soil samples were air-dried, and coarsely shredded and sieved through a 5 mm mesh, then finely ground in a mill. Prior to the analysis of the contents of organic carbon, nitrogen, and phenolic compounds, a sub-samples of the finely ground samples was oven-dried at 70°C to constant weight and re-ground to pass through a 0.25 mm mesh sieve.

Total organic carbon and total nitrogen contents of the peat samples were determined by the dry combustion method using an NC analyzer (Sumigraph NC-800-13N, Sumitomo, Osaka, Japan) after pretreatment with a dilute HCl solution to remove carbonates. Ash content was determined by dry combustion overnight at 440°C.

Kaila's pyrophosphate index (PPI) was determined and used as a key measure of the degree of decomposition of peat soils. A 500-mg air-dried and finely ground sample in a plastic bottle was shaken for 18 h with 50 mL of 0.025 M Na-pyrophosphate, and filtered through a dry filter paper (No. 6, Advantec Toyo, Tokyo, Japan). Ten milliliters of the filtrate was diluted to 50 mL. The absorbance at 550 nm was determined using a UV-VIS spectrophotometer (UV-1200, Shimadzu, Kyoto, Japan), multiplied by 100 and expressed on a dry weight basis. The value obtained was equivalent to the Kaila's PPI.

The phenolic compounds liberated upon alkaline CuO oxidation were analyzed by the procedures described by Kögel-Knabner (1995). A 50-mg oven-dried and ground sample in a pressure bomb was oxidized with 250 mg CuO, 50 mg $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 15 mL 2 M NaOH under N_2 atmosphere, heated at 170°C for 2 h and was centrifuged. The supernatant was acidified to pH 2 with 6 M HCl, and kept in the dark for about 1 h. Then the supernatant was recentrifuged and used for the determination of eleven phenolic compounds by HPLC according to the procedure described by Nambu and Yonebayashi (1999).

RESULTS AND DISCUSSION

Organic carbon content, ash content, and pyrophosphate index

Peat depth and organic carbon and nitrogen contents, carbon / nitrogen ratio, ash content, and PPI are presented in Table 1. The average values of the carbon and nitrogen contents, carbon / nitrogen ratio, ash content, and PPI for the soil profiles were obtained from the number of depthwise samples in each profile, while those for the inland and marginal peats were obtained from the number of depthwise samples in each group. The inland peats were deeper than the marginal peats with a few exceptions. The inland peats showed a higher content of total carbon and lower content of ash compared with the marginal peats. The average values of the nitrogen content and PPI were lower and that of the carbon to nitrogen ratio was higher in the inland peats than in the marginal peats, although the differences were not significant.

Yield and composition of phenolic oxidation products

Eleven major lignin-derived phenolic compounds liberated upon alkaline CuO oxidation were classified as monomethoxyl-substituted vanillyl phenols (V; vanillic acid, acetovanillon, and vanillin), dimethoxyl-substituted syringyl phenols (S; syringic acid, acetosyringone, and syringaldehyde), propenoic acid-substituted cinnamyl phenols (C; ferulic acid and *p*-coumaric acid), and non-methoxyl-substituted *p*-hydroxyl phenols (H; *p*-hydroxybenzoic acid, *p*-hydroxyacetophenone, and *p*-

Table 2. Average phenolic yields on organic carbon basis and some ratio parameters ($n = 48$).

Phenols	Yield (mg g ⁻¹ carbon)	Ratio parameter	Value
H	5.92 ± 1.23	S / V	0.86 ± 0.17
V	17.8 ± 4.72	C / V	0.07 ± 0.04
S	15.8 ± 6.68	H / V	0.35 ± 0.08
C	1.16 ± 0.58	(ac / al)h	3.19 ± 1.89
Acids	12.7 ± 2.34	(ac / al)v	0.69 ± 0.29
Ketones	7.93 ± 2.78	(ac / al)s	0.58 ± 0.25
Aldehydes	18.8 ± 8.94	(ac / al)hvs	0.83 ± 0.38
HVSC	40.7 ± 11.6		

H, *p*-hydroxyl phenols; V, vanillyl phenols; S, syringyl phenols; C, cinnamyl phenols. Acids, phenolic acids; Ketones, phenolic ketones; Aldehydes, phenolic aldehydes. HVSC: sum of H + V + S + C, represents total phenolic yields. S / V, C / V, and H / V: ratio of syringyl, cinnamyl, and *p*-hydroxyl to vanillyl phenols, respectively. (ac / al)h, (ac / al)v, (ac / al)s, and (ac / al)hvs: ratio of acid to aldehyde of *p*-hydroxyl, vanillyl, syringyl, and total of *p*-hydroxyl, vanillyl, and syringyl phenols, respectively.

hydroxy-benzaldehyde) on the basis of chemical substitution. Based on the type of functional group at the C-1 site, they were also classified as phenolic acids (acids), phenolic ketones (ketones), phenolic aldehydes (aldehydes), and cinnamic acids. Cinnamyl phenols in the first category were identical with cinnamic acids in the second category. The composition of the chemical substitution compounds retained the characteristic substitution pattern of the different lignin types of plants and tissues (Hedges and Mann 1979), while that of the functional groups could be used to characterize the degree of alteration of lignin (Hedges et al. 1988).

Chemical substitution. Among the CuO oxidation products of the tropical peat soils (Table 2) the V compounds ($17.8 \pm 4.72 \text{ mg g}^{-1}$) or otherwise the S compounds ($15.8 \pm 6.68 \text{ mg g}^{-1}$) predominated across the samples, followed by the H compounds ($5.92 \pm 1.23 \text{ mg g}^{-1}$), while C was a minor compound ($1.16 \pm 0.58 \text{ mg g}^{-1}$). V, S, and C were exclusively derived from lignin and mostly occurred in insoluble forms, while H contained both lignin and nonlignin sources and was mostly found in soluble forms (Ertel et al. 1993). For these reasons the H compounds have often not been considered to be unambiguously lignin-derived compounds in sedimentary mixtures (Ertel et al. 1993). In this study, however, a highly significant positive correlation ($r = 0.796^{***}$) was observed between the sum of V, S, and C ($34.7 \pm 11.0 \text{ mg g}^{-1}$) and the sum of H, V, S, and C (HVSC; $40.7 \pm 11.6 \text{ mg g}^{-1}$), suggesting that they contributed in the same way to the dynamics of lignin compounds in tropical peats. In this paper, we

selected HVSC to represent the total yield of lignin-derived phenols.

As shown in Table 3, the yields of H, V, and S on an organic carbon basis showed highly significant positive correlations with each other. They also showed highly significant positive correlations with HVSC, suggesting that they displayed relatively the same behavior in relation to the dynamics of lignin decomposition in the tropical peat soils. In contrast, C did not show any significant correlation with other phenols or HVSC. The results also suggested that tropical peat soils were primarily derived from plants containing S and V as predominant lignin units, and that the sources of C did not show a constant contribution but acted only as admixture to the tropical peat soil materials.

The percentages of H, V, S, and C to HVSC averaged 15.2 ± 3.5 , 44.1 ± 3.7 , 37.6 ± 5.4 , and $3.05 \pm 1.55\%$, respectively. In addition to being the predominant constituents, the percentages of V and S did not fluctuate appreciably across all the profiles and depths, suggesting that the contribution of the major organic precursors was relatively identical. The percentage of these constituents was different from that of temperate peat soils. Temperate peat soils derived from Sphagnum and grass vegetation (Tsutsuki and Kondo 1995; Williams et al. 1998) contained higher percentages of H and C, while those derived from gymnosperms (Williams et al. 1998) contained a lower percentage of S. From the composition of phenolic oxidation products based on the chemical substitution, it was assumed that the tropical peat samples in this study had been derived from woody veg-

Table 3. Pearson correlations with Bonferroni probabilities among phenolic yields and pyrophosphate index.

	H	V	S	C	Acids	Ketones	Aldehydes	HVSC
V	0.468							
S	0.387	0.886***						
C	0.148	-0.127	-0.155					
Acids	0.445	0.272	0.053	-0.214				
Ketones	0.415	0.893***	0.939***	-0.176	0.147			
Aldehydes	0.429	0.906***	0.963***	-0.052	-0.064	0.881***		
HVSC	0.526*	0.960***	0.969***	-0.076	0.177	0.939***	0.965***	
PPI	-0.367	-0.697***	-0.813***	-0.115	0.166	-0.761***	-0.834***	-0.796***

	%H	%V	%S	%C	%Acids	%Ketones	%Aldehydes
%V	-0.018						
%S	-0.717***	-0.628***					
%C	0.292	-0.143	-0.379				
%Acids	0.756***	0.341	-0.788***	0.236			
%Ketones	-0.226	-0.013	0.194	-0.139	-0.155		
%Aldehydes	-0.696***	-0.339	0.738***	-0.199	-0.961***	-0.123	
HVSC	-0.694***	-0.285	0.770***	-0.443	-0.834***	0.132	0.801***
PPI	0.604***	0.423	-0.742***	0.222	0.851***	-0.182	-0.804***

* and ***: significantly correlated at 5% and 0.1%, respectively ($n = 48$). PPI, pyrophosphate index. %H, %V, %S, and %C: percentages of *p*-hydroxyl, vanillyl, syringyl, and cinnamyl phenols, respectively. %Acids, %Ketones, and %Aldehydes: percentages of phenolic acids, ketones, and aldehydes, respectively. For abbreviations of other labels, see Table 2 and text.