

Lignin-Derived Phenolic Compounds in Different Types of Peat Profiles in Hokkaido, Japan

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How is the composition of organic matter of peat related to the environment of the peatland? How does it change with the process of peat formation? How does it change when the peatland is affected by the lowering of the ground water table? What are the relationships between the organic matter composition of peat and peatland plants? These are problems which we attempted to address in this study. Peat samples were collected layer-wise from four different peat profiles formed under different environments in Hokkaido, Japan. The basic properties of the peat profiles, i.e. major peat-forming plants, contents of carbon and nitrogen, C/N ratio, pH, degree of humification analyzed by several methods, were described and compared. As one of the keys to answer the above-mentioned questions, we selected lignin-derived phenolic compounds that are released by CuO-NaOH oxidation. The composition of the phenolic compounds varied remarkably among the peat layers differing in peat-forming plants and in the mode of accumulation. The classification into high-moor, transitional moor, and low-moor peat was not sufficient to explain the composition of the phenolic compounds of peat. Differences in major peat-forming plants, i.e. sphagnum moss or sedges in high-moor peat, and Phragmites or Alnus in low-moor peat exerted significant effects on the phenolic composition.

Key Words: CuO-oxidation products, humification, lignin, peat, phenolic compounds.

The ecosystem of peatland which is important in terms of hydrological function, biological resources, and environmental conservation is very fragile and readily affected by human activities such as agricultural use, land reform, and chemical pollution, etc. (Reddy and Patrick 1993; Barber 1993). Due to the anaerobic environment of peatland, the organic matter composition of peat hardly changes with time, and, therefore, information on the past peatland plant communities is interred. When the peatland is exposed to environmental changes induced naturally or artificially, however, organic matter composition may also record it. Our present and the forthcoming papers will focus on the role of organic constituents of peat as an environmental marker, that can be compared among peat profiles formed under different environments in Hokkaido, Japan. In this paper, we analyzed the degree of humification as well as the composition of lignin-derived phenolic compounds released by CuO-NaOH oxidation which have been found to be suitable biomarkers to follow the

dynamics of sediments, soil and peat organic matter (Ertel and Hedges 1985; Tsutsuki et al. 1992, 1994; Kögel-Knabner 1993; Ertel et al. 1993).

MATERIALS AND METHODS

Peat samples. Peat samples were collected layer-wise from four peat profiles formed under different environments in Hokkaido. Tables 1-4 show the description of the sampling sites, peat profiles, and dominant peat forming plants. Fibric, hemic, and sapric peat layers were designated as Oi, Oe, and Oa layers, respectively, according to Everett (1983). Samples were air-dried and powdered with a disk mill.

Carbon and nitrogen. Carbon and nitrogen contents were determined by the dry-combustion method using a CN analyzer (Yanaco-MT500). Finely ground and oven-dried samples equivalent to ca. 50 mg of carbon were mixed with 2 g of CuO (special analytical grade from Wako Chemical Co.) and subjected to the analysis. Hippuric acid was used as a standard.

pH. The pH of peat was measured in 0.01 M CaCl₂ according to the recommendations

Table 1. Description of Oikamanai^a peat profile.

Layer name	Sample name	Depth (cm)	pH CaCl ₂	Dominant peat forming plants	Type of layer
Oa ₁	Oa1	0-9	4.03	<i>Phr.</i> , <i>Aln.</i>	low-moor
IC		9-18			volcanic ash
IIC		18-24			volcanic ash
Oa ₂	Oa2	24-32	3.90	<i>Phr.</i>	low-moor
IIIC		32-40			volcanic ash
Oa ₃	Oa3	40-54	3.95		sandy
Oa ₄	Oa4	54-65	3.85	<i>Phr.</i>	low-moor
Oa ₅	Oa5	65-75	3.91		sandy
Oa ₆	Oa6	75-100+	3.91	<i>Phr.</i>	low-moor

^a Oikamanai: This sample was collected on the eastern shore of the Oikamanai coastal lagoon (42-33-24-N, 143-30-22-E, altitude 1 m) in Taiki-cho, Hiroo-gun, Hokkaido, Japan, on August 30, 1991. *Phr.*, *Phragmites communis*; *Aln.*, *Alnus japonica*.

Table 2. Description of Sarobetsu high-moor^a peat profile.

Layer name	Sample name	Depth (cm)	pH CaCl ₂	Dominant peat forming plants	Type of layer
A _p		0-12			amended soil
Oe ₁	SH1	12-28	3.02	<i>Sph.</i> , <i>Car.</i>	high-moor
Oe ₂	SH2	28-40	3.00	<i>Car.</i> , <i>Sph.</i> , <i>Vac.</i>	high-moor
Oi ₁	SH3	40-50	3.00	<i>Sph.</i> , <i>Car.</i> , <i>Vac.</i>	high-moor
Oi ₂	SH4	50-65	3.00	<i>Car.</i> , <i>Sph.</i>	high-moor
Oe ₃	SH5	65-70	3.26	<i>Car.</i> , <i>Vac.</i>	high-moor
Oa ₁		70-105		<i>Phr.</i> , <i>Aln.</i>	low-moor
	SH6	70-88	3.43		
	SH7	88-105	3.45		
Oa ₂	SH8	105-	3.70	<i>Aln.</i>	low-moor

^a Collected at Nishitoyotomi (45-07-34-N, 141-41-07-E, altitude 6 m), Toyotomi-cho, Teshio-gun, Hokkaido, Japan, on June 23, 1992. This site was amended with mineral soil, drained, and used as grassland. *Car.*, *Carex middendorffii*; *Sph.*, *Sphagnum* spp.; *Vac.*, *Vaccinium middendorffii*.

Table 3. Description of Sarobetsu low-moor^a peat profile.

Layer name	Sample name	Depth (cm)	pH CaCl ₂	Dominant peat forming plants	Type of layer
Oa ₁	SL1	0-12	3.20	<i>Phr.</i>	low-moor peat
Oa ₂	SL2	12-32	3.20	<i>Phr.</i>	low-moor peat
Oa ₃	SL3	32-39	4.20	<i>Phr.</i>	low-moor peat
Oa ₄	SL4	39-49	3.79	<i>Phr.</i>	low-moor peat
Oa ₅		49-87		<i>Phr.</i>	low-moor peat
	SL5U	49-68	3.77		
	SL5L	68-87	4.01		
Oe ₁	SL6	87-117+	4.01	<i>Phr.</i>	low-moor peat

^a Collected at Wakkasakanai (45-04-39-N, 141-40-07-E, altitude 4 m), Toyotomi-cho, Teshio-gun, Hokkaido, Japan, on June 23, 1992. This site was drained, and used as grassland without soil amendment.

Table 4. Description of Bibai high-moor^a peat profile.

Layer name	Sample name ^b	Depth (cm)	pH CaCl ₂	Dominant peat forming plants	Type of layer
Oa ₁	B0	0-10	3.2	<i>Sph., Car., Vac.</i>	high-moor peat
Oe ₁	B13, B18, B23, B28, B33, B38, B43	10-50	3.4	<i>Sph., Car., Vac.</i>	high-moor peat
Oe ₂	B48, B53, B58, B63	50-68	3.7	<i>Mol., Phr., Aln.</i>	transitional moor peat
Oe ₃	B68, B73, B78, B83, B88	68-92	3.7	<i>Phr., Aln.</i>	low-moor peat
Oe ₄	B93, B98, B103, B108	92-113	3.8	<i>Phr., Aln.</i>	low-moor peat
Oe ₅	Samples not collected	113-140	3.7	<i>Phr., Aln.</i>	low-moor peat
C	Samples not collected				clay

^a Collected at the Bibai Branch of Hokkaido Natl. Agric. Exp. Stn. (43-19-35-N, 141-49-00-E, altitude 18 m).

^b Samples were collected in blocks 5 cm thick each, except for the top layer sample (0-13 cm). Numbers in the sample name denote the depth in the upper border. *Mol.*, *Moliniopsis japonica*.

of the Soil Survey Staff (1975).

Degree of humification of peat. Degree of humification was determined by the method of Kaila (1956) on a reduced (1/5) scale. To 100 mg of sample (air-dried and finely ground), 10 mL of 0.025 M sodium pyrophosphate solution was added. The sample was shaken for 18 h and filtered through a dry filter paper (Advantec No. 6). Five milliliters of the filtrate was diluted to 25 mL. The absorbance at 550 nm was determined with a Hitachi Type 101 Spectrophotometer and multiplied by 100. The value obtained is equivalent to the degree of humification determined by the Kaila method (1956). The degree of humification was expressed both on a dry matter basis and on an organic matter basis. The absorbance at 340 nm was also determined after appropriate dilution and multiplied by 100 and a factor of dilution, which corresponds to the modified Kaila's degree of humification at 340 nm.

The absorbances at 600 and 400 nm were also determined to obtain $\Delta \log K (= \log E_{400}/E_{600})$, another index of humification, which is considered to decrease along with the development of the unsaturated coupled double-bond system in the structure of humic substances (Kumada 1987).

The amount of carbon extracted with 0.025 M sodium pyrophosphate by the Kaila

method was determined according to the colorimetric dichromate oxidation method of Tatsukawa (1966) using glucose as standard.

Analysis of phenolic compounds released by CuO-NaOH oxidation. The method of CuO-NaOH oxidation was described by Tsutsuki et al. (1994). The analysis of the phenolic compounds was carried out by applying the gas-chromatographic method (Silicone SE30, 2 m glass column) using Hitachi 163 GC, described by Tsutsuki and Kuwatsuka (1991). Phenolic compounds were grouped as follows. *p*-Hydroxybenzoic acid, *p*-hydroxybenzaldehyde, and *p*-hydroxyacetophenone were grouped into *p*-hydroxyphenyl compounds and designated as H in short. Vanillic acid, vanillin, and acetovanillone were grouped into vanillyl compounds and designated as V. Syringic acid, syringaldehyde, and acetosyringone were grouped into syringic compounds and designated as S. *p*-Coumaric acid and ferulic acid were grouped into cinnamyl compounds and designated as C.

RESULTS AND DISCUSSION

Description of Oikamanai peat profile

Oikamanai low-moor peat was formed on the shore of a lagoon under an eutrophic environment. The vegetation consisted of bush of *Alnus japonica* and *Phragmites communis* (Table 1).

The pH was very low, ranging between 3.8 and 4.0, throughout the profile (Table 1), though this value was higher than in the other profiles studied in this paper.

As shown in Table 5, the contents of carbon and nitrogen were rather low due to the in-flow of mineral materials. Layers Oa₃ and Oa₅ were excluded from the categories of peat due to their low carbon content, but they were included in the samples for comparison. Low C/N ratios were considered to be associated with organic matter decomposition. Degree of humification by the Kaila method (1956) also showed that the largest amount of dark-colored humic substances was extracted from the Oikamanai samples compared with other peat profiles. The amount of carbon extracted by the Kaila procedure is also given in Table 5. This value, calculated on a carbon basis, was very high in the Oikamanai samples. In addition, $\Delta \log K$ values of Oikamanai peats were remarkably lower than those of the high-moor peats and slightly lower than those of the other low-moor peats, indicating that the humic substances extractable with pyrophosphate exhibited a very high degree of humification in this peat profile.

Description of Sarobetsu high-moor peat profile

Sarobetsu high-moor peat was formed from sphagnum moss, sedges (*Carex*), and bog cranberry (*Vaccinium*) up to 70 cm (Table 2). The pH of peat was highly acidic. The pH was as low as 3.0 in the upper 65 cm high-moor layer. These samples were characterized by a high carbon content, low nitrogen content, and consequently a high C/N ratio (Table 5). The degree of humification was low both on a dry matter and organic matter basis. The amount of carbon extracted by sodium pyrophosphate was also low. The $\Delta \log K$ value was high, showing that the extracted humic substances were not condensed.

The degree of humification at 550 and 340 nm as well as the amount of extracted carbon tended to increase slightly in the upper layers (SH1 and SH2, Table 5). Such a tendency was also observed in the Sarobetsu low-moor and Bibai high-moor peat profiles. The high value of $\Delta \log K$ in these layers indicated that the increase in the degree of humification was not due to the condensation of humic substances but to the increase in the amount of alkali-

Table 5. Contents of carbon and nitrogen, C/N ratio, and degree of humification of peat samples.

Layer sample	Carbon g kg ⁻¹	Nitrogen g kg ⁻¹	C/N	Kaila's deg. of humific. at 550 nm			Ext-C/ total C g kg ⁻¹	$\Delta \log K$
				/DM	/OM	/OM		
Oikamanai low-moor peat								
Oa ₁ Oa1	202	13.8	14.6	45.8	132	1160	271	0.753
Oa ₂ Oa2	297	14.8	20.1	96.1	188	823	174	0.509
Oa ₃ Oa3	16.4	0.31	52.9	3.4	120	820	255	0.670
Oa ₄ Oa4	182	8.7	20.8	41.9	133	698	179	0.582
Oa ₅ Oa5	19.9	1.04	19.1	5.5	161	1040	368	0.644
Oa ₆ Oa6	237	11.6	20.4	39.9	97.9	640	181	0.667
Sarobetsu high-moor peat								
Oe ₁ SH1	582	17.6	33.0	18.5	18.4	202	68	0.944
Oe ₂ SH2	600	18.9	31.7	12.4	12.0	125	47	0.903
Oi ₁ SH3	566	11.4	49.7	9.9	10.1	93.2	39	0.759
Oi ₂ SH4	609	15.8	38.5	10.0	9.5	79.0	31	0.775
Oe ₃ SH5	578	15.4	37.5	7.9	7.9	72.0	28	0.823
Oa ₁ SH6	520	20.5	25.4	9.4	10.5	91.8	37	0.812
SH7	626	28.9	21.6	9.0	8.4	73.7	28	0.809
Oa ₂ SH8	505	23.2	21.7	14.4	16.5	108.6	35	0.617
Sarobetsu low-moor peat								
Oa ₁ SL1	536	31.9	16.8	57.1	61.8	399	125	0.662
Oa ₂ SL2	622	28.2	22.0	59.0	55.0	334	95	0.635
Oa ₃ SL3	608	25.7	23.6	52.2	49.8	287	73	0.641
Oa ₄ SL4	616	27.5	22.4	52.4	49.3	280	68	0.631
Oa ₅ SL5U	648	22.6	28.7	31.3	28.0	184	47	0.678
SL5L	501	25.9	19.3	37.5	43.4	262	79	0.661
Oe ₁ SL6	621	26.7	23.3	40.3	37.7	234	60	0.671
Bibai high-moor peat								
Oa ₁ B0	352	13.7	25.7	37.5	61.8	704	218	0.903
Oe ₁ B13	585	15.0	38.9	32.8	32.6	425	127	0.997
B18	577	21.5	26.8	27.5	27.7	352	107	1.000
B23	613	19.4	31.6	17.1	16.2	183	58	0.925
B28	614	21.5	28.5	16.2	15.3	136	44	0.792
B33	658	22.5	29.2	14.9	13.1	119	39	0.804
B38	661	24.4	27.1	13.6	11.9	113	38	0.814
B43	664	20.7	32.1	15.0	13.1	131	41	0.842
Oe ₂ B48	640	31.7	20.2	17.6	16.0	138	42	0.796
B53	655	31.2	21.0	19.9	17.6	150	45	0.791
B58	649	34.2	19.0	25.7	23.0	180	54	0.757
B63	630	29.9	21.0	26.4	24.3	187	58	0.734
Oe ₃ B68	586	22.1	26.5	19.4	19.2	161	57	0.789
B73	476	27.8	17.1	25.5	31.1	266	84	0.817
B78	362	18.9	19.1	21.0	33.6	282	87	0.800
B83	453	22.4	20.2	40.1	51.3	321	111	0.654
B88	514	24.7	20.8	34.9	39.4	301	89	0.759
Oe ₄ B93	574	26.5	21.6	31.6	31.9	238	72	0.726
B98	564	27.2	20.8	24.6	25.3	204	63	0.785
B103	577	35.4	16.3	22.4	22.5	175	56	0.762
B108	597	30.3	19.7	24.8	24.1	185	57	0.742

/DM, dry matter basis; /OM, organic matter basis.

extractable humic substances. This is considered to be the result of the enhancement of organic matter decomposition in the surface peat layers, because the Sarobetsu high-moor

and low-moor profiles used in this study were drained and used as grasslands.

The lower layers (Oa₁ and Oa₂; SH6, SH7, and SH8) of this peat profile consisted of low-moor peat formed from *Phragmites*. The pH increased slightly in these layers. These layers were characterized by a slightly higher nitrogen content and lower C/N ratio. Degree of humification was almost the same compared with the upper high-moor peat layers.

Description of Sarobetsu low-moor peat profile

Sarobetsu low-moor peat was formed mainly from *Phragmites* (Table 3). The pH was low (3.2) in the upper layers (SL1, SL2), but increased considerably (3.8–4.2) in the lower layers. Samples were characterized by a higher nitrogen content, lower C/N ratio, higher degree of humification, and larger amount of extracted carbon compared with the Sarobetsu high-moor peat samples (Table 5). In the uppermost layers, the degree of humification and the amount of extracted carbon increased while the carbon content and C/N ratio decreased. These findings suggested that organic matter decomposition was enhanced in the surface peat layer as mentioned above. Similar tendencies were also observed in the SL5L layer, indicating that the environment was favorable for organic matter decomposition when this layer accumulated.

Description of Bibai peat profile

The succession from the low-moor peat, via transitional peat, to the high-moor peat was observed in the profile of the Bibai peat (Table 4). The pH was very low (3.2–3.4) in the high-moor peat layer, but increased slightly (3.7–3.8) in the transitional moor and low-moor peat layers.

During the past 30 years, the surrounding area of this peatland had been transformed into upland crop fields and paddy fields by drainage of water, and amendment of mineral soils. These land use led to the lowering of the water table in wetlands and the colonization of plants adapted to drier environments (e.g. *Sasa palmata* and bush). The decrease in the carbon content and C/N ratio as well as the increase in the degree of humification and the amount of extracted humic substances in the uppermost layer (Oa₁; B0) is considered to correspond to this drying effect in the peatland (Table 5). In the lower half of the high-moor layer (Oe₁), the degree of humification and the amount of extractable humic substances approached the levels recorded in the Sarobetsu high-moor peat.

In the transitional peat layer (Oe₂), the nitrogen content increased and the C/N ratio decreased remarkably, while the degree of humification and the amount of extractable humic substances increased slightly compared with the overlying high-moor peat samples.

From the transitional peat layer (Oe₂) to the low-moor peat layer (Oe₃), the carbon and nitrogen contents decreased slightly, while the C/N ratio remained almost constant (from 20.3 to 20.7 on an average). On the other hand, Kaila's degree of humification on an organic matter basis (from 164 to 266 at 340 nm on an average) and the amount of extractable humic substances (from 49.8 to 86.0 in average) increased remarkably. When the Oe₃ and Oe₄ layers were compared, Oe₃ layer was more decomposed, in accordance with the slightly lower carbon content in Oe₃ (Table 5).

Relationships between parameters for decomposition and humification of peat layers

Correlation coefficients were calculated between the carbon and nitrogen contents, C/N ratio, and the degree of humification (Table 6). As a whole, the degree of humification

Table 6. Correlation coefficients between C, N, and humification parameters.

	Nitrogen	C/N	$\Delta \log K$	HI550	HI340 (organic matter basis)	Ext-C
Carbon	0.748***	0.022	0.373*	-0.851***	-0.876***	-0.900***
Nitrogen		-0.527***	0.034	-0.568***	-0.617***	-0.664***
C/N			0.325*	-0.195	-0.151	-0.094
$\Delta \log K$				-0.572***	-0.327*	-0.265
HI550 (/OM)					0.928***	0.874***
HI340 (/OM)						0.967***
Ext-C (/OM)						
HI550 (/DM)						
HI340 (/DM)						

	HI550	HI340 (dry matter basis)	Ext-C
Carbon	-0.126	-0.030	0.067
Nitrogen	0.146	0.142	0.193
C/N	-0.447**	-0.360*	-0.306
$\Delta \log K$	-0.513***	-0.033	0.142
HI550 (/OM)	0.535***	0.333*	0.155
HI340 (/OM)	0.408**	0.403**	0.271
Ext-C (/OM)	0.249	0.274	0.189
HI550 (/DM)		0.833***	0.696***
HI340 (/DM)			0.958***

Carbon and nitrogen: content (g kg^{-1}) on a dry matter basis. $\Delta \log K$: $\log(E_{400}/E_{600})$ of the $\text{Na}_4\text{P}_2\text{O}_7$ extract. HI550 and HI340: Degree of humification determined by the Kaila method (1956) at 550 and 340 nm, expressed on an organic matter and dry matter basis. Ext-C: Amount of carbon extracted with $\text{Na}_4\text{P}_2\text{O}_7$, expressed on an organic matter and dry matter basis. Level of significance: 0.1% (***), $r > 0.490$; 1.0% (**), $r > 0.393$; 5.0% (*), $r > 0.304$.

at 550 nm determined by Kaila method was positively correlated ($r = 0.874$ ***, significant at 0.1% level) with the amount of extracted humic substances. The degree of humification determined at 340 nm showed an even higher correlation ($r = 0.967$ ***) with the amount of extracted humic substances. From these correlations, the degree of humification determined by Kaila method may be characterized as an index of the quantity of extractable humic substances.

The amount of extractable carbon on an organic matter basis showed a negative correlation ($r = -0.900$ ***) with the carbon content of the peat. Even when the Oikamanai peats which showed a very low carbon content and a very high extractable carbon content were excluded, this correlation was still highly significant ($r = -0.635$ ***). This fact suggested that the proportion of extractable humic substances increased as the decomposition of peat proceeded or as the mixing of mineral materials with peat proceeded. The degree of humification determined by Kaila method on an organic matter basis was also correlated negatively with the carbon content. This finding can be attributed to the same phenomenon as that described above, because the amount of extractable organic matter and Kaila's degree of humification showed a highly positive correlation.

The correlation between the nitrogen content and Kaila's degree of humification on an organic matter basis was also highly significant. The C/N ratio showed a positive correlation (5% level of significance) with $\Delta \log K$, and a negative correlation (1% level of significance) with Kaila's degree of humification at 550 nm on a dry matter basis. However, the correlations of the C/N ratio with Kaila's degree of humification on an organic matter basis

as well as with the extractable organic matter content were not significant.

The value of $\Delta \log K$, which is a negative index of the degree of condensation of humic substances was negatively correlated ($r = -0.572^{***}$ and -0.513^{***}) with Kaila's degree of humification determined at 550 nm on an organic matter basis and a dry matter basis, respectively. The significance of the correlation was rather low in the relationship with the degree of humification at 340 nm. This finding suggests that Kaila's degree of humification at 550 nm also represents the degree of condensation of the extracted humic substances, while the degree of humification at 340 nm represents mainly the amount of extractable humic substances.

In the high-moor peat profile, since the value of $\Delta \log K$ tended to be high, the degree of condensation of humic substances was low. With increasing depth in the high-moor peat profile, the $\Delta \log K$ value decreased and the degree of condensation increased. On the other hand, the value of $\Delta \log K$ tended to be low, and the humic substances were more condensed, in the low-moor peat.

Yield and composition of phenolic compounds in different peat profiles (Fig. 1)

Phenolic substances liberated upon CuO-NaOH oxidation have been used as a suitable biomarker to estimate the vegetational origin of organic matter in soils, peats, and sediments (Ertel and Hedges 1985; Tsutsuki et al. 1992, 1994; Kögel-Knabner 1993; Ertel et al. 1993). Relationships between the composition of these phenolic compounds and plant taxonomy and tissue type have been studied in detail by Hedges and Mann (1979). The authors have also studied the CuO-NaOH oxidation products of various major peatland plants in Hokkaido and the results will be published elsewhere. In reference to this information, past

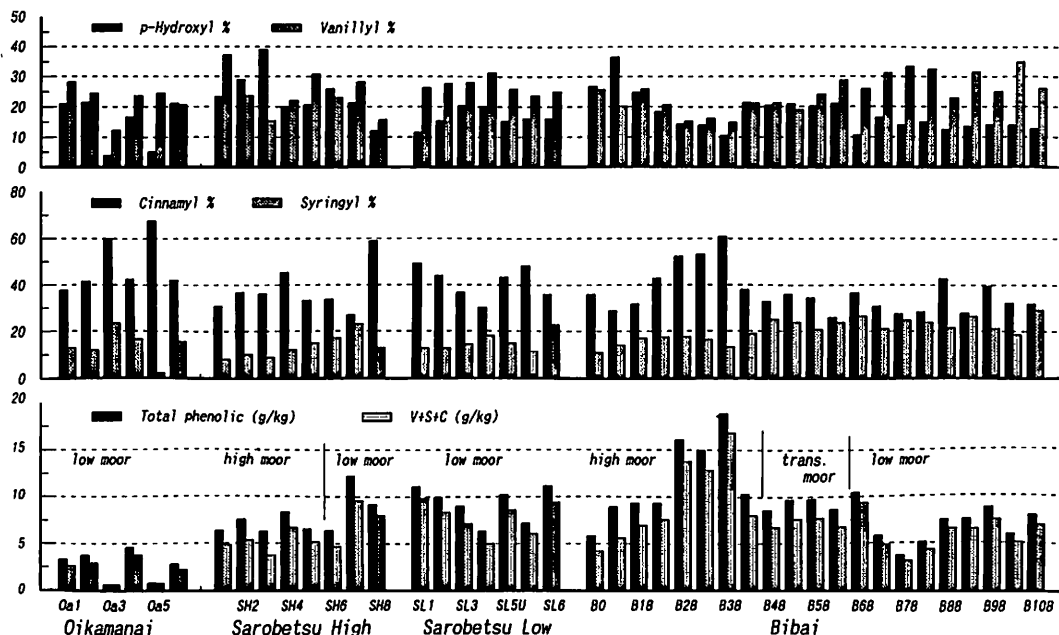


Fig. 1. Yield (g kg^{-1} dry matter basis) of total phenolic compounds and lignin derived phenolic compounds (V+S+C) from different peat profiles, as well as the percentage of each group of phenolic compounds.

vegetation and environments of peatland were estimated based on the CuO-oxidation products of peat layers.

The yield of the phenolic compounds was lowest in the Oikamanai low-moor peat on a dry matter basis. However, when normalized to an organic matter basis, Oikamanai peat layers except for Oa₃ and Oa₅ gave almost the same yield of total phenolic compounds (7.0–14.7 g kg⁻¹ OM) as the other peat profiles, while the Oa₃ and Oa₅ layers gave extremely high yields (both 25 g kg⁻¹ OM). In the Oa₃ and Oa₅ layers which contained a large amount of mineral matter, the decomposition of non-lignin organic constituents was considered to be promoted under an eutrophic condition.

In the Oikamanai peat, the percentage of cinnamyl compounds was also high. Since the cinnamyl compounds are derived solely from non-woody tissues of vascular plants (Hedges and Mann 1979), and the contribution of gymnosperms can be neglected in peatlands, they were considered to reflect the dominant grass vegetation.

Total yields of phenolic compounds were slightly lower in the high-moor layers of the Sarobetsu high-moor peat than in the Sarobetsu low-moor peat. In the upper layers of the Sarobetsu high-moor peat, the percentages of *p*-hydroxyl compounds were high, while those of syringyl compounds were low.

Upon CuO-NaOH oxidation of sphagnum moss, *p*-hydroxyphenyl compounds are produced predominantly (>60%) and vanillin (ca. 35%) and acetovanillone accounted for the remaining part. No syringyl and cinnamyl compounds were formed from sphagnum (Tsutsuki et al. unpublished). Syringyl compounds have been considered to be a good indicator of the presence of angiosperm wood tissues (Hedges and Mann 1979), although non-woody peatland plants, i.e. sedges and gramineous plants, also produced a considerable proportion of syringyl compounds upon CuO-NaOH oxidation (Tsutsuki et al. unpublished).

These facts suggest that the contribution of the sphagnum vegetation was important in the Sarobetsu high moor peat layers. Cinnamyl compounds in these layers are considered to originate from sedges (*Carex*).

In the Sarobetsu low moor peat profile, a slight increase in the total phenolic compounds was accompanied by a decrease in the percentages of *p*-hydroxyl compounds and the slight increase in the percentages of cinnamyl compounds, compared with the Sarobetsu high-moor peat, presumably due to the contribution of *Phragmites* in the low-moor peat.

In the upper layers of the Bibai high-moor peat (B0–B23), the yield of total phenolic compounds was low and the percentages of *p*-hydroxyl compounds were high, due to the contribution of the sphagnum vegetation. In the lower part of the high-moor peat layers (B28–B38), the yield of the phenolic compounds and the percentages of cinnamyl compounds increased, while the percentages of *p*-hydroxyl compounds decreased, due to the contribution of sedges (*Carex*).

In the transitional peat layers of the Bibai profile (B48–B63), the yield of the total phenolic compounds and the percentages of cinnamyl compounds decreased again, presumably due to the decrease in the proportion of grass vegetation.

In the low moor peat layers of the Bibai profile, the yield of phenolic acids decreased further, along with the decrease in the percentages of *p*-hydroxyl compounds and the increase in the percentages of vanillyl and syringyl compounds. Compared with the Sarobetsu low-moor peat, the percentages of syringyl and vanillyl compounds were higher and those of cinnamyl compounds were lower. These findings may correspond to the relatively high contribution of wood (*Alnus*) vegetation in the low-moor peat layers of the Bibai

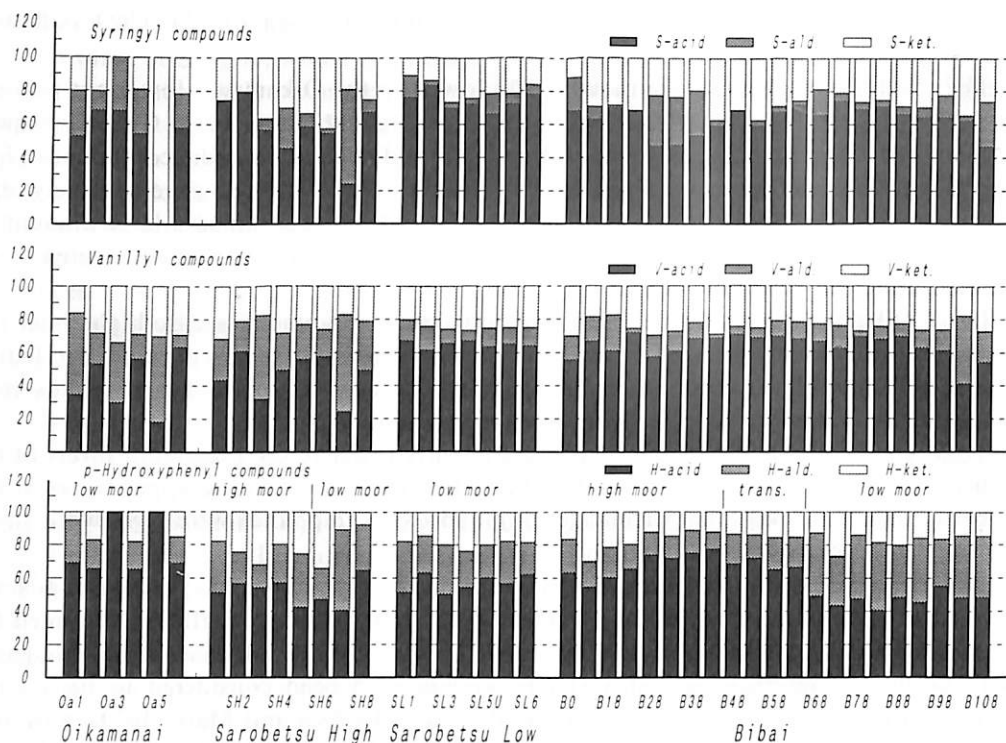


Fig. 2. Composition of phenolic acids, aldehydes, and ketones in each group of phenolic compounds in different peat profiles. H-acid, *p*-hydroxybenzoic acid; H-ald., *p*-hydroxy-benzaldehyde; H-ket., *p*-hydroxy-acetophenone; V-acid, vanillic acid; V-ald., vanillin; V-ket., acetovanillone; S-acid, syringic acid; S-ald., syringaldehyde; S-ket., acetosyringone.

profile, while the Sarobetsu low-moor peat was dominated by reeds, *Phragmites*.

Composition of phenolic acids, aldehydes, and ketones in different peat profiles (Fig. 2)

In the Oikamanai low-moor peat, the proportion of *p*-hydroxybenzoic acid was very high in the *p*-hydroxyphenyl compounds. On the other hand, the proportion of phenolic acids in the vanillyl and syringyl compounds was lower compared with other low-moor peat layers in the Sarobetsu and Bibai profiles.

In the Sarobetsu high-moor peat profile, the proportions of each phenolic acid were generally lower and those of aldehydes and ketones were higher compared with the Sarobetsu low-moor peat, though variations among the layers were large. Among the CuO-NaOH oxidation products of sphagnum, vanillin, *p*-hydroxy-benzaldehyde and *p*-hydroxy-acetophenone were dominant (Tsutsuki et al. unpublished). This characteristic of sphagnum phenols may be reflected in the composition of the *p*-hydroxyl and vanillyl compounds in the Sarobetsu high-moor peat. Composition of syringyl phenols may reflect the characteristics of *Vaccinium* and *Carex* which were found in peat with sphagnum.

In the Sarobetsu low-moor peat, phenolic acids predominated in each group. The composition of the phenolic compounds did not change appreciably among the layers of this profile, presumably because the peat-forming plants consisted mainly of *Phragmites*

throughout the profile. Though the phenolic composition of *Phragmites* was rather higher in aldehydes and ketones, the phenolic composition of peat may result from the diagenetic change of plant phenolic compounds.

The upper part (B0-B23) of the high-moor peat layers of the Bibai profile showed a similar phenolic compound composition to that of the upper layers of the Sarobetsu high-moor peat, suggesting that in both cases peat layers were mainly formed from sphagnum.

In the lower part (B28-B38) of the high-moor peat layers of the Bibai profile, the proportion of syringaldehyde increased among the syringic compounds, which is in agreement with the increase in the contribution of sedges, *Carex*, that are rich in syringaldehyde (Tsutsuki et al. unpublished).

In the transitional peat layers of the Bibai profile, the composition of the phenolic compounds was relatively stable. In general, the composition was similar to that of the Sarobetsu low-moor peat, presumably because in both cases the layers originated mainly from grass vegetation.

From the transitional peat to the low-moor peat layers in the Bibai profile, the proportion of *p*-hydroxy-benzaldehyde increased significantly while that of *p*-hydroxybenzoic acid decreased.

Composition of phenolic compounds of peat in relation to the types of peat and to the surface drying of peatland (Figs. 1-3)

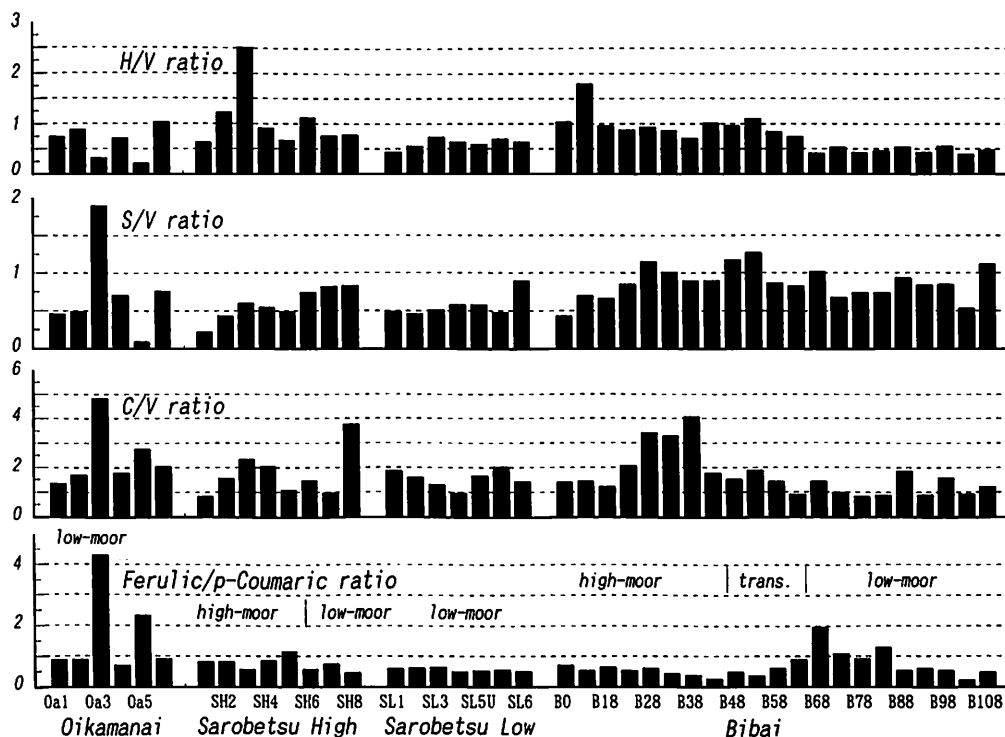


Fig. 3. Ratios of phenolic groups and compounds in different peat profiles. Ferulic/*p*-Coumaric ratio, yield ratio of ferulic acid/*p*-coumaric acid; C/V, cinnamyl phenol/vanillyl phenol; S/V, syringyl phenol/vanillyl phenol; H/V, *p*-hydroxyphenol/vanillyl phenol.

It was demonstrated in this study that the composition of the phenolic compounds is complex and can not be explained only by the classification of peat into high-moor, transitional moor, and low-moor peat layers. The composition of the phenolic compounds differed in the high-moor peat layers depending on whether the peat-forming plants were mainly sphagnum moss or sedges (*Carex*). They differed also in the three types of low-moor layers, one was very eutrophic due to the mixing of mineral materials (Oikamanai), another was formed mainly from *Phragmites* (Sarobetsu low-moor), and the other was formed from *Alnus* (Bibai).

The yield of the phenolic compounds determined by CuO-NaOH oxidation was low in the high-moor peat formed mainly from sphagnum moss but high in the high-moor peat dominated by sedges (Fig. 1). Low-moor peat formed from *Phragmites* showed larger contents of phenolic compounds compared with sphagnum peat. The yield was slightly lower in wood (*Alnus*)-derived low-moor peat than in the *Phragmites* peat. The yield of the phenolic compounds decreased in the well-decomposed low-moor peat (Oikamanai), but it remained almost at the same level as in the other peat profiles when compared on an organic matter basis.

Percentage of cinnamyl compounds was higher in the high-moor peat derived from sedges as well as in the low-moor peat derived from *Phragmites*, but significantly lower in the low-moor and transitional moor peat dominated by woods (Figs. 1 and 3).

Percentage of *p*-hydroxyphenyl compounds and H/V ratio tended to be high in sphagnum moss peat and low in wood-derived peat (Figs. 1 and 3). In contrast, the percentage of syringyl compounds and S/V decreased in sphagnum peat and increased in the wood and sedge peats.

Low-moor peat from woods was also characterized by a larger vanillyl and syringyl percentage, as well as by lower *p*-hydroxyl percentage, H/V and C/V ratios. The ratio of ferulic acid to *p*-coumaric acid was high in the wood-derived low-moor peat layers (Fig. 3). This ratio was also very high in the mineral layers (Oe₃ and Oe₅) of the Oikamanai profile. Ferulic acid is considered to originate from non-woody tissues (leaves and barks) of angiosperm woods.

The lowering of the ground water table and subsequent surface drying of peatland led to the increase of Kaila's degree of humification as well as of the amount of alkali-extractable carbon in the surface layers of the Bibai and Sarobetsu high-moor peat profiles (Table 5). However, no distinctive tendency related to the decomposition of organic matter was observed in the composition of phenolic compounds (Figs. 1-3). This is considered to be due to the refractory nature of lignin compared with other plant constituents. However, the environmentally induced changes in the lignin composition of peat are an important subject to be studied in detail further.

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REFERENCES

- Barber, K.E. 1993: Peatlands as scientific archives of past biodiversity. *Biodiv. Conserv.*, 2, 474-489
- Ertel, J.R. and Hedges, J.I. 1985: Sources of sedimentary humic substances: vascular plant debris. *Geochim. Cosmochim. Acta*, 49, 2097-2107
- Ertel, J.R., Caine, J.M., and Thurman, E.M. 1993: Biomarker compounds as source indicators for dissolved

- fulvic acids in a bog. *Biogeochemistry*, **22**, 195-212
- Everett, K.R. 1983: Histosols. In *Pedogenesis and Soil Taxonomy II. The Soil Orders*. Ed. L.P. Wilding, N.E. Smeck, and G.F. Hall, p. 1-53, Elsevier, Amsterdam
- Hedges, J.I. and Mann, D.C. 1979: The characterization of plant tissues by their lignin oxidation products. *Geochim. Cosmochim. Acta*, **43**, 1803-1807
- Kaila, A. 1956: Determination of the degree of humification in peat samples. *J. Agric. Sci. Finland*, **28**, 18-35
- Kögel-Knabner, I. 1993: Biodegradation and humification processes in forest soils. In *Soil Biochemistry*, Vol. 8, Ed. J.-M. Bollag and G. Stotzky, p. 101-135, Marcel Dekker Inc., New York
- Kumada, K. 1987: Chemistry of Soil Organic Matter, p. 17-33, Japan Scientific Society Press, Tokyo, and Elsevier, Amsterdam
- Reddy, K.R. and Patrick, W.H., Jr. 1993: Wetland soils—opportunities and challenges. *Soil Sci. Soc. Am. J.*, **57**, 1145-1147
- Soil Survey Staff 1975: Soil Taxonomy, U.S. Dept. Agric. Handbook 436, 754 pp., U.S. Dept. Agric., Washington, D.C.
- Tatsukawa, R. 1966: Rapid determination of soil organic matter with special reference to sugars, uronic acids, and amino sugars. *J. Sci. Soil Manure, Jpn.*, **37**, 28-33 (in Japanese)
- Tsutsuki, K. and Kuwatsuka, S. 1991: Characterization of humin metal complexes in a buried volcanic ash soil profile and a peat soil. *Soil Sci. Plant Nutr.*, **38**, 297-306
- Tsutsuki, K., Kondo, R., Shiraishi, H., Kuwatsuka, S., and Ohnohara Wetland Research Group 1992: Composition of lignin-degradation products, lipids, and opal phytoliths in a peat profile accumulated since 32,000 years B.P. in central Japan. *Soil Sci. Plant Nutr.*, **39**, 463-474
- Tsutsuki, K., Esaki, I., and Kuwatsuka, S. 1994: CuO-oxidation products of peat as a key to the analysis of the paleo-environmental changes in a wetland. *Soil Sci. Plant Nutr.*, **40**, 107-116