Organic matter composition of peat as related to drying and vegetation change in a high-moor peatland

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Abstract

The composition of organic matter in the peat soil was investigated to clarify the effect of drying and vegetation change in a high-moor peatland at Bibai, Hokkaido, Japan. Yields of p-hydroxyphenyl compounds and vanillyl compounds were larger at the sites of *Sphagnum* community, while those of syringyl and cinnamyl compounds were larger at the sites of *Sasa senanensis* community. The yields of p-hydroxyphenyl compounds and vanillyl compounds were also larger in the finer (< 2 mm) peat fractions, while those of cinnamyl compounds were larger in coarser fractions (> 2 mm). Composition of fatty acids in peat was bimodal, peaking at palmitic acid and at lignoceric / cerotic acid. Total yield of fatty acid was larger in the finer peat fraction as well as at the sites where the peat was severely oxidised. β-Sitosterol, campesterol, and stigmasterol were more abundant in the coarse fraction than in the fine fraction as well as at the sites with dense *Sasa senanensis* vegetation than at *Sphagnum* vegetation.

Key words: Capillary gas chromatography, CuO-NaOH oxidation, fatty acid composition, lignin, phenolic compounds, sterol

Introduction

The development of drainage system in the surrounding agricultural field caused severe changes in hydrology and vegetation in a high-moor peatland at Bibai, Hokkaido, Japan. Such environmental change in peatland accompanied the changes in fundamental properties of peat, such as carbon and nitrogen contents, C/N, ash contents, fiber contents and bulk density as well as the changes in degrees of humification and decomposition of peat (Kondo and Tsutsuki 2001). In the present study, the detailed compositions of phenolic compounds, fatty acids, and sterols in peat were analysed further because they are important constituents of plants and are relatively stable under anaerobic condition which prevails in peat soils. Therefore, we have assumed that the composition of organic constituents in peat also reflects the changes in vegetation and hydrology in a peatland.

Materials and methods

Peat samples were the same as those used in the previous paper (Kondo and Tsutsuki 2001). Peat samples were separated to coarse and fine fractions using a 2-mm sieve. Phenolic compounds were liberated from peat sample by CuO-NaOH

oxidation at 150 C for 6 h in a degassed sealed tube, extracted with ethylacetate from the acidified extract, silylated with N,O-bis-trimethylsilyl-acetamide, and analysed by capillary gas chromatography (Tsutsuki *et al.*, 1994). Long chain fatty acids were extracted with chloroform-methanol (2:1), treated with methanol-HCl, then extracted with hexane and determined by capillary GC according to Tsutsuki *et al.,* (1997). Sterols were silylated by heating with N-TMS imidazole a portion of the same sample prepared for fatty acid analysis and determined by capillary GC. The same capillary GC column, Neutrabond-1 (id.: 0.25 mm, film thickness: 0.4 micrometer, length: 60m, GL-Science, Japan) was used for the above three analyses.

Results and discussion

1) Phenolic compounds obtained by CuO-NaOH oxidation of peat.

Phenolic compounds derived by CuO-NaOH oxidation are grouped into p-hydroxyphenyl, vanillyl, syringyl, and cinnamyl compounds according to the type of substitution on the aromatic ring. It is known that composition of these compounds differ according to the taxonomy of plants and to the type of the tissue (Hedges and Mann 1979). Proportion of each phenolic compounds in total phenolic compounds is shown in Fig. 1. The yields of four phenolic acids which represent the above groups are shown in Fig. 2.
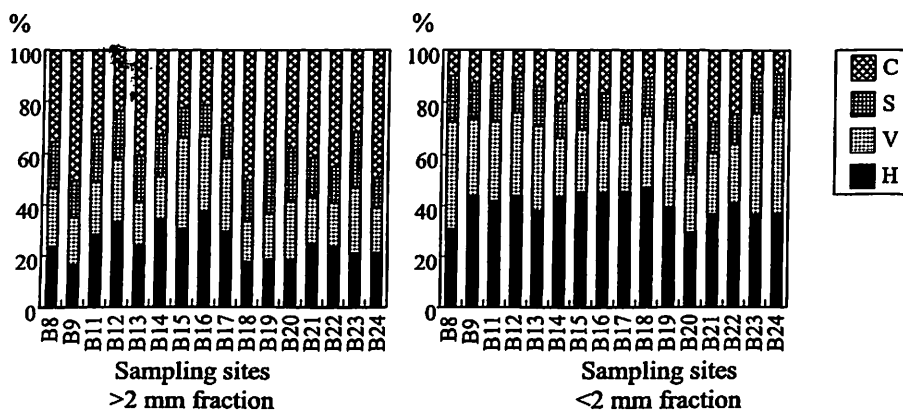
Figure 1 Relative proportion of phenolic compounds according to functional groups. C: cinnamyl, S: syringyl, V: vanillyl, H: p-hydroxyphenyl compounds, respectively.

The coarse fraction (> 2 mm) may represent the relatively undecomposed fraction of plant residue and peat, while the finer fraction (< 2 mm) represent the decomposed fraction. Four types of phenolic compounds, p-hydroxyphenyl (H), vanillyl (V), syringyl (S) and cinnamyl (C) behaved quite differently in these fractions.

The yield of p-hydroxybenzoic acid and vanillic acid showed a similar tendency in the coarse peat fraction. Their yields were relatively high at the central part of the peatland, which corresponded to the community of *Sphagnum* (Kondo and Tsutsuki 2001). The fresh *Sphagnum* yields only p-hydroxyphenyl and vanillyl compounds on CuO-NaOH oxidation.
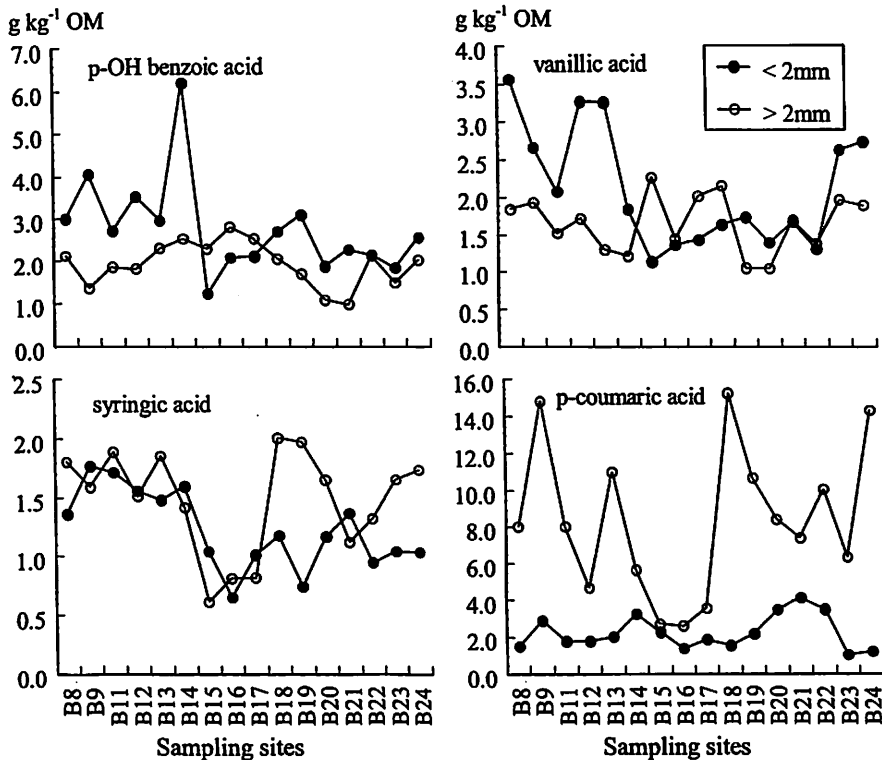
Figure 2 Yields of phenolic acids from coarse and fine fractions of peat in Bibai mire.

Though the yield of p-coumaric acid was largest and that of syringic acid was lowest among the four phenolic acids, distribution of p-coumaric acid and syringic acid were similar to each other. Their yields were tended to be larger in the peripheral area of the peatland, where the community of *Sasa senanensis* invaded, and lower in the central part of the peatland where the community of *Sphagnum* remained. As *Sphagnum* itself do not contain cinnamyl and syringyl compounds, even the small amounts of these compounds were considered to originate from the sedges (*Carex middendorfi* and *Eriophorum vaginatum*) which co-existed within the *Sphagnum* community. Cinnamyl compounds are characteristic to the non-woody tissues of Angiosperm plants, especially *Gramineae* (Hedges and Mann 1979). On the other hands, syringyl compounds were liberated in large amounts from the Angiosperm wood tissue (Hedges and Mann 1979). Therefore, the larger yields of p-coumaric acid and syringic acid in the coarse fraction of peat obtained from the peripheral area of peatland may be explained by the predominance of *Sasa senanensis* and shrubs of *Myrica gale L.* and *Rhus trichocarp L.* which invaded the dried area of this peatland.

When the relative proportion of phenolic compounds were compared between the coarse (> 2mm) and fine (< 2mm) fractions, the proportions of p-hydroxyphenyl and vanillyl compounds were larger in the fine fraction while that of cinnamyl compounds was larger in the coarse fraction (Fig. 1). These tendencies were especially remarkable in the peripheral area of the peatland. The difference in the yields of p-

hydroxybenzoic and vanillic acids between the coarse and fine peat fractions were especially large in the western part of the mire, B8-14, where the drying tendency was the most severe (Fig. 2). The increase in p-hydroxyphenyl and vanillyl compounds as well as the decrease in cinnamyl compounds in the fine peat fraction compared with those in the coarse fraction are considered to result from the decomposition of lignin structure in the plant debris. As the decomposition of p-hydroxyphenyl-propane and guaiacyl propane units in the lignin structure proceed, p-hydroxyphenyl and vanillyl phenols are exposed to the surface of lignin molecule, and easily released by CuO-NaOH oxidation. On the other hand, it is considered that cinnamyl compounds are bonded on the surface of lignin through ester linkages and very vulnerable to the oxidation. The lower yield of cinnamyl compounds (p-coumaric acid and ferulic acid) in the finer fraction is considered to be due to the oxidative decay of plant residues and peat.

2) Long chain fatty acids composition

Histogram of long chain fatty acids in peat were compared at B8 site where the drying tendency of peat was the most severe and at B15 site where *Sphagnum* community still remained intact (Fig. 3). Difference in the composition between the coarse and fine peat fractions were also shown in the same figure. The distribution of the yield of fatty acids were bimodal, peaking at palmitic acid (C16) as well as at lignoceric (C24) or cerotic acids (C26) with respect to the saturated fatty acids. Oleic acid (C18:1) was the most abundant unsaturated fatty acid. Oleic acid, palmitic acid and palmitoleic acid were abundant in the relatively intact *Sphagnum* peat.
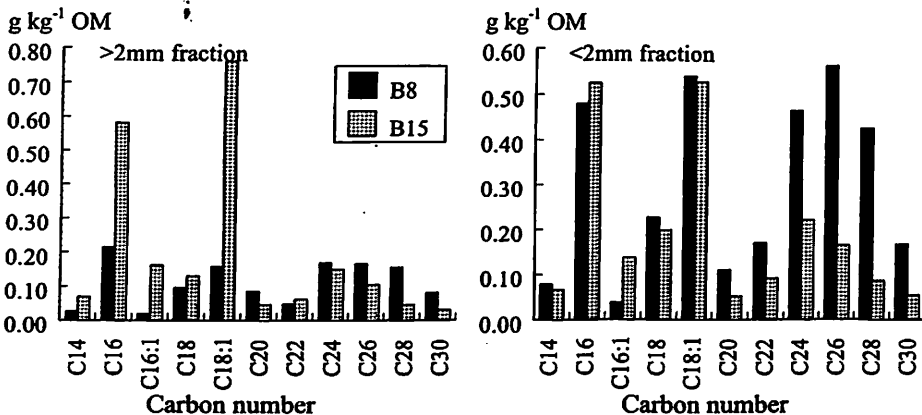

Figure 3 Histogram of long chain fatty acids obtained from the peat of Bibai mire.

Except oleic acid and palmitic acid in *Sphagnum* peat, the yields of fatty acids were larger in the fine peat fraction than in the coarse one. This may be because fatty acids are relatively stable among the plant constituents and increase their proportion as other plant constituents are decomposed preferentially. Especially the long chain fatty acids with carbon numbers 22-30 increased remarkably in the fine peat fraction at the severely oxidised site (B8).

The yields of arachidic acid (C20) and lignoceric acid (C24) were compared on the transect line (Fig. 4). Arachidic acid favored the site of *Sasa senanensis* vegetation and showed low yields at the site of *Sphagnum* community. On the other

hand, lignoceric acid favored the site of *Sphagnum* community. However, its yield increased remarkably where peat underwent severe oxidative decay especially in the western part of the mire. Stearic acid (C18), behenic acid (C22), cerotic acid (C26), montanic acid (C28), and melissic acid (C30) showed the similar tendency with lignoceric acid.
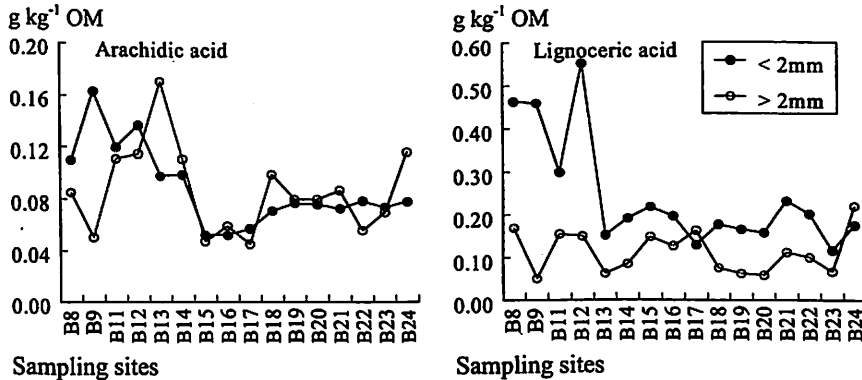

Figure 4 Yields of arachidic acid and lignoceric acid from the peat of Bibai mire

3) Composition of sterols

Dominant sterols detected in the peat were β-sitosterol, campesterol and stigmasterol, which originate from plants. Cholesterol which is contained in animal and microbial tissues was also detected in very small amounts. Yield of each sterol in the coarse and fine fractions was shown in Fig. 5. The yields of β-sitosterol and campesterol were larger in the coarse fraction. They were also large in the area where *Sasa senanensis* thrived, and low where *Sphagnum* community remained. The yield was also low in the western part of the mire, where the drying of peatland was the most severe. This tendency was similar to the yields of p-coumaric acid. This is considered to be because these compounds originated mainly from higher plants and not from *Sphagnum* and also because these compounds were readily decomposed as plant materials were decomposed. The yield of stigmasterol was lower than those of β-sitosterol and campesterol. The difference in the yields of stigmasterol were also small among different sites as well as between the coarse and fine fractions, because stigmasterol was contained in *Sphagnum*. Contrarily, the yields of cholesterol was larger in the fine peat fraction. This may be because cholesterol was produced by soil animals and microbes in accompany with the decomposition of plant materials.

4) Conclusion

The above results indicated that composition of phenolic compounds, fatty acids, and sterols reflect not only the difference in the vegetation but also the degree of the decomposition of peat in the mire. Intact *Sphagnum* peat was characterised by relatively large yields of p-hydroxyphenyl and vanillyl compounds, oleic acid, stearic acid, lignoceric acid and stigmasterol. On the other hand, coarse peat fraction from the community of *Sasa senanensis* and shrubs was characterised by relatively large yields of cinnamyl and syringyl compounds, palmitic acid, arachidic acid, β-sitosterol and campesterol. The decomposition of peat in the dried area caused the decrease in yields of cinnamyl compounds, β-sitosterol and campesterol, and the increase in

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yields of p-hydroxyphenyl and vanillyl compounds, long chain fatty acids with carbon numbers 20-30. Therefore, the drying tendency and the accompanied vegetation change in the mire was followed quantitatively by the characteristic organic constituents in the peat.
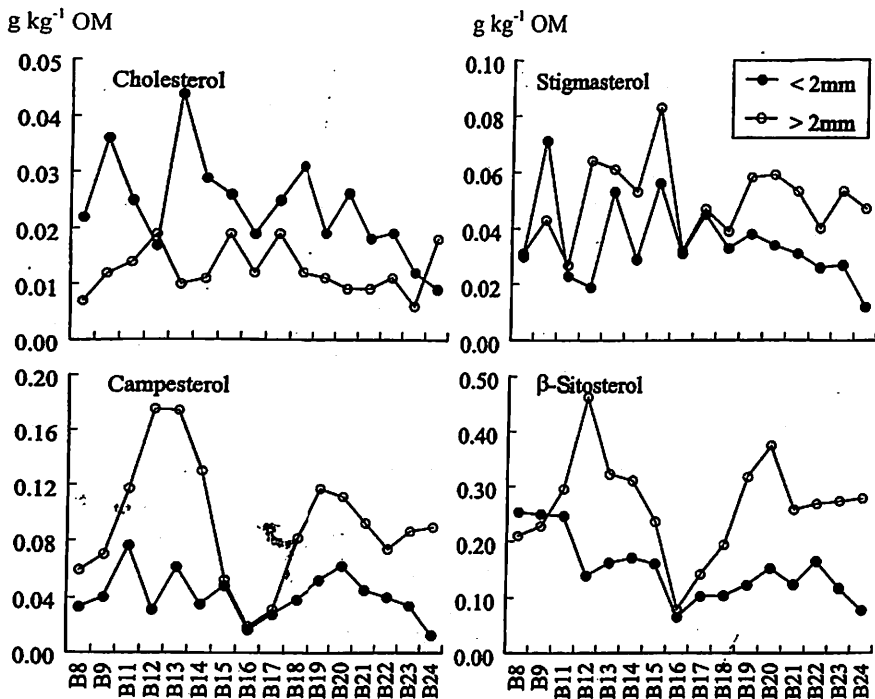

Figure 5 Yields of sterols from peat of Bibai mine

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