## Humus composition of soils under forest, coffee and arable cultivation in hilly areas of south Sumatra, Indonesia

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#### Summary

To understand the effect of land use changes on the composition of humus in tropical soils, samples from land under primary forest, secondary forest, coffee plantation, and arable crops were investigated at three sites in south Sumatra, Indonesia. Total carbon and total nitrogen contents were 1.7 to 4.3 times and 1.1 to 2.8 times greater in the topsoil under primary forest than under the other types of land use. Following change from primary forest to other uses, the proportion of humic acids in the organic matter of the topsoils decreased while that of the fulvic acid fraction increased. Within the range of land uses, differences in the yields of humic acids and fulvic acid fractions were, respectively, larger and smaller than those in total carbon content. The humic acids were classified into the low and middle classes in the degree of humification. Absorption due to the green fraction of humic acids, Pg, was detected in the UVvisible spectra of almost all the humic acids. No relation was observed between the degree of humification of humic acids or the strength of Pg absorption in their spectra and land use change. The fulvic acid fractions were fractionated on insoluble polyvinylpyrrolidone (PVP) into the adsorbed fractions consisting of humic substances and the non-adsorbed fractions consisting of non-humic substances. A positive correlation between the amount of the fulvic acid fraction and the percentage of the PVP-adsorbed fraction within it indicated that the variation in the amount of the fulvic acid fraction was attributable to acid-soluble humic substances. The ionization difference spectra of solutions between pH12 and pH7 suggested that the chemical structures of the PVP-adsorbed fulvic acids have been altered by land use change.

## Introduction

Land use in Indonesia has changed drastically during the past 30 years because of transmigration and changes in the rural economy. In the hilly areas of West Lampung, south Sumatra, the cover of primary forests decreased from 57% to 13% of the total land area between 1970 and 1990, whereas plantations (mainly coffee) increased from 0% to 60% (Lumbanraja *et al.*, 1998). Deforestation and ensuing cultivation alter the physical, chemical, and biological properties of soils.

Soil organic matter, which plays an important role in sustaining soil fertility, is also influenced by land use change. The clearing and burning of forests can lead to a temporary small increase in soil organic matter as a result of the degradation of dead roots (Nye & Greenland, 1964). However,

Correspondence: A. Watanabe. E-mail: akiraw@agr.nagoya-u.ac.jp Received 5 May 2000; revised version accepted 3 April 2001 this organic matter is decomposed rapidly, and the net consequence is a loss of organic matter from the soil (Schimel et al., 1985; Ellert & Gregorich, 1996; Shang & Tiessen, 1997) except where grassland is established (Feigl etal., 1995; De Moraes etal., 1996). Detwiler (1986) estimated that the C content in tropical forest soils decreased by 40% where deforestation was followed by arable land use. Microbial C and N are also greater in natural forest soils than in agricultural soils (Schimel et al., 1985), and the rates of evolution of CO<sub>2</sub> from the soil decline after cultivation (Schimel et al., 1985). In addition to the reduction in fresh plant litter on the mineral soil, tillage accelerates decomposition of organic matter by increasing the oxygen supply and access by microbes. Furthermore, the disappearance of the litter layer and the alteration of the soil's physical properties by tillage increase the risk of erosion. Abandoning agriculture or reafforestation increases the C content of the soil. However, Detwiler (1986) reported that about 35 years are needed before the organic matter of soil under secondary forest returns to its original amount under primary forest in the tropics.

The rates of decomposition of native organic matter and accumulation of organic matter derived from new vegetation have been estimated from the change in the stable C isotope ratios of soils. Bonde *et al.* (1992) estimated a rapid decline in initial C in topsoil (0–10 cm) of an Oxisol in southeastern Brazil during the first 12 years after deforestation. Losses ranged from 40% in the clay fraction to 93% in the fine sand fraction, with a much slower decrease during the following 38 years. Cadisch *et al.* (1996) reported that 73% of the initial C in the 0–2 cm depth layer and 40% of that in the 5–15 cm depth layer of the soil were lost in 18 years following the clearing of rainforest in Brazil.

Change in land use affects not only quantity but also quality of soil organic matter. Guggenberger et al. (1994) showed that organic matter in cultivated soil was richer in carbohydrates than that in forest soil, while phenolic compounds yielded by CuO oxidation appeared to be richer in forest soil than in cultivated soil. Larger concentrations of the sum of vanillyl, syringyl, and cinnamyl phenolic CuO oxidation products and smaller concentrations of neutral sugars and uronic acids in soil under secondary forest compared with continuous farming were also reported by Amelung et al. (1998). The results of pyrolysis-field ionization mass spectrometry also suggested the depletion of lipids and lignin compounds and a predominance of carbohydrates caused by the change from forest to agriculture (Gregorich et al., 1996). However, these compounds are minor constituents of soil organic matter. The major components of soil organic matter are defined by classical extraction and separation procedures, based on solubility in alkali and acid, into three fractions, namely humic acids, fulvic acids, and humin (Stevenson, 1994, pp. 24-58). Each fraction makes its particular contribution towards soil fertility according to changes in humus composition and the chemical structure.

This paper describes the humus composition of soils collected from primary forests, secondary forests, coffee plantations, and cultivated lands in hilly areas of south Sumatra, Indonesia. The humic and fulvic acids were characterized by spectrophotometry in the UV-visible region. The fulvic acid fraction extracted from soil with an alkali solution and separated from humic acids by acidifying the extract consists of both humic substances, highly acidic darkcoloured polyelectrolytes (generic fulvic acids), and nonhumic substances, such as polysaccharides and peptides. In the present study, the proportion of humic and non-humic substances in the fulvic acid fraction was estimated by fractionating them using a cross-linked insoluble polyvinylpyrrolidone (PVP). In this procedure, humic and non-humic substances are concentrated into the PVP-adsorbed and nonadsorbed fractions, respectively (Lowe, 1975; Saiz-Jimenez & de Leeuw, 1984; Watanabe & Kuwatsuka, 1992). Their

proportions have been found to vary depending on the type of soil (Watanabe & Kuwatsuka, 1991).

### Materials and methods

#### Soil samples

Samples of topsoil corresponding to the A horizon (0-13 or 23 cm) and subsoil corresponding to the B horizon (13 or 23-32 or 40 cm) were collected from the four kinds of land use at three sites, namely Bukit Ringgis, Sekincau, and Trimulyo in West Lampung, Sumatra, Indonesia. The climate is B1 (7-9 months wet season and less than 2 months dry season) according to Köppen's classification, with an annual rainfall of 1500-2000 mm. The land ranges between 780 m and 2115 m above sea level. All the soils are heavy Cambisols containing more than 30% clay. The major clay mineral is halloysite at all sites. Soil chemical properties are described by Lumbanraja et al. (1998). At all sites, the predominant trees in the primary forests are Shorea spp., Hopea, Dipterocarpus spp., and Dryobalanops spp., and those in the secondary forests are Ficus septica, F. ampelas, F. variegata, and Hibiscus spp. Cultivated crops are tomato, long bean, cowpea, and red pepper.

Four soil profiles were exposed under each land use at each site, and four soil samples were collected and mixed to give a composite sample. Then the samples were air-dried, sieved (<2 mm), and the humic and fulvic acid fractions were extracted from them. Plant debris and roots were removed by hand as far as possible. For determination of total C and total N contents, aliquots of the soil samples were further pulverized using a vibrating sample mill (TI-100, HEIKO Ltd).

## Extraction and fractionation of humic acids and fulvic acid fractions

The humic and fulvic acid fractions were extracted with 0.1 M NaOH for 48 h under an  $N_2$  atmosphere at 25°C with intermittent shaking. The ratio of alkali to soil sample was set at  $300 \text{ cm}^3 \text{ g}^{-1}$  C, except for some subsoil samples containing less C, for which 100 cm<sup>3</sup> alkali was applied to 20 g soil. The extract was separated by centrifuging at 3000gfor 15 minutes after an addition of 30 mg cm<sup>-3</sup> of Na<sub>2</sub>SO<sub>4</sub> as coagulant. The soil residue was washed twice with the same volume of 0.1 M NaOH containing Na<sub>2</sub>SO<sub>4</sub>. The washings were combined with the extract. Then the extract was acidified to pH1.5 and allowed to stand overnight. After separation of the humic acids from the fulvic acid fraction by centrifuging, the precipitated humic acids were dissolved in 0.1 M NaOH and re-precipitated by the addition of 1.5 M H<sub>2</sub>SO<sub>4</sub>. The supernatant obtained by centrifuging was combined with the fulvic acid fraction. The precipitate was re-dissolved in 0.1 M NaOH, and clay contaminants were removed by addition of  $Na_2SO_4$  (30 mg cm<sup>-3</sup>), followed by centrifuging at 15 000 g for 20 minutes. The supernatant was re-acidified, centrifuged, and the precipitate was re-dissolved in a small volume of 0.2 M NaOH, and diluted in a volumetric flask with 0.1 M NaOH.

The fulvic acid fraction was diluted in a volumetric flask with distilled water. Then portions of the fraction were fractionated using columns packed with PVP (Polyclar SB-100, purchased from Gokyo Sangyo Inc.) into the adsorbed and non-adsorbed fractions as described by Watanabe & Kuwatsuka (1991). The PVP-adsorbed fractions were eluted with 0.01 M NaOH, acidified with  $1.5 \text{ M H}_2\text{SO}_4$ . Both the PVP-adsorbed and non-adsorbed fractions obtained were diluted in volumetric flasks with distilled water.

The extraction and fractionation of humic and fulvic acid fractions were done in duplicate.

#### Determination of carbon and nitrogen contents

Total C and total N contents of the soil samples were determined using an NC analyser (Sumigraph NC-800, Shimadzu). The total C and inorganic C contents in the solution samples were determined using a dissolved carbon analyser (TOC-500, Shimadzu). The total C content after removal of dissolved CO<sub>2</sub> by bubbling with N<sub>2</sub> was regarded as the organic C content in the fulvic acid fractions and their PVP-adsorbed and non-adsorbed fractions. For the humic acid solutions the measurement was done after  $1/15 \text{ M KH}_2\text{PO}_4$  was added at a ratio of 4:1 to regulate pH at around 4, and the difference between total C and inorganic C contents was regarded as the organic C content.

# Measurement of UV-visible spectra and expression of their characteristics

The UV-visible spectra from 230 nm to 700 nm and the absorbances at 600 nm and 400 nm ( $E_{600}$  and  $E_{400}$ ) of the humic acid solutions were recorded on a Shimadzu UV-2200 spectrophotometer. The values of RF and  $\Delta \log K$  were calculated using the following equations:

and

$$RF = 15 E_{600}/C,$$

$$\Delta \log K = \log E_{400} - \log E_{600}$$

where *C* is the organic carbon concentration of the sample solution  $(\text{mg ml}^{-1})$ . The *RF* indicates the relative depth of colour of humic acids, and  $\Delta \log K$  expresses the slopes of UV-visible spectra which are almost straight on the logarithmic scale. Based on these variables, humic acids were classified into four types, A, B, P, and Rp (Figure 1; Kumada *et al.*, 1967; Kumada, 1987).

The green fraction of humic acids designated 'Pg' has absorption maxima at 615, 570, and 450 nm in alkali (Sato, 1974; Watanabe *et al.*, 1996). The relative strength of Pg absorption was judged from the shape (flat, shoulder, or peak)



**Figure 1** Classification diagram of humic acids based on RF and  $\Delta \log K$ .

at these wavelengths, and expressed using the symbols  $\pm$ , +, ++, and +++ in the subscript form following the type of humic acids (Kumada *et al.*, 1967; Kumada, 1987).

## Measurement of ionization difference spectra

Equal volumes of the PVP-adsorbed fractions of the fulvic acid fraction, corresponding to an organic C content of 0.5 mg, were placed in two beakers, and their pHs were adjusted to 12.0 and 7.0, respectively, using HCl and NaOH. The total volume of each sample was adjusted to  $25 \text{ cm}^3$  using the appropriate HCl or NaOH diluents. The pH 7.0 and pH 12.0 solutions were set in a reference cell and sample cell, respectively, and the spectra were recorded between 230 m and 700 nm on the Shimadzu UV-2200 spectrophotometer.

#### Statistical analyses

The contents of various fractions and the spectrophotometric variables of humic acids were analysed by two-factor analysis of variance for both the topsoil and the subsoil. The average values from the three sampling sites were used (n=3) for comparison between the types of land use. The relation between the amount of fulvic acid fraction in soil and the percentage of the PVP-adsorbed fraction in the fulvic acid fraction was estimated by Pearson's correlation coefficient.

#### **Results and discussion**

#### Total carbon and total nitrogen contents of soils

Total carbon and total nitrogen contents in the topsoil under primary forest were 1.7 to 4.3 times and 1.1 to 2.8 times greater than those under the other three types of land use at the three sites, respectively (Table 1; P < 0.05). Although the total C and total N contents in the topsoil samples under secondary forest were 1.1 to 2.3 times and 1.1 to 1.4 times greater than those from cultivated lands, respectively, the differences were not statistically significant.

The altitude of the sampling sites decreased from primary forest to secondary forest (150-160 m), and secondary forest to coffee plantation (200-280 m), with a smaller difference between coffee plantation and cultivated land (-20 to 70 m). Because the lower temperatures at higher altitudes increase the accumulation of organic matter, the differences in altitude might have an effect, albeit small, on the differences in the organic matter content of the topsoil between primary forest and the other types of land use. Van Noordwijk et al. (1997), for example, reported that the organic C content in the topsoil increases by a factor of only 1.04 per 100 m increase in altitude in Indonesia when the types of soil and land use are identical. We therefore think that the clearance of primary forest and the use of the land for coffee or arable crops caused a decrease in organic matter in the topsoils at the three sites, and that the organic matter has not returned to the initial values even under secondary forest.

The C/N ratios of the topsoils from the coffee and arable lands are less than those under primary forest (P < 0.05), which suggests a larger decrease in C than in N after deforestation. Ellert & Gregorich (1996) obtained similar results for Canadian soils.

The total C contents in the subsoil tended to be greater in the forest soils than in the agricultural ones (Table 1). Whilst they are 3.2 to 6.8 times greater at Sekincau, they are less than twice as large at Bukit Ringgis and Trimulyo.

## Contents of humic acids and fulvic acid fraction

The proportions of humic acids and fulvic acid fraction in total organic matter in the topsoil varied among land uses (Figure 2). At all the sites the proportion of humic acids was greater while that of fulvic acid fraction was smaller under primary forest than under the other land uses (P < 0.05).

The proportion of fulvic acid fraction in the subsoil ranged between 21% and 50%, while that of humic acids was less than 8%. There was no relation between the proportion of humic acids or the fulvic acid fraction and the type of land use.

The differences in the amount of humic acids in the topsoil between primary forest and the other land uses (2.2 to 14 times; P < 0.05) were greater than those noted for the total C content (Figure 3a). The differences in the amounts of the fulvic acid fraction between different land uses were smaller (not significant; Figure 3b). More than twice the difference in the amount of fulvic acid fraction was observed between cultivated land and the other land uses at Sekincau and between primary forest and the others at Trimulyo.



**Figure 2** Percentages of humic acids and fulvic acid fraction in total soil organic matter under the four types of land use (C basis).  $\bullet$ , Topsoil under primary forest;  $\blacktriangle$ , topsoil under secondary forest;  $\blacksquare$ , topsoil under coffee plantation;  $\times$ , topsoil under cultivated land;  $\bigcirc$ , subsoil under primary forest;  $\bigtriangleup$ , subsoil under secondary forest;  $\Box$ , subsoil under cultivated land.

Table 1 Total carbon and total nitrogen contents and	the C/N ratio of soil samples
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Site	Land use	Total C /g kg <sup>-1</sup>		Total N /g kg <sup>-1</sup>		C/N ratio	
		Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Bukit Ringgis	Primary forest	53.8	9.8	2.74	0.78	20.2	12.6
	Secondary forest	32.4	10.9	2.42	1.01	13.4	10.7
	Coffee plantation	26.0	7.3	2.27	0.69	11.5	10.7
	Cultivated land	27.6	8.8	2.12	0.77	13.0	11.4
Sekincau	Primary forest	147.4	49.4	7.65	2.40	19.3	20.6
	Secondary forest	80.2	56.3	4.43	2.89	18.1	19.5
	Coffee plantation	80.1	15.6	5.64	1.21	14.2	12.9
	Cultivated land	34.6	8.3	3.13	0.75	11.0	11.0
Trimulyo	Primary forest	96.2	18.8	7.21	2.10	13.3	8.9
	Secondary forest	37.9	13.8	3.55	1.57	10.7	8.8
	Coffee plantation	25.4	12.5	2.60	1.38	9.8	9.1
	Cultivated land	27.2	10.0	2.68	1.14	10.2	8.8



Figure 3 Amounts of humic acids and fulvic acid fraction in soils under the four types of land use. (a) Humic acids in topsoil; (b) fulvic acid fraction in topsoil; (c) humic acids in subsoil; (d) fulvic acid fraction in subsoil.

Fable 2 Spectrophotome	tric variables	of humic	acids
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Site	Land use	$RF^{\mathrm{a}}$		$\Delta \log K^{a}$		Type of HA <sup>a</sup>	
		Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Bukit Ringgis	Primary forest	46.3	39.5	0.721	0.580	B <sub>±</sub>	P+++
	Secondary forest	41.4	34.6	0.747	0.720	B_+	Rp_++
	Coffee plantation	35.5	33.5	0.777	0.671	Rp <sub>+</sub>	P_+++
	Cultivated land	30.8	36.6	0.840	0.680	Rp+	P+++
Sekincau	Primary forest	48.5	63.7	0.721	0.734	$B_{+}$	B++
	Secondary forest	64.0	32.2	0.669	0.542	B <sub>++</sub>	P_+++
	Coffee plantation	31.2	38.4	0.790	0.766	Rp <sub>++</sub>	Rp <sub>++</sub>
	Cultivated land	50.3	41.0	0.771	0.713	B <sub>+</sub>	B <sub>++</sub>
Trimulyo	Primary forest	19.5	24.1	0.955	0.855	Rp	Rp+
	Secondary forest	20.4	44.6	0.884	0.819	Rp +	B_++
	Coffee plantation	39.4	42.5	0.711	0.780	Rp <sub>+</sub>	B <sub>++</sub>
	Cultivated land	35.4	25.4	0.737	0.756	Rp <sub>+</sub>	Rp+++

<sup>a</sup>See text for explanation.

The amount of humic acids in the subsoil under primary forest was 1.9 to 67 times and 4.4 to 27 times larger than under coffee and arable crops, respectively (Figure 3c), although these differences were not statistically significant. The amount of fulvic acid fraction in the subsoil was 3.4 to 8.7 times larger under both kinds of forest than under agriculture at Sekincau, and was similar between different types of land use at Bukit Ringgis and Trimulyo (Figure 3d).

When a mixture of 0.1 M NaOH and 0.1 M  $Na_4P_2O_7$  was used as extractant, larger yields of humic acid C under forest than under arable rotation have been reported (Guggenberger *et al.*, 1995). A decrease in humus as a result of cultivation was also found for a crusting soil in Zimbabwe by Pardo *et al.* (1997), who used a mixture of 0.1 M NaOH and 0.1 M  $Na_4P_2O_7$ to extract the humus. The humic acids and fulvic acid fraction decreased by 28% and 57%, respectively, in the topsoil (0–20 cm) and by 38% and 61% in the subsoil (20–45 cm). This contrasts with our results and could be because humic acids extracted with chelating agents such as  $Na_4P_2O_7$  but not extractable with dilute NaOH form stable complexes with polyvalent cations, and because there is much less fulvic acid fraction in such forms (Kumada, 1987).

#### Spectrophotometric properties of humic acids

The *RF* and  $\Delta \log K$  values as well as the type of humic acids classified according to Kumada (Kumada *et al.*, 1967; Kumada, 1987) are shown in Table 2. The increases in *RF* values or the decrease in  $\Delta \log K$  values indicate the increase in the degree of humification. Many other properties of humic



Figure 4 Yields of the PVP-adsorbed and non-adsorbed fractions from fulvic acid fractions (C basis).

acids have been shown to be related to the *RF* and  $\Delta \log K$  values. For example, the contents of carboxyl and carbonyl groups (Tsutsuki & Kuwatsuka, 1978) and the aromatic C content estimated from <sup>13</sup>C-NMR (Tate *et al.*, 1990) correlate positively with *RF*, whereas the contents of methoxyl and phenolic hydroxyl groups (Tsutsuki & Kuwatsuka, 1978) and molecular size (Tsutsuki & Kuwatsuka, 1984) decrease with increasing degree of humification. Thus this classical technique gives valuable information about composition and structure of humic acids.

The humic acids from the topsoil samples were classified into Type B or Type Rp, the middle or low class in the degree of humification. The Pg absorption, although not very strong, was observed in the UV-visible spectra of the humic acids from all the topsoils, except for that from primary forest at Trimulyo. Four humic acids from the subsoil samples were classified into Type  $P_{+++}$ , and most other humic acids also showed distinct Pg absorption (++ or +++) in their UV-visible spectra.

The relation between land use and the degree of humification of humic acids varied from site to site. At Sekincau, the degree of humification of humic acids in the topsoil was greatest under secondary forest and least under coffee. It was greater under forests than under agriculture at Bukit Ringgis, whilst the opposite was the case at Trimulyo. The increase in the degree of humification with decreasing amount of humic acids due to changing land use suggests selective decomposition of the molecules or moieties of humic acids with low degrees of humification. Burning could also increase the degree of humification. On the other hand, the decrease in humic acids due to erosion may be non-selective in relation to the degree of humification. A decrease in the degree of humification suggests the accumulation of or substitution with new humic acids under the new land use. They were uncommon, however, at our research sites.

The green fraction, which has a 4,9-dihydroxyperylene-3,10-quinone skeleton as the chromophore, has been found in many countries from the tropics to the subarctic (Kumada, 1987). Our report of its presence is the first in Indonesia. The absorption due to the green fraction was measured to determine its potential as an index of the degradation of complex aromatic materials. Orlov (1968) and Sato (1976) suggested that Pg is degraded by cultivation, based on their finding it in subsoil but not the plough layer. The relative strength of Pg absorption was also greater for the humic acids from the subsoil than for those from the topsoil (Table 2). However, we assumed this difference to be due to the readier movement of Pg than that of the other humic acids, because the relative strength of Pg absorption in topsoil humic acids was often greater under agriculture than under primary forest. This result also suggested that Pg was more stable than the other humic acids against changes in land use.

## Distribution of fulvic acid fraction between the PVPadsorbed and non-adsorbed fractions, and the ionization spectra of the PVP-adsorbed fractions

The distribution of fulvic acid fraction between the PVPadsorbed and non-adsorbed fractions is shown in Figure 4. The percentage of the PVP-adsorbed fractions ranged from 17% to 49%. A larger percentage of the PVPadsorbed fraction compared with the other types of land use was observed for the topsoil from primary forest at Trimulyo. A smaller percentage of the PVP-adsorbed fraction than that in the other fulvic acid fractions from the same site was observed for the topsoil and subsoil from the cultivated land at Sekincau. There the amount of fulvic acid fraction was also smaller than in the soil under forest and coffee. A positive correlation (n=24; r=0.803) was detected between these two variables for both the topsoil and subsoil samples. Therefore, it seems that change of land use has diminished the humic substances rather than non-humic substances in the fulvic acid fraction, with the latter possibly increasing under the new regime. This accords with the findings of Amelung et al. (1998) and



**Figure 5** Ionization difference spectra of the PVP-adsorbed fractions of fulvic acid fractions obtained from the topsoil under the four types of land use. (a) Bukit Ringgis; (b) Sekincau; (c) Trimulyo. PF, primary forest; SF, secondary forest; CF, coffee plantation; CL, cultivated land. A vertical bar indicates the length of 0.1 of absorbance.

Guggenberger *et al.* (1994) that a cultivated soil contained more carbohydrate than did one under secondary forest.

The *RF* and  $\Delta \log K$  are less useful for characterizing the fulvic acids, and the elementary composition, molecular size distribution, infrared and <sup>13</sup>C-NMR spectra are similar between the generic fulvic acids from different types of soils (Watanabe & Kuwatsuka, 1992). The  $\Delta E_{7-12}$  spectra, in which peaks appear due mainly to ionization of hydroxyls having p $K_a$  between pH7 and 12, were found to differ in pattern between the PVP-adsorbed fulvic acids from different types of soils (Watanabe & Kuwatsuka, 1991). Differences in structure such as the number of hydroxyls on an aromatic skeleton and the length of conjugated system lead to differences in the wavelengths of the peaks.

Figure 5 shows the  $\Delta E_{7-12}$  spectra of the PVP-adsorbed fulvic acids. They are drawn on the same scale but offset vertically. The  $\Delta E_{7-12}$  spectra of the PVP-adsorbed fulvic acids from the soils under primary forest differed from site to site. The strong and sharp peaks at 245, 295, and 335 nm in the spectrum of the sample from the primary forest at Trimulyo could be assigned to lignin-like structures (Terashima, 1982). The strong shoulder at 400 nm suggested the co-occurrence of a longer conjugated system. Two maxima at 245 and around 340–350 nm as well as a shoulder at around 400 nm were observed for the sample from Bukit Ringgis. There was no peak at around 300 nm that could be assigned to the phenols having saturated or unconjugated side chain (Terashima, 1982). Similar spectra were typical for fulvic acids in Japanese brown forest soils (Watanabe & Kuwatsuka, 1991). The Sekincau sample showed peaks at 285 and 360 nm.

The PVP-adsorbed fulvic acids obtained from coffee plantations (Bukit Ringgis and Trimulyo) and cultivated lands (Sekincau and Trimulyo) had spectra with peaks at 260, 285, 350, and around 465 nm as well as shoulders at 400 nm. Similar  $\Delta E_{7-12}$  spectra have been observed for the fulvic acids in Japanese Ando soils (Watanabe & Kuwatsuka, 1991), although the peak strength at around 465 nm, suggesting the presence of polynuclear aromatic structures, was much less marked for the fulvic acids in the Sumatra soil. The amount of the PVP-adsorbed fulvic acids in these agricultural soils suggested that 40-80% of that in the soils under primary forest was lost (Figures 3 and 4). Materials remained after clearing forest because of their greater stability towards biodegradation; materials formed by oxidative degradation of humic acids under cultivation, or materials produced during burning, may account for the absorptions. Thus the variations in  $\Delta E_{7-12}$ spectra, which were less conspicuous than those detected among the various kinds of soil (Watanabe & Kuwatsuka, 1991), suggested the change in chemical structure of fulvic acids after deforestation.

## Conclusions

Based on the analyses of humus composition and spectrophotometric properties of humic and fulvic acids, land use changes in hilly areas in south Sumatra, Indonesia affect soil organic matter as follows.

**1** Clearing primary forest and using the land for coffee or arable crops caused a decrease in organic matter in the topsoil. The organic matter content was less even under secondary forest.

**2** Changing land use from primary forest to other forms led to a decrease in the proportion of humic acids and an increase in that of fulvic acid fraction in the total organic matter in the topsoil.

**3** There was no relation between the variation in the degree of humification of humic acids and the land use.

**4** The decrease in the amount of fulvic acid fractions corresponded to the decrease in the proportion of humic substances (generic fulvic acids) in them.

**5** The chemical structure of generic fulvic acids also changed as a result of the forest clearance.

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## References

- Amelung, W., Zech, W., Zhang, X., Sajjapongse, A. & Niamskul, C. 1998. Lignin and carbohydrates in soils under secondary forest, alley-cropping, and continuous farming, Thailand. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **161**, 297–302.
- Bonde, T.A., Christensen, B.T. & Cerri, C.C. 1992. Dynamics of soil organic matter as reflected by natural <sup>13</sup>C abundance in particle size fractions of forested and cultivated Oxisols. *Soil Biology and Biochemistry*, **24**, 275–277.
- Cadisch, G., Imhof, H., Urquiaga, S., Boddey, R.M. & Giller, K.E. 1996. Carbon turnover ( $\delta^{13}$ C) and nitrogen mineralization potential of particulate light soil organic matter after rainforest clearing. *Soil Biology and Biochemistry*, **28**, 1555–1567.
- De Moraes, J.F.L., Volkoff, B., Cerri, C.C. & Bernoux, M. 1996. Soil properties under Amazon forest and changes due to pasture installation in Rondônia, Brazil. *Geoderma*, **70**, 63–81.
- Detwiler, R.P. 1986. Land use change and the global carbon cycle: the role of tropical soils. *Biogeochemistry*, **2**, 67–93.
- Ellert, B.H. & Gregorich, E.G. 1996. Storage of carbon, nitrogen and phosphorus in cultivated and adjacent forested soils of Ontario. *Soil Science*, **161**, 587–603.
- Feigl, B.J., Melillo, J. & Cerri, C.C. 1995. Changes in the origin and quality of soil organic matter after pasture introduction in Rondônia (Brazil). *Plant and Soil*, **175**, 21–29.
- Gregorich, E.G., Monreal, C.M., Schnitzer, M. & Schulten, H.-R. 1996. Transformation of plant residues into organic matter: chemical characterization of plant tissue, isolated soil fractions, and whole soils. *Soil Science*, **161**, 680–693.
- Guggenberger, G., Christensen, B.T. & Zech, W. 1994. Land-use effects on the composition of organic matter in particle-size separates of soil: I. Lignin and carbohydrate signature. *European Journal of Soil Science*, **45**, 449–458.
- Guggenberger, G., Zech, W., Haumaier, L. & Christensen, B.T. 1995. Land-use effects on the composition of organic matter in particlesize separates of soils: II. CPMAS and solution <sup>13</sup>C NMR analysis. *European Journal of Soil Science*, **46**, 147–158.
- Kumada, K. 1987. Chemistry of Soil Organic Matter. Elsevier, Amsterdam.
- Kumada, K., Sato, O., Ohsumi, Y. & Ohta, S. 1967. Humus composition of mountain soils in central Japan with special reference to the distribution of P type humic acid. *Soil Science and Plant Nutrition*, **13**, 151–158.
- Lowe, L.E. 1975. Fractionation of acid-soluble components of soil organic matter using polyvinyl pyrrolidone. *Canadian Journal of Soil Science*, **55**, 119–126.
- Lumbanraja, J., Syam, T., Nishide, H., Mahi, A.K., Utomo, M., Sarno & Kimura, M. 1998. Deterioration of soil fertility by land use

changes in South Sumatra, Indonesia (from 1970 to 1990). Hydrological Processes, **12**, 2003–2013.

- Nye, P.H. & Greenland, D.J. 1964. Changes in the soil after clearing tropical forest. *Plant and Soil*, **21**, 101–112.
- Orlov, D.S. 1968. Adsorption and distribution of spectra of P-type humic acids in USSR soils. *Soviet Soil Science*, 1384–1393.
- Pardo, M.T., Giampaolo, S. & Almendros, G. 1997. Effect of cultivation on physical speciation of humic substances and plant nutrients in aggregate fractions of crusting soil from Zimbabwe. *Biology and Fertility of Soils*, 25, 95–102.
- Saiz-Jimenez, C. & de Leeuw, J.W. 1984. Pyrolysis-gas chromatography-mass spectrometry of soil polysaccharides, soil fulvic acids and polymaleic acid. *Organic Geochemistry*, 6, 287–293.
- Sato, O. 1974. Methods for estimating Pg content in P type humic acid and for calculating  $\Delta \log K$  of its Pb fraction. *Soil Science and Plant Nutrition*, **20**, 343–351.
- Sato, O. 1976. The distribution of Pg (green fraction of P type humic acid) and the degree of humification of Pb (brown fraction of P type humic acid) in soils of central Japan. *Soil Science and Plant Nutrition*, **22**, 159–167.
- Schimel, D.S., Coleman, D.C. & Horton, K.A. 1985. Soil organic matter dynamics in paired rangeland and cropland toposequences in North Dakota. *Geoderma*, **36**, 201–214.
- Shang, C. & Tiessen, H. 1997. Organic matter liability in a tropical Oxisol: evidence from shifting cultivation, chemical oxidation, particle size, density, and magnetic fractionations. *Soil Science*, 162, 795–807.
- Stevenson, F.J. 1994. Humus Chemistry: Genesis, Composition, Reactions, 2nd edn. John Wiley & Sons, New York.
- Tate, K.R., Yamamoto, K., Churchman, G.J., Meinhold, R. & Newman, R.H. 1990. Relationships between the type and carbon chemistry of humic acids from some New Zealand and Japanese soils. *Soil Science and Plant Nutrition*, **36**, 611–621.
- Terashima, N. 1982. Physical properties. In: *Chemistry of Lignin* (ed. J. Nakano), pp. 169–173. Uni Publishing Company, Tokyo (in Japanese).
- Tsutsuki, K. & Kuwatsuka, S. 1978. Chemical studies on soil humic acids. II. Composition of oxygen-containing functional groups of humic acids. *Soil Science and Plant Nutrition*, 24, 547–560.
- Tsutsuki, K. & Kuwatsuka, S. 1984. Molecular size distribution of humic acids as affected by the ionic strength and the degree of humification. *Soil Science and Plant Nutrition*, **30**, 151–162.
- Van Noordwijk, M., Cerri, C., Woomer, P.L., Nugroho, K. & Bernoux, M. 1997. Soil carbon dynamics in the humid tropical forest zone. *Geoderma*, **79**, 187–225.
- Watanabe, A. & Kuwatsuka, S. 1991. Fractionation of soil fulvic acids using polyvinylpyrrolidone and their ionization difference spectra. *Soil Science and Plant Nutrition*, **37**, 611–617.
- Watanabe, A. & Kuwatsuka, S. 1992. Chemical characteristics of soil fulvic acids fractionated using polyvinylpyrrolidone (PVP). *Soil Science and Plant Nutrition*, **38**, 31–41.
- Watanabe, A., Fujimori, H., Nagai, Y., Miyajima, T. & Kuwatsuka, S. 1996. Analysis of the green fraction of humic acids. *European Journal of Soil Science*, **47**, 197–204.