

Characterization of Humin-Metal Complexes in a Buried Volcanic Ash Soil Profile and a Peat Soil

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Received July 29, 1991

Humin was prepared from samples of a buried humic volcanic ash soil profile and a peat soil by the HF/HCl treatment method as well as by the DMSO extraction method. Recovery of humin carbon was 35-86% by HF/HCl treatment and 9-22% by DMSO extraction. With respect to the elementary composition, DMSO-humin was characterized by higher H/C and N/C ratios and a lower degree of unsaturation compared with HF-humin. The elementary composition of the humin from the peat soil was similar to that of lignin. Both HF-humin and DMSO-humin contained a large amount of ash. In HF-humin, aluminum was the predominant metal accompanied by small amounts of magnesium and calcium. In DMSO-humin, iron was the predominant metal accompanied by a small amount of titanium. Other elements were contained in trace amounts in both humin preparations. Though both HF-humin and DMSO-humin were insoluble in aqueous alkaline solution, a large part of them could be solubilized in alkaline solution by treatment with Chelex 100, a chelating resin, which suggested that HF-humin occurred as a complex with aluminum while DMSO-humin with iron. Only HF-humin from the peat soil was hardly soluble in alkaline solution after treatment with Chelex 100 presumably because the humin in the peat soil occurred as a hardly soluble polymer like lignin and not as a metal complex.

Key Words: humin, metal-humic complex, peat, volcanic ash soil.

Humin is a fraction of soil organic matter that cannot be extracted either with alkali or with acid. Although it accounts for 50-80% of the soil organic matter, humin is the least studied fraction of humic substances (Rice and MacCarthy 1988). The difficulty in extraction, purification, and solubilization prevents the determination of the chemical composition and structure of humin. Though humin has been isolated after HF treatment very often, the substance obtained may have been modified due to hydrolysis and/or condensation under the drastic conditions of HF treatment (Stevenson 1982). In this study humin was extracted from samples of a buried humic volcanic ash soil profile and a peat soil with acidified dimethylsulfoxide (DMSO), which has been used as a mild and effective extractant of soil humic substances (Law et al. 1984; Hayes 1985; Piccolo 1988), and the chemical

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composition of the preparation thus obtained was compared with that of HF-treated humin. Since both preparations were insoluble in aqueous solvents and contained still large amounts of ash, an effective purification method using a chelating resin was proposed.

MATERIALS AND METHODS

1. Soil samples. Buried volcanic ash soil profile: Samples from a surface and buried layers of a humic volcanic ash soil profile were collected at Ashitaka-Onoue, Numazu City, Shizuoka Prefecture, Japan. Description of the profile has been reported previously (Tsutsuki and Kuwatsuka 1989).

Peat soil: Peat soil samples were collected at Tsukude, Minami-Shitara-gun, Aichi Prefecture, Japan (35 N, 137.5 E). A well decomposed peat sample collected from the 56 to 68 cm deep layer was used. According to the tephro-chronology of the volcanic ash layers interposed between peat layers, this peat sample was slightly younger than 6,300 yBP (K-Ah tephra). Another peat sample was collected from the buried layer overlaid by a sandy loam. Radio-carbon date 32,140 yBP (NUTA-697) of this sample was determined by the authors using the Tandetron accelerator mass spectrometer at Nagoya University.

2. Methods of preparation of humin. Preparation of humin fractions (residue of extraction): Soil samples of the humic volcanic ash soil profile were air-dried and passed through a 2 mm mesh sieve. The soil samples were further crushed in water and passed through a 0.1 mm mesh sieve to remove fine roots, and then extracted with 0.1 mol L⁻¹ NaOH for 48 h under a N₂ atmosphere at room temperature, washed two times with 0.1 mol L⁻¹ NaOH containing 30 g L⁻¹ Na₂SO₄, two times with 30 g L⁻¹ Na₂SO₄, and two times with water. The humin fraction was obtained by freeze-drying of the residue.

Peat samples were freeze-dried and crushed to pass through a 0.2 mm mesh sieve. Sixty grams of sample was extracted 5 times with 1 L of 0.1 mol L⁻¹ NaOH, washed two more times with 0.1 mol L⁻¹ NaOH, 2 times with 30 g L⁻¹ NaCl, 2 times with 0.1 mol L⁻¹ HCl, and 2 times with water. The residue (humin fraction) was freeze-dried and subjected to further preparation of humin.

Preparation of humin by HF treatment: Two hundred milliliters of 0.46 kg kg⁻¹ HF/2 mol L⁻¹ HCl (1 : 1) solution was added to 10 g of the residue of alkaline extraction in a plastic centrifuge tube. The mixture was allowed to react at 80°C under shaking for 1 h. The supernatant was discarded after centrifugation, and the residue was treated three more times with the above HF/HCl solution. After the final supernatant was discarded, the residue was washed 4 times with water and freeze-dried to yield the HF-humin preparation.

Preparation of humin by extraction with DMSO: Five grams of the residue of extraction was soaked with 3–8 mL of conc. HCl (12 mol L⁻¹) depending on the bulk of the sample. The soaked sample was shaken with 250 mL of dimethylsulfoxide (DMSO) for 30 min, left to stand overnight and centrifuged to obtain the dark colored extract. The residue of the DMSO extraction was extracted again with 100 mL of DMSO, and the first and second extracts were combined together. Saturated NaOH solution was added dropwise to the extract and the pH of the solution was adjusted at 8–9 to precipitate humin. The pellet was collected by centrifugation, suspended in water, and acidified slightly with HCl. The suspension was transferred into a dialysis bag and dialyzed against distilled water until the outer solution became free of chloride ion. Finally, the material in the dialysis bag was freeze-dried to obtain the humin preparation (DMSO-humin).

Treatment of humin preparations with a chelating resin: Ten to 20 mg of humin

preparations and 1 g of Chelex 100 resin (100–200 mesh) were weighed in a 10 mL centrifuge tube and extracted three times with 0.1 mol L⁻¹ NaOH (5 mL+3 mL+3 mL). For the extraction, the mixture was treated with ultrasonics for 30 min and shaken for 1 h with a reciprocal shaker. Organic carbon concentration in the combined extract was determined by a colorimetric dichromate oxidation method (Tatsukawa 1966) and ultraviolet and visible absorption spectra were recorded after proper dilution.

3. Analytical methods. Elementary composition: Carbon and nitrogen contents in the soil samples and residues of extraction were determined using a CN analyzer (Yanaco, MT-500) with cobalt oxide as an oxidizing agent. Elementary composition (C, H, N, ash) of humin preparations, HA and FA was analyzed by the staff of the Micro-analysis Laboratory of the Faculty of Agriculture, Nagoya University.

Composition of metal elements determined by AAS method: Ten to 20 mg of humin preparations were weighed in a Pyrex test tube with a teflon-lined screw cap and soaked with 2 mL of perchloric acid (0.70 kg kg⁻¹). The tube was capped tightly and the preparation digested at 150°C for 5 h in an oil bath. The non-colored digest was filled up to 10 mL with distilled water and the concentrations of the metal elements (Al, Fe, Ca, Mg, Cu, Mn, Ti) were determined by AAS (atomic absorption spectrometry) using a Hitachi Z-6100 spectrometer after proper dilution.

Fluorescence X-ray spectrography (powder method): Inorganic elements in DMSO-humin were analyzed by Fluorescence X-ray spectrography following the method of Ishii et al. (1987). A 175 mg aliquot of the finely ground powder of humin preparation was placed on a filter paper (Toyo, No. 4A) attached to a half-size slide mount and covered by a plastic film (Rigaku Denki Ltd., Cell-sheet). It was analyzed with a fluorescence X-ray analyzer, KeveX Ultratrace 0600. Molybdenum was used as an X-ray target for the measurements of Fe, Ti, Mn, Cu, V, As, and Br, while titanium was used as a target for elements such as Al, Si, S, K, and Ca. The voltage and current of the X-ray source were 35 kV and 20 mA, respectively. Time of measurement was 300 s.

Infrared absorption spectra: Infrared spectra of the humin preparations were recorded by the KBr disc method with a Jasco A-30 Infrared spectrometer.

Ultraviolet and visible absorption spectra: Ultraviolet and visible absorption spectra of the DMSO-humin preparations were recorded in the DMSO solutions using a Shimadzu UV-240 spectrophotometer. To promote the dissolution, the preparations were wetted with a few drops of conc. HCl. Spectra of the humin fractions solubilized with Chelex 100 were determined in 0.1 mol L⁻¹ NaOH solution.

RESULTS AND DISCUSSION

1. Yields of humin fractions

Table 1 shows the yields of humin fractions as well as those of humic acid and fulvic acid fractions on a carbon basis. In the samples from the Ashitaka humic volcanic ash soil profile, the carbon contained in the residue of alkaline extraction accounted for 65–80% of the total carbon in soils. From the carbon in the residue (humin fraction), 35–82% of carbon was recovered in the HF-humin fraction, and 14–22% was recovered in the DMSO-humin fraction. The yields of the humin fractions were higher compared with those of humic acid (10–15%) and fulvic acid (6.6–21%).

In the samples of Tsukude peat, 51–59% of the soil carbon was distributed in the residue of alkaline extraction. Almost the same amount (40–48%) was distributed in the humic acid

Table 1. Distribution of carbon among HA, FA, and humin fractions (% (fraction C/total C×100)).

	Humin fraction	HF-humin	DMSO-humin	Humic acid	Fulvic acid	Total
Volcanic ash soil						
Ashitaka A	64.9	53.3	13.0	14.6	20.5	100.0
Ashitaka D	73.6	25.9	10.2	12.4	14.0	100.0
Ashitaka 4	79.5	36.2	17.3	13.8	6.7	100.0
Ashitaka 8	80.3	43.8	16.5	13.1	6.6	100.0
Ashitaka 20	72.7	29.9	10.3	9.9	17.5	100.0
Peat soil						
Tsukude 56	51.2	39.9	4.5	47.5	1.3	100.0
Tsukude 280	59.2	51.1	5.0	40.1	0.7	100.0

Table 2. Elementary composition of HF-humin and DMSO-humin fractions.

	Elementary composition (weight %)				Atomic ratio				
	C	H	N	O	H/C	N/C	O/C	US	CQ
HF-humin									
Ashitaka A	45.9	4.69	1.77	47.6	1.22	0.033	0.78	40.7	1.12
Ashitaka D	51.2	3.08	1.19	44.5	0.72	0.020	0.65	65.1	1.19
Ashitaka 4	52.5	3.20	1.36	43.0	0.73	0.022	0.61	64.8	1.17
Ashitaka 8	51.0	3.06	1.21	44.8	0.72	0.020	0.66	65.3	1.20
Ashitaka 20	50.6	3.06	1.12	45.2	0.72	0.019	0.67	64.9	1.20
Tsukude 56	61.4	5.20	1.75	31.7	1.01	0.025	0.39	50.7	0.96
Tsukude 280	59.6	6.00	1.17	33.3	1.20	0.017	0.42	40.8	0.93
DMSO-humin									
Ashitaka A	38.6	5.62	2.31	53.4	1.73	0.051	1.04	15.9	1.14
Ashitaka D	36.9	4.73	1.81	56.5	1.52	0.042	1.15	25.9	1.29
Ashitaka 4	44.6	4.15	1.70	49.5	1.11	0.033	0.83	46.3	1.20
Ashitaka 8	45.6	3.60	1.46	49.3	0.94	0.028	0.81	54.4	1.24
Ashitaka 20	33.3	3.92	1.22	61.6	1.41	0.031	1.39	31.3	1.58
Tsukude 56	55.0	5.89	2.24	36.9	1.28	0.035	0.50	37.9	0.96
Tsukude 280	63.2	7.23	1.48	28.1	1.36	0.020	0.33	32.9	0.86

US: degree of unsaturation, $US = (2[C] - [H] + [N]) \times 100 / 2[C]$; CQ: combustion quotient, $CQ = 4[C] / (4[C] + [H] - 3[N] - 2[O])$; where [C], [H], [N], [O] denote the number of elements in %.

fraction, while the carbon content in the fulvic acid fraction was very low (0.7–1.3%). From the carbon in the residue, 78–86% of carbon was recovered in the HF humin fraction, while only 8–9% was recovered in the DMSO humin fraction.

2. Ash content of humin fractions

Removal of ash from the humin preparations was very difficult in the case of the humic volcanic ash soil samples. Ash content of each humin preparation is given in Table 3. Ash content of HF-humin ranged from 28–60% and that of DMSO-humin ranged from 44–60% in the Ashitaka soils. In the peat soils, on the other hand, the ash content of HF humin ranged from 2.9–4.4% and that of DMSO humin from 7.7–12%.

3. Elementary composition of humin fractions

Elementary composition of the humin preparations is shown in Table 2. The degree of unsaturation, which indicates the deficit of hydrogen compared with the putative saturated

structure containing neither a double bond nor a ring, was always higher in the HF-humin preparation than in the DMSO-humin preparation in the volcanic ash soil and peat soil. In the volcanic ash soil profile, the degree of unsaturation of HF-humin which was low in the surface soil showed a high and constant value in the buried layers. The trend was similar also in the DMSO-humin fractions. Combustion quotient (Tamiya 1932), on the other hand, was not appreciably different between the HF-humin and DMSO-humin preparations. Nitrogen contents of DMSO-humin were higher than those of HF-humin in both the volcanic ash soil and peat soil.

To analyze the trend in the elementary composition of the humin preparations more clearly, a H/C-O/H diagram was drawn (Fig. 1). Using this diagram, Kumada (1987) showed that the plots of soil humic acids were distributed within a narrow arc shaped band, and different types of HAs (buried A type, A type, B type, and Rp type) were separated in different areas within the band. The area of FA was also different from the HA band, and located in the area with higher H/C and O/H ratios.

Plots for the HF-humin of the buried layers of the Ashitaka soil were located in the upper margin of the buried HA area, while the plot for the HF-humin of the surface layer was located slightly outside the upper margin of the A type HA area. These results indicate that the elementary composition of the HF-humin preparations of the samples of the surface and buried volcanic ash soil profiles was different from that of HAs and was characterized by higher H/C ratios.

The area for the DMSO-humin of the volcanic ash soil samples differed entirely from the HA band and was located in or around the FA area, due to the higher H/C ratios of DMSO-humin. Based on the procedure of separation of humin, it is considered that lipid constituents may be contained in the humin fraction. Based on the ^{13}C -NMR spectra Hatcher et al. (1985) also indicated that terrestrial humin contained a remarkably larger amount of highly aliphatic components than humic acid. The high H/C ratio of humin observed in this study may also be due to the presence of lipid and highly branched aliphatic structures.

Plots for both HF-humin and DMSO humin of the peat soil samples were located within the B and Rp type HA area. H/C ratios of the DMSO-humin of the peat soil samples were slightly higher than those of the HF-humin preparation. Area of the peat soil humin fractions was also located in or near the lignin area, which suggested that the chemical composition of the peat humin fractions was similar to that of lignin.

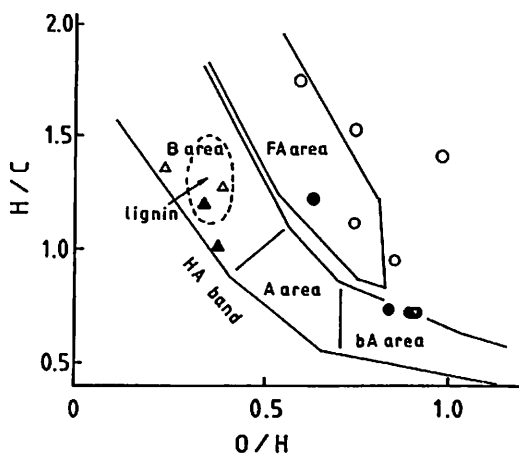


Fig. 1. H/C-O/H diagram of HF-humin and DMSO-humin obtained from Ashitaka humic volcanic ash soil and Tsukude peat soil. ●, HF-humin of Ashitaka soil; ○, DMSO-humin of Ashitaka soil; ▲, HF-humin of Tsukude peat soil; △, DMSO-humin of Tsukude peat soil.

Therefore, DMSO-humin was considered to display a highly aliphatic character and to be stabilized at the early stage of humification, while HF-humin was more oxidized and condensed in the samples of both soils.

4. Contents of metals in humin fractions

Table 3 shows the metal contents of the HF-humin and DMSO-humin fractions. The predominant metal element in the HF humin of the samples of Ashitaka humic volcanic ash soil was Al, the content of which ranged from 6.0 to $13.7 \times 10^{-2} \text{ kg kg}^{-1}$. Besides aluminum, $1.7\text{--}3 \times 10^{-2} \text{ kg kg}^{-1}$ Mg and $0.4\text{--}2.5 \times 10^{-2} \text{ kg kg}^{-1}$ Ca were recorded while other elements were present in trace amounts in the HF humin of the volcanic ash soil. In the uppermost layer, Ca was present in larger amounts than Mg, while Mg was more abundant than Ca in the buried layers.

Metal content in the HF humin from the peat soil samples was much lower than that in the humin from the volcanic ash soil samples. The predominant metal was also Al ($0.6\text{--}1.7 \times 10^{-2} \text{ kg kg}^{-1}$) followed by Mg ($0.2\text{--}0.7 \times 10^{-2} \text{ kg kg}^{-1}$). The contents of the other metal elements were very low compared with those of the two elements.

Composition of metal elements in DMSO humin was very different from that in HF humin. DMSO humin in the volcanic ash soil contained $30\text{--}42 \times 10^{-2} \text{ kg kg}^{-1}$ iron accompanied by ca. $1 \times 10^{-2} \text{ kg kg}^{-1}$ titanium, while the contents of the other elements were much lower. The DMSO-humin from the peat soil also contained $1\text{--}5 \times 10^{-2} \text{ kg kg}^{-1}$ iron and ca. $1 \times 10^{-2} \text{ kg kg}^{-1}$ titanium as the sole dominant metal.

The composition of the inorganic constituents in the DMSO-humin was also investigated semi-quantitatively by the fluorescence X-ray method (Table 4). Using molybdenum as X-ray target, Fe, Ti, Mn, Cu, Ca, As, and Br were detected. Elements other than Fe and Ti were all in trace amounts. Using titanium as X-ray target, trace amounts of Al, Si, P, S, Cl, K, and Ca were detected. DMSO-humin of the volcanic ash soil samples contained larger amounts of Fe, Ti, V, Mn, Br than that of peat soil samples. On the other hand, DMSO-humin of the peat soil contained larger amounts of Cu, As, Si, P, S, Cl, K, and Ca than that of volcanic ash soil, which may reflect the reduced state of the peat soil.

Table 3. Metal contents of humin preparations (in $10^{-2} \text{ kg kg}^{-1}$, oven dry basis).

	Al	Fe	Ca	Mg	Mn	Cu	Ti	Total	Ash
HF-humin									
Ashitaka A	13.7	0.93	2.46	1.69	0.07	0.00	0.00	18.8	41.0
Ashitaka D	6.49	0.43	1.10	2.86	0.05	0.00	0.00	10.9	27.8
Ashitaka 4	5.96	0.50	0.72	2.96	0.05	0.00	0.00	10.2	29.1
Ashitaka 8	6.89	0.61	0.64	2.77	0.06	0.00	0.00	10.9	60.2
Ashitaka 20	6.49	0.60	0.38	2.46	0.05	0.00	0.00	10.0	29.6
Tsukude 56	1.70	0.18	0.08	0.72	0.00	0.01	0.00	2.69	4.4
Tsukude 280	0.59	0.02	0.01	0.21	0.00	0.00	0.00	0.84	2.9
DMSO-humin									
Ashitaka A	0.38	38.1	0.00	0.04	0.16	0.02	1.3	40.0	55.0
Ashitaka D	0.30	41.9	0.00	0.03	0.18	0.05	1.46	43.9	60.0
Ashitaka 4	1.41	33.3	0.01	0.07	0.17	0.08	1.05	36.1	52.0
Ashitaka 8	1.36	30.4	0.00	0.06	0.10	0.06	0.49	32.4	44.0
Ashitaka 20	0.44	36.1	0.00	0.22	0.09	0.03	1.02	37.9	51.0
Tsukude 56	0.77	5.19	0.01	0.05	0.01	0.07	0.99	7.08	12.0
Tsukude 280	0.74	1.01	0.00	0.01	0.01	0.06	1.02	2.84	7.7

Table 4. Content (10^{-2} kg kg $^{-1}$) of co-existing elements in DMSO-humin fraction determined by semi-quantitative fluorescence X-ray analysis (powder method).

DMSO-humin	Ti	Fe	Cu	V	Mn	As	Br
Ashitaka A	3.80	38.1	0.02	0.61	0.27	0.04	0.01
Ashitaka D	4.02	41.9	0.02	0.67	0.32	0.04	0.05
Ashitaka 4	2.95	33.3	0.04	0.58	0.27	0.02	0.09
Ashitaka 8	1.32	30.4	0.03	0.33	0.18	0.02	0.15
Ashitaka 20	2.88	36.1	0.03	0.79	0.22	0.03	0.14
Tsukude 56	0.66	5.2	0.05	0.10	0.00	0.06	0.01
Tsukude 280	0.65	1.0	0.04	0.07	0.00	0.04	0.01

DMSO-humin	Ca	K	Cl	S	P	Si	Al
Ashitaka D	0.007	0.006	0.019	0.060	0.048	0.33	0.30
Tsukude 56	0.037	0.047	0.067	0.330	0.189	0.67	0.77

Contents of Ti, Cu, V, As, Mn, and Br were calculated from the Fe-content (determined by atomic absorption) by multiplying the relative peak height divided by the relative sensitivity of each element to Fe in the fluorescence X-ray spectrum. Contents of Ca, K, Cl, S, P, and Si were also calculated from the Al-content by multiplying the relative peak height divided by the relative sensitivity of each element to Al.

Table 5. Characteristics of humin preparations solubilized by Chelex 100.

	Yield % from humin C	Yield % from total C	RF	$\Delta \log K$
HF-humin				
Ashitaka A	30.0	16.0	101.9	0.434
Ashitaka D	67.4	17.5	193.7	0.457
Ashitaka 4	62.8	22.7	209.7	0.459
Ashitaka 8	73.6	32.2	197.1	0.470
Ashitaka 20	67.9	20.3	215.5	0.453
Tsukude 56	8.4	3.35	124.7	0.489
Tsukude 280	4.6	2.35	56.0	0.676
DMSO-humin				
Ashitaka A	43.0	5.59	82.0	0.713
Ashitaka D	44.8	4.57	169.2	0.660
Ashitaka 4	65.9	11.4	120.1	0.578
Ashitaka 8	68.6	11.3	167.0	0.534
Ashitaka 20	78.8	8.12	132.7	0.558
Tsukude 56	84.1	3.78	41.4	0.721
Tsukude 280	84.1	4.20	17.6	0.883

5. Solubilization of humin by removal of metals

A large portion of both HF-humin and DMSO-humin could be solubilized in an alkaline solution after bound metals were removed by treating the humin preparations with Chelex 100, a complex-forming resin.

Table 5 shows the yields of solubilized humin preparations and their degree of humification. In the Ashitaka volcanic ash soil, 30% of HF-humin carbon in the uppermost layer and 62–74% of HF-humin in the buried layers could be solubilized by the treatment with Chelex 100, suggesting that a large part of HF-humin was present as a metal complex with aluminum.

On the other hand, the proportion of HF-humin solubilized by the Chelex 100 treat-

ment was low and amounted to only 4.6–8.4% in the peat soil. These findings suggested that the HF-humin in the peat soil occurred mainly in the form of a high polymer with a low solubility such as lignin and cellulose, and not in the form of a metal complex. This fraction seemed to correspond to the category of inherited humin defined by Duchofour (1982).

The proportion of DMSO humin solubilized by the Chelex 100 treatment ranged from 43–79% and increased with increase in the depth of the buried layers. A large portion (84%) of the DMSO-humin of the peat soil samples could also be solubilized by Chelex 100, suggesting that most part of DMSO-humin was present as a Fe-complex.

In the previous paper (Tsutsuki and Kuwatsuka 1989), the authors reported the results of successive extractions of humic constituents, indicating that the amount of the bound type humic substances ranged from 5 to 23%, bound type humic acid from 2.1 to 13.7%, and bound type fulvic acid from 2.9 to 11.2% of the total soil carbon. Because the sum of the amount of HF-humin and DMSO-humin (22–34%) was larger than the amount of bound type humus determined by successive extraction, the treatment with Chelex 100 was considered to be more effective in separating bound type humus from soil.

6. Spectrometric characteristics of humin preparations

Figure 2 shows the ultraviolet and visible absorption spectra of DMSO-humin of the Ashitaka soil samples in the DMSO solution. The DMSO-humin of the volcanic ash soil showed a remarkable peak or shoulder at 350 nm, which was assumed to be due to the

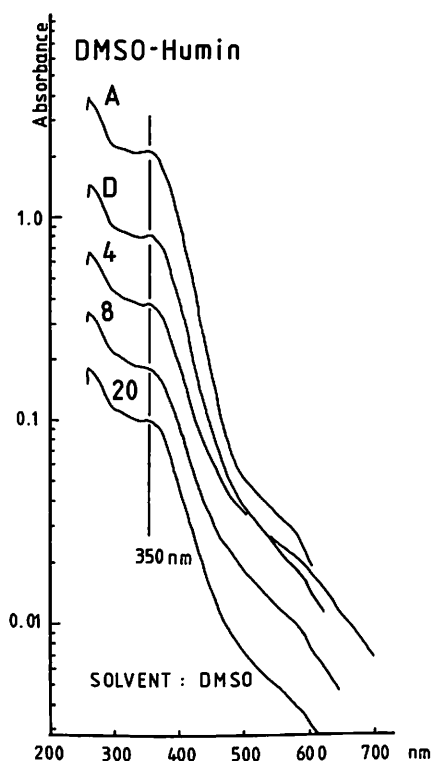


Fig. 2. Ultraviolet and visible absorption spectra of DMSO-humin before Chelex 100 treatment (measured in DMSO solution).

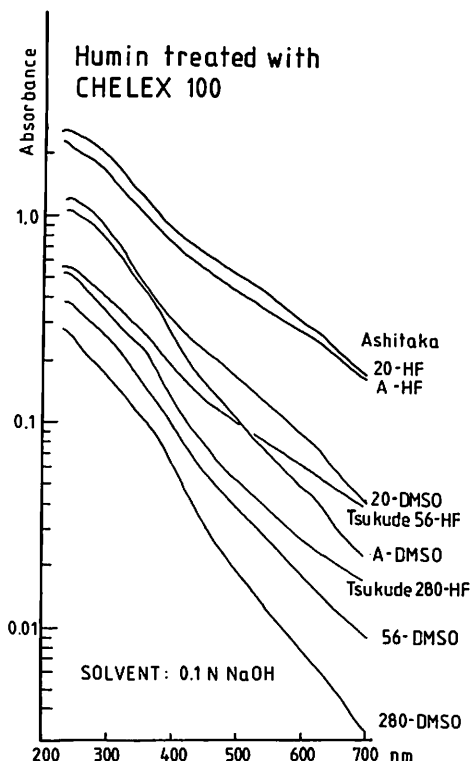


Fig. 3. Ultraviolet and visible absorption spectra of DMSO-humin treated with Chelex 100 (measured in 0.1 N NaOH).

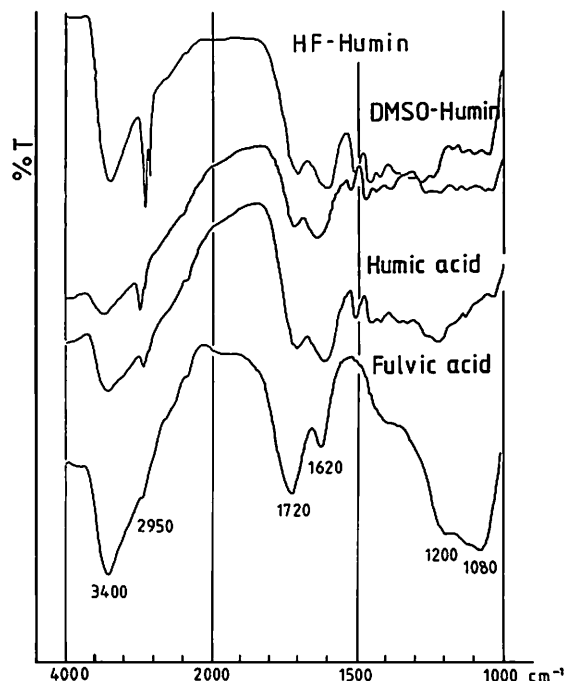


Fig. 4. Infrared absorption spectra of HF-humin, DMSO-humin, humic acid, and fulvic acid obtained from Tsukude 280 peat soil.

formation of complex with Fe. The spectra of DMSO-humin treated with Chelex 100 resin (Fig. 3) did not show such an absorption peak or shoulder at that wavelength and they appeared to be very similar to the spectra of A type humic acids. The ultraviolet and visible absorption spectra of HF-humin after the Chelex 100 treatment were characterized by a very low inclination, implying the development of a condensed structure.

Figure 4 shows the IR spectra of HF-humin, DMSO-humin, humic acid, and fulvic acid obtained from the Tsukude 280 peat soil. Prominent feature of the spectra was the strong absorption at ca. 2950 cm^{-1} in the spectra of HF- and DMSO-humins, suggesting the predominance of an aliphatic structure in the humin fractions.

7. Characteristics of the solubilized humins

As shown in Table 5, the degree of humification of the solubilized HF-humin fraction was very high. In the uppermost layer of the Ashitaka profile, the RF value of solubilized HF-humin was 102, while in the buried horizons it ranged from 193-215. On the other hand, the value of $\Delta\log K$ ($\log E_{400}/E_{600}$) was the lowest (0.434) in the uppermost layer, and it increased slightly to 0.45-0.47 in the buried layer. The structure of humin and humic acid is likely to be composed of two parts, i.e. the structure which contributes to the strong visible absorption, and the structure which does not contribute to the visible absorption (Tsutsuki and Kuwatsuka 1984). The high RF and low $\Delta\log K$ values and their change with depth in the Ashitaka volcanic ash soil profile suggested that the structure which was responsible for the strong visible absorption was already fully developed in the uppermost layer and that its contribution increased with depth, while it underwent a slight degradation as evidenced by the slight increase in the $\Delta\log K$ value. The RF value of the solubilized HF-humin of the peat soil samples was also very high (56-125) as compared with the value for humic acids.

The degree of humification of solubilized DMSO-humin was considerably lower than

that of the solubilized HF-humin both in the volcanic ash soil and in the peat soil, as indicated by the lower RF and higher $\Delta \log K$ values. DMSO-humin is therefore considered to have been stabilized in the earlier stage of humification by forming a complex with Fe.

Duchaufour (1982) considers that there are several kinds of humin with marked differences in their behavior and origin such as (a) inherited humin, (b) insolubilized humin, (c) microbial humin, and (d) developed humin. Our present study indicated that humin in a volcanic ash soil is mainly insolubilized by complex formation with two major metals, aluminum and iron, where iron-humate and aluminum-humate corresponded to different humin fractions that could be technically separated.

Acknowledgments. The authors are indebted to Mr. S. Kitamura, Micro-Analysis Laboratory, School of Agriculture, Nagoya University, for the analysis of C, H, N, and ash, to the Research Center for Resource and Energy Conservation of Nagoya University for the use of a fluorescence X-ray analyzer Kevex 0600, and to Ms. E. Moroto (Sato), a student of the authors' laboratory for her technical help.

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