Investigation on the Stabilization of the Humus in Mollisols

Kiyoshi Tsutsuki*, Chikage Suzuki*, Shozo Kuwatsuka*, Peter Becker-Heidmann, and Hans-Wilhelm Scharpenseel****

* Faculty of Agriculture, Nagoya University, Chikusa, Nagoya, 464 Japan

** Ordinariat für Bodenkunde, Universität Hamburg, Allende Platz 2, 2000 Hamburg 13, Federal Republic of Germany

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Summary - Zusammenfassung

Soil organic matter in Mollisols is often preserved for an extremely long period (e.g. > 3000 years). We confirmed that the stable organic matter in Mollisols is the medium to coarse sized (0.2-2.0 μm) clay-humus complex with humic acid combined with calcium as the main organic constituent. The argillic horizon contained relatively large amounts of clay-humus complexes and had relatively high carbon contents, humic acid/fulvic acid ratios and degrees of humification of humic acid. Medium clay and coarse clay fractions preserved the organic carbon most efficiently. Highly humified humic acid could be detected even in the uppermost part of the Ah horizon and was probably stabilized in lower horizons by forming a complex with clay fractions.

Untersuchung der Humus-Stabilisierung in Mollisolen

In Schwarzerden ist die organische Substanz häufig über sehr lange Zeiträume vor Abbau geschützt, manchmal mehr als 3000 Jahre. Diese Untersuchungen bestätigen, daß die geschützte organische Substanz in Schwarzerden als Komplex mit Mittel- oder Grobton (0.2-2.0 μm) vorliegt, und zwar hauptsächlich als Humat mit Calcium-Brücken. Die Ton-angereicherten Horizonte enthalten nicht nur größere Mengen an Ton-Humus-Komplexen sondern weisen auch merklich höhere C-Gehalte, höhere Huminsäure/Fulvosäure-Verhältnisse sowie höhere Humifizierungsgrade der Huminsäuren auf. Mittel- und Grobtonfraktionen konservieren den organischen Kohlenstoff am besten. Eine stark humifizierte Huminsäure konnte selbst im oberen Bereich des Ah-Horizonts nachgewiesen werden. Es wird angenommen, daß diese Struktur in den tieferliegenden Horizonten durch Komplexbildung mit Tonmineralen stabilisiert wird.

Introduction

Mollisols have up to 1-m thick Ah horizons often with a radiocarbon age of several thousands of years. Besides polycondensation of the organic matter, complexation with clay minerals and sesquioxides has been used to explain the high stability of the organic matter (*Gerasimov* 1971, *Stout* et. al. 1981). Previously *Scharpenseel* et. al. (1986) reported that the maximum radiocarbon age was in the medium or coarse clay fraction. In this study, the quality and quantity of soil humus contained in the particle size (p.s.) fractions obtained from different horizons were investigated to throw further light on the question how soil organic matter is stabilized in Mollisols.

Materials and Methods

1. Soils used

Two Mollisol profiles, a cultivated soil at Söllingen village to the south of Schöningen, and a forest soil at Asel village near Hildesheim, Federal Republic of Germany, were investigated. Selected soil characteristics including radiocarbon ages of soil samples collected from these profiles are listed in Table 1.

2. Fractionation of organo-mineral complexes in soils according to their particle-sizes

None of the methods proposed for the particle-size fractionation of organo-mineral complexes in soils (*Edwards* and *Bremner* 1967, *Sato* and *Yamane* 1972, *Yonebayashi* et. al., 1974, *Turchenek* and *Oades* 1979, *Sakai* and *Kumada* 1985) was suitable for preparing large fractions required for the radiocarbon dating. In this study, the < 2 μm fraction was further fractionated by adding 90 ml of distilled water to 10 g of soil sample. The pH of the suspension was adjusted at 8.5 by adding dropwise 0.004M sodium pyrophosphate. The solution was treated with ultrasound (Sharp ultrasonic water bath UTA 152) for 15 min, centrifuged at a fixed rpm for a calculated time and the supernatant was transferred into a tall beaker. These procedures were repeated 6 times for the fine clay fraction (< 0.2 μm) and 5 times for medium and coarse clay fractions (0.2-0.63 μm and 0.63-2.0 μm). The suspensions were combined and acidified with 10 ml of 0.1N sulfuric acid, left overnight and centrifuged at 3000 rpm for 15 min. Fractions with smaller particle-size were separated prior to larger fractions. The silt fraction (2.0-20 μm) was obtained from the non-clay residue by the pipet method. The remaining sand fraction (20 μm) was recovered by centrifugation.

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Table 1: Characteristics of the two Mollisols used in this study.
Tabelle 1: Kenndaten der beiden Schwarzerden.

HORIZON	Name of Horizon	depth (cm)	org. C (%)	CaCO$_3$-C (%)	pH(H$_2$O)	pH(KCl)	^{14}C-Age (YBP)	Texture in % Fine clay <0.2 µm	 Medium clay 0.2-0.63 µm	 Coarse clay 0.63-2 µm	 Silt 2-20 µm	 Sand >20 µm
Söllingen												
S1	AlAh$_1$	10-25	2.38	0.00	7.86	6.72	1028	2.1	5.5	7.3	22.9	57.2
S2	AlAh$_2$	25-45	2.14	0.00	7.84	6.74	2312	2.7	5.6	7.4	22.6	56.5
S3	(Bt)Ah$_1$	45-65	2.23	0.00	7.85	6.65	2660	4.4	7.9	8.4	24.4	51.5
S4	(Bt)Ah$_2$	65-85	1.84	0.019	7.85	6.53	3033	5.2	7.8	7.5	23.8	53.0
S5	(Bt)AhC	85-110	1.34	0.029	8.17	6.35	3885	7.6	6.7	6.0	22.9	54.1
Asel												
A1	(Al)Ah$_1$	5-20	2.42	0.00	4.67	3.69	modern	8.1	6.6	4.1	18.1	57.0
A2	(Al)Ah$_2$	20-40	1.87	0.00	7.05	5.60	1245	6.5	6.8	5.5	18.5	57.1
A3	(Bt)Ah$_1$	40-60	1.68	0.00	7.73	6.55	2621	7.3	6.7	5.8	18.5	58.5
A4	(Bt)Ah$_2$	60-80	0.916	0.03	7.87	6.85	2946	3.8	5.0	5.9	19.8	55.0
A5	(Bt)AhC	80-100	0.139	1.54	8.15	7.33	2668					

These p.s. fractions were further washed with water, centrifuged (up to 10,000 rpm), lyophilized and weighed.

3. Measurements of carbon contents of unfractionated soil samples and p.s. fractions

Carbon contents of untreated soil samples were measured with a CN corder (Yanaco MT 500) using cobalt oxide as an oxidizing agent. The C contents of the p.s. fractions were not sufficient for the analysis with a CN corder, and were determined by the Walkley- Black method (*Walkley* 1946) in its 1/5 scale.

4. Analysis of humus composition in unfractionated soils and their p.s. fractions

Aliquotes of p.s. fractions containing ca. 100 mg of carbon were weighed and extracted with 0.1 N NaOH (30 + 20 + 20 ml) according to the method of *Kumada* et. al. (1967). The extracted solution was acidified to pH 1 with sulfuric acid and filtered (Toyo filter paper No. 5B) to separate humic and fulvic acids. The humic acid fraction (after dissolved again in 0.1N NaOH) and fulvic acid fraction were made up to a fixed volume. The carbon contents of these solutions were determined by acid permanganate (0.1N) titration. Ultraviolet and visible absorption spectra of humic acid solution in 0.1N NaOH were measured in the range of 230-700 nm. Following parameters (RF and Δ logK) were calculated according to *Kumada* et. al. (1967) for the degree of humification:

$RF = (E_{600}/\text{Cons.KMnO}_4) \times 1000$

and $\Delta \log K = \log (E_{400}/E_{600})$

where E_{600} and E_{400} are the extinction at 600 and 400 nm and Cons.KMnO$_4$ is the consumed ml of 0.1N KMnO$_4$ by 30 ml of the humic acid solution.

Results and Discussion

1. Yields of particle-size (p.s.) fractions

The recovery rates, 95-98% for the Söllingen profile, and 90-97% for the Asel profile, were considered satisfactory. Yields of the silt fraction (ca. 20% and the sand fraction (51-59%) did not vary greatly among the horizons. Total clay contents were 15-20% in both profiles.

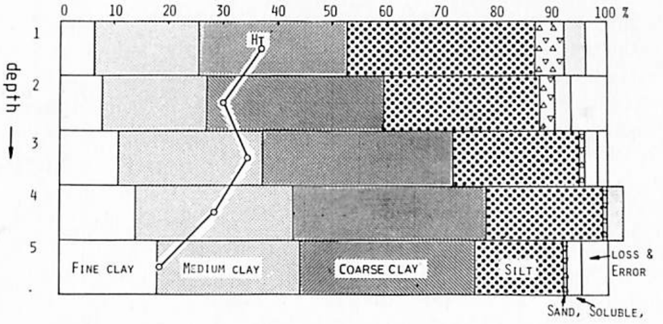

Figure 1: Distribution of carbon among different particle size fractions of a Mollisol (Söllingen). Depth: 1) 10-25 cm, 2) 25-45 cm, 3) 45-65 cm, 4) 65-85 cm, 5) 85-110 cm. H$_t$: consumed amount of 0.1N KMnO$_4$ (ml) per g unfractionated soil (the graduation is the same as that for %).

Abbildung 1: Verteilung des Kohlenstoffs auf die verschiedenen Korngrößenfraktionen einer Schwarzerde (Söllingen).
Tiefen: 1) 10-25 cm, 2) 25-45 cm, 3) 45-65 cm, 4) 65-85cm, 5) 85-110 cm. Ht: Verbrauch an 0.1 N KMnO$_4$ in ml pro g des nicht fraktionierten Bodens (gleiche Skalierung).

2. Distribution of carbon among the particle size fractions

The amount of solubilized organic matter were very low in all the horizons in both soils. The sum of carbon contents in the p.s. fractions was almost equal to the total organic carbon contents of the original soil (Fig. 1). These results indicated that the dispersion method of soils was appropriate for physical fractionation of the Mollisols studied.

The distribution of soil organic carbon among p.s. fractions suggests that humus in clay fractions, especially the coarse clay fraction, was most stable, while humus in sand and silt fractions are decomposed more easily. Our results are similar to those by *Yonebayashi* et. al. (1974) while *Turchenek* and *Oades* (1979) and *Scharpenseel* (1971) showed

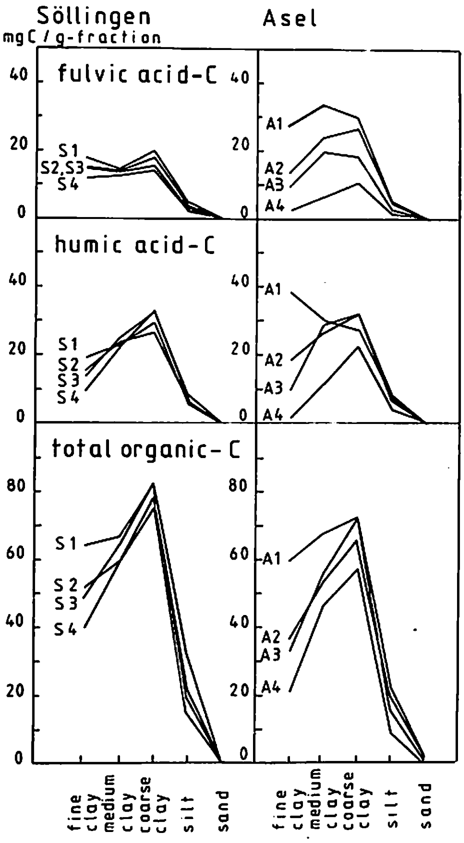

Figure 2: Total organic-, humic acid-, and fulvic acid-carbon contents of the particle-size fractions of two Mollisols.

Abbildung 2: Gehalte an Gesamt-C_{org}, Huminsäure-, und Fulvosäure- C der Korngrößenfraktionen zweier Schwarzerden.

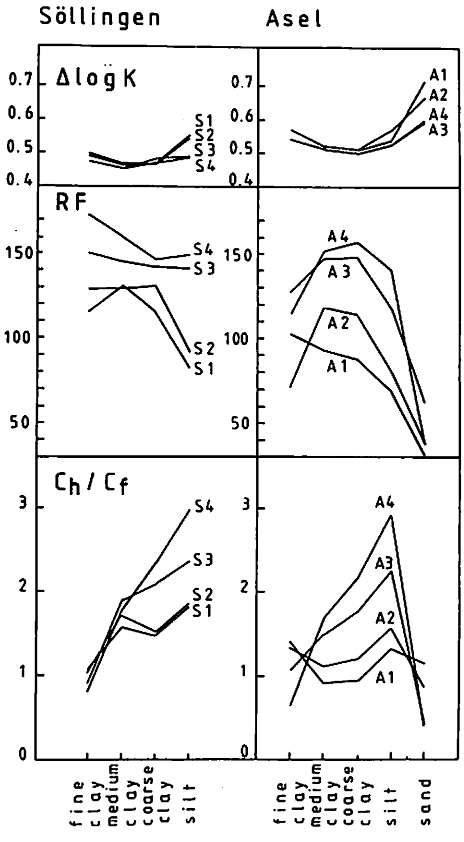

Figure 3: Humic acid-/fulvic acid- ratio (C_h/C_f), and Humic acid RF- and Δ logK- values of particle-size fractions of two Mollisols.

Abbildung 3: Huminsäuren-/Fulvosäuren-Verhältnis (C_h/C_f), Huminsäuren-RF- und ΔlogK-Werte der Korngrößenfraktionen zweier Schwarzerden.

that silt fractions are more important in stabilizing organic matter. In our study the silt fraction was most important in the retention of organic matter only in the uppermost horizon of Mollisols.

3. Analysis of humic and fulvic acids extracted from particle size fraction

Fig. 2 shows the carbon contents of the p.s. fractions obtained from different horizons in forms of total organic, humic acid, and fulvic acid. The coarse clay fraction invariably had the highest carbon content. The carbon contents of the medium clay and coarse clay fractions were 2-4 times higher than the carbon content of the unfractionated soil and tended to be higher in the argillic horizons than in the eluvial horizons. In both soils, the extracted amounts of humic acids from sand, silt and fine clay fractions decreased with depth, but those from medium clay and coarse clay fractions showed a maximum in the lower horizons (S3 and S4 in Söllingen, A2 and A3 in Asel profile). On the other hand, extracted amounts of fulvic acid decreased with depth in all p.s. fractions in both soils.

Ratios of Ch/Cf of medium clay, coarse clay and silt fractions increased with depth in the Ah horizon in both soils (Fig. 3). This suggests that fulvic acid has been leached out or decomposed preferentially with increasing soil age. On the other hand, Ch/Cf ratios of fine clay and sand fractions decreased with depth. The Ch/Cf ratio in the fine clay fraction was considered to have decreased with depth due to the leaching of fulvic acid from the upper horizons. The decrease of the Ch/Cf ratio in the sand fraction with depth may be due to poor protection of organic matter in this fraction as a result of weak linkage of organic matter and mineral constituents.

Fig. 3 also shows the change in two parameters, RF and Δ logK, with depth. RF values almost invariably increased with depth in all p.s. fractions. The RF values of humic acids in the p.s. fraction also showed a remarkable jump from the eluvial horizons (S1, S2, A1, A2) to the argillic horizons (S3, S4, A3, A4) in both profiles. RF can be related to the amount of well developed conjugated system in the humic acid structure and has been reported to be correlated positively with the degree of unsaturation of humic acids (*Tsutsuki* and *Kumada* 1980). Therefore, the trend of RF-values indicate that highly unsaturated structure and/or components in humic acid increased in the profile with depth. In the early stage of humic acid formation, the humic acid may largely retain the nature of its original material such as lignin, protein and polysaccharides, which have a rather low absorption in the range of 400 - 600 nm. As humic acid undergoes oxidation and polycondensation with age, such structure and/or component decreases relatively.

Compared with the RF, ΔlogK of humic acids (Fig. 3) changed little with depth or with particle-size, except for the slight drop in ΔlogK from the eluvial horizons to the argillic horizons. ΔLogK qualitatively shows the development of conjugated systems in humic acids. The constancy of Δ logK with depth suggests that highly developed conjugated system exists already in humic acids of the uppermost horizon, while in the lower horizons little further development of the conjugated system has taken place. Because such conjugated systems are protected against decomposition due to their strong bond with mineral constituents in soils, its relative abundance in humic acid increases with age as does the RF value. Non-parallel patterns in RF and Δ logK were also observed in humic acids fractionated according to the molecular size (*Tsutsuki* and *Kuwatsuka* 1984). The value of ΔlogK is probably not affected by the structure or component which has very low visible absorption, while the RF value does vary depending on the amount of such structure or component.

4. Radiocarbon age of texture fractions and its relation to the dynamics of soil humus

Using the same soil samples, *Scharpenseel* et. al. (1986) showed that the fraction which showed the oldest age was the 0.5- 1.0 µm fraction in Söllingen soil, and the 0.25- 0.5 µm fraction in Asel soil. Younger ages were observed in both larger and smaller p.s. fractions.

All results discussed so far suggest that the humus in Mollisols forms organo-mineral complexes especially with medium or coarse clay, and is preserved best in the form of humic acid. Although humic acid with very high degree of humification (high RF and low ΔlogK) also occurred in the fine clay fraction of the argillic horizon, the age of the fine clay fraction was young. This may be attributed to young organic matter in the form of fulvic acid leached out from the upper horizons. Organic carbon in silt and sand fractions is considered to be rejuvenated due to the effect of plant roots, microbial cells and their degradation products. *Ahmed* and *Oades* (1984) concluded, that while fine clay may be a matrix for the metabolic products of organisms, the silt fraction a matrix for cells, and macroorganic matter contains most of the plant debris. Their findings are also in agreement with our results.

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