

## **Degradation and Stabilization of Humus in Buried Volcanic Ash Soils**

### **II. Humus Composition in Fractions with Different Particle Sizes**

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Soil samples with different ages collected from a buried volcanic ash profile were fractionated according to particle size and the characteristics of organic matter contained in these fractions were investigated. Humus composition differed largely between the top layer of soil and buried layers of soil. In buried humic volcanic ash soils, the humus composition varied with age according to the particle size. It was considered that the formation of highly humified humic substances occurred first on the surface of clay particles but that humic substances were stabilized further in larger aggregates in buried soils. Sand particle size fraction ( $>0.02$  mm), which was assumed to be composed of aggregates of finer organo mineral complexes and rotted scoria with minor contribution from free organic matter, was the most important fraction in holding and stabilizing the humus in buried volcanic ash soils.

**Key Words:** buried volcanic ash soil, humus composition, particle size fraction, soil age.

This series of papers aimed to clarify the mechanism of degradation and stabilization of humus in buried volcanic ash soils by investigating the changes in the quality and quantity of humus with age. In our previous report (Tsutsuki and Kuwatsuka 1989) using the same soil profile, the humus composition and sugar composition of soils, as well as the molecular size distribution of humic acids, were investigated, and it was suggested that the humus and polysaccharides of buried volcanic ash soils are stabilized in bound forms with mineral components, and that the decomposition of unprotected humic substances proceeds in the buried layers.

Assuming that the humus composition in soil is not homogeneous and the diagenetic dynamics of humus differs even depending on the particle size of soil (Tsutsuki et al. 1988), changes with age in several important characteristics of humus in buried humic volcanic ash soils were investigated with reference to the size of the soil particles in this paper.

#### **MATERIALS AND METHODS**

**1. Soils used.** Soil samples were collected from the archeological excavation site at Ashitaka-Onoue in Numazu, Shizuoka, Japan. The scheme of the soil profile was illustrated

in the previous paper (Tsutsuki and Kuwatsuka 1989). The following layers with high organic matter contents and known ages were chosen for the detailed analysis of the humus in the particle size (p.s.) fractions: Layer A, <1,000 YBP, 16.9% C; Layer D,  $8.0 \times 10^3$  YBP, 7.95% C; Layer 4,  $18.0 \times 10^3$  YBP, 6.87% C; Layer 8,  $27.2 \times 10^3$  YBP, 6.15% C; Layer 15,  $>28.1 \times 10^3$  YBP, 4.23% C; Layer 20,  $30.0 \times 10^3$  YBP, 5.84% C. Used buried soils were also characterized by their scoriaceous nature.

**2. Determination of the particle size distribution.** Particle size distribution of soils was determined by the pipette method for the samples in which organic matter had been removed with  $H_2O_2$ . Particle size limits defined by the International Soil Sci. Soc. were adopted in this study. Samples were dispersed at pH 4.0 adjusted by dil. HCl with a pH meter. To facilitate the dispersion, the suspension was subjected to ultrasonics (100 W, 30 min).

**3. X-ray diffraction of clay fractions.** X-ray diffraction of clay samples saturated with sodium ion was recorded in the range of  $2\theta$  between 3 and 30 degree in selecting  $Cu-K\alpha$  as X-ray source and using a Rigaku Denki Geigerflex X-ray diffractometer.

**4. Fractionation of particle size (p.s.) fractions without removal of organic matter.** Particle size fractions without organic matter removal which corresponded to coarse sand ( $d > 0.2$  mm), fine sand ( $0.2 \text{ mm} > d > 0.02$  mm), silt ( $20 \mu\text{m} > d > 2 \mu\text{m}$ ), coarse clay ( $2 \mu\text{m} > d > 0.63 \mu\text{m}$ ), medium clay ( $0.63 \mu\text{m} > d > 0.2 \mu\text{m}$ ), and fine clay ( $0.2 \mu\text{m} > d$ ) were fractionated according to the method of Tsutsuki et al. (1988). Soils were dispersed by subjecting the soil suspension (pH 8.5) to ultrasonics (100 W, 30 min). Clay fractions were separated by centrifugation, silt fraction by the pipette method, and the remaining sand fraction was further divided into fine and coarse sand fractions by sieving. Suspensions of fine, medium, and coarse clay fractions were slightly acidified with dil. HCl, allowed to settle, and centrifuged. Supernatants of the fine clay suspensions exhibited a brown color especially in the upper two layers, while those of the medium and coarse clay suspensions were pale or hardly colored. Therefore, the supernatant of the fine clay suspension was concentrated with a rotary evaporator, and the carbon content in the solution was determined as the amount of solubilized organic matter.

**5. Measurements of carbon contents of unfractionated soil samples and p.s. fractions.** Carbon contents of untreated soil samples were measured with a CN coder (Yanaco MT 500) using cobalt oxide as an oxidizing agent. The C contents of the p.s. fractions were determined according to the Walkley-Black method (Walkley 1946) in the 1/5 scale due to the small amount of sample.

**6. Analysis of humus composition in unfractionated soil samples and their p.s. fractions.** This analysis was carried out also on a reduced scale. Aliquots of p.s. fractions containing *ca.* 3–5 mg of carbon were weighed and extracted three times with 3 ml of 0.1 N NaOH containing 3%  $Na_2SO_4$  by heating in a steam bath for 30 min. The extracted solution was acidified with 0.5 ml of dil. sulfuric acid (1 : 5) and made up to 10 ml. After being allowed to stand overnight, the suspension was centrifuged to separate the humic acid (HA) and fulvic acid (FA) fractions. The precipitated HA fraction was washed with dil. sulfuric acid (1 : 100) and dissolved again in 0.1 N NaOH and made up to 10 ml. To 2 ml portions of HA and FA solutions, 4 ml of 0.5 N  $K_2Cr_2O_7$  in concentrated sulfuric acid was added and the green color which developed was determined at 645 nm (Tatsukawa 1966). The calibration curve was made using sucrose. Ultraviolet and visible absorption spectra of the humic acid solution in 0.1 N NaOH were measured in the range of 230–700 nm. The following parameters (*RF* and  $\Delta \log K$ ) were calculated as degrees of humification after modification

of the original method (Kumada et al. 1967):

$$RF = (E_{600}/\text{HA conc.}) \times 15,$$

and

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

where  $E_{600}$  and  $E_{400}$  are the coefficients of extinction at 600 and 400 nm and HA conc. is the value of mg C in 1 ml of the HA solution (Kumada 1987). The  $RF$  value indicated above was comparable to that obtained by the original method. Humin-C was calculated by subtracting the HA-C and FA-C contents from the total C content in the p.s. fractions.

## RESULTS AND DISCUSSION

### 1. Yields of particle size fractions

Table 1 shows the particle-size distribution of the Ashitaka-Onoue volcanic ash soil profile either with organic matter removal prior to dispersion or without organic matter removal. The soil texture consisted of clay loam in the top layer A, loam in layers D and 4, and sandy loam in layers 8, 15, and 20. There was a remarkable difference in the soil texture between the top layer and buried layers. The clay content decreased while the fine sand content increased in deeper layers. In this study, organic matter was removed but free iron oxides were not removed for the determination of the soil texture, for the purpose of investigating the effect of organic matter on the particle size distribution. Cementing of smaller particles into larger aggregates by iron oxides or aluminum oxides may also be responsible for the changes in the soil texture with age. By X-ray diffraction, the clay fractions of all the layers were found to be amorphous (Fig. 1), and no crystalline clay minerals were observed.

In the presence of organic matter, the proportion of the clay fraction increased and that of the sand and silt fractions decreased in the top layer, while in buried layers only the proportion of coarse sand increased remarkably and that of the other fractions decreased. These results suggest that not only amorphous minerals but also organic matter contribute significantly to the formation of macroaggregates in buried layers.

Particle size distribution in the presence of organic matter may be also influenced by the predominance of scoriaceous particles in used buried soils and also by the compression of soil particles in buried layers.

The predominance of fractions with a finer particle size in the top layer than in buried layers may be ascribed to the weaker aggregation of organo mineral particles with each other.

### 2. Distribution of carbon among fractions with different particle sizes

Table 2 shows the distribution of carbon among different p.s. fractions. In the uppermost layer (Layer A), more than half of total carbon was distributed into silt and smaller p.s. fractions. However, in the buried layers, the contribution of carbon in these finer p.s. fractions to the total carbon was low and most of the carbon (>90%) was found in the sand size (>0.02 mm) fraction. The amount of carbon distributed in the coarse and fine sand fractions was similar in the buried layers. Implication of these results was investigated by analyzing the humus composition of each p.s. fraction.

**Table 1.** Particle-size distribution of a buried volcanic ash profile at Ashitaka-Onoue excavation plot.

Layer	Coarse-sand	Fine-sand	Silt	Clay
<b>I. Texture analysis (% on organic matter free basis)</b>				
A	9.4	30.3	42.9	17.4
D	1.1	60.7	23.7	14.4
4	4.0	50.6	32.1	13.3
8	1.3	69.5	19.2	10.0
15	2.5	65.5	25.1	6.8
20	1.4	73.6	15.7	9.4
<b>II. Texture analysis (% on dry soil basis)</b>				
A	6.2	19.8	28.0	11.4
D	1.0	52.9	20.7	12.6
4	3.2	40.5	25.7	10.6
8	1.2	61.9	17.1	8.9
15	2.4	61.6	23.6	6.4
20	1.3	66.7	14.2	8.5
<b>III. Particle-size distribution without H<sub>2</sub>O<sub>2</sub> treatment (% on dry soil basis)</b>				
A	8.8	39.2	40.3	4.3
D	70.0	14.6	1.8	0.1
4	72.0	17.3	4.3	0.3
8	69.6	12.7	5.6	0.4
15	52.4	20.8	11.1	1.2
20	68.6	17.4	3.9	0.4
<b>IV. Effect of organic matter on particle size distribution (III - II) (% on dry soil basis)</b>				
A	2.6	19.4	12.3	-7.1
D	69.0	-38.3	-18.8	-12.4
4	68.8	-23.3	-21.4	-10.3
8	68.8	-49.2	-11.5	-8.5
15	50.0	-40.8	-12.5	-5.2
20	67.3	-49.3	-10.3	-8.1

### 3. Content of carbon in different humic fractions

The content of carbon (total organic C, humin C, HA-C, and FA-C) in different p.s. fractions was compared as shown in Fig. 2. Carbon contents in the fine and medium clay fractions are not shown because the yield was very low. Though the yield of the coarse clay fractions was also low, an accurate determination of the humus composition in these fractions was possible. The contamination of this fraction with soluble organic matter was also unlikely, because soluble organic matter was almost completely removed by the preceding separation of finer clay fractions.

The total organic C contents of the p.s. fractions increased remarkably with decreasing particle size especially in the uppermost layer. The total organic C contents were highest in the coarse clay fraction and almost at the same level in silt, fine sand, and coarse sand fractions in buried layers. These trends imply that finer mineral particles have a larger capacity to adsorb soil organic carbon per unit weight at the beginning of organic matter accumulation.

Though the content of the humin form of C was also highest in the coarse clay fraction in the uppermost layer, it decreased remarkably with age and the fine sand fraction showed the highest humin C content in the buried layers.

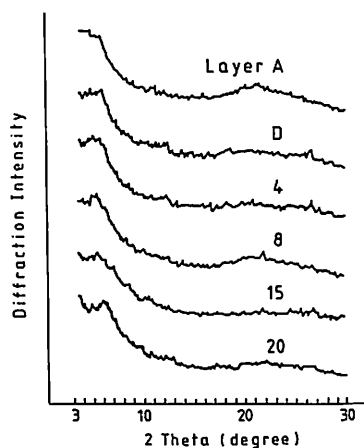


Fig. 1. X-ray diffraction patterns of clay fractions (Na form) of Ashitaka-Onoue soil profile.

Table 2. Distribution of organic carbon among fractions with different particle size (% to the total carbon in the unfractionated soil).

Layer	Coarse-sand	Fine-sand	Silt	Coarse-clay	Medium-clay + fine-clay + loss
A	5.6	34.3	40.0	4.5	15.6
D	66.2	14.6	1.8	0.16	17.2
4	72.3	17.6	4.6	0.34	5.2
8	77.5	14.3	5.6	0.27	2.3
15	62.6	23.1	7.3	0.69	6.3
20	74.5	17.9	3.9	0.29	3.4

The trend of the distribution of HA-C was quite different from that of humin C. In the uppermost layer, the content of HA-C was highest in the silt fraction, while in the buried layers it was highest in the coarse clay fraction and decreased with increasing particle size. FA-C contents were high in the uppermost layer but they were very low in all the p.s. fractions of buried layers. FA-C contents were relatively high in the coarse clay and the coarse sand fractions and slightly lower in the silt and fine sand fractions. However, the difference in FA-C contents among the p.s. fractions was not as remarkable as that of the humin- or HA-C contents.

The above results indicate that the coarse clay and fine sand fractions showed a very different humus composition after a long burial time (> 10,000 years). The HA-C was held preferentially by the coarse clay fraction, while the humin C by the fine sand fraction with increasing age.

As shown in Table 1, the sand fractions without organic matter removal were actually not sand fractions, but consisted of aggregates of fractions with finer particles. Therefore, the results obtained in this study suggest that organic matter adsorbed onto the clay particles was stabilized further, when organo-mineral particles were cemented into larger aggregates, and that the organic matter adsorbed onto fine particles is likely to be decomposed for a very long period of time in spite of its protection by organo-mineral aggregation.

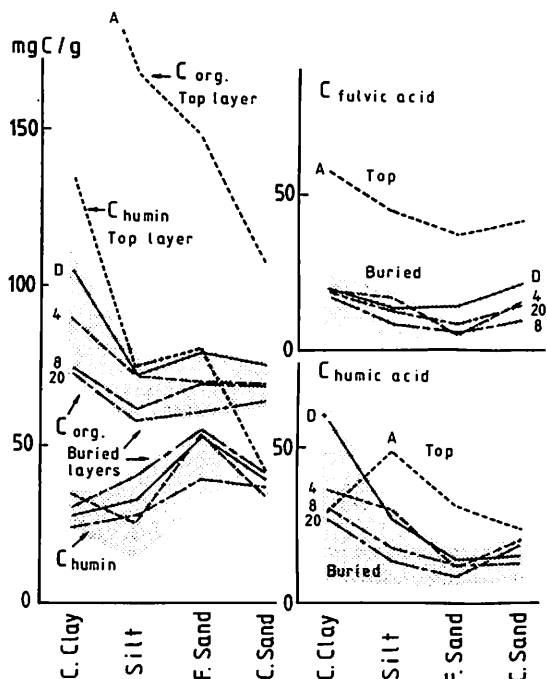


Fig. 2. Relationship between the amount of carbon in each humus form and the particle size fractions.

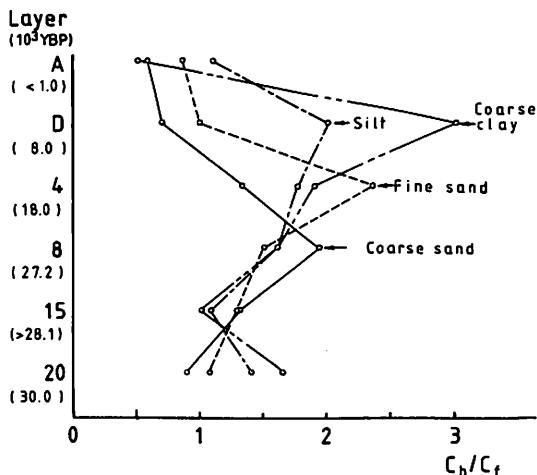


Fig. 3. Changes with age of the  $C_h/C_f$  ratios of particle size fractions.

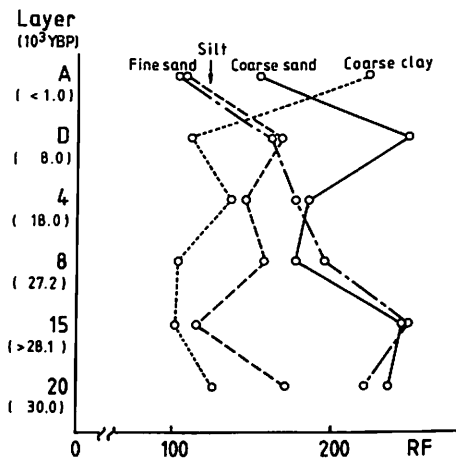


Fig. 4. Changes with age of  $RF$  value of HAs obtained from fractions with different particle sizes.

**4. Changes with age of  $C_h/C_f$  ratios of fractions with different particle sizes**

The ratio of HA-C/FA-C ( $C_h/C_f$ ) has been used as a useful indicator to characterize the humus composition of different soils. The change with age of the  $C_h/C_f$  of the fractions with different p.s. is shown in Fig. 3. In all the p.s. fractions the  $C_h/C_f$  ratio increased once with age and after a peak was attained the ratio decreased again with age. The age at the peak of  $C_h/C_f$ , however, differed among the p.s. fractions. The peak was observed at 8,000

YBP for the coarse clay and silt fractions, at 18,000 YBP for the fine sand fraction, and at 27,200 YBP for the coarse sand fraction. To sum up, it took a longer time for the  $C_h/C_f$  of the coarser fractions to attain a peak.

In the early stage of humus formation, FA consisted mainly of slightly decayed bio-polymers and was decomposed more readily than HA, which resulted in the increase of the  $C_h/C_f$  ratio. After easily decomposable constituents in FA are exhausted, however, the main constituents of FA become the decomposition products of HA and humin, which leads to the decrease in the  $C_h/C_f$  ratio with age. The rate of such dynamic processes differed with the size of the soil particles, and the humus composition of finer particles changed more quickly presumably due to their larger surface area. Partial decrease with age of the molecular size of HA (Tsutsuki and Kuwatsuka 1989) also agrees with the above results. The importance of the degradative pathway for the formation of humic substances was also pointed out by Hatcher and Spiker (1988).

##### **5. Changes with age of the degree of humification of HAs obtained from fractions with different particle sizes**

The  $RF$  value, which indicates the relative intensity in the visible absorption of HA, also changed differently with age in the p.s. fractions (Fig. 4). In the uppermost layer (Layer A), the  $RF$  value was highest in the coarse clay fraction and lowest in the fine sand fraction. In buried layers, however, the  $RF$  value of coarse clay HAs became lowest among all the p.s. fractions, and that of fine sand HAs increased steadily with age, reaching the highest value among the p.s. fractions at 27,200 YBP. The  $RF$  value of silt HAs was intermediate between those of coarse clay HAs and sand HAs. The changes in the  $RF$  value with age also suggested that highly humified HAs were formed first on the surface of clay particles but that they became more stable in larger aggregates, while the HAs remaining in the clay fraction were decomposed in the buried layers with time. The values of  $\Delta \log K (= \log E_{400}/E_{600})$  were similar among HAs of the p.s. fractions and soils with different ages.

##### **6. Stabilization of humus in the buried volcanic ash soils**

With respect to the relationship between the  $^{14}C$  age of organic matter and the particle size of soil, the oldest fraction was the silt fraction (Scharpenseel 1971), coarse clay fraction (Paul 1984) or medium and coarse clay fractions in two Mollisols (Scharpenseel et al. 1986). From the viewpoint of the distribution of organic carbon and the degree of humification of HAs, the silt and coarse clay fractions are known to play a major role in the stabilization of organic matter in various kinds of soils (Yonebayashi et al. 1974; Turchenek and Oades 1979; Tsutsuki et al. 1988). Ahmed and Oades (1984), on the other hand, confirmed that biomass accumulates in silt size aggregates in calcareous soils. The biomass accumulated in the silt fraction undergoes degradation, and is considered to be stabilized on the coarse clay and medium clay particles which have a larger surface area.

As reported in other studies, soil organic matter was stabilized by clay-organic and silt-organic aggregation in the top layer soil also in this study. However, the fine and coarse sand fractions played a major role in holding organic matter in buried volcanic ash soils. These results suggest that even though protected by organo-mineral aggregation organic matter in a clay-organic complex is also subjected to degradation after a long period of accumulation. When clay-organic complexes are cemented into larger sand aggregates by organic matter as well as amorphous minerals by compression in buried volcanic ash soils, however, they are assumed to become more resistant to degradation. Oades (1984) also

considers that large aggregates can be stabilized if sufficient quantities of mucilage or humic materials associated with metal ions are spread uniformly through the soil.

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