# Amorphous Materials of Andosols (Kuroboku) in Japan

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As Japan is situated in a part of the Circum-Pacific Orogenic zone, volcanic ash, cinders and other volcanic materials are found in most parts of the country from Hokkaido to the Southern Kyushu. Volcanic ash derived soils in Japan, occupying 16.4% of the total land, are used for common crops, grasslands and locally as paddy fields. Such soils can be easily distinguished from other soils becasue of dark fluffy surface soils and natural vegetation, and often turn out speciality in land use and in farming system.

Andosols in Japan are characterized by the following properties mainly coming from a high amount of amorphous material including allophane in the clay fraction; at first as the chemical properties, they have high organic carbon content from about 5 to 20% in the A horizon, high phosphorus absorption coefficient from about 1,500 to 3,440 $P_2O_5$ mg/100 g, and cation exchange capacity varying with pH directly owing to the chemical property of allophane. Secondly, as the physical properties, they have low bulk density from 0.50 to 0.90 g/cc except for volcanic coarse textured horizons, consequently Andosols are of high water holding capacity, plowed with ease, and subject to severe wind erosion.

Ando soils (Ando was coined from Japanese words referring to dark soils), first given by Thorp and Smith (1949)[9] are included in Andepts suborder of Soil Taxonomy of USDA (1975)[8], and in Andosols, one of the soil units of FAO/UNESCO soil map of the world (1969)[11]. In most countries, the soils are called Andosols, however, they are known under different names; Kuroboku soils in Japan, Black Andean soils or Paramo soils in Columbia and Ecuador, Trumao soils in Chile, Amorphic soils or Yellow Brown loams in New Zealand, Humic Allophane soils or Volcanic soils in USSR. The soil Taxonomy defined Andepts as the soils that have the exchange complex dominated by amorphous material, however, quantitative determination method of amorphous material has not been described.

In this paper the characteristics and determination of amorphous material in soils are roughly reviewed, and analytical results of amorphous material by the author's method are briefly summarized in order to know the characteristics of Andosols in Japan.

## Characteristics of allophane and amorphous materials

The mineralogical composition of Andosols mostly depends on the petrography of the original ashes. The weathering of volcanic glass, the principal component of ash, tends to produce amorphous materials predominantly represented by allophane. Halloysite and metahalloysite are formed by weathering or transformation of different kinds of minerals, but mainly they are formed directly from allophane by molecular rearrangement in the course of time. It is generally conceived that the formation of allophane starts from the solution or gel containing a high proportion of silica and aluminum liberated from the primary minerals of volcanic glass and plagioclases, and that the environmental condition stimulates the silica and aluminum to co-precipitate isoelectrically forming a colloidal amorphous fraction.

From the mineralogical composition of the clays, Andosols are divided into two categories; a) soils with clays of dominant allophane, b) soils with clays of dominant allophane and halloysite. The former soils may be in a first weathering stage and include most of Andosols. The latter soils are found in soils with well developed soil profile, preferably in soils formed by ash influenced or by redeposited volcanic materials.

Dudal (1966)[2] reported from the reconnaissance soil survey in Java, Indonesia, that the soils deriving from unconsolidated andesitic or basaltic ashes under climate condition varying from humid to subhumid tropical are composing of Dark Red Latosols, Dark Reddish Brown Latosols, Brown Latosols and Andosols, and that the Latosols occupy the lower slope, and with increasing elevation the soils range progressively into Andosols. It is suggested that these great group soils can be differentiated from the characteristics of soils and the properties of clay, especially of amorphous material.

The term "amorphous material" in this paper is used for clay fraction (less than 2 microns) amorphous to X-ray, composed of inorganic colloidal materials including allophane. Because the clays of Andosols are of widely varying chemical composition and mineralogical characteristics, it is difficult to separate allophane from other amorphous constituents.

## Review on determination of amorphous materials in soils

Hashimoto and Jackson (1960)[3] reported that most allophane, free alumina and silica were dissolved from clay by boiling for 2.5 min in 0.5 N NaOH, but some crystalline clay minerals were also dissolved during the treatment. Higashi and Ikeda (1974)[4] employed an oxalate solution to dissolve allophane from clay, and recommended shaking a 100 mg sample for 1 hour at 30°C in 200 ml of 0.15 M Na-oxalate solution of pH 3.5. Segalen (1968)[7] employed a differential dissolution method of treating the sample with 8N HCl for 30 min, and boiling for 5 min in 0.5 N NaOH, and determining the amorphous inorganic products from the cumulative curve of extracted amorphous constituents. Recently Kitagawa (1976)[5,6] reported that the weight loss from heating clay between 105° and 200°C is highly correlated with the amount of allophane and amorphous matter determined by the alternate dissolution method of Segalen (1968)[7]. Kitagawa's method is one of simple and convenient methods, but it is not to determine the amount of each amorphous constituent, accordingly the author tried to establish the following method.

## Proposed dissolution method of amorphous materials in soils

A 100 mg soil sample sieved through a 0.5 mm screen is put in a 100 ml tall beaker covered with a watch glass, and the organic matter is decomposed by 30% $H_2O_2$ on a boiling water bath. Following complete removal of excess $H_2O_2$, 100 ml of 0.2 N oxalic acid solution of pH 1.40 is added. The beaker is placed in a thermobath at 40°C under 10,000 lux irradiation by a fluorescent lamp, and treated for 6 hours with stirring by a glass rod every hour. The treated mixture is transferred to a 200 ml measuring flask, and made to volume. A portion of the solution is centrifuged at 3,000 rpm for 10 to 15 min. An aliquot of the supernatant is used for determination of silica by Weaver's method (1968)[10], and aluminum and iron are determined by the colorimetric method using ferron reagent (Belyayeva, 1966)[1] following complete decomposition of oxalic acid on a sand bath using a mixture of $H_2SO_4$, $HNO_3$ and a small quantity of $H_2O_2$.

The most effective particle size for treatment was soil passed through a 0.5 mm sieve,

**Table 1. Some properties of selected**

| Soils | Horizon | Depth (cm) | Amorphous materials (%)[1] | | | |
|---|---|---|---|---|---|---|
| | | | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | Total |
| **First group soils** | | | | | | |
| Jonouchi | B22 | 98+ | 13.9 | 5.8 | 23.1 | 42.8 |
| Isehara | B1 | 70+ | 11.5 | 15.8 | 12.7 | 40.0 |
| Hachioji | B1 | 40–67 | 10.0 | 13.9 | 15.8 | 39.7 |
| Miura | A3 | 30–60 | 7.3 | 12.4 | 13.8 | 33.5 |
| Miyagasaki | B1 | 36–65 | 8.0 | 8.6 | 14.1 | 30.7 |
| Kanuma | A12 | 18–43 | 6.9 | 6.2 | 14.4 | 27.5 |
| | B1 | 82–95 | 8.7 | 6.3 | 13.9 | 28.9 |
| Kuju | A12 | 20–38 | 4.0 | 7.1 | 14.7 | 25.8 |
| | AB | 82–109 | 7.2 | 4.3 | 13.0 | 24.5 |
| Takizawa | A3 | 42–66 | 7.1 | 6.2 | 11.5 | 24.8 |
| Kikyogahara | B1 | 25–45 | 4.0 | 7.9 | 10.3 | 22.2 |
| Hirusen | B1 | 46–64 | 4.9 | 4.2 | 11.4 | 20.5 |
| **Second group soils** | | | | | | |
| Shinshiro | A12 | 10–36 | 3.0 | 5.9 | 9.5 | 18.4 |
| | B1 | 80–120 | 4.9 | 8.3 | 6.2 | 19.4 |
| Kitagami | B2 | 76–112 | 3.7 | 6.2 | 7.3 | 17.2 |
| Sekigahara | A3 | 37–51 | 2.0 | 4.4 | 5.5 | 11.9 |
| Kanazawa | A3 | 52–67 | 2.2 | 5.0 | 4.2 | 11.4 |
| **Third group soils** | | | | | | |
| Asama | Ab1 | 4– 9 | 1.1 | 1.3 | 1.8 | 4.2 |
| | IIIBb2 | 26–39 | 2.0 | 1.1 | 3.3 | 6.4 |

1) Per cent is based on the weight dried at 105°C
2) A. M. is abbreviation of amorphous materials
3) Phosphorus absorption coefficient is expressed on the oven-dry basis

and no great difference of extracted amorphous constituents from samples ground more finely was observed. The most appropriate soil-solution ratio was determined as 100 mg per 100 ml. A series of experiments to determine the effect of irradiation on extractable inorganic amorphous materials showed that, for amorphous material dominant soils such as the Miyagasaki, there was no great effect of the degree of irradiation. Even in the dark room, free oxides were dissolved by the acidity of oxalic acid. However for crystallized clay mineral dominant soils such as the Shinshiro, the effect of irradiation was considerable, especially for aluminum. The duration of treatment on the proposed method was decided by the fact that the extracted amount of amorphous consituents for 6 hours treatment at 40°C under irradiation are highly correlated with the amount determined by the method of the alternate dissolution with 8N HCl and 0.5 N NaOH solutions (Segalen, 1968). It appears that the treatment is not selective dissolution for amorphous material, extracting some inorganic constituents from poorly crystallized or crystallized minerals in the course of continual treatment, though the extracted amount after 6 hours treatment is not considerable. It was confirmed through X-ray analysis of treated clay fractions that the samples treated for 6 hours produced intense and sharper peaks than those treated for 4 or 8 hours.

**soils derived from volcanic ash**

| Clay (%)[1] | A. M.[2]/Clay (%) | Organic carbon (%)[1] | Phosphorus absorption coefficient[3] |  | Bulk density (g/cc) | Deposition mode of parent material |
|---|---|---|---|---|---|---|
|  |  |  | (P mg/g) | ($P_2O_5$ mg/100 g) |  |  |
| 43.4 | 99 | 0.83 | 12.20 | 2800 | 0.74 | Wind-blown |
| 44.8 | 89 | 1.04 | 12.56 | 2880 | 0.72 | Wind-blown |
| 53.8 | 74 | 1.46 | 14.56 | 3340 | 0.70 | Wind-blown |
| 47.5 | 71 | 5.91 | 11.90 | 2730 | 0.75 | Wind-blown |
| 35.3 | 87 | 2.95 | 12.08 | 2770 | 0.67 | Wind-blown |
| 40.6 | 68 | 5.48 | 14.39 | 3300 | 0.67 | Wind-blown |
| — | — | 1.51 | 12.08 | 2770 | 0.74 | Wind-blown |
| 38.6 | 67 | 21.47 | 15.00 | 3440 | 0.52 | Wind-blown |
| — | — | 5.77 | 12.86 | 2950 | 0.62 | Wind-blown |
| 31.3 | 79 | 2.48 | 11.16 | 2560 | 0.70 | Wind-blown |
| 42.4 | 52 | 3.16 | — | — | — | Wind-blown |
| 34.4 | 60 | 5.04 | 11.21 | 2570 | 0.69 | Wind-blown |
| 51.4 | 36 | 13.70 | 14.82 | 3400 | 0.60 | Redeposited |
| — | — | 0.65 | — | — | 0.79 | Redeposited |
| 58.4 | 29 | 0.96 | 9.90 | 2270 | 0.91 | Wind-blown |
| 52.7 | 23 | 5.17 | 11.21 | 2570 | 0.80 | Redeposited |
| 50.6 | 23 | 5.01 | — | — | 0.80 | Redeposited |
| 4.4 | 95 | 2.19 | 4.14 | 950 | 0.87 | Wind-blown |
| 7.4 | 86 | 2.97 | 6.88 | 1580 | 0.96 | Wind-blown |

## Amount of amorphous materials of selected Andosols

To obtain the quantitative information on the amount of amorphous materials of Andosols, numbers of different kinds of the soils are required. As the first step, for the most part, the lower A horizons or B horizons of the selected Andosols were analysed. The whole horizons of representative soil profile are being analysed.

In Table 1, the soils are ranked in the order of the amount of amorphous material. The first group of soils from Jonouchi to Hirusen are derived from wind-blown volcanic ash, and contain amorphous material ranging from 42.8 to 20.5% on the oven-dry basis. The amount of amorphous material in the clay fraction ranged from 99 to 52%. The soils range in bulk density from 0.75 to 0.52 g/cc, and phosphorus absorption coefficients vary from 15.00 (3440) to 11.16 (2560) P mg/g ($P_2O_5$ mg/100 g). It is noted that the lowest bulk density of the Kuju A12 among them depends upon the dominant amorphous material, besides upon the higher content of organic carbon amounting to 21.47%.

In the second group, the Shinshiro, Sekigahara, and Kanazawa are deriving from volcanic ash influenced or from redeposited parent material. The amounts of amorphous material for those soils are 19.4, 11.9 and 11.4% on the oven-dry basis respectively. They contain from 36 to 23% amorphous material in the clay fraction, and have bulk density of 0.80 to 0.79 g/cc. The Kitagami soil is derived from wind-blown volcanic ash, and developed in a condition imperfectly drained throughout the year. Therefore it is composed of relatively well crystallized clay. The amount of amorphous material is less than 20% on the oven-dry basis, and occupies about 30% in the clay fraction.

The third group of soils, exemplified by the Asama, are derived from young volcanic ejecta, about 200 years old, and developed in cool climate. Coarse textured as it is, the amount of amorphous material in the clay fraction is 95 to 86%. The clay mineralogical investigation showed that a small quantity of poorly crystallized halloysite was recognized and clay was dominated by amorphous materials. The soil has developed in the piedmont of the Asama, and for the most part, the sand fraction consists of pyroclastic materials.

The amount of amorphous material of the first group soils is higher than the second group soils as mentioned above, however, their values of phosphorus absorption coefficient are similarly high. On the other hand, the bulk densities of the two groups are slightly different, corresponding to the amount of amorphous material.

In general, the amount of amorphous material, its percentage in the clay fraction, bulk density, pyroclastic material content in the coarse fraction, and phosphorus retention are very important factors for identification and classification of Andosols. However, the relationship of phosphorus absorption coefficient and the amount of amorphous material should be further studied.

It can be evaluated from the definition of Andepts in Soil Taxonomy (1975) that the soils of the first group and third group are included in Andepts suborder, however, that the soils of second group having amorphous material of less than 50% in the clay fraction, and less than 20% on the oven-dry basis, are not included in Andepts, but in Andeptic subgroups outside of Andepts, if the word "dominated" in the definition means more than 50% in the clay fraction. In Japanese soil classification system, on the other hand, these soils from the first group to third group including second group are included in Kuroboku soils. This system has been traditionally accepted for a long period, because they have higher phosphorus absorption coefficient, one of the important characters of soils. The difference between these two systems has to be made clear by further studies.

## Summary

With reference to the amount of amorphous materials of the selected soils, it is summarized that Andosols (Kuroboku soils) in Japan may be divided into three groups: 1) soils that have the amount of amorphous material of more than 20% on the oven-dry basis, and more than 50% in the clay fraction, deriving from wind-blown volcanic ash, 2) soil that have more than 10% on the oven-dry basis, and more than 20% in the clay fraction, deriving from ash influenced or redeposited and/or from wind-blown volcanic ash with well developed soil profile, and 3) soils that have less than 5% on the oven-dry basis, but more than 85% in the clay fraction, deriving from young coarse textured volcanic material.

Phosphorus absorption coefficients ranged from 15.00 (3440) to 9.90 (2270) P mg/g ($P_2O_5$ mg/100 g) except for young coarse textured horizons, and it seems not directly related to the amount of amorphous material.

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