Symposium Paper

Organic Carbon Accumulation in Andosols: (2) Contribution of Aluminum-humus Complexes to Carbon Accumulation in Non-allophanic Andosols

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Abstract

Andosols, especially non-allophanic Andosols, accumulate organic carbon (OC) in large amounts mainly due to stabilization of the OC by formation of aluminum-humus (Al-humus) complexes, low soil pH and high Al toxicity. These factors can be easily changed by soil management, and this may lead to a considerable decrease in the OC.

Introduction

Andosols accumulate large amounts of soil organic matter (SOM). Andosols cover only 0.8% of the earth's surface (Kimble et al., 2000), but they contain approximately 1.8% of the global soil carbon (Hillel and Rosenzweig, 2009). This is because not only of vigorous vegetation growth due to the high fertility of the soils, but of the high stability of the SOM against decomposition. It is generally considered that the SOC stabilization is related to 1) formation of the SOM in organo-mineral and/or organo-metallic (Al-humus) complexes (Torn et al., 1997; Inoue and Higashi, 1988; Nanzyo et al., 1993; Percival et al., 2000), 2) low activity of soil microorganisms due to the low soil pH and the high level of toxic Al (Tokashiki and Wada, 1975; Tonneijck, 2009), 3) physical protection of the SOM by the high porosity of the soils (Baldock and Nelson, 2000), and 4) the presence of charcoals (especially in melanic Andosols) (Nishimura et al., 2006). In this paper, we will briefly review the role of the Al-humus complexes, soil pH and toxic Al in the OC accumulation, and introduce our recent studies showing that these factors are rather easily controlled by soil management.

Importance of Al-humus complexes on OC accumulation in Andosols

Among the factors listed above, Al-humus complexes are considered to be the most important regarding the accumulation of OC. Inoue and Higashi (1988) showed that accumulation of OC in the upper 35 cm depth is strongly related to the pyrophosphate-extractable Al (r = 0.89, $P < 0.01$) or Al + Fe (r = 0.88, $P < 0.01$) using the data of Andosols that form under widely different climatic conditions around the world. Nanzyo et al. (1993) also confirmed the close positive correlation (r = 0.84, $P < 0.01$) between the content of pyrophosphate-extractable Al and the OC concentration using the A horizon data of the Andisol Tohoku University Database that consists of soil mostly from the Tohoku and Hokkaido districts in Japan and Alaska and Oregon in the United States. Similarly, in New Zealand soils, the pyrophosphate-extractable Al strongly correlated to the OC, whereas allophanic materials were not related to the OC (Percival et al., 2000). It is considered that the complexation of multivalent cations (e.g., Al^{3+} and Fe^{3+}) by humic substances results in functional groups becoming more condensed and less susceptible to biological attack (Baldock and Nelson, 2000).

With a lower soil pH, organic matter may be protected against decomposition by the Al toxicity to microorganisms (Tokashiki and Wada, 1975). In Andean Andosols, the KCl-extractable Al (toxic Al) concentration and soil pH value were also closely related to

the OC amounts (Tonneijck, 2009).

### High SOM accumulation in non-allophanic Andosols

Andosols are divided into two major groups on the basis of their colloidal compositions, i.e., allophanic Andosols and non-allophanic Andosols. Non-allophanic Andosols are characterized by the dominance of Al-humus complexes in their active Al. They usually show low soil pH values (pH (H$_2$O) of about 5 or less) and a high Al toxicity. Therefore, as compared to allophanic Andosols, non-allophanic Andosols tend to accumulate larger amounts of SOM as summarized by Nanzyo et al. (1993). Even in allophanic Andosols, when soils are strongly acidified (such as observed in Japanese tea gardens), the SOM significantly increases in comparison to the inorganic noncrystalline materials (Mitamura, 2005; Takahashi et al. 2008). This is due to the increase in the Al-humus complexes, namely the non-allophanic-andosolization of allophanic soils.

### Stability of Al-humus complexes – are all of them highly stable?

As mentioned above, the Al-humus complexes are highly stable and contribute to the OC accumulation. However, it has been revealed that a part of the complexes can be rather unstable as described below.

We determined the Al solubility in A horizon soils of allophanic and non-allophanic Andosols based on an equilibrium study (Fig. 1) (Takahashi et al., 1995). For the allophanic Andosol, the solubility was identi-

cal to that of gibbsite, indicating that the solubility is controlled by the soil minerals. On the other hand, the solubility of the non-allophanic Andosols deviated from that of gibbsite (Fig. 1). This indicates that the solubility is mainly controlled by the Al-humus complexes, or the exchange reaction of Al ions and H$^+$ on the charges of humus. Accordingly, it was shown, using many A horizon samples of non-allophanic soils from Japan, that the amounts of easily exchangeable Al from soils (an indicator of Al toxicity) are closely related to the soil pH and the organically-complexed Al (pyrophosphate-extractable Al) concentration (Fig. 2) (Takahashi et al. 2003).
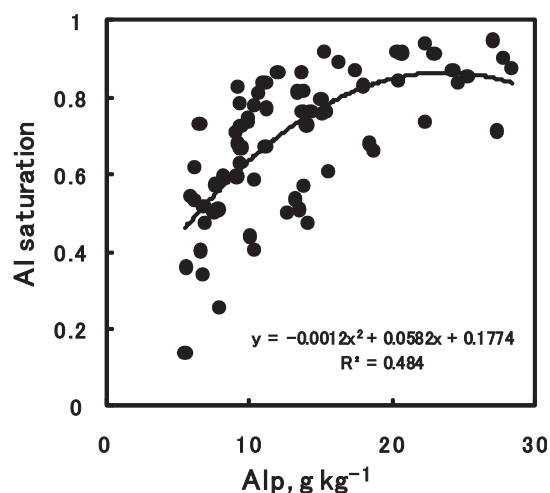

Fig. 2. Relationship between the concentration of pyrophosphate-extractable Al (Al$_p$) and Al saturation (KCl-extractable Al / effective cation exchange capacity) for A horizon samples of non-allophanic Andosols from northeastern Japan (Takahashi et al., 2003).
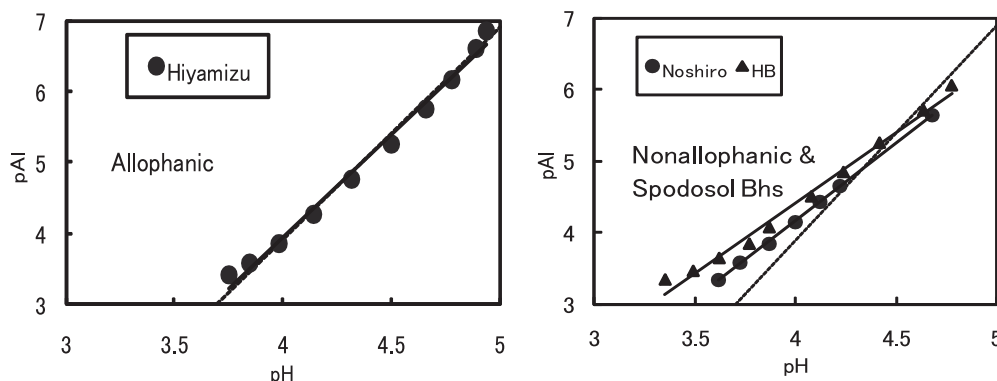
Fig. 1. Plot of equilibrium Al solubility versus pH for A horizons of an allophanic Andosol (Hiyamizu soil) and a non-allophanic Andosol (Noshiro soil), and Bhs horizon of a Podzol (Hubbard Brook soil) (Takahashi et al., 1995). The soil samples (3 g) suspended in 0.01 M CaCl$_2$ solution (30 mL) were incubated for 30 days at 25 °C, and the supernatant was obtained after centrifugation for the analyses. The dotted line indicates the solubility of synthetic gibbsite.
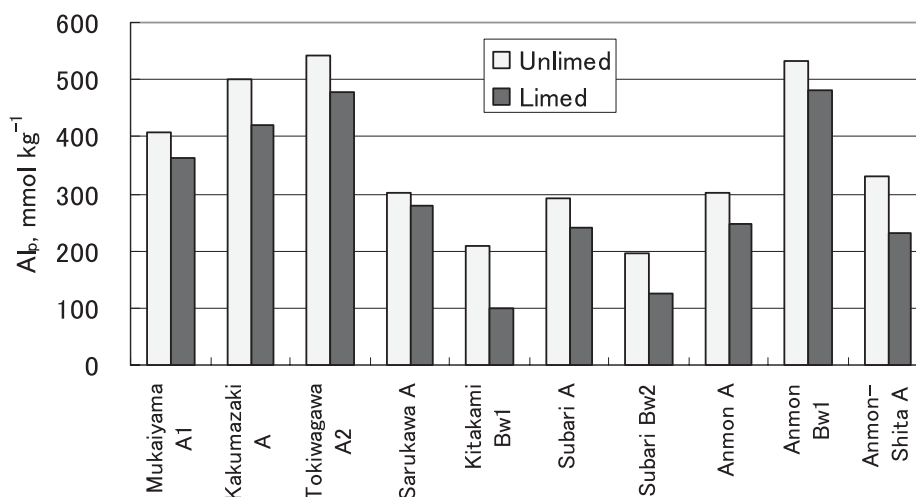
Fig. 3. Amounts of pyrophosphate-extractable Al from unlimed and limed soil samples (Takahashi et al., 2006). The limed soil samples were prepared by the incubation of a mixture of soil samples and calcium carbonate at field water capacity at room temperature (approximately 25 ˚C) for 30 days.

The root growth of Al sensitive plants in synthetic Al-humus complexes showed that the complexes directly cause Al-toxicity to the plant roots (Takahashi et al., 2007). These results indicate that the toxic Al of non-allophanic Andosols, at least, partly originates from the Al-humus complexes.

These facts about the non-allophanic Andosols demonstrate that a part of the Al-humus complexes is rather unstable. This is supported by the fact that even liming significantly decreases the organically complexed Al (pyrophosphate- and $CuCl_2$-extractable Al fractions) (Fig. 3) (Takahashi et al. 2006).

Changes in the land-use of non-allophanic Andosols will affect the extent of carbon accumulation. For example, liming increases the soil pH and decreases the Al toxicity, and thus the activity of microorganisms will increase as shown in the result of the denaturing gradient gel electrophoresis (DGGE) band pattern of eubacterial 16s rRNA (Fig. 4). Liming may accelerate the decomposition of the highly humified SOM due to the liberation of a part of the Al-humus complexes (Fig. 3). Fertilizer application will also activate the activity of microorganisms as observed for the nitrogen and phosphate treatments (Fig. 4). The effects of the soil pH change, the associated change in the Al-humus complexes, and fertilizer application on the OC accumulation potential of soils require further investigation.
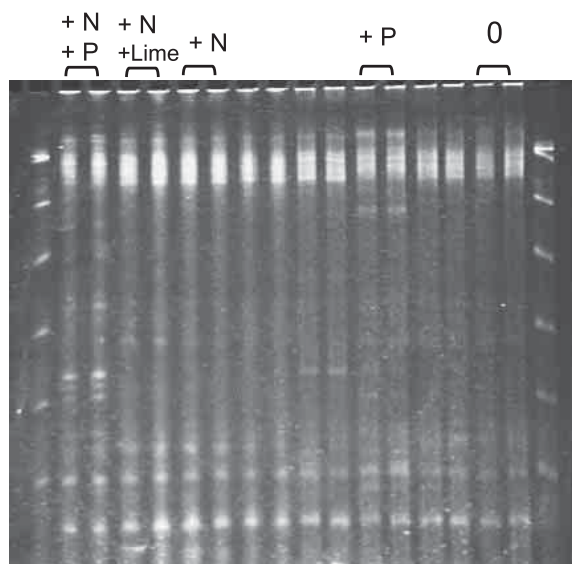
Fig. 4. Denaturing gradient gel electrophoresis (DGGE) band patterns of eubacterial 16s rRNA genes for A horizon samples of Kawatabi soil (non-allophanic Andosol) after several treatments and incubation (30 ˚C) (Yamada et al., unpublished data). +P: 30 days after the treatment of 40 g KH_2PO_4 kg^{-1} soil, +N: 14 days after the treatment of 1.18 g $(NH_4)_2SO_4$ kg^{-1} soil, +N+Lime: 14 days after the treatment of 1.18 g $(NH_4)_2SO_4$ kg^{-1} soil plus liming with $CaCO_3$ (pH 6.5), +N+P: 14 days after the treatment of 1.18 g $(NH_4)_2SO_4$ kg^{-1} soil plus 40 g KH_2PO_4 kg^{-1} soil, 0: 0 day after no treatment.

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