Nature, properties and function of aluminum–humus complexes in volcanic soils

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ABSTRACT

Andosols (or Andisols) possess several distinctive properties that are rarely found in other groups of soils. These properties are largely due to the dominance of short-range-ordered minerals (allophane, imogolite and ferrihydrite) and/or metal–humus complexes (Al/Fe–humus complexes) in their colloidal fraction. While several papers have extensively reviewed the nature and properties of short-range-ordered minerals, there is no comprehensive review of the genesis, characteristics and management implications of Al–humus complexes, the dominant form of active Al in non-allophanic Andosols. In this review, we survey the chemical characteristics of Al–humus complexes and discuss the pedogenic environment favoring their formation in non-allophanic Andosols. The role of Al–humus complexes in carbon cycling and soil organic carbon accumulation is emphasized as an important mechanism controlling organic dynamics in Andosols. While non-allophanic Andosols share many common properties with allophanic Andosols, they display several distinct characteristics associated with Al–humus complexes, such as strong acidity and high exchangeable Al content that impair agricultural productivity due to Al phytotoxicity. Thus, we focus on the role of Al–humus complexes in regulating aqueous Al^{3+} solubility and release/retention kinetics, Al phytotoxicity, phosphorus dynamics, and suppression of soil-borne diseases. Knowledge of these soil properties as related to Al–humus complexes is necessary to develop effective soil management practices to assure sustainable agricultural productivity in non-allophanic Andosols. Finally, future research needs are identified concerning the role of Al–humus complexes in regulating soil biogeochemical processes.

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Contents

1. Introduction

Andosols (Obara et al., 2011; The Fourth Committee for Soil Classification and Nomenclature, 2003; WRB, 2014) or Andisols (Soil Survey Staff, 1999; Soil Survey Staff, 2014), the typical soils developed from volcanoclastic materials, cover approximately 124 million hectares, about 0.84% of the world's land surface (Leamy, 1984; McDaniel et al., 2012). While Andosols comprise a relatively small extent of the world's land surface, they represent a crucial land resource due to the disproportionately high human population densities often supported by these soils (Mohr, 1938; Leamy, 1984; Shoji et al., 1993). The high human-carrying capacity implies that Andosols have favorable

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physical, chemical and biological properties for sustainable agricultural production.

Andosols possess several distinctive properties that are rarely found in other groups of soils. These properties include variable charge, high water retention, high phosphate retention, low bulk density, high friability, highly stable soil aggregates, and excellent tilth (Shoji et al., 1993). These distinctive properties are largely due to the formation of short-range-ordered minerals (mainly allophane, imogolite and ferrihydrite) and Al/Fe – humus complexes. For soil management purposes, Andosols are often divided into two groups based on the major colloidal composition of surface horizons: allophanic Andosols dominated by allophanic clays (allophane and imogolite) and non-allophanic Andosols dominated by Al–humus complexes and often containing 2:1 layer silicates (Shoji, 1985, 1985; Shoji and Ono, 1978). In the World Reference Base for Soil Resources (WRB, 2014), the term "silandic" is used to describe allophanic Andosols and "aluandic" to designate non-allophanic Andosols. Non-allophanic Andosols represent about 30% of all Andosols in Japan (Saigusa and Matsuyama, 1998) and are distributed worldwide (e.g., Japan, USA, Indonesia, Spain, Italy, Portugal, Chili, New Zealand, Western Samoa, Taiwan) (Chen et al., 1999; Johnson-Maynard et al., 1997; Leamy et al., 1988; Madeira et al., 1994; Shoji et al., 1985, 1987).

In this review, we assess the nature, genesis, properties and significance of Al–humus complexes in soils formed on volcanoclastic materials. Al–humus complexes are the dominant form of active Al (acid oxalate-extractable Al) in the colloidal fraction of non-allophanic Andosols, and also comprise a significant portion of the colloidal fraction of humus-rich horizons in most Andosols and Podzols. Specific topics covered by this review include the role of Al–humus complexes in organic carbon accumulation, aqueous Al solubility and kinetics, Al phytotoxicity, phosphorus dynamics, and suppression of soil-borne diseases. This synthesis informs management practices related to maximizing agricultural productivity of soils dominated by Al–humus complexes.

2. Characterization of Al–humus complexes and origin of the organic carbon

Humic substances are anionic polyelectrolytes with a large degree of heterogeneity in terms of physical and chemical properties. The structure, molecular mass and functional groups of humic substances vary depending on origin and degree of humification of the organic material. The majority of humic substances in soils occurs as insoluble forms such as macromolecular complexes, macromolecular complexes bound together by multivalent cations (e.g., Fe^{3+}, Al^{3+}), or in combination with soil minerals (e.g., clay–metal–humus) through bridging by polyvalent cations, hydrogen bonding and van der Waal's forces (Stevenson, 1985). Humic substances are often strongly bound to mineral surfaces through specific adsorption by ligand exchange with protonated surface hydroxyl groups to form metal–organic–mineral coatings on soil mineral surfaces. As a result, the surface chemistry of the soil is transformed from primary control by inorganic constituents to organo-mineral coatings.

Humic substances have two primary types of metal binding sites, carboxylic and phenolic functional groups. Two main types of chelate linkages have been suggested: one involving a COOH and an adjacent phenolic OH group to form a salicylate-like ring and the other involving two COOH groups in close proximity to form a phthalate-like ring (Schnitzer and Skinner, 1965; Gamble, 1970). The maximum binding capacity of humic substances is approximated by the content of acidic functional groups, primarily COOH moieties. Exchange acidities of humic substances, approximating COOH content, range widely but generally fall within the range of 1500–5000 $mmol_c$/kg (Stevenson, 1985). Polyvalent cations (e.g., Al^{3+}, Fe^{3+}) may form multi-dentate complexes (mono-, di- and tri-dentate) with humic substances, but bidentate complexes are believed to be the most prevalent (Rouff et al., 2012).

The stability constants for metal–humic complexes display a curvilinear decrease with increasing metal coverage (Perdue and Lytle, 1983; Stevenson and Chen, 1991). Stevenson and Chen (1991) described the relationship between the stability constant and metal coverage of humic substances by a continuous distribution model that results from (i) complexation sites with different binding energies, (ii) increasing electrostatic repulsion with increased metal saturation, and (iii) increasing aggregation of humic substances with increasing metal saturation thereby reducing metal accessibility. Thus, the stability of metal–humic complexes will depend on the metal/ligand ratio (i.e., degree of metal saturation on humic substance functional groups) and the concentration of competitive cations, especially protons (Hargrove and Thomas, 1982; Gerke, 1994).

The Al/Fe – humus complex fraction has historically been operationally defined as the Al, Fe and organic carbon extracted by pyrophosphate reagent (0.1 M Na-pyrophosphate at pH 10) (McKeague, 1967). In spite of its long-term use, caution must be exercised in interpreting pyrophosphate extractable metal and organic matter concentrations as pyrophosphate reagent has been shown to dissolved some Al from gibbsite and amorphous $Al(OH)_3$ in soil (Kaiser and Zech, 1996). Due to the lack of specificity for metal–humic compounds by pyrophosphate reagent, other extraction reagents have been proposed for characterization of metal–humic substances with the following general extractability pattern (Dahlgren, 1994): pyrophosphate (McKeague, 1967) > Na-EDTA (Borggaard, 1976) > Na-tetraborate (Higashi and Shinagawa, 1981) > $CuCl_2$ (Hargrove and Thomas, 1981).

Solid-state cross polarization magic angle spinning (CPMAS) ^{13}C-nuclear magnetic resonance (NMR) spectra of A horizons from Andosols usually show the presence of C in aliphatic, O-alkyl, aromatic and carbonyl functional groups. Among them, the aromatic C and carbonyl C were shown to be concentrated in humic substances extracted by alkaline solutions (pyrophosphate or NaOH) (Hiradate et al., 2004; Takahashi et al., 2007). This evidence supports the assumption that metal–humus complexes are formed primarily by the interaction of metals with carboxylic functional groups. The complexing capacity of humus increases as the degree of humification increases. The Al–humus fraction is generally much higher (~10:1) than the Fe–humus fraction owing to the greater stability of iron in Fe (hydr)oxides as compared to humus complexes (Dahlgren et al., 1993; Ugolini and Dahlgren, 2002; Wada and Higashi, 1976). The degree of metal complexation by humic substances can be evaluated by examining pyrophosphate extractable Al, Fe, and C (Al_p, Fe_p, C_p) using atomic ratios: Al_p/C_p or $(Al_p + Fe_p)/C_p$. For most A horizons of Andosols, the Al_p/C_p ratio ranges between 0.05 and 0.2 (Higashi, 1983) while the $(Al_p + Fe_p)/C_p$ ratio ranges between 0.1 and 0.2 (Inoue and Higashi, 1988). These ratios are likely over-estimated due to the non-specificity of pyrophosphate reagent for the Al/Fe fraction. Assuming a bidentate metal chelate with COOH and an adjacent phenolic OH group (salicylate-like complex), metal saturation with humic substances having a 5000 mmol COOH/kg organic C content and 50% carbon content would be metal saturated at a metal/C_p atomic ratio of approximately 0.12.

As for the origin of organic carbon in humic substances of Andosols, especially for very dark colored A horizons with highly humified organic matter (melanic epipedon), grass vegetation such as *Miscanthus sinensis* has been implicated as the primary source (Arai et al., 1986; Kumada, 1987; Mitsuchi, 1985; Shoji et al., 1990). Ishizuka et al. (2014) showed that the melanic index correlates negatively with $\delta^{13}C$ values of A horizons in Japanese forest soils, indicating that C4 grasses played an important role in generating dark-colored organic matter. Hiradate et al. (2004) further showed that the contribution of C4 plants, such as *Miscanthus sinensis,* to organic C was ~50% in dark-colored humic acids using $\delta^{13}C$ values of humic substances in A horizons of Japanese volcanic soils. This indicates that C3 plants, including tree vegetation, are also an important source of humic materials in melanic epipedons (Shindo et al., 2005; Hiradate et al., 2006). Furthermore, Inoue et al. (2001, 2006) and Takahashi et al. (1994) showed that C4 plants were