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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 Al³⁺ 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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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 dissolve some Al from gibbsite and amorphous $\text{Al}(\text{OH})_3$ 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 $(\text{Al}_p + \text{Fe}_p)/\text{C}_p$. For most A horizons of Andosols, the Al_p/C_p ratio ranges between 0.05 and 0.2 (Higashi, 1983) while the $(\text{Al}_p + \text{Fe}_p)/\text{C}_p$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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

not necessary for formation of melanic epipedons. In addition to these grass and tree vegetation types, pteridophyte vegetation, such as bracken fern (*Pteridium aquilinum*), has been shown to preferentially form Al–humus-rich melanic or melanic-like surface horizons (Birrell et al., 1971; Johnson-Maynard et al., 1997; Leamy et al., 1980; Lowe and Palmer, 2005).

Takahashi et al. (1994) documented the presence of high concentrations of charred materials across a range of melanic epipedons in northern California. A subsequent analysis of these samples indicated that charcoal comprised up to 20% of the total organic C pool (Dahlgren, unpublished data). These results suggest that fire may be an important factor in the formation of melanic epipedons in the xeric moisture regime of northern California where fire return frequencies of less than 30 years were historically common. Many studies by Shindo and coworkers further demonstrated that considerable amounts of charred plant fragments are found in Andosols from Japan (Miyazaki et al., 2009, 2010; Nishimura et al., 2006, 2008, 2009; Shindo et al., 2003, 2004). There were strong positive correlations between concentrations of the charred materials and humic substances (e.g., humic acid, fulvic acid) (Miyazaki et al., 2009, 2010; Nishimura et al., 2009; Shindo et al., 2004). They attributed the charred plant fragments as important contributors to the formation of humic substances in Japanese Andosols, especially the A-type humic acid that represents the highest degree of humification.

3. Formation of Al–humus complexes

Under humid weathering conditions in volcanoclastic materials, aluminum in the colloidal fraction generally forms a continuum between pure Al–humus complexes and pure allophane/imogolite (Mizota and van Reeuwijk, 1989), corresponding to aluandic and silandic horizons, respectively, in WRB classification (WRB, 2014). Pedogenic environments favoring formation of Al–humus complexes and allophanic materials are sharply contrasting in Andosols. Non-allophanic soils dominated by Al–humus complexes form preferentially in pedogenic environments dominated by organic acid weathering and are therefore rich in organic matter and have pH values of 5 or less (Shoji and Fujiwara, 1984). Contributing to soil acidification are base-poor volcanic deposits (e.g., rhyolitic, dacitic, or andesitic) having non-colored volcanic glass, annual precipitation amounts greater than about 1000 mm, and older parent materials that have experienced a greater degree of weathering. At pH values less than 5, organic acids are the dominant proton donor lowering pH and aqueous Al^{3+} activities through formation of Al–humus complexes. Aqueous Al^{3+} may also be incorporated into the interlayer of 2:1 layer silicates when present (Dahlgren and Ugolini, 1989). Under this weathering environment, humus and 2:1 layer silicates effectively compete for dissolved Al, leaving little Al available for co-precipitation with silica to form aluminosilicate materials, such as allophane/imogolite. This preferential incorporation of Al into Al–humus complexes and hydroxy-Al interlayers of 2:1 layer silicates has been termed the anti-allophanic effect (Shoji et al., 1993) and leads to the formation of non-allophanic Andosols.

In contrast, allophanic clays form preferentially in pedogenic environments where the dominant proton donor is carbonic acid, pH values are in the range of 5–7, and the content of complexing organic compounds is low (Ugolini and Dahlgren, 1991). Shoji et al. (1982) and Shoji and Fujiwara (1984) showed that allophanic soils are favored in base-rich parent materials (e.g., andesitic basalt, basalt) having colored volcanic glass, humid climates having less than 1000 mm of annual precipitation, and in younger volcanic deposits. These conditions favor higher pH values (pH > 5), which promotes formation of Al–polymers relative to Al–humus complexes (Jackson, 1963a,b). The Al–polymers are able to react with silica and form allophane/imogolite leading to formation of allophanic Andosols.

It is important to note that allophanic and non-allophanic Andosols are distinguished based on the dominance of Al–humus complexes

versus allophanic materials in the upper soil horizons (e.g., generally upper 30 cm). As such, Al–humus complexes are also common in the A horizons of allophanic Andosols where they often suppress formation of allophanic materials relative to underlying B horizons (Dahlgren et al., 2004). Similarly, non-allophanic Andosols often have allophanic materials in their lower horizons as the organic acid weathering regime in the upper soil horizons is replaced by carbonic acid in the lower soil horizons (Ugolini et al., 1988; Dahlgren et al., 1991, 2004).

In Japan, allophanic Andosols are mainly distributed in areas having thick deposition of Holocene and/or late-Pleistocene volcanic deposits, while non-allophanic Andosols are found in areas with older tephra deposits. Older tephra deposits are generally more acidified and have been exposed to eolian deposition of exogenous materials containing 2:1 layer silicates or their precursors, such as loess from China (Bautista-Tulin and Inoue, 1997; Inoue and Naruse, 1987; Mizota and Inoue, 1988; Mizota et al., 1990; Saigusa and Matsuyama, 1998). Mixing of alluvial or residual deposits with volcanic materials may also result in formation of non-allophanic Andosols. For example, Takahashi et al. (2001) showed that non-allophanic Andosols in several forest soils of Aomori and Akita Prefectures were formed in Pleistocene sedimentary rocks and Miocene green tuff mixed by landslides with no evidence of tephra deposition. Recent studies in forested areas in Japan indicate widespread distribution of non-allophanic Andosols mixed with Brown forest soils (Imaya et al., 2005, 2007, 2010a,b).

4. Organic carbon accumulation in Andosols

Accumulation of soil organic matter (SOM) is a characteristic property of Andosols (Wada, 1985). Andosolization is the darkening of the soil due to an accumulation of stable humic substances under subacid conditions (Duchaufour, 1977; Ugolini et al., 1988). Andosolization is a case of melanization in which Al^{3+} is the dominant exchangeable cation, as opposed to Ca^{2+} that produces a mollic epipedon. While Andosols cover 0.84% of the Earth's land surface (Leamy, 1984; Soil Survey Staff, 1999), they contain a disproportionate amount of SOM, approximately 1.8% of the global soil organic carbon (Hillel and Rosenzweig, 2009). The large accumulation of organic matter results from a combination of high detritus inputs associated with the generally high fertility and productivity of Andosols and from effective stabilization of SOM against decomposition. Research has shown that plant-derived SOM is strongly degraded and that it is the microbial SOM fraction that contributes substantially to SOM pools in Andosols (Buurman et al., 2007). Stabilization of SOM in Andosols has been attributed to i) formation of the SOM in organo-mineral and/or organo-metallic (Al/Fe–humus) complexes (Inoue and Higashi, 1988; Nanzyo et al., 1993; Neculman et al., 2013; Percival et al., 2000; Rumpel et al., 2012; Torn et al., 1997), ii) low activity of soil microorganisms due to low soil pH, Al toxicity, low base cation content, and/or P deficiency (Tokashiki and Wada, 1975; Tonnejck, 2009), iii) physical protection of the SOM in stable microaggregates characteristic of variable charge soils (Huygens et al., 2005; Baldock and Broos, 2011), iv) sorption and deactivation of exoenzymes involved in the extracellular depolymerization component of SOM decomposition (Saggar et al., 1994; Miltner and Zech, 1998), v) burial of organic-rich surface horizons by repeated additions of airfall tephra deposition, and vi) the presence of microbially-recalcitrant charcoal (especially in melanic epipedons) (Miyazaki et al., 2009, 2010; Nishimura et al., 2006). The stabilization of SOM is reflected in the ^{14}C age of humic acids extracted from A horizons of Andosols which is reported to range from modern to 30,000 YBP, with the majority in the range 1000–5000 YBP (Inoue and Higashi, 1988). It was concluded that mean residence time of SOM in Andosols was appreciably greater than for Mollisol A horizons and Podzol/Spodosol Bh horizons. This supports the assertion that the mean residence time of SOM in Andosols is generally much longer than for other soil types (Arnalds, 2008; Torn et al., 1997).

Several studies have suggested that chemical stabilization of SOM via formation of Al–humus complexes is an important process for SOM accumulation in Andosols (e.g., Zunino et al., 1982; Inoue and Higashi, 1988; Egashira et al., 1997; Baldock and Skjemstad, 2000; Percival et al., 2000; Rasmussen et al., 2006; Takahashi et al., 2012). Al–humus complexes may facilitate protection of organic C directly by rendering functional groups more condensed and less assessable to enzymatic attack and indirectly by promoting adsorption to mineral surface (as Al–humic–mineral complexes), particle cementation, and the formation of stable micro- and macro-aggregate structures (Oades, 1988). However, the specific role of Al–humus complexes in chemical stabilization of SOM is not yet fully understood. Studies examining extensive global datasets for Andosol A horizons find a strong correlation between pyrophosphate-extractable Al and SOM ($r = 0.89, P < 0.01$, Inoue and Higashi, 1988; $r = 0.84, P < 0.01$, Nanzyo et al., 1993). In New Zealand volcanic soils, the pyrophosphate-extractable Al was similarly strongly correlated to SOM, whereas allophanic materials were not related to SOM (Percival et al., 2000). It is considered that the complexation of multivalent cations (e.g., Al^{3+}) by humic substances results in functional groups becoming more condensed and less susceptible to biological attack (Baldock and Broos, 2011). The role of Al–humus complexes in enhancing the resistance of humic substances to microbial decomposition has been demonstrated by incubation experiments (Martin et al., 1966; Juste et al., 1975; Martin et al., 1982; Rasmussen et al., 2006). However, a pyrolysis-GC/MS investigation of soil organic matter in Andosols from Costa Rica did not support the theory of strong chemical protection of plant-derived components through binding to allophane, iron or aluminum (Buurman et al., 2007). Therefore, other processes may be important in SOM sequestration in Andosols.

Al–humus complexes may also participate in physical protection of SOM, along with allophanic materials, through formation of micro- and macro-aggregates that are prevalent in Andosols (Warkentin et al., 1988). Asano and Wagai (2014) demonstrated strong evidence for aggregate hierarchy in Andosols A horizons with Al–humus complexes likely contributing as a binding agent to form both micro- and macro-aggregates. Gijsman and Sanz (1998) investigated the physical protection of macro-aggregates in Andisols and found elevated CO_2 mineralization after crushing of macro-aggregates. Macro-aggregate breakdown results in the exposure of labile organic matter rendering it accessible for microbial decomposition. Due to high water retention

by micro-aggregates, it is plausible that anaerobic conditions may hinder aerobic decomposers in the aggregate interiors, even under otherwise well-aerated conditions at the soil pedon scale. For example, Buurman et al. (2007) reported incorporation of SOM into 10 μ m-diameter aggregates that remained saturated with water throughout much of the year, thereby hindering microbial decomposition. As fluid migration is reduced inside the fractal structure of the aggregates, the SOM adsorbed or trapped in these fractal pore structures is less available to microbes and enzymes (Chevallier et al., 2010).

With the lower soil pH characteristic of non-allophanic Andosols ($pH < 5$), organic matter may also be protected against decomposition by Al toxicity to some microorganisms (Tokashiki and Wada, 1975). In Andean Andosols, soil pH and KCl-extractable Al concentration were closely related to the SOM content (Tonnejck, 2009). Takahashi et al. (2012) determined the relationship between SOM content and selected soil properties such as $pH(H_2O)$, KCl-extractable aluminum (KCl-Al, exchangeable Al), pyrophosphate-extractable Al and Fe (Al_p and Fe_p , Al/Fe–humus complexes), and acid oxalate-extractable Si (Si_o , Si in allophanic materials) for 293 A horizons in the Tohoku University World Andosol Database (Shoji et al., 1996). A path analysis was used to examine direct and indirect effects of soil properties on SOM content (Fig. 1 and Table 1). The results showed a high correlation coefficient between SOM content and Al_p ($r = 0.69, P < 0.01$) indicating a strong direct effect of Al_p (path coefficient = 0.52, $P < 0.01$) on SOM content. Strong correlations between SOM and KCl-Al ($r = 0.60, P < 0.01$) or $pH(H_2O)$ ($r = -0.58, P < 0.01$) were not only due to direct effects (path coefficient = 0.21 and -0.27, respectively, $P < 0.01$), but also to indirect effects of other properties, especially that of Al_p . Thus, it is considered that, in the humus horizons of many Andosols, Al–humus complexation strongly contributes to SOM accumulation, and low soil pH and Al toxicity may be partially responsible for this humus accumulation through depressing microbial activity (Takahashi et al., 2012).

Al–humus complexes are believed to be highly stable under natural conditions in non-allophanic Andosols. As previously discussed, Al–humus complexes are assumed to protect soil humus from decomposition by microorganisms and enzymes (Baldock and Broos, 2011; Mikutta et al., 2007; Schneider et al., 2010). However, Takahashi et al. (2006a) showed a remarkable decrease of Al_p values (7–52%) following liming of A horizon soils from non-allophanic Andosols in a laboratory study. The authors postulated that the reduction of Al–humus complexes could lead to an increase in C mineralization by liming

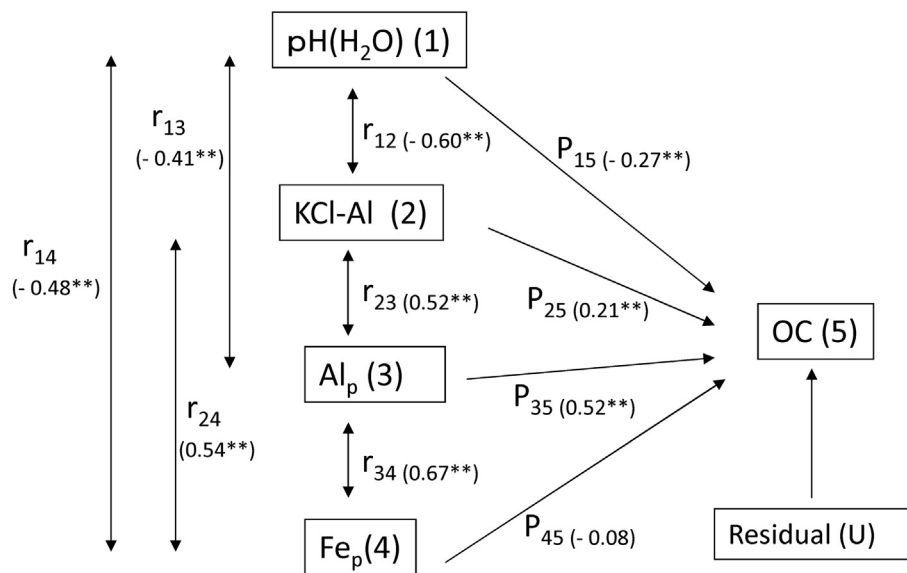


Fig. 1. Path analysis diagram for the relationships between organic carbon (OC) content and soil properties using data ($n = 293$) from the Tohoku University World Andosol Database. The path coefficient (P_{ij}) of soil properties is represented by single-headed arrows, and the simple correlation coefficients (r_{ij}) between variables are represented by double-headed arrows. **Significant at $P < 0.01$. (Takahashi et al., 2012).

Table 1

Direct effect (diagonal, underlined> and indirect effect (off diagonal) of soil properties on organic carbon content from the results of the path analysis ($n = 293$). (Takahashi et al., 2012).

	pH(H ₂ O)	KCl-Al ^a	Al _p ^b	Fe _p ^c	r	R^2	U^d
pH(H ₂ O)(1)	−0.27**	−0.13*	−0.21**	0.04	−0.58**	0.61	0.63
KCl-Al (2)	0.16**	0.21**	0.27**	−0.04	0.60**		
Al _p (3)	0.11	0.11	0.52**	−0.05	0.69**		
Fe _p (4)	0.13*	0.11	0.35**	−0.08	0.52**		

^a 1 M KCl-extractable Al.

^b Pyrophosphate-extractable Al.

^c Pyrophosphate-extractable Fe.

^d Uncorrelated residue.

** Significant at $P < 0.01$.

* Significant at $P < 0.05$.

(Takahashi et al., 2006a), as was later verified in a laboratory incubation (Miyazawa et al., 2013). These results are consistent with field studies that demonstrated a marked decrease in Al_p and SOM contents of Ap horizons in Andosols following cultivation and liming (Saigusa et al., 1988; Verde et al., 2005).

5. Role of Al–humus complexes in aluminum solubility and release/retention kinetics

Aluminum solubility and release/retention kinetics are closely related to the dominant pools of active Al in allophanic and non-allophanic Andosols. In turn, Al dynamics play an important role in agricultural productivity, especially related to Al toxicity that is often closely tied to the easily exchangeable Al fraction. Studies examining Al solubility and release/retention kinetics in Andosols show fast reaction kinetics and rapid attainment of equilibrium (Dahlgren and Saigusa, 1994; Dahlgren and Walker, 1993; Takahashi and Dahlgren, 1998; Takahashi et al., 1995). In soils containing hydroxy-Al polymers (interlayered 2:1 layer silicates), allophane/imogolite, Al–humus complexes, and exchangeable Al, there appears to be a simultaneous equilibrium among all phases (Fig. 2; Dahlgren and Walker, 1993). In particular, the release/retention kinetics associated with exchangeable Al and Al–humus complexes are very rapid with an apparent equilibrium from both over- and under-saturation occurring within a 20-min residence time (Dahlgren et al., 1989). Hydroxy-Al polymers appear to ultimately regulate Al solubility with a solubility product similar to that of synthetic gibbsite: $\log K^*_{so} = 8.1$ for the reaction $\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$ (May et al., 1979). Dahlgren and Walker (1993) obtained a slope of about 2.7 for several Spodosol Bs horizons, compared to a theoretical value of 3.0 for an $\text{Al}(\text{OH})_3$ phase. A slope less than 3.0 may indicate that the formula for the hydroxy-Al polymer is $\text{Al}(\text{OH})_{2.7}^+$, the positive charge satisfying the negative charge of the 2:1 layer silicate hosting the interlayer material (Huang, 1988). As for allophanic Andosol A horizons, Takahashi et al. (1995) observed a slope of 2.9, which was very close to the value expected for an $\text{Al}(\text{OH})_3$ phase (Fig. 3 and Table 2).

In contrast, humus-rich soils such as non-allophanic Andosol A horizons and Podzol/Spodosol Bh horizons have significantly lower

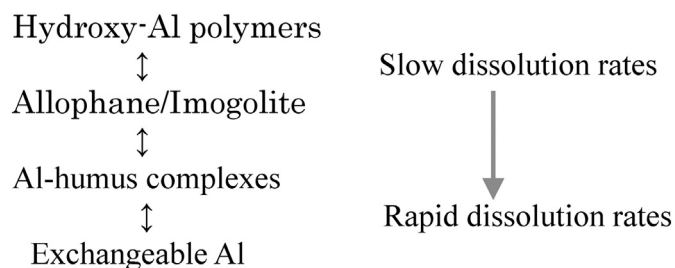


Fig. 2. The active Al fractions in Andosols appear to form a simultaneous equilibrium between the various solid-phase constituents. (Dahlgren et al., 2004).

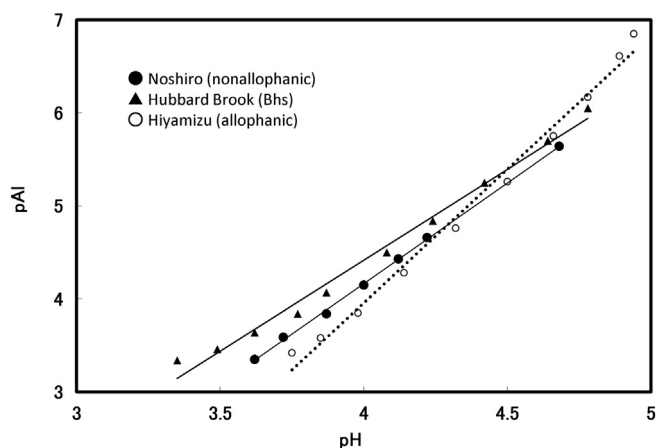


Fig. 3. Plots of equilibrium Al solubility versus pH at 25 °C for A horizons of non-allophanic and allophanic Andosols and a Bh horizon of a Podzol. The solubility of synthetic gibbsite is indicated by the dotted line for comparison. (Takahashi et al., 1995).

Al^{3+} activities and pAl/pH slopes (1.3 – 2.4) than expected for hydroxy-Al polymers ($\text{pAl/pH} = 3.0$) (Table 2 and Fig. 3; Dahlgren and Ugolini, 1989; Takahashi et al., 1995). These studies suggest that exchange of Al^{3+} with humic substances (Al–humus complexes) controls the relationship between Al^{3+} and H^+ . In this case, the degree of Al^{3+} saturation of carboxyl groups on humic substances will determine the pAl versus pH solubility relationship (i.e., slope and intercept) (Cronan et al., 1986).

The kinetics of Al release from soils containing a variety of active Al forms show that Al release rates are rapid from both allophanic and non-allophanic soils (Dahlgren and Saigusa, 1994; Takahashi et al., 1995). To determine the source of Al released, soil samples were sequentially treated with KCl (exchangeable Al), pyrophosphate (Al–humus complexes) and acid oxalate (allophane/imogolite) to isolate the effects of each active Al pool on Al release rates. The KCl treatment resulted in a large decrease in Al release rates for non-allophanic soils, but an increase in release rates for allophanic soils. The decrease in Al release rates for non-allophanic soils is explained by the removal of easily exchangeable Al having rapid release kinetics (Fig. 4). In contrast, the increase in Al release rates observed in the allophanic soils (Fig. 4) is believed to be due to the mechanism of “induced hydrolysis” (Wada, 1987a,b). Induced hydrolysis results from the release of adsorbed Al to the aqueous phase in the exchange process with K^+ . The exchangeable Al is considered to be mostly from weakly held Al–humus complexes. Following release, the Al undergoes hydrolysis and releases H^+ that is adsorbed on the surface of variable charge materials. Saturation indices for the KCl-treated soil were near apparent equilibrium to slightly super-saturated with respect to synthetic gibbsite suggesting that the precipitation of displaced Al was thermodynamically favorable. These precipitates are most likely adsorbed to soil surfaces making them readily available for subsequent dissolution by acidic solutions (Dahlgren and Saigusa, 1994; Dahlgren and Walker, 1993).

Among soil samples rich in Al–humus complexes and having a virtual absence of allophanic materials, Takahashi and Dahlgren (1998) found several samples showing an increase of Al release rates after 1M KCl treatment as previously found for allophanic soils. The saturation

Table 2

Slopes and $\log K^*_{so}$ (intercept) values obtained from linear regression of Al solubility data for A horizons of Andosols and a Bh horizon of a Podzol. (Takahashi et al., 1995).

Soil type	Non-allophanic			Podzol Bhs	Allophanic
	Mukaiyama	Noshiro	Wakami	Hubbard Brook	Hiyamizu
Slope	2.4	2.2	2.3	2.0	2.9
$\log K^*_{so}$	5.2	4.5	4.8	3.4	7.5

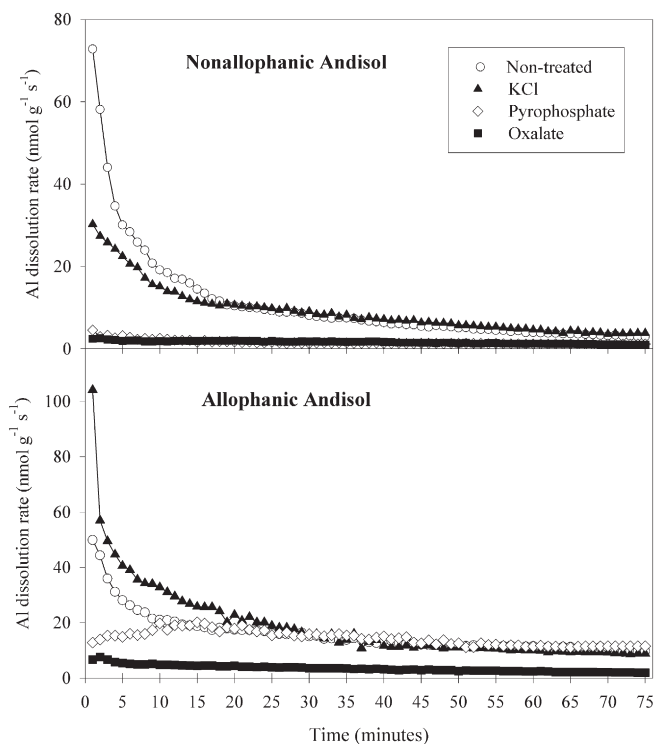


Fig. 4. Aluminum release rates at pH 3.3 for nontreated soil samples and residues following selected dissolution treatment for a Bw horizon from allophanic and non-allophanic Andosols. Samples were treated with KCl, pyrophosphate, and oxalate to remove the various Al pools for determining their effect on the overall Al dissolution rates. (Dahlgren and Saigusa, 1994).

indices indicated that the precipitation of an $\text{Al}(\text{OH})_3$ phase was thermodynamically possible. The probable “induced hydrolysis” of non-allophanic soils was assumed to be related to high contents of active Al (Al_o and Al_p) (Takahashi and Dahlgren, 1998). Lee (1988) also demonstrated that the extraction of Al from Spodosol Bh horizons by KCl solution was controlled by the solubility of an $\text{Al}(\text{OH})_3$ phase. Thus, these phenomena may occur widely in acidic soils with an active Al fraction dominated by Al–humus complexes.

Removal of Al–humus complexes with pyrophosphate reagent resulted in a substantial decrease in Al release rates for both allophanic and non-allophanic soils (Fig. 4). This suggests that Al–humus complexes are a labile source of dissolved Al, especially for non-allophanic soils. Further treatment with acid oxalate had little effect on Al release from non-allophanic soils; however, Al release from allophanic soils decreased to very low rates, suggesting that allophane/imogolite are an important source of dissolved Al in allophanic soils.

Allophanic soils usually have $\text{pH}(\text{H}_2\text{O})$ values greater than ~5. However, the heavy application of ammonium-based fertilizers over many years has resulted in allophanic Andosols becoming strongly acidified (Inamatsu et al., 1991; Matsuyama et al., 2005; Morikawa et al., 2002; Saigusa et al., 1988). Changes in soil chemical properties and Al solubility characteristics for acidified allophanic soils in tea plantations were investigated by Takahashi et al. (2008) (Fig. 5). Samples were derived from both alleyways and under the tea canopy. The less fertilized soils beneath the tea canopy showed limited acidification ($\text{pH}(\text{H}_2\text{O})$ 4.9–5.0) and demonstrated Al solubility characteristics typical of allophanic Andosols (Takahashi et al., 2008). In contrast, the alleyway soils were strongly acidified due to heavier application of ammonium-based fertilizers ($\text{pH}(\text{H}_2\text{O}) \approx 3.6$ –3.8) and displayed a decrease in allophanic materials with a concomitant increase in Al–humus complexes. This study clearly demonstrates the conversion of allophanic to non-allophanic (Al–humus complexes) materials upon prolonged acidification. The ion activity products for the strongly acidified soils were largely under-saturated with respect to allophane/imogolite and gibbsite.

Similarly, the pAl/pH slope was <3.0 , consistent with Al solubility being controlled by Al–humus complexes (Fig. 5). Similar Al solubility characteristics were reported by Yagasaki et al. (2006) for an acidified A horizon initially dominated by allophanic materials. Thus, long-term acidification of allophanic soils leads to a change in the active Al fraction to a dominance by Al–humus complexes and the Al solubility and kinetic characteristics are then controlled by Al–humus complexes.

6. Aluminum phytotoxicity

In acidic Andosols, toxicities (H^+ and Al^{3+}), deficiencies (P, Ca, Mg and micronutrients), and suppression of microbial activity may limit agricultural productivity. Among these agricultural impairments, Al toxicity is often recognized as the most important constraint on plant growth in acidic Andosols. The importance of Al toxicity in Andosols is recognized by the “alic” subgroup/qualifier ($>2.0 \text{ cmol}_{(+)} \text{ kg}^{-1}$ KCl-extractable Al) in Soil Taxonomy. Among Andosols significant differences in Al toxicity potential are recognized between allophanic and non-allophanic soils. Allophanic Andosols are moderate to slightly acidic ($\text{pH}(\text{H}_2\text{O}) \approx 5$ –7), even when the base saturation is very low, and rarely contain toxic levels of KCl-extractable Al. In contrast, non-allophanic Andosols are strongly acidic ($\text{pH} \leq 5$) when the base saturation is low and possess high KCl-extractable Al concentrations ($>2.0 \text{ cmol}_{(+)} \text{ kg}^{-1}$) that are toxic to Al-sensitive plants (Saigusa et al., 1980; Shoji et al., 1980). Unbuffered salt solutions, such as 1 M KCl solution, are generally believed to extract exchangeable Al ions electrostatically bonded to permanently charged sites of clay minerals (Jardine and Zelazny, 1996) and the weakly complexed fraction from Al–humus complexes (Dahlgren and Saigusa, 1994).

Humus-rich horizons of non-allophanic Andosols generally contain abundant amounts of organically complexed Al (Al–humus complexes). The potential for Al toxicity is believed to be controlled by the degree of Al^{3+} saturation of clay minerals and humic substances. Evidence suggests that KCl-extractable Al is considerably influenced by Al–humus complexes (Takahashi and Dahlgren, 1998). To support this assumption, the relationship between Al saturation (KCl-extractable Al/effective CEC) and Al_p was examined (Takahashi et al., 2003). The results showed that there is a strong relationship ($P < 0.001$) in the humus-rich mineral horizons of non-allophanic Andosols from an extensive area of eastern Japan ($n = 70$) (Fig. 6). Another dataset of 105 humus-rich mineral horizons showed a strong negative correlation between KCl-extractable Al and $\text{pH}(\text{KCl})$ values ($P < 0.01$) and a strong relationship between KCl-extractable Al and Al_p ($P < 0.05$) (Takahashi et al., 2011). Thus, it is suggested that the KCl-extractable Al fraction from Andosols consists of the easily exchangeable Al fraction plus Al associated with the pyrophosphate-extractable fraction (i.e., Al–humus complexes) (Takahashi et al., 2011). This evidence supports the origin of a portion of the exchangeable Al fraction as aqueous Al equilibrated with Al–humus complexes, as indicated in the Al equilibration scheme discussed above (Fig. 2). Thus, it is also considered that the organically complexed Al may contribute to Al phytotoxicity.

To confirm the potential phytotoxicity of Al–humus complexes, plant culture tests were performed using synthetic Al–humus complexes (Takahashi et al., 2007). Humic substances were extracted from the A horizon of a non-allophanic Andosol using NaOH and subsequently reacted with partially neutralized AlCl_3 solution ($\text{pH} = 4.0$ –5.5) to prepare purified Al–humus complexes. The synthetic complexes showed Al solubility characteristics similar to that of non-allophanic soils. Plant growth tests using the Al–humus complexes revealed that root growth of burdock (*Arctium lappa* L.) and barley (*Hordeum vulgare* L.) was significantly reduced and the roots showed symptoms typical of Al toxicity (Figs. 7 and 8). These results indicate that, in soils dominated by Al–humus complexes, the Al from the Al–humus complexes, as well as other exchangeable Al forms, are highly toxic to plant roots.

Strong acidification of allophanic Andosols as a result of changes in vegetation or the heavy application of ammonium-based fertilizers

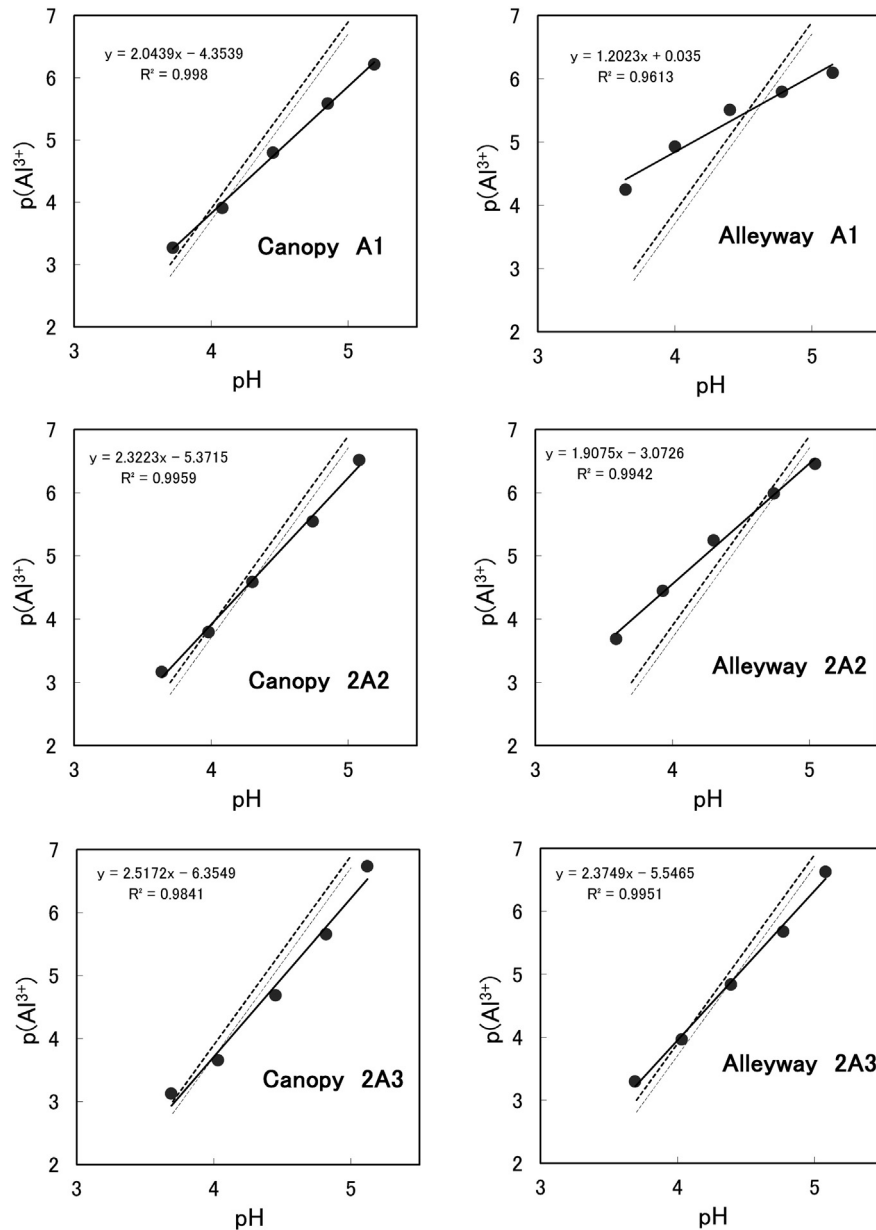


Fig. 5. Plots of equilibrium Al solubility versus pH at 25 °C for acidified allophanic Andosols. The dotted lines are synthetic and soil gibbsites for the reaction: $\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$. (Takahashi et al., 2008).

can result in a transformation of Al solubility control from allophane/imogolite-gibbsite control to that of Al–humus complexes (Takahashi et al., 2008; Yagasaki et al., 2006). In these situations, it is considered that Al ions are released from Al–humus complexes as a function of pH resulting in high concentrations of aqueous Al^{3+} that are phytotoxic (Inamatsu et al., 1991; Matsuyama et al., 2005; Mitamura, 2005; Morikawa et al., 2002; Saigusa et al., 1988; Takahashi et al., 2008). Yamada et al. (2011) performed intensive plant cultivation experiments using non-allophanic and allophanic soils (including some acidified allophanic soils) over a wide range of pH values ($\text{pH}(\text{H}_2\text{O}) = 4.4\text{--}7.0$). The results indicated that Al–humus complexes significantly contributed to Al toxicity in the allophanic Andosol at lower pH values, as well as non-allophanic Andosols (Yamada et al., 2011).

Lime materials are generally applied to acidic soils to ameliorate Al toxicity potential. However, liming of surface soils is not effective for amelioration of subsoil acidity because of its low solubility and lack of transport to the subsoil. As a result, gypsum or phosphogypsum, which have higher solubility, have been investigated for their ability

to ameliorate subsoil acidity following surface application. Phosphogypsum application to Andosols with high humus (Al–humus complexes) content was not effective for reducing plant root toxicity, whereas application to Andosols with low humus content was effective (Saigusa and Toma, 1977; Saigusa et al., 1996; Toma and Saigusa, 1997). This was explained by the changes in Al release rates from soils with acetate buffer solution (pH 3.5) following gypsum application (Takahashi et al., 2006b). The Al release rates from soils with low humus content were markedly decreased due to Al precipitation as low-solubility compounds (e.g., gibbsite-like phases). In contrast, Al release rate from soils rich in Al–humus complexes showed little or no change indicating that Al release from Al–humus complexes remained the primary source of the labile Al causing the phytotoxicity (Takahashi et al., 2006b).

7. Phosphorus dynamics

Mature Andosols commonly possess high phosphate (P) sorption capacity. As a result, P retention (>85%) is used as a criterion to define

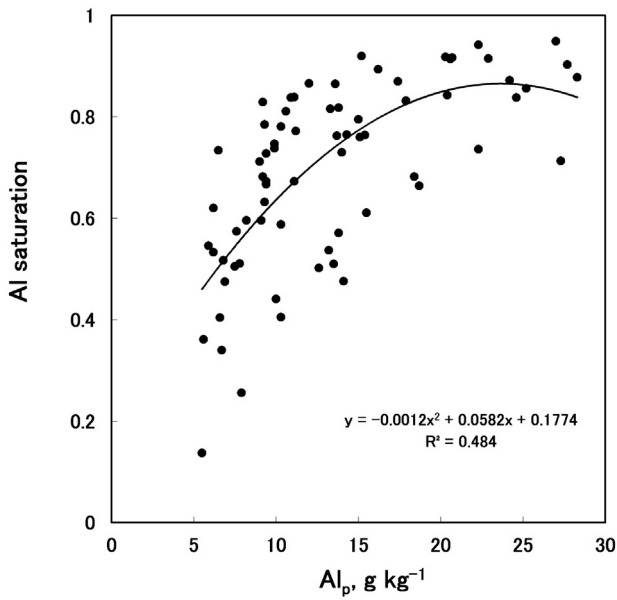


Fig. 6. Relationship between the concentration of pyrophosphate-extractable Al (Al_p) and Al saturation (KCl-extractable Al/effective cation exchange capacity). (Takahashi et al., 2003).

andic soil properties (Soil Survey Staff, 1999; Soil Survey Staff, 2014; WRB, 2014). The major colloidal constituents responsible for P sorption in allophanic Andosols are allophane/imogolite and Al–humus complexes, while Al–humus complexes are the dominant component in non-allophanic Andosols. The amount of P adsorbed per mole of active Al (acid oxalate-extractable Al) is higher in non-allophanic Andosols (0.13 mol/mol) as compared to allophanic Andosols (0.09 mol/mol) (Matsuyama et al., 1999; Saigusa et al., 1991). Phosphorus sorption has been shown to be strongly pH dependent with a maximum P sorption capacity generally occurring between pH values of 3–4 (Nanzyo et al., 1993). The pH dependency for P sorption by Al–humus complexes is considerably lower as compared to allophanic materials (Gunjigake and Wada, 1981; Nanzyo et al., 1993).

Using Al–humus complexes synthesized from humic acids and $Al_x(OH)^{3x-y}$, Appelt et al. (1975) demonstrated adsorption of ortho-phosphate by the $Al_x(OH)^{3x-y}$ –humus complex. P sorption increased with increasing OH content of the $Al_x(OH)^{3x-y}$ –humus complex. They postulated that a ligand exchange reaction occurred between the ortho-phosphate anion and the $Al_x(OH)^{3x-y}$ –humus complex: $humus-Al_x(OH)^{3x-y} + H_2PO_4 \rightarrow humus-Al-H_2PO_4 + OH^-$. It has also been shown that organic C is often released from non-allophanic Andosols via P sorption suggesting that Al may be removed from the



Fig. 8. Root tips of burdock planted in a medium containing Al–humus complexes. (Takahashi et al., 2007).

Al–humus complex upon reaction with PO_4 (Nanzyo, 1991). In this case the Al released from the Al–humus complex may combine with PO_4 to form noncrystalline aluminum phosphate compounds, such as $Al(OH)_2H_2PO_4$ and $NaAl(OH)_2HPO_4$ (Veith and Sposito, 1977).

Due to the higher P sorption potential of non-allophanic Andosols, P availability is generally higher for agricultural crops in allophanic Andosols. Matsuyama et al. (1994) showed that dent corn (*Zea mays indentata*) absorbed more P from allophanic Andosols as compared with non-allophanic Andosols when the ratio of total P/active Al was similar for both types of Andosols. Similarly, Ito et al. (2011) demonstrated that for soils with similar levels of available P (Truog-P or Bray II-P), P uptake by grain sorghum (*Sorghum bicolor*) was larger from allophanic Andosols than from non-allophanic Andosols. These results support the contention that P retention by Al–humus complexes is stronger than for allophane/imogolite resulting in lower availability of P to agricultural plants in non-allophanic Andosols.

To improve phosphorus fertilizer utilization efficiency in Andosols, especially in non-allophanic soils, Nanzyo et al. (2002) showed that localized application (banding) of P fertilizer to avoid extensive mixing of the fertilizer with the soil was very effective. For the P-deficient non-allophanic Andosols, the roots of *Brassica* plants and buckwheat (*Fagopyrum esculentum*) completely covered the P fertilizer particles resulting in P recovery rates of about 40%, which was two times greater than conventional broadcast P fertilizer application (Nanzyo et al., 2004).

Given the pH dependency for P sorption by Al–humus complexes (Gunjigake and Wada, 1981; Nanzyo et al., 1993), liming of non-allophanic Andosols may be expected to decrease P sorption due to an increase in soil pH. In addition, a decrease in P sorption by liming of

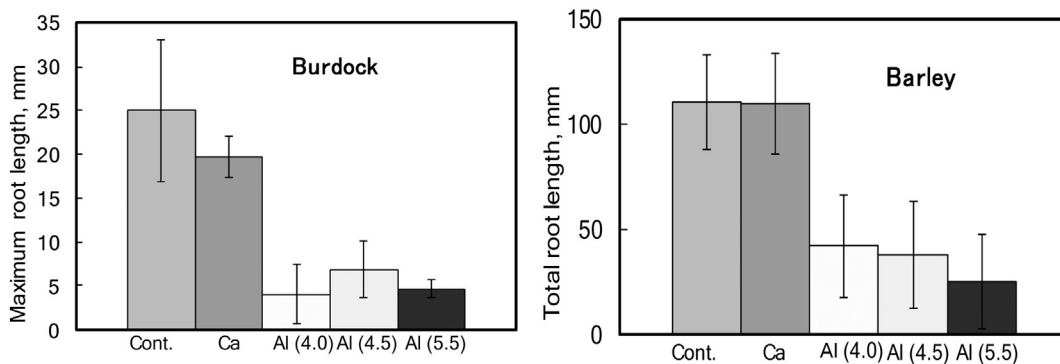


Fig. 7. Root growth of burdock and barley cultured in perlite media containing synthetic Al–humus complexes (Al(4.0), Al(4.5) and Al(5.5); numerical values showing the pH at the start of the trial), Ca–humus complex (Ca) and perlite medium only (Cont.). Bars indicate standard deviation. (Takahashi et al., 2007).

non-allophanic Andosols may also be expected due to a considerable decrease in Al_p (Al–humus complexes) following lime addition (Takahashi et al., 2006a). These results are supported by Saigusa et al. (1988) who showed a significant decrease in Al_p and a decrease of P retention in Ap horizons of non-allophanic Andosols following cultivation and lime addition.

8. Soil borne diseases and microbial processes in non-allophanic Andosols

Elevated levels of aqueous and exchangeable Al in Andosols sometimes provide benefits for some types of agricultural production through suppression of soil borne diseases. Root rot of common bean (*Phaseolus vulgaris* L.) caused by *Fusarium solani* f. sp. *Phaseoli* (Furuya et al., 1996) and common scab of potato (*Solanum tuberosum* L.) caused by *Streptomyces scabies* (Mizuno and Yoshida, 1993) are common in Hokkaido, Japan where allophanic Andosols are widely distributed. Suppression of these soil-borne pathogens was reported in non-allophanic Andosols because the higher levels of exchangeable and associated aqueous Al inhibit these pathogens. In the case of root rot for common bean, inhibition of macroconidial germination and disease incidence was observed in soils with exchangeable Al contents greater than $0.4 \text{ cmol}_c \text{ kg}^{-1}$ (Furuya et al., 1999). Similarly, potato common scab was suppressed in soils having relatively higher amounts of exchangeable Al and aqueous Al concentrations ($>0.3 \text{ mg L}^{-1}$). To enhance control of potato common scab by Al, a single basal application of ammonium sulfate is applied to each planting row. This application effectively lowers the soil pH and increases the concentration of aqueous Al to effectively suppress disease incidence (Mizuno et al., 1998, 2000).

In addition to Al inhibition of these specific soil-borne pathogens, several other soil-borne pathogens have been shown to be sensitive to elevated Al concentrations on the basis of *in vitro* tests, including *Aphanomyces euteiches* (Lewis, 1973), *Phytophthora capsici* (Muchovej et al., 1980), *Phytophthora parasitica* (Benson, 1993; Fichtner et al., 2001), *Verticillium albo-atrum* (Orellana et al., 1975), *Rhizoctonia solani* Kühn (Kobayashi and Ko, 1983, 1985), and *Thielaviopsis basicola* (Meyer, 1994). Thus, acidic Andosols with abundant Al–humus complexes possess the potential to reduce damage from selected soil-borne pathogens through inhibition by exchangeable and aqueous Al.

Recently, Oshima et al. (2015) reported that amendment of Andosol subsoil horizons with Al-containing humic acid suppressed root rot of lettuce (*Lactuca sativa* var. *capitata* L.) caused by *Fusarium oxysporum* f. sp. *Lactucaee* even when the soil pH was about 6.0, suggesting very low exchangeable and aqueous Al concentrations. Fichtner et al. (2001) also demonstrated that Al–peat complexes (generally considered non-toxic) suppressed damping off of Vinca (*Catharanthus roseus*) caused by *Phytophthora parasitica*. Similarly, microbial processes related to emission of reduced greenhouse gases (such as methane and N_2O) may also be suppressed by active Al compounds (e.g., Al–humus) explaining the lower N_2O emission observed in several studies (Kusa et al., 2006; Muñoz et al., 2011; Yazaki et al., 2011). While a direct mechanism for microbial suppression has not been elucidated, further exploration is warranted as manipulation of soil aluminum levels through pH regulation may provide an effective and natural strategy to alleviate selected microbial pathogens and lower greenhouse gas emissions from non-allophanic Andosols.

9. Future research needs

As new molecular techniques become available, further elucidation of the chemical nature of Al–humus complexes will contribute to our understanding of their genesis and reactivity in soil biogeochemical processes. The molecular characterization of Al–humus complexes will likely yield important information on their role in stabilization of SOM. Understanding the physical, chemical and biological mechanisms by which Al–humus complexes contribute to carbon sequestration in

Andosols is a critical research need that could provide management strategies to enhance carbon storage in Andosols. This leads not only to conservation of soil quality, but also to provision against global climate change.

While a considerable amount of research has explored the role of Al–humus complexes in regulating aqueous Al^{3+} activities, there is further need to quantitatively model these relationships for application to understanding clay mineralogy, phytotoxicity, soil microbial communities and controls on nutrient availability. The model should address microsites of heterogeneous soil systems (e.g., rhizosphere soil) in addition to bulk soil systems because Al^{3+} activity may be easily changed with fluctuations of pH and ion strength thereby affecting chemical and biological processes. A better understanding of how Al–humus complexes affect P retention and phosphorus availability to plants will contribute to enhanced P fertilizer-use efficiency, especially in developing countries where high fertilizer costs hinder agricultural production. Further, the role of Al–humus complexes as a potential source of Al toxicity to agricultural plants and soil microbial communities requires further investigation as Al toxicity is often a major impairment to agricultural productivity in non-allophanic Andosols. Remediation methods, other than the use of lime amendments, for strong acidity and Al toxicity in both surface and subsoil horizons will further enhance agricultural productivity. Finally, there is a critical need for research that examines the role of Al–humus complexes on soil microbial processes, especially with regard to organic matter decomposition, trace gas emissions (N_2O , CH_4), and suppression of soil borne diseases.

References

- Appelt, H., Coleman, N.T., Pratt, P.F., 1975. Interactions between organic compounds, minerals, and ions in volcanic-ash-derived soils: II. Effects of organic compounds on the adsorption of phosphate. *Soil Sci. Soc. Am. J.* 39, 628–630.
- Arai, S., Honna, T., Oba, Y., 1986. Humus characteristics. In: Wada, K. (Ed.), *Ando Soils in Japan*. Kyushu University Press, Fukuoka, Japan, pp. 57–68.
- Arnalds, O., 2008. Andosols. In: Chesworth, W. (Ed.), *Encyclopaedia of Soil Science*. Springer, Dordrecht, The Netherlands, pp. 39–46.
- Asano, M., Wagai, R., 2014. Evidence of aggregate hierarchy at micro- to micron scales in an allophanic Andisol. *Geoderma* 216, 62–74.
- Baldock, J.A., Broos, K., 2011. Soil Organic Matter. In: Huang, P.M., Sumner, M.E. (Eds.), *Handbook of Soil Sciences*. CRC Press, pp. 1–52.
- Baldock, J.A., Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Org. Geochem.* 31 (7–8), 697–710.
- Bautista-Tulin, A.T., Inoue, K., 1997. Hydroxy-interlayered minerals in Japanese soils influenced by eolian deposition. *Soil Sci. Soc. Am. J.* 61 (2), 631–640.
- Benson, D.M., 1993. Suppression of *Phytophthora parasitica* on *Catharanthus roseus* with aluminum. *Phytopathology* 83, 1303–1308.
- Birrell, K.S., Pullar, W.A., Heine, J.C., 1971. Pedological, chemical, and physical properties of organic horizons of paleosols underlying the Tarawera Formation. *N. Z. J. Sci.* 14, 187–218.
- Borggaard, O.K., 1976. The use of EDTA in soil analysis. *Acta Agric. Scand.* 26 (2), 144–150.
- Buurman, P., Peterse, F., Almendros Martin, G., 2007. Soil organic matter chemistry in allophanic soils: A pyrolysis-GC/MS study of a Costa Rican Andosol catena. *Eur. J. Soil Sci.* 58 (6), 1330–1347.
- Chen, Z.-S., Asio, V.B., Yi, D.-F., 1999. Characteristics and genesis of volcanic soils along a toposequence under a subtropical climate in Taiwan. *Soil Sci.* 164 (7), 510–525.
- Chevallier, T., Woignier, T., Toucet, J., Blanchart, E., 2010. Organic carbon stabilization in the fractal pore structure of Andosols. *Geoderma* 159 (1–2), 182–188.
- Cronan, C.S., Walker, W.J., Bloom, P.R., 1986. Predicting aqueous aluminum concentrations in natural waters. *Nature* 324, 140–143.
- Dahlgren, R.A., 1994. Quantification of allophane and imogolite. In: Amonette, J.E., Zelazny, L.W. (Eds.), *Quantitative Methods in Soil Mineralogy*. Soil Science Society of America, pp. 430–451.
- Dahlgren, R.A., Saigusa, M., 1994. Aluminum release rates from allophanic and nonallophanic Andosols. *Soil Sci. Plant Nutr.* 40, 125–136.
- Dahlgren, R.A., Ugolini, F.C., 1989. Formation and stability of imogolite in a tephritic Spodosol, Cascade Range, Washington, U.S.A. *Geochim. Cosmochim. Acta* 53, 1897–1904.
- Dahlgren, R.A., Walker, W.J., 1993. Aluminum release rates from selected Spodosol Bs horizons: Effect of pH and solid-phase aluminum pools. *Geochim. Cosmochim. Acta* 57, 57–66.
- Dahlgren, R.A., Driscoll, C.T., McAvoy, D.C., 1989. Aluminum precipitation and dissolution rates in Spodosol Bs horizons in the northern USA. *Soil Sci. Soc. Am. J.* 53, 1045–1052.
- Dahlgren, R.A., Ugolini, F.C., Shoji, S., Ito, T., 1991. Soil-forming processes in alic Melanudans under Japanese pampas grass and oak. *Soil Sci. Soc. Am. J.* 55, 1049–1056.
- Dahlgren, R., Shoji, S., Nanzyo, M., 1993. Mineralogical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), *Volcanic Ash Soil – Genesis, Properties and Utilization*. Elsevier, The Netherlands, pp. 101–143.

- Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. The nature, properties and management of volcanic soils. *Adv. Agron.* Academic Press, pp. 113–182.
- Duchauffour, P., 1977. *Pédologie. 1-Pédogénèse et classification*. Masson, Paris.
- Egashira, K., Uchida, S., Nakashima, S., 1997. Aluminum-humus complexes for accumulation of organic matter in black-colored soils under grass vegetation in Bolivia. *Soil Sci. Plant Nutr.* 43, 25–33.
- Fichtner, E.J., Hesterberg, D.L., Shew, H.D., 2001. Nonphytotoxic aluminum-peat complexes suppress phytophthora parasitica. *Phytopathology* 91, 1092–1097.
- Furuya, H., Wakui, A., Takahashi, T., Uti, T., 1996. Inhibition of macroconidial germination of *Fusarium solani* f. sp. *Phaseoli* by soil aluminum. *Ann. Phytopathol. Soc. Jpn.* 62, 69–74 (in Japanese with English summary).
- Furuya, H., Takahashi, T., Matsumoto, T., 1999. Suppression of *Fusarium solani* f. sp. *phaseoli* on bean by aluminum in acid soils. *Phytopathology* 89, 47–52.
- Gamble, D.S., 1970. Titration curves of fulvic acid: the analytical chemistry of a weak acid polyelectrolyte. *Can. J. Chem.* 48 (17), 2662–2669.
- Gerke, J., 1994. Aluminum complexation by humic substances and aluminum species in the soil solution. *Geoderma* 63, 165–175.
- Gijsman, A.J., Sanz, J.L., 1998. Soil organic matter pools in a volcanic-ash soil under fallow or cultivation with applied chicken manure. *Eur. J. Soil Sci.* 49 (3), 427–436.
- Gunjigake, N., Wada, K., 1981. Effects of phosphorus concentration and pH on phosphate retention by active aluminum and iron of Ando soils. *Soil Sci.* 132, 347–352.
- Hargrove, W.L., Thomas, G.W., 1981. Extraction of aluminum from aluminum-organic matter complexes. *Soil Sci. Soc. Am. J.* 45, 151–153.
- Hargrove, W.L., Thomas, G.W., 1982. Titration properties of Al-organic matter. *Soil Sci.* 134, 216–225.
- Higashi, T., 1983. Characterization of Al/Fe-humus complexes in Dystrandeps through comparison with synthetic forms. *Geoderma* 31 (4), 277–288.
- Higashi, T., Shinagawa, A., 1981. Comparison of sodium hydroxide-tetraborate and sodium pyrophosphate as extractants of Al/Fe-humus "complexes" in Dystrandeps, Japan. *Geoderma* 25, 285–292.
- Hillel, D., Rosenzweig, C., 2009. Soil carbon and climate change – carbon exchange in the terrestrial domain and the role of agriculture. *CSA News* 54 (6), 4–11.
- Hiradate, S., Nakada, T., Shindo, H., Yoneyama, T., 2004. Carbon source of humic substances in some Japanese volcanic ash soils determined by carbon stable isotopic ratio, delta C-13. *Geoderma* 119 (1–2), 133–141.
- Hiradate, S., Hirai, H., Hashimoto, H., 2006. Characterization of allophanic Andisols by solid-state ¹³C, ²⁷Al, and ²⁹Si NMR and by C stable isotopic ratio, delta C-13. *Geoderma* 136 (3–4), 696–707.
- Huang, P.M., 1988. Ionic factors affecting aluminum transformations and the impact on soil and environmental sciences. *Adv. Soil Sci.* 8, 1–78.
- Huygens, D., Boeckx, P., Van Cleemput, O., Oyarzún, C., Godoy, R., 2005. Aggregate and soil organic carbon dynamics in South Chilean Andisols. *Biogeosciences* 2, 159–174.
- Imaya, A., Ohta, S., Tanaka, N., Inagaki, Y., 2005. General chemical properties of Brown forest soils developed from different parent materials in the submontane zone of the Kanto and Chubu districts. *Jpn. Soil Sci. Plant Nutr.* 51 (6), 873–884.
- Imaya, A., Inagaki, Y., Tanaka, N., Ohta, S., 2007. Free oxides and short-range ordered mineral properties of brown forest soils developed from different parent materials in the submontane zone of the Kanto and Chubu districts. *Jpn. Soil Sci. Plant Nutr.* 53 (5), 621–633.
- Imaya, A., Yoshinaga, S., Inagaki, Y., Tanaka, N., Ohta, S., 2010a. Proposal for advanced classification of brown forest soils in Japan with reference to the degree of volcanic ash additions. *Soil Sci. Plant Nutr.* 56 (3), 454–465.
- Imaya, A., Yoshinaga, S., Inagaki, Y., Tanaka, N., Ohta, S., 2010b. Volcanic ash additions control soil carbon accumulation in brown forest soils in Japan. *Soil Sci. Plant Nutr.* 56 (5), 734–744.
- Inamatsu, K., Kikuchi, M., Shibuya, K., 1991. Acidification of mulberry field soil - In case of volcanic ash soils on Tsukuba upland. *Jpn. J. Soil Sci. Plant Nutr.* 62, 351–356 (in Japanese with English summary).
- Inoue, K., Higashi, T., 1988. Al- and Fe-humus complexes in Andisols. In: Kinlock, D.L., Shoji, S., Beinroth, M., Eswaran, H. (Eds.), *Proceedings of 9th Int. Soil Classification Workshop, Japan*. Japanese Committee for 9th International Soil Classification Workshop and Soil Management Support Services, Washington D.C., pp. 535–546.
- Inoue, K., Naruse, T., 1987. Physical, chemical, and mineralogical characteristics of modern eolian dust in Japan and rate of dust deposition. *Soil Sci. Plant Nutr.* 33 (3), 327–345.
- Inoue, Y., Yoneyama, T., Sugiyama, S., Okada, H., Nagatomo, Y., 2001. Variations in natural abundance of stable carbon and nitrogen isotopes in a cumulative Andisol in Miyakonojo Basin, Southern Kyushu, with reference to vegetation changes from phytolith. *Quat. Res.* 40, 307–318.
- Inoue, Y., Nagaoka, S., Sugiyama, S., 2006. The genesis of humic soil with interlayered Aira-Tn tephra in the southeast part of Shimabara Peninsula, Japan. *Q. Res.* 45, 303–311.
- Ishizuka, S., Kawamuro, K., Imaya, A., Torii, A., Morisada, K., 2014. Latitudinal gradient of C4 grass contribution to Black Soil organic carbon and correlation between delta C-13 and the melanin index in Japanese forest stands. *Biogeochemistry* 118 (1–3), 339–355.
- Ito, T., Kikawa, N., Saigusa, M., 2011. Phosphorus sorption and bioavailability in allophanic and non-allophanic Andosols. *Pedologist* 55 (2), 84–88 (in Japanese).
- Jackson, M.L., 1963a. Aluminum bonding in soils: a unifying principle in soil science. *Soil Sci. Soc. Am. J.* 27 (1), 1–10.
- Jackson, M.L., 1963b. Interlayering of expansible layer silicates in soils by chemical weathering. *Clay Clay Miner.* 11, 29–46.
- Jardine, P.M., Zelazny, L.W., 1996. Surface reactions of aqueous aluminum species. In: Sposito, G. (Ed.), *The Environmental Chemistry of Aluminum*, Second Edition CRC Press LLC, Boca Taton, Florida, pp. 221–270.
- Johnson-Maynard, J.L., McDaniel, P.A., Ferguson, D.E., Falen, A.L., 1997. Chemical and mineralogical conversion of Andisols following invasion by bracken fern. *Soil Sci. Soc. Am. J.* 61 (2), 549–555.
- Juste, C., Delas, J., Langon, M., 1975. C. R. Acad. Se., série D 281, 1685–1688.
- Kaiser, K., Zech, W., 1996. Defects in estimation of aluminum in humus complexes of podzolic soils by pyrophosphate extraction. *Soil Sci.* 161 (7), 452–458.
- Kobayashi, N., Ko, W.H., 1983. Screening of *Rhizoctonia*-suppressive soil in Hawaii Islands and their mechanism of suppressiveness. *Soil Microorg.* 25, 1–8.
- Kobayashi, N., Ko, W.H., 1985. Nature of suppression of *Rhizoctonia solani* in Hawaiian soils. *T. Brit. Mycol. Soc.* 84 (4), 691–694.
- Kumada, K., 1987. *Chemistry of Soil Organic Matter*. Japan Scientific Societies Press, Tokyo.
- Kusa, K., Hu, R., Sawamoto, T., Hatano, R., 2006. Three years of nitrous oxide and nitric oxide emissions from silandic Andosols cultivated with maize in Hokkaido. *Jpn. Soil Sci. Plant Nutr.* 52 (1), 103–113.
- Leamy, M.L., 1984. International Committee on the Classification of Andisols (ICOMAND) Circular letter No. 6, New Zealand Soil Bureau. DSIR, Lower Hutt.
- Leamy, M.L., Smith, G.D., Colmet-Daage, F., Otowa, M., 1980. The morphological characteristics of Andisols. In: Theng, B.K.G. (Ed.), *Soils with Variable Charge*. New Zealand Society of Soil Science, pp. 17–34.
- Leamy, M.L., Clayden, B., Parfitt, R.L., Kinloch, D.L., Childs, C.W., 1988. The Andisol Proposal 1988, Final Proposal of the International Committee on the Classification of Andisols (ICOMAND). New Zealand Soil Bureau, Lower Hutt, New Zealand.
- Lee, R., 1988. The extraction of aluminum from a New Zealand podzol by KCl solutions of varying concentration. *Commun. Soil Sci. Plant Anal.* 19, 183–192.
- Lewis, J.A., 1973. Effect of mineral salts on *Aphanomyces euteiches* and *Aphanomyces* root rot of peas. *Phytopathology* 63, 989–993.
- Lowe, D.J., Palmer, D.J., 2005. Andisols of New Zealand and Australia. *J. Integr. Field Sci.* 2, 39–65.
- Madeira, M., Furtado, A., Jeanroy, E., Herbillon, A.J., 1994. Andisols of Madeira Island (Portugal). Characteristics and classification. *Geoderma* 62 (4), 363–383.
- Martin, J.P., Ervin, J.O., Shepherd, R.A., 1966. Decomposition of the iron, aluminum, zinc, and copper salts or complexes of some microbial and plant polysaccharides in soil. *Soil Sci. Soc. Am. J.* 30 (2), 196–200.
- Martin, J.P., Zunino, H., Peirano, P., Caziozzi, M., Haider, K., 1982. Decomposition of ¹⁴C-labeled lignins, model humic acid polymers, and fungal melanins in allophanic soils. *Soil Biol. Biochem.* 14 (3), 289–293.
- Matsuyama, N., Saigusa, M., Kudo, K., 1994. Phosphorus response of dent corn young plants and evaluation of phosphorus availability in Andosols. *Tohoku J. Crop Sci.* 37, 57–58 (in Japanese).
- Matsuyama, N., Kudo, K., Saigusa, M., 1999. Active aluminum of cultivated Andosols and related soil chemical properties in Japan. *Bull. Fac. Agric. Life Sci. Hirosaki Univ.* 1, 30–36.
- Matsuyama, N., Saigusa, M., Sakaiya, E., Tamakawa, K., Oyama, Z., Kudo, K., 2005. Acidification and soil productivity of allophanic Andosols affected by heavy application of fertilizers. *Soil Sci. Plant Nutr.* 51 (1), 117–123.
- May, H.M., Helmke, P.A., Jackson, M.L., 1979. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25 °C. *Geochim. Cosmochim. Acta* 43, 861–868.
- McDaniel, P.A., Lowe, D.J., Arnalds, O., Ping, C.L., 2012. Andisols. In: Huang, P.M., Li, Y., Sumner, M.E. (Eds.), *Handbook of Soil Science*, 2nd edition Vol. 1: Properties and Processes. CRC Press (Taylor & Francis), Boca Raton, FL, p. 33 29–33.48.
- McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. *Can. J. Soil Sci.* 47, 95–99.
- Meyer, J.R., 1994. Inhibition of germination and growth of *Thielaviopsis basicola* by aluminum. *Phytopathology* 84, 598–602.
- Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., Jahn, R., 2007. Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochim. Cosmochim. Acta* 71 (10), 2569–2590.
- Miltner, A., Zech, W., 1998. Carbohydrate decomposition in beech litter as influenced by aluminium, iron and manganese oxides. *Soil Biol. Biochem.* 30 (1), 1–7.
- Mitamura, A., 2005. Chemical properties and phosphate fertility of allophanic Andisols used for tea fields Masters thesis, Tohoku University, Japan (in Japanese).
- Mitsuchi, M., 1985. Studies on differentiating characteristics and criteria in soil classification. Part 3. Properties of soil humus. *Jpn. J. Soil Sci. Plant Nutr.* 56, 197–203 (in Japanese with English summary).
- Miyazaki, K., Inoue, Y., Nishimura, S., Shindo, H., 2009. Relationship between the vertical distribution of charred plants and the humus composition or the carbon storage in the soil profile of a cumulative Andisol. *Pedologist* 53, 77–85 (in Japanese with English summary).
- Miyazaki, K., Inoue, Y., Nishimura, S., Shindo, H., 2010. Relationship between the vertical distribution of low specific gravity fraction (charred plants) and the soil age or organic C storage in the soil profile of a cumulative Andisol. *Jpn. J. Soil Sci. Plant Nutr.* 81, 112–117 (in Japanese with English summary).
- Miyazawa, M., Takahashi, T., Sato, T., Kanno, H., Nanzyo, M., 2013. Factors controlling accumulation and decomposition of organic carbon in humus horizons of Andosols – a case study for distinctive non-allophanic Andosols in northeastern. *Jpn. Biol. Fertil. Soils* 49, 929–938.
- Mizota, C., Inoue, K., 1988. Eolian dust contribution to soil development on volcanic ashes in Japan. In: Kinlock, D.L., Shoji, S., Beinroth, F.M., Eswaran, H. (Eds.), *Proceedings 9th Int. Soil Classification Workshop, Japan*. Japanese Committee for 9th International Soil Classification Workshop and Soil Management Support Service, Washington, DC, pp. 547–557.
- Mizota, C., van Reeuwijk, L.P., 1989. *Clay Mineralogy and Chemistry of Soils Formed in Volcanic Material in Diverse Climatic Regions*. Soil Monograph 2. Wageningen, ISRIC.

- Mizota, C., Kusakabe, M., Noto, M., 1990. Oxygen isotope composition of quartz in soils developed on late Quaternary volcanic ashes in Japan. *Geoderma* 46 (4), 319–327.
- Mizuno, N., Yoshida, H., 1993. Effect of exchangeable aluminum on the reduction of potato scab. *Plant Soil* 155/156, 505–508.
- Mizuno, N., Yoshida, H., Nanzyo, M., Tadano, T., 1998. Chemical characterization of conductive and suppressive soils for potato scab in Hokkaido. *Jpn. Soil Sci. Plant Nutr.* 44, 289–295.
- Mizuno, N., Yoshida, H., Tadano, T., 2000. Efficacy of single application ammonium sulfate in suppressing potato common scab. *Soil Sci. Plant Nutr.* 46 (3), 611–616.
- Mohr, E.C.J., 1938. The relation between soil and population density in the Netherlands Indies. *Comptes Rendus du Congres International de Geographie, Section IIIc. Tome Deuxieme*, pp. 478–493.
- Morikawa, K., Saigusa, M., Dahlgren, R., 2002. Origin of 1 M KCl extractable Al in strongly acidified allophanic Andosol used for tea garden, 17th World Congress of Soil Science, 14–21 August 2002 Bangkok, Thailand pp. No. 1274.
- Muchovej, J.J., Maffia, L.A., Muchovej, R.M.C., 1980. Effect of exchangeable soil aluminum and alkaline calcium salts on the pathogenicity and growth of *Phytophthora capsici* from green pepper. *Phytopathology* 70, 1212–1214.
- Muñoz, C., Paulino, L., Vera, J., Zagal, E., 2011. CO₂ and N₂O emissions from an Andisols in Chile under a no till system using non-fixed closed chambers. *Chil. J. Agr. Res.* 71 (2), 275–282.
- Nanzyo, M., Dahlgren, R., Shoji, S., 1993. Chemical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), *Volcanic Ash Soils - Genesis, Properties and Utilization*. Dev. Soil Sci. Elsevier, pp. 145–187.
- Nanzyo, M., Shibata, Y., Wada, N., 2002. Complete contact of *Brassica* roots with phosphates in a phosphorus-deficient soil. *Soil Sci. Plant Nutr.* 48, 847–853.
- Nanzyo, M., Wada, N., Kanno, H., 2004. Phosphorus foraging root development of *Brassica rapa* nothovar. grown in a phosphorus-deficient nonallophanic Andisol. *Plant Soil* 265, 325–333.
- Nanzyo, M., 1991. Chemisorption of phosphate on Andisols (volcanic ash soils) – material balance and the sorption product. *Phosphorus Res. Bull.* 1, 471–476.
- Neculman, R., Rumpel, C., Matus, F., Godoy, R., Steffens, M., Luz Mora, M., 2013. Organic matter stabilization in two Andisols of contrasting age under temperate rain forest. *Biol. Fertil. Soils* 49, 681–689.
- Nishimura, S., Hirota, T., Hirahara, O., Shindo, H., 2006. Contribution of charred and buried plant fragments to humic and fulvic acids in Japanese volcanic ash soils. *Soil Sci. Plant Nutr.* 52 (6), 686–690.
- Nishimura, S., Noguchi, T., Shindo, H., 2008. Distribution of charred plant fragments in particle size fractions of Japanese volcanic ash soils. *Soil Sci. Plant Nutr.* 54 (4), 490–494.
- Nishimura, S., Tani, M., Fujitake, N., Shindo, H., 2009. Relationship between distribution of charred plant residues and humus composition in chernozemic soils. *Pedologist* 53 (2), 86–93.
- Oades, J.M., 1988. The retention of organic matter in soils. *Biogeochemistry* 5 (1), 35–70.
- Obara, H., Ohkura, T., Takata, Y., Kohyama, K., Maejima, Y., Hamazaki, T., 2011. Comprehensive soil classification system of Japan – first approximation. *Bull. Nat. Inst. Agro-environmental Sci.* 29, 1–73 (in Japanese with English summary).
- Orellana, R.G., Foy, C.D., Fleming, A.L., 1975. Effect of soluble aluminum on growth and pathogenicity of *Verticillium albo-atrum* and *Wetzelinia sclerotiorum* from sunflower. *Phytopathology* 65, 202–205.
- Oshima, H., Goto, D., Goto, I., Maeda, Y., 2015. Effect of organic matter removal treatments and addition of aluminum-containing substances on incidence of *Fusarium* wilt of lettuce. *Soil Sci. Plant Nutr.* <http://dx.doi.org/10.1080/00380768.2015.1014295>.
- Percival, H.J., Parfitt, R.L., Scott, N.A., 2000. Factors controlling soil carbon levels in New Zealand grasslands: is clay content important? *Soil Sci. Soc. Am. J.* 64 (5), 1623–1630.
- Perdue, E.M., Lytle, C.R., 1983. A distribution model for binding of protons and metal ions by humic substances. *Environ. Sci. Technol.* 17 (11), 654–660.
- Rasmussen, C., Southard, R.J., Horwath, W.R., 2006. Mineral control of organic carbon mineralization in a range of temperate conifer forest soils. *Glob. Chang. Biol.* 12 (5), 834–847.
- Rouff, A.A., Phillips, B.L., Cochiara, S.G., 2012. The effect of dissolved humic acids on aluminosilicate formation and associated carbon sequestration. *Appl. Environ. Soil Sci.* 2012. <http://dx.doi.org/10.1155/2012/430354>.
- Rumpel, C., Rodríguez-Rodríguez, A., González-Pérez, J.A., Arbelo, C., Chabbi, A., Nunan, N., González-Vila, F.J., 2012. Contrasting composition of free and mineral-bound organic matter in top- and subsoil horizons of Andisols. *Biol. Fertil. Soils* 48 (4), 401–411.
- Saggar, S., Tate, K.R., Feltham, C.W., Childs, C.W., Parshotam, A., 1994. Carbon turnover in a range of allophanic soils amended with ¹⁴C-labelled glucose. *Soil Biol. Biochem.* 26 (9), 1263–1271.
- Saigusa, M., Matsuyama, N., 1998. Distribution of allophanic Andosols and non-allophanic Andosols in Japan. *Tohoku J. Agr. Res.* 48, 75–83.
- Saigusa, M., Toma, M., 1977. Mechanism of reduction of exchangeable aluminum by gypsum application in acid Andosols. *Soil Sci. Plant Nutr.* 43 (2), 343–349.
- Saigusa, M., Shoji, S., Takahashi, T., 1980. Plant root growth in acid Andosols from northeastern Japan: 2. Exchange acidity Y1 as a realistic measure of aluminum toxicity potential. *Soil Sci.* 130, 242–250.
- Saigusa, M., Matsuyama, N., Honna, T., Abe, T., 1991. Chemistry and fertility of acid Andisols with special reference to subsoil acidity. In: Wright, R.J., Baligar, V.C., Murrmann, R.P. (Eds.), *Plant–Soil Interactions At Low pH. Developments in Plant and Soil Sciences*. Springer, Netherlands, pp. 73–80.
- Saigusa, M., Toma, M., Nanzyo, M., 1996. Alleviation of subsoil acidity in nonallophanic Andosols by phosphogypsum application in topsoil. *Soil Sci. Plant Nutr.* 42, 221–227.
- Saigusa, M., Shoji, S., Ogata, Y., 1988. Land use and physico-chemical properties of non-allophanic Andosols. *Kawatabi Noujo Hokoku, Kawatabi Farm Bull. Tohoku Univ.* 4, 9–13 (in Japanese).
- Schneider, M.P.W., Scheel, T., Mikutta, R., van Hees, P., Kaiser, K., Kalbitz, K., 2010. Sorptive stabilization of organic matter by amorphous Al hydroxide. *Geochim. Cosmochim. Acta* 74 (5), 1606–1619.
- Schnitzer, M., Skinner, S.I.M., 1965. Organo-metallic interactions in soils: 4. Carboxyl and hydroxyl groups in organic matter and metal retention. *Soil Sci.* 99 (4), 278–284.
- Shindo, H., Ushijima, N., Honna, T., Yamamoto, S., Honma, H., 2003. Relationship between distribution of charred plant fragments and humus composition or amorphous Al components in Ando soils. *Jpn. J. Soil Sci. Plant Nutr.* 74, 485–492 (in Japanese with English summary).
- Shindo, H., Honna, T., Yamamoto, S., Honma, H., 2004. Contribution of charred plant fragments to soil organic carbon in Japanese volcanic ash soils containing black humic acids. *Org. Geochem.* 35, 235–241.
- Shindo, H., Yoshida, M., Yamamoto, A., Honma, H., 2005. δ¹³C values of organic constituents and possible source of humic substances in Japanese volcanic ash soils. *Soil Sci.* 170, 175–182.
- Shoji, S., 1985. Genesis and properties of non-allophanic Andisols in Japan. *Appl. Clay Sci.* 1 (1–2), 83–88.
- Shoji, S., Fujiwara, Y., 1984. Active aluminum and iron in the humus horizons of Andosols from northeastern Japan: Their forms, properties, and significance in clay weathering. *Soil Sci.* 137 (4), 216–226.
- Shoji, S., Ono, T., 1978. Physical and chemical properties and clay mineralogy of Andosols from Kitakami. *Jpn. Soil Sci.* 126, 297–312.
- Shoji, S., Saigusa, M., Takahashi, T., 1980. Plant root growth in acid Andosols from northeastern Japan: 1. Soil properties and root growth of burdock, barley and orchard grass. *Soil Sci.* 130, 124–131.
- Shoji, S., Fujiwara, Y., Yamada, I., Saigusa, M., 1982. Chemistry and clay mineralogy of Ando soils, brown forest soils, and Podzolic soils formed from recent Towada ashes, northeastern Japan. *Soil Sci.* 133 (2), 69–86.
- Shoji, S., Ito, T., Saigusa, M., Yamada, I., 1985. Properties of nonallophanic Andosols from Japan. *Soil Sci.* 140, 264–277.
- Shoji, S., Suzuki, Y., Saigusa, M., 1987. Clay mineralogical and chemical properties of nonallophanic Andepts (Andisols) from Oregon. *USA. Soil Sci. Soc. Am. J.* 51 (4), 986–990.
- Shoji, S., Kurebayashi, T., Yamada, I., 1990. Growth and chemical composition of Japanese pampas grass (*Miscanthus sinensis*) with special reference to the formation of dark-colored Andisols in northeastern Japan. *Soil Sci. Plant Nutr.* 36, 105–120.
- Shoji, S., Nanzyo, M., Dahlgren, R.A., 1993. *Volcanic Ash Soils – Genesis, Properties and Utilization*. Elsevier, Amsterdam.
- Shoji, S., Nanzyo, M., Dahlgren, R.A., Quantin, P., 1996. Evaluation and proposed revisions of criteria for Andosols in the World Reference Base for Soil Resources. *Soil Sci.* 161 (9), 604–615.
- Soil Survey Staff, 1999. *Soil Taxonomy. A Basic System Of Soil Classification For Making And Interpreting Soil Surveys*. 2nd edition. Natural Resources Conservation Service, USDA, Washington DC, USA.
- Soil Survey Staff, 2014. *Keys to Soil Taxonomy Twelfth Edition*. United States Department of Agriculture, Natural Resources Conservation Service.
- Stevenson, F.J., 1985. Geochemistry of soil humic substances. In: Aiken, G.R. (Ed.), *Humic Substances in Soil Sediment and Water*. John Wiley and Sons, New York.
- Stevenson, F.J., Chen, Y., 1991. Stability constants of copper(II)-humate complexes determined by modified potentiometric titration. *Soil Sci. Soc. Am. J.* 55 (6), 1586–1591.
- Takahashi, T., Dahlgren, R.A., 1998. Possible control of aluminum solubility by 1 M KCl treatment in some soils dominated by aluminum-humus complexes. *Soil Sci. Plant Nutr.* 44 (1), 43–51.
- Takahashi, T., Dahlgren, R.A., Sase, T., 1994. Formation of melanic epipedons under forest vegetation in the xeric moisture regime of northern California. *Soil Sci. Plant Nutr.* 40, 617–628.
- Takahashi, T., Fukuoka, T., Dahlgren, R.A., 1995. Aluminum solubility and release rates from soil horizons dominated by aluminum-humus complexes. *Soil Sci. Plant Nutr.* 41, 119–131.
- Takahashi, T., Sato, T., Sato, A., 2001. Chemistry and clay mineralogy of four soil profiles from Mts. Shirakami. *Pedologist* 45, 118–129 (in Japanese with English summary).
- Takahashi, T., Sato, T., Sato, A., Nanzyo, M., 2003. Relationship between 1 M KCl-extractable aluminum and pyrophosphate-extractable aluminum in A horizons of non-allophanic Andosols. *Soil Sci. Plant Nutr.* 49 (5), 729–733.
- Takahashi, T., Ikeda, Y., Fujita, K., Nanzyo, M., 2006a. Effect of liming on organically complexed aluminum of nonallophanic Andosols from northeastern Japan. *Geoderma* 130 (1–2), 26–34.
- Takahashi, T., Ikeda, Y., Nakamura, H., Nanzyo, M., 2006b. Efficiency of gypsum application to acid Andosols estimated using aluminum release rates and plant root growth. *Soil Sci. Plant Nutr.* 52 (5), 584–592.
- Takahashi, T., Nanzyo, M., Hiradate, S., 2007. Aluminum status of synthetic Al-humic substance complexes and their influence on plant root growth. *Soil Sci. Plant Nutr.* 53 (2), 115–124.
- Takahashi, T., Mitamura, A., Ito, T., Ito, K., Nanzyo, M., Saigusa, M., 2008. Aluminum solubility of strongly acidified allophanic Andosols from Kagoshima Prefecture, southern Japan. *Soil Sci. Plant Nutr.* 54 (3), 362–368.
- Takahashi, T., Kanno, H., Tsujimura, N., Nanzyo, M., 2011. What does 1 M potassium chloride-extractable aluminum from non-allophanic Andosols measure? *Jpn. J. Soil Sci. Plant Nutr.* 82 (1), 1–6 (in Japanese with English summary).
- Takahashi, T., Kanno, H., Nanzyo, M., 2012. Factors affecting organic carbon accumulation in humus horizons of volcanic soils from the Tohoku University World Andosol Database: a path analysis. *Pedologist* 56 (2), 58–62.
- The Fourth Committee for Soil Classification and Nomenclature, 2003. *The Japanese Society of Pedology. Unified Soil Classification System of Japan – 2nd Approximation (2002) – Hakuyusha, Tokyo (in Japanese)*.

- Tokashiki, Y., Wada, K., 1975. Weathering implications of the mineralogy of clay fractions of two Ando soils, Kyushu. *Geoderma* 14 (1), 47–62.
- Toma, M., Saigusa, M., 1997. Effects of phosphogypsum on amelioration of strongly acid nonallophanic Andosols. *Plant Soil* 192 (1), 49–55.
- Tonneijck, F.H., 2009. Volcanic ash soils in Andean ecosystems – unravelling organic matter distribution and stabilisation. Thesis Universitet van Amsterdam.
- Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., Hendricks, D.M., 1997. Mineral control of soil organic carbon storage and turnover. *Nature* 389 (6647), 170–173.
- Ugolini, F.C., Dahlgren, R.A., 1991. Weathering environments and occurrence of imogolite/allophane in selected Andisols and Spodosols. *Soil Sci. Soc. Am. J.* 55, 1166–1171.
- Ugolini, F.C., Dahlgren, R.A., 2002. Soil development in volcanic ash. *Glob. Environ. Res.* 6 (2), 69–81.
- Ugolini, F.C., Dahlgren, R., Shoji, S., Ito, T., 1988. An example of andosolization and podzolization as revealed by soil solution studies, southern Hakkoda, northeastern Japan. *Soil Sci.* 145 (2), 111–125.
- Veith, J.A., Sposito, G., 1977. Reactions of aluminosilicates, aluminum hydroxides, and aluminum oxide with o-phosphate: The formation of X-ray amorphous analogs of variscite and montebasite. *Soil Sci. Soc. Am. J.* 41, 870–876.
- Verde, J.R., Camps Arbestain, M., Macías, F., 2005. Expression of andic properties in soils from Galicia (NW Spain) under forest and agricultural use. *Eur. J. Soil Sci.* 56 (1), 53–64.
- Wada, K., 1985. The distinctive properties of Andosols. *Adv. Soil Sci.* 2, 173–229.
- Wada, S.-I., 1987a. Adsorption of Al (III) on allophane, imogolite, goethite and noncrystalline silica and the extractability of the adsorbed Al (III) in 1 M KCl solution. *Soil Sci. Plant Nutr.* 33, 487–491.
- Wada, S.-I., 1987b. A critical evaluation of 1 M KCl-extraction method for determining exchangeable Al ions in variable charge soils. *Soil Sci. Plant Nutr.* 33, 153–160.
- Wada, K., Higashi, T., 1976. The categories of aluminum- and iron-humus complexes in Ando soils determined by selective dissolution. *J. Soil Sci.* 27 (3), 357–368.
- Warkentin, B.P., Maeda, T., Soma, K., 1988. Physical characteristics for classification of Andisols. In: Kinloch, D.I., Shoji, S., Beinroth, F.M., Eswaran, H. (Eds.), *Proceedings 9th Int. Soil Classification Workshop, Japan*. pp. 97–107. Japanese Committee for 9th International Soil Classification Workshop and Soil Management Support Service, Washington, DC.
- WRB, I.W.G., 2014. World Reference Base for Soil Resources 2014. International Soil Classification System For Naming Soils And Creating Legends For Soil Maps. World Soil Resources Report No. 106. FAO, Rome.
- Yagasaki, Y., Mulder, J., Okazaki, M., 2006. The role of soil organic matter and short-range ordered aluminosilicates in controlling the activity of aluminum in soil solutions of volcanic ash soils. *Geoderma* 137 (1–2), 40–57.
- Yamada, K., Ito, K., Takahashi, T., Kanno, H., Nanzyo, M., 2011. Inhibitory effect of acid Andosols on plants – is aluminum toxicity true for allophanic Andosols? *Soil Sci. Plant Nutr.* 57 (4), 491–499.
- Yazaki, T., Nagata, O., Sugito, T., Hamasaki, T., Tsuji, H., 2011. Nitrous oxide emissions from an Andosol upland field cropped to wheat and soybean with different tillage systems and organic matter applications. *J. Agric. Meteorol.* 67 (3), 173–184.
- Zunino, H., Borie, F., Aguilera, S., Martin, J.P., Haider, K., 1982. Decomposition of ¹⁴C-labeled glucose, plant and microbial products and phenols in volcanic ash-derived soils of Chile. *Soil Biol. Biochem.* 14 (1), 37–43.