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Microstructural development in volcanic ash soils from South Chile

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ABSTRACT

Streaming potential measurements and amplitude sweep tests were performed on a range of Andosols from South Chile to find out about aggregation strength and mechanisms, as well as thixotropy and microstructural stability. Different stages in soil development and types of land use (pasture vs. natural forest) were considered and compared. Younger, alu-andic Andosols along with Al-humus-complexes contained higher levels of volcanic glass, indicated by their low pH values ($pH_{H_2O} < 5$), and high ratios of sodium pyrophosphate extractable Al (Al_p) to acid ammonium oxalate extractable Al (Al_o) ($Al_p/Al_o > 0.5$). Alu-andic Andosols were also found to have (super)hydrophobicity in addition to typically high contents of amorphous iron (ferrihydrite). On the contrary, in well-developed, sil-andic Andosols ($Al_p/Al_o < 0.5$), allophane contents increased, accompanied by higher pH values ($pH_{H_2O} > 5$ and <7). Based on rheological data, the gel–sol–gel transformation (thixotropy) was better defined in sil-andic Andosols. Integral *z*, a dimensionless rheological parameter that represents quasi-elasticity was used to quantify stiffness degradation, and to identify single stages of thixotropy in allophanic Andosols. Scanning electron micrographs revealed that mineralogical components were predominated by volcanic glass (e.g. vesicular) and amorphous iron oxides in addition to fungal hyphae in younger acidic Andosols, while these characteristics were absent in well-developed Andosols. Here weathered minerals e.g. biotite, as well as halloysite, (proto)imogolite and allophanes were identified, indicating desilication and a shift from alu-andic to sil-andic Andosols. Zeta potentials derived from conducted particle charge density (PCD) measurements supported the assumptions that (i) Al-humus-complexes promoted aggregation in partially superhydrophobic topsoils of alu-andic Andosols, especially at ungrazed sites (or 1 year under pasture), and that (ii) thixotropic behaviour is related to allophanic, sil-andic Andosols, and better pronounced at sites which had been under pasture for 50 years.

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1. Introduction

Andosols are highly sensitive to any mechanical disturbance, but they have the potential to recover their structure after a certain resting time (Rao, 1995). However, the mechanism of thixotropy in these soils on the particle-to-particle scale is still not well understood. The investigation of thixotropy in volcanic ash soils is relevant for a better comprehension of mechanical behaviour at different scales, as induced by e.g. trampling or remoulding, and also to understand dynamic processes such as e.g. landslides.

Although the thixotropic behaviour of Andosols or allophanes is well-described in e.g. Maeda et al. (1977), Nanzyo et al. (1993a,b), Dahlgren et al. (2004), or Woignier et al. (2007), few authors have reported the rheological properties (e.g. bulk density < 0.9 g cm^{-3}, high contents in SOC) and the mineralogical components (e.g. presence of short range order minerals which have a large specific surface area and variable surface charge) of these soils. The general physicochemical properties of South Chilean soils in a toposequence as presented in this investigation were described by Grez (1977). The surface charge properties of the mineralogical components found in volcanic ash soils, i.e. ferrihydrite, allophane, imogolite, and halloysite, dependent on climate, vegetation, and soil development, are given in e.g. Wada (1989), Theng et al. (1982), Dahlgren et al. (1993a,b), and Nanzyo et al. (1993a,b), and are supposed to influence the soils' (micro)mechanical behaviour.

The penetration resistance in four South Chilean Andosols was investigated by Hartge et al. (1978), whereas Ellies and Gayoso (1986) delivered data about consistency limits and pointed out that allophanic Andosols tend to form stable microaggregates, which remain stable even at high water contents. Furthermore, Wells and Childs (1988) investigated the flow behaviour of allophane and ferrihydrite and Jacquet (1990) highlighted the sensitivity of remoulded volcanic ash soil. Rao (1995) gave a

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Nomenclature

a	particle radius (mm)
Al_o	acid ammonium oxalate extractable aluminium
Al_p	sodium pyrophosphate extractable aluminium
AST	amplitude sweep test
CA_{WPM}	contact angle determined according to Wilhelmy-Plate-Method
CEC	cation exchange capacity ($cmol_c\ kg^{-1}$)
CSD	controlled shear deformation
d_B	bulk density ($Mg\ m^{-3}$)
DLVO	Derjaguin–Landau–Verwey–Overbeek
E	electric field strength ($V\ m^{-1}$)
EDS	energy dispersive scan
Fe_d	dithionite–citrate extractable iron
Fe_o	acid ammonium oxalate extractable iron
G	grassland
G'	storage modulus (Pa)
G''	loss modulus (Pa)
MCR	modular compact rheometer
NF	native forest
P-retention	phosphate retention (%)
Past.	pasture
Poly-DADMAC	polydiallyldimethylammonium chloride
pzc	point of zero charge
SD	standard deviation
SEM	scanning electron microscopy
Si_o	acid ammonium oxalate extractable silicon
SOC	soil organic carbon
v	particle velocity ($m\ s^{-1}$)
$\tan\delta$	loss factor
ε	relative dielectric constant (80.1 $As\ V^{-1}\ m^{-1}$ for water at 20.1 °C)
ε_0	absolute dielectric constant ($\approx 8.8541 \times 10^{-12}\ As\ V^{-1}\ m^{-1}$)
γ	deformation (%)
η	dynamic viscosity ($N\ s\ cm^{-2}$)
κ	Debye–Hückel length (nm)
υ	electrophoretic mobility ($\mu m\ s^{-1}\ (V\ cm^{-1})^{-1}$)
ζ	zeta potential (mV)

mechanistic approach to the shear strength of allophanic soils and revealed that Andosols have a silt-like shear behaviour and angles of internal friction of 35° on average.

Aggregate stability in Andosols is influenced by Al-humus-complexes, which are formed under acidic conditions ($pH_{H_2O} < 5$) in alu-andic Andosols, and results from high allophane contents in sil-andic Andosols ($pH_{H_2O} > 5$ and <7) (Matus et al., 2006). Ellies et al. (2003) reported on soil water repellence and consequences for aggregate stability and soil hydraulic functions. These water repellent properties were investigated by Bachmann et al. (2000), who applied the sessile drop method for measuring contact angles and reported highly pronounced hydrophobicity, especially in topsoils of South Chilean Andosols caused by the organic matter constituents.

Soil physical parameters, such as soil structure, hydraulic conductivity, shear strength or cohesion of South Chilean Andosols as a function of land use have been determined by Hartge et al. (1978), Ellies et al. (2000), and Dörner et al. (2010, 2011), whereas Seguel and Horn (2005) provided data for soils under pasture, and Dec et al. (2012) reported the temporal variation of an Andosol's soil physical properties under (long-term) pasture. Ellies and Funés (1980) reported on the water stability and morphology of aggregates in topsoil of holocenic and pleistocenic formed volcanic ash soils in comparison. They found that holocenic ash revealed rough, rounded particles with higher porosity than pleistocenic, and that soil maturation was leading to smaller, more stable aggregates, despite higher silt contents. Moreover, Ellies and Gayoso (1986) stated that the determination of consistency limits was strongly influenced by water-stable microaggregates due to allophane, which is reflected in an increase of the silt fraction.

However, the investigation of microstructural changes in soils has undergone significant advancements in the last six years (Markgraf et al., 2006; Holthusen et al., 2010; Baumgarten et al., 2012). The application of rheometry has been well-established in the research area of soil micromechanics and soil physicochemistry. Rheometry has often been used as a method capable of linking the colloidal and aggregate scales (=meso scale), combining e.g. scanning electron microscopy, streaming potential measurements, and cyclic loading tests with amplitude sweep (Baumgarten et al., 2012). This approach has been applied to study the microstructural changes and stiffness degradation in a wide range of soils, i.e. in South Brazilian Oxisols and a Vertisol (Markgraf and Horn, 2007), in Luvisols which originated from the Rothamsted Broadbalk Wheat Experiment site (Markgraf et al., 2012b), or in salt affected Fluvisols from northern Germany and South Spain (Baumgarten et al., 2012; Markgraf et al., 2012a).

Hence, we hypothesize that

(i) with increasing allophane content, thixotropy is better pronounced, that
(ii) Al-humus-complexes in alu-andic as well as allophane and (amorphous) Fe-oxides in sil-andic Andosols increase microstructural stability, and
(iii) stiffness degradation is dependent on land use and soil development.

Thus, the aim of this study was to elaborate a concept for a classification of non-allophanic and allophanic Andosols regarding their micromechanical, thixotropic behaviour and stiffness degradation. Rheometry was supplemented by streaming potential measurements (PCD) and scanning electron microscopy (SEM), and used for a quantification of stiffness degradation. Hence, (i) specific physicochemical properties of the investigated Andosols were taken into account, i.e. allophane and ferrihydrite contents, SOC contents, as well as (ii) their management, i.e. native forest, grassland and pastures (1–50 years), and (iii) soil development.

2. Materials and methods

2.1. Sampling sites

A toposequence (~200 km) of three Andosols from South Chile were sampled. These soils developed in different positions in relation to the Andes Mountain Range (from less and more developed Andosols). The Liquiñe Serie (Acrudoxic Hapludands according to Soil Survey Staff, 2006 or Acroxi-Vitric Andosol, IUSS WRB, 2006) is a moderately deep soil (till 130 cm depth) derived from recent volcanic ashes which were deposited on the pumitic material located in the Andes Mountain Range (39°35′ S and 72°05′ W, 620 m a.s.l.). The topography presents hills with slopes between 30 and 50% (CIREN, 2003). The soil samples were collected from a soil under a native forest (e.g. *Nothofagus dombeyi*, *Embothrium coccineum*) and grassland (*Holcus lanatus*, *Poa annua*). According to Donoso et al. (2007) rainfalls can reach 4000 mm per year and the mean annual temperature varies between 4 and 8 °C. More information about this soil series can be found in Donoso et al. (2007).

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