



## Charge fingerprint in relation to mineralogical composition of Quaternary volcanic ash along a climatic gradient on Java Island, Indonesia

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### ABSTRACT

We studied the relationship between the mineralogical composition and surface charge properties of representative Quaternary volcanic ash soils, classified as Andosols, along an East-West sequence on Java Island in Indonesia. The soil charge characteristics were determined using ‘charge fingerprinting’ procedures. Most of the studied soils have a limited ability to retain cations under their forest or grass vegetation. The surface charge properties of these soils are mainly related to allophane and organic matter contents and, to a lesser degree, to ferrihydrite content and layer silicate characteristics. In East Java, the soils are Andosols with low allophane content, dominated either by halloysitic clays or by a mixture of 2:1 and 1:1 layer silicate clays; these soils are characterized by a low to moderate permanent charge. In West Java, the soils are rich in allophane, with subordinate kaolinitic clays, gibbsitic material or a mixture of 1:1 and 2:1 layer silicate clays; in contrast to the allophane-poor soils of East Java, these soils have extreme variable charge characteristics, creating a net ‘positive’ variable surface charge at soil pH. Differences in mineralogical composition of the clay fraction are attributed mainly to more pronounced seasonality in East Java, with variations in parent ash composition, becoming more acidic from east to west, as subordinate factor. The more severely leaching environment in West Java results in a higher degree of desilication, which led to a higher point of zero net charge (PZNC) and pH<sub>o</sub> in the allophane-rich soils. This study demonstrates how a climatic gradient can affect regional variations in charge properties, through the impact of climate on the mineralogical composition of the clay fraction. Regional patterns of this type must be understood to correctly assess of variations in soil fertility status and to make correct soil management choices for sustainable crop production.

### 1. Introduction

Andosols (IUSS Working Group WRB, 2015) developed on a rather wide variety of Quaternary volcanic ashes are widespread across the island of Java (Hutchison, 1989). Their physico-chemical and mineralogical properties have been studied by several authors (e.g., Tan and van Schuylenborgh, 1959; Tan, 1965; Supriyo et al., 1992; Utami, 1998; Van Ranst et al., 2002, 2004, 2008), revealing a close relationship between certain physico-chemical properties (e.g., base status, phosphate fixation, bulk density, water retention) and the mineralogical composition of the soils. They concluded that the development of these soils is affected by parent ash composition and climatic conditions. Some data on surface charge properties of selected B horizons of volcanic ash soils from Java have been published (Van Ranst et al., 2002), but complete characterization through charge fingerprinting, for

both A and B horizons, has not yet been reported in the literature. A soil ‘charge fingerprint’ constitutes the graphical representation of changes in soil cation and anion exchange capacities versus pH. It provides an unambiguous assessment of a soil’s inherent chemical properties, which are crucial in defining management strategies (Gillman, 2007). Surface charge properties of highly weathered soils have been extensively studied in other regions (Gillman, 1979), where those properties have been found to be closely related to the nature of the parent material (Gillman and Sinclair, 1987) and to the mineralogical composition of the soil (Tessens and Zauyah, 1982; Van Ranst et al., 1998; Qafoku et al., 2000).

Surface charge properties of Andosols are controlled by the relative amounts of short-range-order minerals (mainly, allophane and ferrihydrite), organic matter (especially Al- and Fe-humus complexes), crystalline Fe oxides, gibbsite, and layer silicate clays (e.g., smectite,

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halloysite, kaolinite) (e.g., Dahlgren et al., 2004; Qafoku et al., 2004; Theng and Yuan, 2008; Parfitt, 2009; McDaniel et al., 2012; Xu et al., 2016; Van Ranst et al., 2017). One of the key factors affecting Andosol properties is the variable surface charge, associated with the clay fraction. Electrical charges on clay particle surfaces can be either positive or negative, and they can change as a function of pH. Allophane, possessing Si-O-Al bonds, carries a negative surface charge at high pH through dissociation of  $H^+$  ions from siloxane groups (Si-OH), whereas at low pH it carries a positive surface charge owing to the acceptance of protons by aluminol groups (Al-OH) (Zhang and Zhao, 1997). Humus contains a large quantity of acid groups and is an important source of variable charge. It has been estimated that the quantity of negative charge carried by humus is within the range of 200 to 500  $cmol\ kg^{-1}$  (Zhang and Zhao, 1997). These negative charges originate mainly from carboxyl groups (C-O-OH), with an acidity constant (pKa) value of 4 to 5. Edge faces of layer silicate particles can also be sites where variable charge originates, through dissociation or adsorption of protons of exposed OH groups of broken bonds. However, because layer silicates, especially 2:1-type minerals, commonly carry a large quantity of permanent charge, this kind of variable charge component generally does not manifest itself strongly.

Andosols consist of both variable-charge minerals and permanent-charge minerals, together with compounds carrying both types of charge. The zero point of charge of the variable surface charge (pHo) is the pH at which the quantity of the net surface charge of the variable charge component in the mixed system equals zero. On the contrary, the point of zero net charge (PZNC) is the pH at which the sum of the permanent charge ( $\sigma_p$ ) and the variable charge ( $\sigma_v$ ) equals zero, which is dependent on electrolyte concentration (e.g., Uehara and Gillman, 1980, 1981; Gillman and Uehara, 1980; Zhang and Zhao, 1997; Qafoku et al., 2004).

The pHo is a characteristic feature that is independent of the permanent charge of the system. However, the pHo may be affected by the presence of specifically adsorbed cations or anions and by the quantity of permanent surface charge. On the other hand, PZNC is a parameter characterizing the relationship between the net surface charge, composed of electric charges of all origins, and pH in a mixed system. Clays with PZNC lower than pHo carry permanent negative surface charge, whereas those with PZNC higher than pHo carry permanent positive surface charge. The larger the difference between PZNC and pHo, the larger the quantity of permanent surface charge.

In the present study, mineralogical and detailed surface charge properties, with special emphasis on charge fingerprints, of A and B horizons of representative volcanic ash soils along an East-West (E-W) climatic gradient in Java have been determined and studied in an attempt to relate differences in mineralogical composition of the clay fraction, assumedly controlled by parent ash composition and rainfall patterns, to changes in surface charge properties as expressed by the charge fingerprints. Topsoils (A horizons) were included in this study in order to assess whether the charge fingerprint approach would be equally effective in characterizing surface soils, containing organic matter that imparts significant amounts of variable surface charge.

## 2. Materials and methods

### 2.1. Selected volcanic ash soils

Six pedons along an E-W sequence in Java were selected for this investigation: EJ1 and EJ2 in East Java, CJ3 and CJ4 in Central Java, and WJ5 and WJ6 in West Java. They are all located between 1250 and 1600 m in altitude, along the slopes of volcanoes (Fig. 1; Table 1). All soils developed on volcanic ash that is attributed to the Early to Mid Holocene (Van Bemmelen, 1949; Hutchison, 1989), with possible rejuvenation by historical eruptions of the 18th and 19th centuries. Based on the total elemental composition of parent ashes across Java (Whitford, 1975), volcanic ash ranges from basaltic in East Java (calc-

alkaline basaltic ash) to more silica-rich types in Central Java (basaltic-andesitic ash) and West Java (andesitic ash). The ashes of the volcanoes of East Java contain more Na (7 to 8%  $Na_2O$ ) but less K (0.5 to 1.5%  $K_2O$ ) and Si (48 to 53%  $SiO_2$ ), compared to the ash of the volcanoes in Central and especially West Java (~3%  $Na_2O$ ; 2 to 3%  $K_2O$ ; 55 to 60%  $SiO_2$ ) (Whitford, 1975).

Java is characterized by distinct wet and dry seasons. Annual rainfall at the studied sites ranges from about 2300 mm in East Java (2292 mm at EJ2) to 2700–2800 mm in Central Java (2754 mm at CJ4) and West Java (2795 mm at WJ6). Large seasonal variations in temperature are absent, with mean monthly temperatures of 18–19 °C at ca. 1400 m altitude (Table 1). This seasonality is more pronounced in the east of Java than in the west (Hendon, 2003; Rodysill et al., 2013). The length of the dry spell period, during which evapotranspiration exceeds precipitation, increases from 1 month in West Java to 4 months in East Java (Fig. 2). During this period, no excess rainfall is available to build up soil moisture reserves and no leaching will occur. All pedons have an isothermic temperature regime and a udic soil moisture regime. All are under (pine) forest, mostly with grass cover, except the CJ4 pedon, which is under grass. Other information about environmental conditions, as well as morphological and physicochemical properties of the selected soils, have been published elsewhere (Van Ranst et al., 2002).

### 2.2. Soil sampling and analysis

Soil samples were collected for A and Bw horizons of all pedons, whereby the Bw horizon was sampled at a depth of about 50 cm. The samples were immediately packed in a polyethylene bag that was tightly closed. Part of each sample was stored at field moisture conditions for moisture retention analysis. The remainder was air-dried and crushed to pass a 2-mm sieve.

Most analyses were done using air-dried fine earth, applying methods recommended for volcanic soils (Mizota and van Reeuwijk, 1989). Particle size distribution was determined by quantitative recovery of clay, silt and sand fractions after sieving and dispersion with  $Na^+$ -saturated resins (Bartoli et al., 1991). Bulk density (BD) was measured on an oven-dry weight basis for 100 ml core samples taken at field-moisture conditions. The pH was measured in  $H_2O$  and 1 M KCl in a 1:2.5 soil:solution ratio after 2 h mechanical shaking, and in 1 M NaF in a 1:50 soil:solution ratio after 2 min stirring. The pH was also determined in 0.002 M  $CaCl_2$  (ionic strength of 0.006 M), referred to as soil pH at field conditions. Organic carbon content was determined by the Walkley-Black wet combustion method (Allison, 1965). Phosphate retention (P-ret.) was determined by the method of Blakemore et al. (1981). Exchangeable base cations (Ca, Mg, K, and Na) were removed by leaching with 1 M-ammonium acetate solution (pH 7) using a Centurion vacuum extractor, followed by leachate analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).

Short-range-order constituents were characterized by selective chemical dissolution. Pyrophosphate solution (0.1  $mol\ l^{-1}$ , pH 10) was applied using a soil:solution ratio of 1:100, with shaking for 16 h and then centrifuging at  $2.10^4\ rpm$  ( $4.10^5\ N\ kg^{-1}$ ) for 30 min after addition of “Superfloc” (McKeague, 1967; McKeague et al., 1971). Oxalate solution (0.2  $mol\ l^{-1}$ , pH 3) was applied using a ratio of 1:100, with shaking for 4 h in the dark (USDA, 1972). Dithionite-citrate-bicarbonate (DCB) extraction was performed following the method of Mehra and Jackson (1960). Contents of pyrophosphate-extractable C, Al and Fe ( $C_p$ ,  $Al_p$  and  $Fe_p$ ), oxalate-extractable Si, Al and Fe ( $Si_o$ ,  $Al_o$ , and  $Fe_o$ ), and DCB-extractable Al and Fe ( $Al_d$  and  $Fe_d$ ) were determined by ICP-OES. Calculation of allophane content was done according to the formula proposed by Parfitt and Wilson (1985): % allophane = % Si \* (100/y), in which y is % Si in allophane, calculated using the equation  $y = 23.4 - 5.1x$ , in which  $x = (Al_o - Al_p)/Si_o$ , with Al and Si expressed as atomic abundance. The content of ferrihydrite was determined using the expression: % ferrihydrite =  $1.7 * Fe_o$  (Childs, 1985).

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