



## Soil carbon storage and stabilisation in andic soils: A review



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### ABSTRACT

Andic soils contain a large amount of stabilised soil organic matter (SOM). The present study aims to review and integrate the determining factors and mechanisms of SOM stabilisation in andic compared with other (non-andic) soil types. We have reviewed recent literature regarding the nature of SOM and its stabilisation processes in the top- and sub-soil to address and discuss the interaction between the SOM and the mineral phase. The carbon (C) storage capacity by the metal-humus-complex formation of volcanic soils is also evaluated. The most important stabilisation processes are related to the incorporation and decomposition of microbial-derived C along with the changing C storage capacity with increasing soil development. The priming and destabilisation of adsorbed SOM are crucial mechanisms influencing the soil C sequestration in subsoils. The C storage capacity of andic soils was closely related to the Na-pyrophosphate extractable Al and Fe. The upper boundary for SOM saturation with Al and Fe was a molar metal:C ratio of 0.18. The influence of climate, mineralogy and soil disturbances on the SOM storage capacity of andic soils also require further attention.

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### 1. Introduction

Volcanic ash soils contain a disproportionate amount of soil C in soil organic matter (SOM) (Batjes, 1996; Eswaran et al., 1993) because they comprise only 0.84% of the global land area but may contain several times more C than non-volcanic soils (Dahlgren et al., 2004). These soils store approximately 5% of the global soil C (Eswaran et al., 1993).

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The hypotheses that explain SOM accumulations in andic soil are the following: 1) phosphorus is a rate-limiting factor for organic matter mineralisation (Munevar and Wollum, 1977), and 2) mineral associations reduce SOM mineralisation (Zunino et al., 1982). Moreover, enzymes and microbial by-products may be deactivated by adsorption on short-range order (SRO) mineral surfaces of andic soils (Saggar et al., 1994). In volcanic soils, the microbial decomposition of organic matter may be limited by Al toxicity (Illmer et al., 2003; Tate and Theng, 1980) and low pH values. This is particularly important in alu-andic soils (dominated by Al-humus-complexes), where the pH is low, versus sil-andic soils (dominated by allophane and allophane-like minerals), or andic soils, where the pH is higher (Dahlgren et al., 2004). Another important factor in the preservation and accumulation of SOM in volcanic soils is burial by repeated additions of volcanic deposits. This rejuvenates landscapes and creates new ecosystems that may sequester organic C (Imaya et al., 2010).

Andic soils, including Andisols, as described by the USDA classification (Soil Survey Staff, 2008), or Andosols in the WRB system classification (FAO-ISRIC-ISSS, 1998), cover more than 120 million hectares worldwide (Dahlgren et al., 2004) and display unique morphological, physical and chemical properties attributed to the composition of their mineral phase. These soils' minerals consist of SRO materials such as allophane, imogolite, ferrihydrite and Al- and Fe-humus complexes lacking a long-range crystal atomic order (Harsh et al., 2002). Based on the mineralogical composition of the A horizons, two groups of Andisols are included: non-allophanic and allophanic Andisols. The latter are dominated by allophane and imogolite-type materials and the former by Fe- and Al-organic complexes (humus-complexes). At a pH > 5, carbonic acid weathering causes the soil to produce allophane formations, allowing the Al to polymerise and co-precipitate with Si, whereas at a pH < 5, the formation of metal (Al and Fe)-humus complexes will be favoured. Allophanes are weathered metastable non-crystalline materials in both temperate and tropical humid environments. As weathering proceeds, the SRO minerals evolve to more stable crystalline minerals (e.g., halloysite, kaolinite, gibbsite) leading to other soil orders (e.g., Ultisols, Inceptisols or Alfisols) (Dahlgren et al., 2004). In perhumid tropical environments, Oxisols occur. Under cool-cold-humid climates, Podzols are often the dominant soil developed under acidic conditions (Ugolini et al., 1977). The high SOM storage capacity of Andisols is a function of the high surface areas of noncrystalline constituents that are available for the sorption of organic matter (Baldock and Nelson, 2000; Saggar et al., 1994). Therefore, Andisols would be expected to have a higher potential for SOM sequestration than non-andic soils.

The present review aims specifically to update and integrate the fundamental aspects determining SOM composition and its stabilisation and destabilisation processes that occur in andic soils (hereafter referred to as Andisols). Stabilisation is defined as the absence of SOM biodegradation (Sollins et al., 1996), where the humification dominates over mineralisation. In particular, we want to note the differences and similarities between Andisols and other soil types to answer the question of why Andisols are able to store more organic matter than any other soil type. We have reviewed recent literature concerning the nature of SOM and its relationship to the stabilisation processes operating in the top- and subsoil. As a result, this review has three sections. First, we focus on the nature and origin of SOM in Andisols and its importance on the stabilisation processes. In the second section, we discuss the interactions between the SOM and the mineral phase and its implications for C-stabilisation. We will also consider the destabilisation processes related to the priming action, dissolved organic matter (DOM) and water extractable organic matter (WEOM). The latter two have been proposed to serve as a crucial mechanism of soil C transport into the subsoil. Lastly, in the third section, the C storage capacity change over time is discussed and the metal-humus-complex formation for C sequestration of Andisols is evaluated.

## 2. Nature and distribution of organic matter in Andisols

### 2.1. Chemical composition

The chemical composition of SOM may provide valuable information regarding SOM precursors and the mechanisms of stabilisation (Derenne and Largeau, 2001). Most studies on the chemical composition of SOM in Andisols were carried out after alkaline extraction of humic and fulvic acids using NaOH and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (Nierop et al., 2005). The chemical properties of humic substances were determined to be different for Andisols and adjacent non-andic soils. The Andisols accumulate more unsaturated C than the non-andic soils. This indicates more carboxyl and methoxyl functional groups from poorly degraded lignin, which may be involved in stable Al complex formation from amorphous materials (Conte et al., 2003). Humic materials extracted from Andisols in Japan have been reported to exhibit a higher degree of condensation compared with those of non-andic soils (Kuwatsuka et al., 1978; Yonebayash and Hattori, 1988). The high aromaticity of these fractions could be related to the presence of charred plants from the regular burning of vegetation and melanic epipedon characteristics (Golchin et al., 1997; Shindo et al., 2004). However, Nierop et al. (2005) indicated that the NaOH extractable SOM of volcanic soils is unaffected by burning; these soils were found to be dominated by polysaccharide-derived compounds. These studies contrast with others noting that the recalcitrant plant-derived compounds are scarcely preserved and that most of the SOM in Andisols is composed of easily degradable microbial-derived material (Buurman and Nierop, 2007; Buurman et al., 2007; González-Pérez et al., 2007; Naafs et al., 2004; Nierop et al., 2005; Suárez-Abelenda et al., 2011). This finding is in accordance with the general literature regarding SOM stabilisation in non-volcanic soils, where the chemical recalcitrance of plant litter compounds is no longer regarded as an SOM stabilisation mechanism (Dungait et al., 2012; Kleber et al., 2011; Marschner et al., 2008). Even black C, a recalcitrant SOM component that is generally preserved in other soil types over centuries (Hammes et al., 2008; Rumpel et al., 2008), does not seem to accumulate in Andisols (Cusack et al., 2013). This may be due to the absence of interactions of this component with soil minerals (Hernández et al., 2012; Rivas et al., 2012). Studies on hydrophobic (HB) and hydrophilic (HI) recalcitrant materials other than black C revealed that HB/HI ratio of forest soils was substantially reduced after cultivation, resulting in an SOM poor in alkyl (aliphatic compounds), except in Andisols (Spaccini et al., 2006). In Andisols, there is a contribution of alkyl C along the soil profile that is resistant to dichromate chemical oxidation and that increases C storage (Rivas et al., 2012). It seems that alkyl structures can be protected from oxidation due to their hydrophobic nature, possibly through encapsulation into their hydrophobic network (Knicker and Hatcher, 2001). Indeed, Barbera et al. (2008) reported that the refractory organic fraction, enriched in aliphatic compounds, did not greatly interacted with kaolinite, smectite or poorly crystalline Fe or Al because part of this fraction (most likely proteins) was bound to crystalline Fe-oxides. Recently, Tonneijck et al. (2010) reported that extremely acidic soil pH conditions possibly lead to Al toxicity along with high microporosity, may enhance the preservation of plant-derived aliphatic C in Andisols. Other studies related to biomarkers showed that intact biopolymers may be chemically protected in the insoluble organic macromolecular network (Naafs and van Bergen, 2002). Recently, Nierop and Jansen (2009) reported that solvent extractable lipids preserved their plant-derived signatures throughout the soil profile, even if the bulk SOM composition no longer resembled the vegetation growing on these soils. Thus, some recalcitrant component of SOM, such as charred materials, seems to be less preserved in comparison with SOM of an aliphatic nature.

The composition of the SOM stabilised by mineral interactions in subsoils of allophanic as well as non-allophanic Andisols was recently studied (Rumpel et al., 2012). This SOM was found to be enriched by N-containing compounds, and is different from those of the A horizon.

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