UC Davis UC Davis Previously Published Works

Title

Long-term response of tropical Andisol properties to conversion from rainforest to agriculture

Permalink https://escholarship.org/uc/item/04w9t892

Authors

Anda, Markus Dahlgren, RA

Publication Date

2020-11-01

DOI

10.1016/j.catena.2020.104679

Peer reviewed

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Long-term response of tropical Andisol properties to conversion from rainforest to agriculture

Markus Anda^{a,b,*}, R.A. Dahlgren^b

^a Indonesian Center for Agricultural Land Resource Research and Development, Agency of Agricultural Research and Development, Jalan Tentara Pelajar No.12, Kampus Penelitian Pertanian, Cimanggu, Bogor 16114, Indonesia⁴

^b Department of Land, Air and Water Resources, University of California Davis, One Shields Avenue, CA 95616, USA

ARTICLEINFO

Keywords: Andisols Land use changes Physical and chemical changes Carbon and Nitrogen stocks Microbial biomass

ABSTRACT

Short-term changes in tropical rainforest soil properties and their impact on C cycling following land-use conversion to agriculture have received intensive study. However, long-term, land-use changes have not been explored for tropical Andisols, whose high carbon stocks and several distinctive properties may differ in their response to land-use conversion. Thus, the primary objective of this study was to assess changes in selected soil properties of Andisols in response to long-term (> 100 years) changes of land use from tropical rainforests to agriculture. Soils were sampled by horizon to a depth of 110-140 cm in pine forests (PF), tea plantation (TP) and horticultural crops with either intensive cultivation (IH) or bare fallow (FH) cropping systems. Selected physical, chemical and biological soil properties were characterized, including microbial biomass carbon (MBC) and laboratory CO₂ mineralization rates. Results showed that land-use change from rainforest to agriculture resulted in increased soil bulk density and meso/micropores that contributed to increased plant-available water retention capacity. Soil carbon and nitrogen stocks in the upper 1 m of soil were higher in agricultural soils (25-29 kg C m^{-2} ; 1.7 – 2.3 kg N m⁻²) than pine forest soil (17 kg C m⁻²; 1 kg N m⁻²) with a redistribution of organic matter from topsoil to subsoil horizons. Organic matter quality was also affected by land-use conversion with the horticultural soils having lower rates of carbon mineralization per unit soil carbon (PF > TP > IH > FH) and lower microbial biomass, especially in topsoil horizons. The MBC sharply decreased in the topsoil horizon due to land-use change from forest (330 mg kg^{-1}) to agricultural production (< 118 mg kg^{-1}). The intensive horticultural soil receiving recent additions of horse manure had higher extractable mineral N (especially NO₃), reduced P fixation, increased available P, higher pH, and higher concentrations of exchangeable base cations $(Ca^{2+}, Mg^{2+} and K^+)$ and micronutrients (Zn, Mn and Cu). The Andisols in this study demonstrated strong resilience to long-term degradation of soil properties following conversion from rainforest to agronomic land use. Further, this study demonstrates the ability of these Andisols to sequester additional C upon conversion to selected agriculture practices, thereby providing a positive impact on C mitigation.

1. Introduction

Net tropical forest loss of 7 million hectares per year occurred between 2000 and 2010, with conversion to agriculture accounting for 86% of deforestation (FAO, 2016). Annual deforestation in tropical Asia during the 1990s reached up to 5.6 million ha yr^{-1} , resulting in the emission of 1.0 Pg C yr^{-1} to the atmosphere (Houghton, 2002; Carlson et al., 2012). In Indonesia, the total forest area of 117 million ha in 1990 (FAO, 2006) dropped to 89 million ha in 2011–2012 with primary, secondary and plantation forests occupying 45.2, 40.8 and 3.0 million ha, respectively (Ministry of Forestry, 2014). The average forest loss of 1.3 million ha yr $^{-1}$ from 1990 to 2012 resulted from burning and conversion to agriculture, mining and infrastructure with Indonesia contributing to $\sim 10\%$ of total global forest loss each year.

Short-term changes in soil properties following conversion of tropical forests to agricultural land use are often pronounced and in most cases detrimental to sustainable agricultural production. In contrast to the Amazon (Brazil) rainforests supported by Oxisols and Ultisols (Cherubin et al., 2015), Indonesia's rainforests are largely supported by volcanic soils, primarily Andisols. These Andisols support high agricultural productivity with some of the world's highest human-carrying capacity being found on volcanic soils in Indonesia (Shoji et al., 1993;

* Corresponding author.

https://doi.org/10.1016/j.catena.2020.104679





CATENA

E-mail address: markusandas@yahoo.com (M. Anda).

¹ Present address.

Received 22 October 2019; Received in revised form 7 May 2020; Accepted 13 May 2020 0341-8162/ © 2020 Published by Elsevier B.V.



Fig. 1. Location of the study site in Lembang region, west Java.

Van Ranst et al., 2002). With respect to greenhouse gases, Andisols are notable for having the highest soil carbon storage capacity among the mineral soil orders in temperate and tropical climatic regimes with an average carbon stock of 25.4 kg C m⁻² (Batjes, 2014). Matus et al (2014) reviewed soil carbon storage and stabilisation in andic soils and concluded that the most important mechanism of sorption of soil organic matter by short range ordered amorphous minerals is the ligand exchange. While short-term (< 30 years) changes in properties of tropical rainforest soils have been extensively studied, there is a paucity of

information concerning long-term (> 100 years) changes in soil properties resulting from changing land use and management practices, especially with respect to Andisols.

Greenhouse gas (GHG) emissions from agriculture are reported to contribute up to 30% of anthropogenic emissions (Tubiello et al., 2013). Soils can be a major source (Smith et al., 2008) or sink (Batjes, 2014) of GHG from terrestrial ecosystems depending on the ecosystem disturbance regime and soil management practices. Soil carbon storage is dependent on soil mineral constituents, with volcanic ash soils typically having exceptionally high potential C stocks owing to their high content of active Al and Fe constituents (e.g., allophane, imogolite, ferrihydrite and metal-organo complexes). In Andisols, Chevallier et al. (2008) showed organic matter transformation to CO_2 via microbial respiration was lower as allophane content increased. In addition, changes in land use/land cover alter organic matter quantity and quality, which are major factors controlling soil microbial biomass and activity (Fierer et al., 2009; Kallenbach and Grandy, 2011). Given the high C stocks in Andisols, it is important to assess the fate of soil C following land-use conversion from forest to intensive agricultural production, especially with regard to rapid deforestation in the tropics.

Andisols have several unique properties that affect agricultural productivity, such as high P fixation, high organic matter concentrations, a clay-size fraction dominated by pH dependent variable charge, low bulk density, high porosity, high water retention capacity and high mesopore (fractal pores) content (Shoji et al., 1993; Auxtero et al., 2004; Chevallier et al. 2008). In particular, high P retention (> 85%) (Soil Survey Staff, 2014) in Andisols can limit agricultural productivity by limiting plant availability of P. Currently, there is little information on how P retention and availability in tropical Andisols change with different land use and agricultural practices. Nitrate leaching characteristics in Andisols are also strongly affected by variable charged constituents as positive charges can retain nitrate enabling higher plantutilization efficiency. In southern Chile, Huygens et al. (2008) reported NH_4^+ and NO_3^- retention of 84 and 69% of N fertilizer additions, respectively, after one year based on ¹⁵N pool-dilution and ¹⁵N tracer studies of forested Andisols. In Japan, the maximum nitrate adsorption by Andisols (Melanudands and Hapludands) ranged from 0.4 to 7.0 cmol_c kg⁻¹ with the highest values occurring in soil horizons with high allophane content and low organic carbon content (Tani et al., 2002). Furthermore, Deng et al. (2011) evaluated the denitrification rates from eight Andisols under three different cropping systems in an intensive livestock catchment of central Japan and reported that N loss via denitrification from upland fields was almost negligible in spite of substantial N inputs (200–800 kg N ha⁻¹yr⁻¹). In addition to retention of NO₃⁻ by positively charged colloids, a laboratory study by Matus et al. (2019) reported high retention of NO_3^- in Andisols through transformation of NO_3^{-} to dissolved organic nitrogen (DON).

In Indonesia, land use/land cover of Andisols is primarily native rainforest, tea plantation, horticultural crops, terraced paddy fields and other food crops. Land-use conversion from tropical rainforest to agriculture has taken place over long periods of time (> 100 years); however, no rigorous studies have examined changes to Andisol soil properties over these time periods. In addition, several studies have examined microbial biomass carbon (MBC) and CO_2 measurements in topsoil horizons, however, MBC and CO2 measurements in subsoil horizons have been ignored although these measurements are crucial for explaining the exceptionally high carbon stocks in Andisols. Given the several unique properties of Andisols, it may be expected that these soils are more resilient to land-use change and agricultural management practices. Therefore, we hypothesize that the unique soil properties of Andisols lessen the negative impacts of land-use change from tropical forest to agriculture on soil physical, chemical and biological properties. The objective of this study was to take advantage of longterm, land-use/land management changes (> 100 years) to examine changes in several physical, chemical and biological properties of Andisols in tropical Indonesia following conversion of rainforest to tea plantation and horticultural crops.

2. Materials and methods

2.1. Environmental setting

The study area is located in Lembang, West Java, Indonesia at $6^{\circ}46'25''$ and $6^{\circ}48'10''$ S and $107^{\circ}38'6''$ and $107^{\circ}38'54''$ E (Fig. 1) with elevations ranging from 1236 to 1530 m above mean sea level (amsl).

Mean annual air temperature and precipitation are 20 °C and 1902 mm, respectively. The rainy season occurs between October and April and accounts for 79% of total annual rainfall. The resulting soil temperature and moisture regimes are isothermic and perudic, respectively (Soil Survey Staff, 2014). Initial vegetation at all study sites was a pine forest (Pinus mercusi) according to information provided by the present third generation of local people. Soils developed from basaltic andesite volcanic ash and were classified as Typic Hapludands and Typic Melanudands (Soil Survey Staff, 2014). The age of soil materials was measured by Chartres and van Reulert (1985) using the ¹⁴C dates based on soil profile excavations to a 270 cm depth. They reported dates for buried A horizons consisting of IIA (40-78 cm), IIIA (141-162 cm) and IVA 8.700 ± 200 . $14.500 \pm 300.$ (210-236 cm)of and $17,700 \pm 580$ years, respectively.

This study examined soil characteristics for four land-use/management practices: pine forest (PF), tea plantation (TP), and horticultural cropland with either intensive cultivation (IH) or bare fallow (FH). All study sites had similar landscape position (convex shoulder slopes), slope (5-8%), and aspect southwest and were located within 3 km of each other. All sites occurred on a similar landform unit (namely middle volcanic slope), derived from similar parent materials, and experienced similar climate conditions. Hence we assumed that the soils at all four study sites had similar soil properties prior to land-use change. Conversion of rainforest to agricultural production occurred > 100 years ago based on historical records. The soils under tea plantation (TP) (Camellia sinensis) currently receive application of KCl, kieserite and urea three times each year. The horticultural treatments were located at the Indonesian Vegetable Research Institute (IVRI) where detailed records of soil management practices were available. Horticultural crops included eggplant (Solanum melongena), cabbage (Brassica oleracea), bell pepper (Capsicum annum), long beans (Vigna unguiculata), French beans (Phaseolus vulgaris), lettuce (Lactuca sativa), and tomato (Solanum lycopersicum). While intensive horticultural cultivation has occurred at this site for > 100 years, soil treatments were initiated 7 years ago on the long-term horticultural site to examine application of horse manure (20 Mg ha^{-1} yr⁻¹) (IH) versus bare fallow (FH) (September 2006 to May 2013). The horse manure trial was established with the intention of reducing inorganic fertilizer application to 50% of that normally applied to horticultural crops. The 50% inorganic fertilizer application rate for the past 7 years was 150 kg N ha $^{-1}$ as urea, 160 kg P ha⁻¹ as superphosphate (SP36) and 120 kg K ha⁻¹ as KCl applied as a split application three times each year. Horse manure $(20 \text{ Mg ha}^{-1} \text{ yr}^{-1} \approx 244 \text{ kg N}; 70 \text{ kg P}; 350 \text{ kg K}; 146 \text{ kg Ca}; 58 \text{ kg Mg})$ was annually incorporated to a depth of 20 cm. For the past 7 years, the IH plot was cropped with cabbage/lettuce from January to March, cover crop Mucuna sp./fallow from April to July (dry season) and cabbage-tomato from August to December. The previously cultivated FH plot was located adjacent (4 m) to the IH plot and was minimally tilled to remove weeds and received no manure or fertilizer additions for the past 7 years.

2.2. Soil characterization

We excavated a soil pedon with the dimensions (width \times length \times depth) of $150 \times 200 \times 110-140$ cm at each of the four land-use/management sites. A composite soil sample was collected for each soil horizon from all sides of the soil pedon; the sample was thoroughly mixed prior to subsampling about 1 kg for analysis. Soils were air dried and passed through a 2-mm sieve to remove coarse fragments and roots prior to further analysis.

Bulk density (D_b) was measured by the core method (Blake and Hartge, 1986) using steel cylinders of 5×5 cm (diameter × length). Intact soil cores were collected at 0–20 cm and 30–50 cm depths at field-moist conditions. The D_b was expressed on an oven-dry weight basis. Particle density (ρ_b) was determined by the submersion method (Blake, 1986). Total porosity (P_T) was estimated by the formula P_T = (1

Table 1

Selected chemical properties of Andisols under different land uses.

| Profile/ | Depth | Partic | le siz | e | pН | | Organic matter | | | CEC Al | | BS^\dagger | Oxalate | | | Al ₀ -Al _p / | Ferri- | Allo- |
|--|------------|-----------|--------|---------|------------------|-----|----------------|--------|------------------|--------|------------------|-----------------------|-----------------|-------------------|-----------------|------------------------------------|----------------------|--------------|
| horizon | cm | Sand % | Silt | Clay | H ₂ O | KCl | C | N % | C/N [‡] | cmol | kg ⁻¹ | % | Al _o | Fe _o % | Si _o | Si _o | hydrite [†] | phane¶ _% |
| TP Typic Hapludand under tea plantation | | | | | | | | | | | | | | | | | | |
| Ар | 0-24 | 41 | 44 | 15 | 4.8 | 4.6 | 6.70 | 0.41 | 16 | 9.28 | 0.39 | 23 | 5.77 | 5.00 | 2.25 | 2.18 | 8.50 | 18.93 |
| Bw1 | 24–54 | 46 | 41 | 13 | 4.7 | 4.6 | 6.40 | 0.39 | 16 | 8.00 | 0.30 | 19 | 5.76 | 5.02 | 2.27 | 2.20 | 8.53 | 19.25 |
| Bw2 | 54-88 | 31 | 48 | 21 | 4.9 | 4.8 | 6.10 | 0.35 | 17 | 7.83 | 0.09 | 19 | 7.63 | 5.32 | 3.20 | 2.14 | 9.04 | 26.53 |
| Bw3 | 88-130 | 25 | 57 | 18 | 4.7 | 4.6 | 3.20 | 0.16 | 19 | 6.17 | 0.05 | 20 | 8.48 | 5.06 | 3.85 | 2.06 | 8.59 | 30.75 |
| FH Typic Melanudand under fallow system (former horticultural crops) | | | ;) | | | | | | | | | | | | | | | |
| Ар | 0-21 | 42 | 40 | 18 | 5.2 | 4.9 | 6.30 | 0.48 | 13 | 9.73 | < 0.01 | 138 | 7.02 | 2.79 | 3.21 | 1.98 | 4.73 | 24.86 |
| Bw1 | 21-48 | 42 | 28 | 30 | 5.6 | 5.3 | 5.70 | 0.53 | 11 | 9.48 | < 0.01 | 151 | 6.99 | 2.20 | 3.31 | 1.94 | 3.73 | 25.25 |
| Bw2 | 48–70 | 32 | 45 | 23 | 5.6 | 5.2 | 7.50 | 0.45 | 17 | 9.44 | < 0.01 | 150 | 6.85 | 2.99 | 3.01 | 2.04 | 5.08 | 23.88 |
| 2Bw3 | 70–118 | 37 | 37 | 26 | 5.6 | 5.5 | 2.70 | 0.16 | 17 | 9.45 | < 0.01 | 130 | 6.63 | 3.77 | 3.84 | 1.65 | 6.42 | 26.18 |
| IH Typi | : Melanuda | nd und | er hor | ticultu | ral cro | ps | | | | | | | | | | | | |
| Ар | 0-21 | 43 | 32 | 25 | 6.1 | 5.6 | 6.10 | 0.56 | 11 | 9.94 | < 0.01 | 312 | 5.95 | 2.16 | 2.76 | 2.00 | 3.66 | 21.54 |
| Bw1 | 21-48 | 38 | 39 | 23 | 5.8 | 5.3 | 5.60 | 0.53 | 11 | 9.22 | < 0.01 | 261 | 6.10 | 2.09 | 2.86 | 1.96 | 3.56 | 21.97 |
| Bw2 | 48–70 | 42 | 40 | 18 | 5.6 | 5.3 | 4.50 | 0.34 | 13 | 8.73 | < 0.01 | 192 | 7.08 | 2.85 | 3.49 | 1.91 | 4.85 | 26.24 |
| Bw3 | 70–110 | 24 | 44 | 32 | 5.7 | 5.3 | 6.00 | 0.33 | 18 | 7.98 | < 0.01 | 163 | 7.21 | 3.78 | 3.51 | 1.90 | 6.43 | 26.30 |
| PF Typi | c Hapludan | d under | r pine | forest | | | | | | | | | | | | | | |
| А | 0-24 | 24 | 56 | 20 | 4.5 | 4.3 | 8.00 | 0.49 | 16 | 8.53 | 1.01 | 23 | 7.28 | 4.36 | 3.48 | 1.87 | 7.40 | 25.78 |
| Bw1 | 24–60 | 29 | 40 | 31 | 4.5 | 4.2 | 3.20 | 0.18 | 18 | 8.97 | 0.29 | 16 | 7.39 | 4.45 | 3.71 | 1.85 | 7.57 | 27.27 |
| Bw2 | 60–100 | 31 | 56 | 13 | 4.5 | 4.2 | 3.30 | 0.17 | 19 | 8.09 | 0.32 | 17 | 7.90 | 4.84 | 3.83 | 1.92 | 8.23 | 28.98 |
| Bw3 | 100–140 | 32 | 46 | 22 | 4.4 | 4.3 | 3.50 | 0.19 | 19 | 7.50 | 0.21 | 18 | 7.65 | 4.66 | 3.67 | 1.95 | 7.92 | 27.97 |

Note:

 † Ferrihydrite% = 1.7*Fe $_{ox}$ % (Parfitt, and Childs, 1988); BS: base saturation.

[¶] Allophane% = Si_o% (100/y), y = 23.4–5.1 ×, where x = (Al_o -Al_p)/Si_o (Parfitt and Wilson (1985).

* C/N ratio reported on a mass basis.

 $- D_b/\rho_b) \times 100$ (Van Ranst et al. 2002).

Particle size of the fine-earth fraction was determined by the pipette method and wet sieving (Soil Survey Staff, 1992). Samples were pretreated with H_2O_2 to remove organic matter and dispersed with dilute Na-hexametaphosphate. Silt- and clay-sized fractions were measured after sedimentation according to Stokes law. The sand fraction was separated from the clay and silt fractions by wet sieving through a 0.05 mm sieve. Water retention (WR) at various tensions was determined using a pressure plate. Plant-available water holding capacity was estimated as the volume fraction of water retained between 33 and 1500 kPa. A sample of < 2-mm (sieved), air-dry soil was placed on a porous ceramic plate and wetted by capillary action; gravimetric water content was measured following attainment of equilibrium at 33 and 1500 kPa.

Soil pH was measured 1:2 (solid:solution) in H₂O and 1.0 M KCl. Phosphate retention was determined using the method of Blakemore et al. (1987) and the Bray-1 extraction was used as an estimate of available P (Olsen and Sommers, 1982). Exchangeable cations were displaced by 1 M NH₄OAc at pH 7.0, then the cations were measured in the supernatant (Soil Survey Staff, 1992) using an atomic absorption spectrometer (AAS). The cation exchange capacity (CEC) was determined in 1 M NH₄OAc (buffered at pH 7.0) after extraction of NH₄⁺ by 10% NaCl as a measure of CEC. Base saturation was calculated as the sum of base cations by 1 M NH₄OAc divided by CEC. Sulfate-sulfur (SO₄-S) was extracted using monocalcium phosphate as outlined by Schulte and Eik (1988) and available micronutrients (Zn, Mn, Cu, and Fe) were determined by DTPA extraction (Lindsay and Norvell, 1978). All weight percent data were reported on an oven-dry basis (105 °C). Non-sequential selective dissolution in Na-pyrophosphate (Blakemore et al., 1987) and ammonium-oxalate (Soil Survey Staff, 1992) was used to characterize Fe, Al and Si in various pedogenic pools.

Total C and N concentrations were determined on ground samples $(< 120 \,\mu\text{m})$ by dry combustion using a Costech C/N analyzer (Analytical Technologies, USA). Soil microbial biomass C (MBC) and N (MBN) were measured using chloroform fumigation and direct extraction with 0.5 M K₂SO₄ (Horwath and Paul, 1994). Briefly, 10 g oven-dry equivalent samples were fumigated for 48 h in the dark, and then C and

N were extracted with $0.5 \text{ M K}_2\text{SO}_4$. Similar extraction was applied for non-fumigated (control) samples. Total dissolved organic C (DOC) and total extractable N were measured using a C/N analyzer (Shimadzu Model TOC/TN). The non-fumigated control values were subtracted from fumigated values as an estimate of microbial C and N. A Kec/Ken factor of 0.35 was applied for both C and N (Voroney et al., 1991).

Carbon mineralization was measured in the topsoil (A horizon) and subsoil (Bw3 horizon) by incubating duplicate soil samples in the dark under laboratory conditions (21 \pm 1 °C; similar to mean annual air temperature of 20 °C) over a 119-day period. Soil moisture was adjusted to $\sim 80\%$ of field capacity and pre-incubated for one week prior to starting the long-term incubation. Soils were incubated in sealed Mason jars fitted with septa. Carbon dioxide in the headspace of each soil sample and blanks with no soil was measured each week using an Infrared Gas Analyzer. The CO₂ emission was normalized to initial total C content of each soil and expressed as CO_2 -C mg kg⁻¹ soil C. In addition, net N mineralization was measured on these same samples at the end of the 119-day incubation by determining concentrations of mineral N (NH₄⁺ and NO₃⁻) in 1 M KCl extracts at time zero and at 119 days. Quantification of NO_3^- used the vanadium chloride method (Doane and Horwath, 2003) and NH_4^+ the Berthelot reaction with a salicylate analog of indophenol blue (Forster, 1995). A correlation analysis was performed to assess soil properties most strongly affected by land-use changes, using IBM SPSS Statistics 22. 2013.

3. Results

3.1. Soil physical properties

All soils were well drained with an A horizon (21–24 cm thick) overlying Bw horizons that extended to the depth of investigation (110–140 cm). Soil particle-size distribution was similar among the four sites with the majority of the horizons having a loam texture (Table 1). Some distinct changes in particle-size distribution within various pedons (e.g., IH at 48 cm; FH at 70 cm) are attributable to more recent tephra deposition that resulted in burial of the former soil profile.

Bulk density (D_b) in subsoil horizons was very low (0.38 -

Table 2

Selected physical properties of Andisols under different land uses.

| Sample | Depth | D_b | ρ_b | P _T | Water conter pF1 | it pF2 | pF2.54 | pF4.2 | Available water | Drainage por Rapid | res Slow | WRC |
|---|-----------|------------------|-----------------|-------------------|---------------------|--------------|--------------|--------------|--------------------|-----------------------|-------------|--------------|
| | cm | g cm | g cm | % volume | | | | | | % | volume | |
| TP Typic Hapludand under tea plantation | | | | | | | | | | | | |
| TP-1 | 0-20 | $0.55~\pm~0.02$ | 1.73 ± 0.12 | 68.53 ± 1.43 | 59 ± 4.6 | 47 ± 2.4 | 40 ± 2.1 | 19 ± 1.2 | $21~\pm~0.8$ | 21 ± 1.5 | 7 ± 0.5 | 53 ± 0.6 |
| TP-2 | 20-40 | $0.46~\pm~0.05$ | 1.66 ± 0.20 | 71.40 ± 9.40 | 64 ± 6.8 | 48 ± 8.9 | 41 ± 4.9 | 20 ± 3.2 | 20 ± 1.2 | 24 ± 0.5 | 8 ± 0.7 | 51 ± 9.4 |
| Typic N | lelanudaı | nds under fallow | v system (FH) a | and intensive hor | ticultural crop | s (IH) | | | | | | |
| FH-1 [†] | 0-20 | $0.59~\pm~0.10$ | $1.85~\pm~0.8$ | 68.13 ± 4.70 | 66 ± 4.5 | 52 ± 4.8 | 47 ± 5.0 | 27 ± 4.8 | $21~\pm~0.6$ | 16 ± 3.2 | 5 ± 0.6 | 44 ± 3.7 |
| FH-2 | 20-40 | 0.43 ± 0.04 | $1.68~\pm~0.12$ | 74.20 ± 1.70 | 72 ± 2.7 | 57 ± 2.2 | 49 ± 2.4 | 26 ± 1.6 | 23 ± 1.2 | 18 ± 0.6 | 7 ± 0.2 | 46 ± 1.5 |
| IH-1 [¶] | 0-20 | $0.80~\pm~0.07$ | $2.00~\pm~0.03$ | 60.20 ± 3.20 | 58 ± 2.5 | 45 ± 3.0 | 39 ± 3.3 | 22 ± 1.2 | 17 ± 2.4 | 15 ± 0.4 | 6 ± 0.4 | 44 ± 3.3 |
| PF Typi | c Haplud | and under pine | forest | | | | | | | | | |
| PF-1 | 0-20 | $0.38~\pm~0.03$ | 1.32 ± 0.14 | 70.75 ± 5.35 | 53 ± 0.9 | 46 ± 5.1 | 39 ± 5.2 | 25 ± 4.1 | 14 ± 1.1 | 25 ± 0.3 | 7 ± 0.1 | 37 ± 2.1 |
| PF-2 | 20–40 | $0.38~\pm~0.01$ | $1.63~\pm~0.01$ | 76.65 ± 0.75 | 68 ± 1.7 | 52 ± 0.4 | 44 ± 0.2 | 24 ± 0.8 | 20 ± 0.6 | 25 ± 0.4 | 8 ± 0.3 | 45 ± 1.5 |

WRC, water retention capacity (available water/pF2.54), $D_b =$ bulk density; $\rho_b =$ particle density; $P_T =$ total porosity.

Note: Numbers within a column are average (\pm standard error) of triplicate samples.

[†] FH Fallow area adjacent to the IH intensively cultivated site fallowed since September 2006.

[¶] IH Intensively cultivated site for horticultural crops with horse manure additions starting in September 2006.

0.46 g cm⁻³), characteristic of soils formed in volcanic ash (Table 2). D_b was also low in the A horizon of the pine forest (PF) (0.38 g cm⁻³), but was higher under agricultural management (0.55–0.80 g cm⁻³) due to traffic compaction resulting in a reduced pore volume. The agricultural soils displayed a distinct increase in D_b and a reduction in total porosity (especially macropores) in the topsoil horizons compared to the pine forest soil. Given the low bulk densities, total porosity was correspondingly high, ranging between 60 and 77%, with values decreasing in surface horizons with agricultural management.

Plant-available soil water (water held between pF2.5 and pF4.2) was generally in a narrow range (mostly 20–22%) with the exception of the surface horizons of the pine forest soil (14%) (Table 2). The water retention capacity (ratio between available water content and pF2.5 water content) varied from 37 to 53% in topsoil horizons and from 45 to 51% in subsoil horizons with the lowest values in the pine forest.

3.2. Soil acidity and exchangeable cations

Soil pH-H₂O increased from very strongly acid in the pine forest (4.4–4.5) and tea plantation (4.7–4.9) to moderately acid in the horticultural crops with fallow (5.2–5.6) and intensive cultivation (5.6–6.1) (Table 1). Regardless of land use, all soils in this study had low CEC (6.2 to 9.9 cmol_c kg⁻¹) characteristic of acidic Andisols dominated by allophanic materials (Table 1). The lowest values occurred in the pine forest and the highest values in the horticultural soils. The pH_{KCI}-pH_{H2O} (Δ pH) values ranging between – 0.1 and – 0.5 were indicative of a soil colloidal fraction dominated by variable charge materials (Nanzyo et al., 1993a). Especially notable is the very low base saturation (16 – 23%) (Table 1) and concentrations of exchangeable Ca and Mg for the PF and TP soils (1.5 and 0.3 cmol_c kg⁻¹, respectively) (Fig. 2). Exchangeable base cations (Ca, Mg and K) are a common limiting factor for horticultural production in the studied Andisols since these nutrient cations are extremely low under pine forest.

While the horticultural management practice of applying horse manure and lime did not appreciably increase the measured CEC, it was remarkably effective in increasing exchangeable base cations (Fig. 2). For example, exchangeable Ca, Mg and K increased from 1.5, 0.3 and 0.2 cmol_c kg⁻¹ in the pine forest to 26.3, 3.5 and 1.0 cmol_c kg⁻¹ in the intensive horticultural crops, respectively (Fig. 2). The high base saturation of over 100% under horticultural land uses (FH and IH) compared to < 23% for the pine forest and tea plantation (PF and TP soils) (Table 1).

3.3. Total and dissolved soil carbon C, and nutrient dynamics

Organic C concentration in A horizons was highest in PF (8.0%) and 1.0 to 2.0% lower under agricultural management (Table 1). In contrast, organic C was lower in the PF subsoil (3.2-3.5%) while the agricultural sites had elevated organic C concentrations (2.7-7.5%) in several subsoil horizons. Organic C stocks in the upper 100 cm of the soil profile were calculated by summing the organic carbon stocks in each individual horizon (thickness × bulk density × organic carbon concentration; no coarse fragments (> 2-mm) were present). Organic carbon stocks followed (kg m⁻²): TP (29.0) \approx IH (28.7) > FH (25.0) > PF (16.7). The agricultural soils contained more organic carbon than the pine forest soil. While horse manure $(20 \text{ Mg ha}^{-1} \text{ yr}^{-1})$ was added to the IH soil for the past 7 years, the TP and FH soils received no organic matter amendments and still had similar pedon organic matter stocks. As a direct comparison, the IH soil receiving horse manure contained only slightly more organic C (29 kg m^{-2}) than the FH soil (25 kg m^{-2}) located 4 m away that received no horse manure and was fallowed over the past 7 years. Dissolved organic carbon (DOC) concentrations (extracted by 0.5 M K₂SO₄) were appreciably higher in the PF topsoil (860 mg kg $^{-1}$) and throughout subsoil horizons of the TP profile (420–900 mg kg $^{-1}$) (Fig. 3). The horticultural soils (IH and FH) tended to have lower overall DOC concentrations $(100-400 \text{ mg kg}^{-1})$ than PF and TP land uses.

Total N concentrations followed a similar distribution to organic C concentrations among sites with total N stocks in the upper one meter of soil following (kg m⁻²): IH (2.3) > FH (1.8) \approx TP (1.7) > PF (1.0) (Table 1). The C:N ratio (mass basis) was lowest in the upper 50 cm of the IH and FH soil profiles (11 – 13), while values for PF, TP and lower soil horizons at all sites were generally in the range 16 to 19. The highest concentrations of inorganic N (KCl-extractable NO₃⁻ and NH₄⁺) were found in the IH pedon (25–40 mg N kg⁻¹) and were dominated by NO₃⁻ (Fig. 4). In contrast to the IH soil dominated by NO₃⁻, inorganic N concentrations were dominated by NH₄⁺ in the TP, FH and PF soils with the highest value in the TP soil and lowest under FH land use.

High P fixation (> 80%), characteristic of Andisols, was exhibited for all land-use types. Under forest vegetation (PF), the soil P retention was consistent at 97% throughout the entire pedon (Fig. 5). Change of land use to TP and FH did not appreciably affect P fixation. However, the IH land use receiving application of horse manure for the past 7 years showed appreciably lower P fixation (< 87%) in the upper 40 cm. Reflecting the high P fixation, available P content was below the detection limit (< 0.5 mg kg⁻¹) for all horizons of all land-use types, except for the upper horizons (0–48 cm) of the IH land use (3.0–7.7 mg kg⁻¹) (Table 3).



Fig. 2. Changes in exchangeable cations of Andisols under different land uses and management: (a) Ca, (b) Mg, (c) K and (d) Na. Notes: TP, tea plantation; FH, fallow area of former intensive horticultural crops; IH, intensive horticultural crops with horse manure application and some inorganic fertilizer (NPK); PF, pine forest.

Extractable SO₄-S content was considerably higher in the PF and TP pedons (524 – 898 mg kg⁻¹) as compared to the horticultural pedons (IH and FH range 52–272 mg kg⁻¹). Change of land use from pine forest to agriculture decreased extractable S content. The exception is the TP pedon that contains high S due to application of kieserite (MgSO₄·H₂O) as an integral part of tea plantation fertilizer management. Extractable micronutrient concentrations showed the following general order of abundance: Fe \gg Mn > Cu > Zn (Table 3). In terms of land-use, micronutrient levels followed the general pattern of IH > FH > TP > PF.

3.4. Microbial biomass C and C mineralization

Microbial biomass C (MBC) sharply decreased in the topsoil (A horizon) due to land-use change from forest (330 mg kg^{-1}) to agricultural production (< 118 mg kg⁻¹) (Fig. 6). In subsoil horizons (Bw3), MBC values were slightly higher in the TP and PF soils

 $(50-90 \text{ mg kg}^{-1})$ as opposed to the intensive horticultural soils (FH and IH; 15–60 mg kg⁻¹). In addition, MBC sharply decreased from topsoil (330 mg kg⁻¹) to subsoil layers (80 mg kg⁻¹) under PF land use, while MBC generally increased with soil depth under IH land use.

Carbon mineralization from the laboratory incubation showed the following rates (mg CO₂-C kg⁻¹ soil C): PF > TP > IH > FH in both topsoil and subsoil horizons (Fig. 7). In topsoil horizons, CO₂ emissions increased to a maximum at day 7, decreased to a relatively stable plateau between 21 and 47 days, and then declined through the remainder of the 119-day incubation. For subsoil horizons, CO₂ emission rates followed the same trend for land-use types as the topsoil horizons. A distinct contrast between topsoil and subsoil horizons was the longer time required to achieve the maximum CO₂ emission rate for the subsoil horizons (35 vs 7 days). In all cases, the CO₂ emission was higher for the topsoil horizon (Fig. 7a) as compared to their corresponding subsoil horizon (Bw3) (Fig. 7b), ranging from 8 – 12 times higher on day 7, to 2–4 times higher over the last 20 days of the incubation.



Fig. 3. Changes in total dissolved organic C of Andisols under different land uses and managements.

3.5. Correlation matrix of important soil properties of Andisols

There were several significant correlations among soil properties (Table 4). Oxalate-extractable Si_o showed a positive correlation with the clay fraction, while Fe_o had a strong negative correlation with pH and exchangeable Ca and Mg. In contrast, Al_o showed no significant correlations with other soil properties. For organo-metal complexes (*i.e.*, pyrophosphate extractable Fe/Al), Al_p had highly negative and positive correlations with the clay fraction and organic C, respectively. However, Fe_p showed no significant correlations with other soil properties. Soil pH showed a highly negative correlation with P retention and Fe_o, along with a positive correlation with exchangeable cations (Ca, Mg and K), total N and D_b. Soil bulk density (D_b) showed a positive correlation with P retention with P retention. P retention had a negative correlation with exchangeable cations (Ca, Mg and K).



Fig. 5. Changes in P retention of Andisols under different land uses and managements. Notes: TP, tea plantation; FH, fallow practice of initially used for intensive horticultural crops; IH, intensive horticultural crops with organic manure (horse manure and inorganic fertilizer); PF, pine forest.

4. Discussion

4.1. Changes in physical properties associated with land use

Andisols are characterized by low D_b and high porosity due to the abundance of amorphous and poorly crystalline materials and organic matter that contribute to highly stable and very well structured soils under natural conditions. However, the low natural D_b may change due to anthropogenic activities. The evidence was revealed by soil tillage under intensive horticultural crops contributing to increased D_b from compaction by potential destruction of soil aggregates due to physical mixing/abrasion by tillage operations. Tillage was reported to destroy macropore pathways of Andisols in Mexico resulting in a lower infiltration and permeability of topsoil horizons (Prado et al., 2011).



Fig. 4. Changes in N mobility of Andisols under different land uses and managements: (a) NO_3 -N and (b) NH_4 -N. Notes TP = Tea plantation, IH intensive horticultural crops, PF pine forest, FH bare fallow system at the site which was initially used for intensive horticultural crops.

Table 3

| Cł | nanges | in | available | Ρ, | S | and | mi | cronutr | ients | under | different | land | uses. |
|----|--------|----|-----------|----|---|-----|----|---------|-------|-------|-----------|------|-------|
|----|--------|----|-----------|----|---|-----|----|---------|-------|-------|-----------|------|-------|

| Soil/ | Depth | Bray-P | SO ₄ -S | DTPA extraction | | | | | | | | | |
|----------|---|------------------------------|----------------------|---------------------|-------|-------|------|--|--|--|--|--|--|
| HOLIZOII | | | | ZII | WIII | Cu | re | | | | | | |
| | cm | | | mg kg ⁻¹ | | | | | | | | | |
| TP Typic | TP Typic Hapludand under tea plantation | | | | | | | | | | | | |
| Ap | 0–24 | < 0.5 | 621 | 0.4 | 1.5 | 1.3 | 29.7 | | | | | | |
| Bw1 | 24–54 | < 0.5 | 524 | 0.2 | 1.7 | 1.4 | 31.8 | | | | | | |
| Bw2 | 54-88 | < 0.5 | 623 | < 0.1 | 1.3 | 0.5 | 30.9 | | | | | | |
| Bw3 | 88-130 | < 0.5 | 898 | < 0.1 | < 0.1 | < 0.1 | 9.7 | | | | | | |
| FH Typic | Melanudan | d under horticultural crops | s with fallow system | | | | | | | | | | |
| Ap | 0-21 | < 0.5 | 158 | 0.5 | 5.4 | 2.3 | 29.3 | | | | | | |
| Bw1 | 21-48 | < 0.5 | 114 | 0.5 | 5.5 | 2.3 | 35.0 | | | | | | |
| Bw2 | 48–70 | < 0.5 | 114 | 0.3 | 4.8 | 1.8 | 29.9 | | | | | | |
| 2Bw3 | 70–118 | < 0.5 | 272 | < 0.1 | 1.0 | 0.5 | 19.9 | | | | | | |
| IH Typic | Melanudano | d under intensive horticultu | ural crops | | | | | | | | | | |
| Ap | 0-21 | 7.7 | 52 | 7.2 | 7.0 | 10.3 | 29.0 | | | | | | |
| Bw1 | 21-48 | 3.0 | 161 | 4.0 | 7.0 | 6.5 | 29.7 | | | | | | |
| Bw2 | 48–70 | < 0.5 | 257 | 0.4 | 3.6 | 1.2 | 21.7 | | | | | | |
| Bw3 | 70-110 | < 0.5 | 223 | 0.1 | 2.3 | 1.0 | 24.4 | | | | | | |
| PF Typic | Hapludand | under pine forest | | | | | | | | | | | |
| Α | 0-24 | < 0.5 | 585 | 0.1 | 1.1 | 0.5 | 19.4 | | | | | | |
| Bw1 | 24-60 | < 0.5 | 874 | < 0.1 | 0.1 | < 0.1 | 6.1 | | | | | | |
| Bw2 | 60-100 | < 0.5 | 874 | < 0.1 | 0.1 | < 0.1 | 6.2 | | | | | | |
| Bw3 | 100–140 | < 0.5 | 835 | < 0.1 | < 0.1 | < 0.1 | 6.7 | | | | | | |



Fig. 6. Microbial biomass C distribution with soil depth in different land uses of Andisols. Notes: PF = pine forest, TP = tea plantation, FH = former intensive horticulture with now fallow system, IH = FH intensive cultivation system for horticulture.

Chemically, the exchangeable cations (Ca, Mg and K) have positive significant correlation with D_b , indicating the increase in soil exchangeable cations gave rise to the increased soil bulk density (D_b). This is probably due to the role of Ca and Mg ions derived from lime and manure in binding soil particles, resulting in the change of soil friable structure under forest to more compact aggregate formation under intensive horticultural cultivation.

The water retention capacity (WRC) varied from 37 to 53% in topsoil horizons and from 45 to 51% in subsoil horizons with the lowest values in the pine forest (37%) (Table 2). These data indicate that the number of soil pores storing plant-available water (0.2–8.6 μ m pore sizes or pF4.2 - pF2.5 suction) is lower in the forest Andisols than those converted for agriculture. In other words, the water retention capacity has increased about 50% following conversion from pine forest to agriculture. This implies that the compaction associated with tillage is responsible for increasing the water retention capacity through conversion of macropores to meso/micropores. The water retention

capacity in this study was higher than for cultivated Mexican Andisols (23% to 45%) reported by Prado et al. (2011). The high water retention in Andisols is caused primarily by their large volume of meso/micropores (Nanzyo et al., 1993b). Formation of these meso/micropores is greatly enhanced by poorly crystalline materials and soil organic matter (Van Ranst et al., 2002). Buytaert et al. (2006) studied toposequece of Andisols in south Ecuador and reported the large water storage capacity as revealed by water content ranges from $2.64 g g^{-1}$ at saturation, down to $1.24 g g^{-1}$ at wilting point.

The long-term (> 100 years) cultivation of agricultural soils in this study has not caused appreciable degradation to the overall Db, porosity or water retention characteristics of these Andisols. While macroporosity was decreased by tillage, the macropore content of topsoil horizons remained > 15% providing adequate infiltration and soil aeration. The loss of macropores is compensated for by the increase in meso/micropores that contribute to increased plant-available water holding capacity. In spite of the increase of bulk density (from 0.4 to 0.6–0.8 g cm⁻³) and loss of macropore capacity, field observations confirmed that the agricultural soils in this study retained their high infiltration capacity with no evidence of surface runoff. In Italy, well developed Andisols on flow-like landslides over 70 years experienced low run off and minimal soil erosion owing to a good infiltration in spite of the high slope steepness and the anthropic pressure associated with land management (Scognamiglio et al., 2019).

4.2. Changes in chemical properties associated with land use

The pine forest soil was very strongly acidic owing to the strong leaching regime associated with the isothermic/perudic climatic regime. Applications of lime and more recently horse manure to the IH soil were effective in raising the pH of the horticultural soils (Table 1). In spite of the low soil pH values in the tea plantation, the potential for Al^{3+} toxicity was not evident as ascribed to the low exchangeable Al^{3+} concentrations (< 0.4 cmol_c kg⁻¹). Threshold values for Al toxicity are generally considered about 2 cmol_c kg⁻¹ for common agricultural crops and 1 cmol_c kg⁻¹ for Al-sensitive crops (Dahlgren et al., 2004). Andisols dominated by allophanic materials generally contain low KCl-extractable Al concentrations; however, these values may be underestimated due to "induced hydrolysis" of displaced Al and subsequent adsorption of polymeric Al to allophanic materials (Wada, 1987a, b). The elevated pH associated with the horticultural soils reduced the exchangeable Al^{3+} concentrations to non-detectable levels (< 0.01)



Fig. 7. Changes in microbial C emission from Andisols as affected by different land uses: (a) topsoil and (b) subsoil. Notes TP = Tea plantation, IH intensive horticultural crops, PF pine forest, FH fallow system at the site which was initially used for intensive horticultural crops.

Murdoch, 2005).

values of the IH soil may contribute to more favorable conditions for

nitrification leading to the lower NH₄⁺ and higher NO₃⁻ concentrations

found in the profile. Similar results were reported following forest

timber harvest where soil NO3- increased up to 8-fold shortly after

harvest (1 yr) as compared to pre-harvest conditions (Burns and

Tani et al., 2002; Katou et al., 1996). This range of AEC values corre-

sponds to 56 to 1700 mg NO₃-N kg⁻¹, which appears sufficient to accommodate the KCl-extractable NO_3^- concentrations that range up to

 35 mg NO_3 -N kg⁻¹ in the IH profile. Evaluation of N content in Java

Island, Indonesia with different soil types and land uses showed higher

soil N content in Andisols was associated with the presence of nano-

crystalline materials (Yanai et al., 2014). Retention of NO₃⁻ within the

soil profile reduces nitrate leaching and provides a readily available N

sistently high (97%) throughout the entire pedon (Fig. 5). In contrast,

the IH land use receiving application of horse manure for the past

Under pine forest vegetation (PF), the soil P retention was con-

supply for deeply-rooted crops (Auxtero et al., 2004).

Previous studies measured anion exchange capacity (AEC) of allophane-rich soils ranging from 0.4 to $12.2 \text{ cmol}_c \text{ kg}^{-1}$ (Ryan et al., 2001;

cmol_ckg⁻¹), further reducing the potential for Al³⁺ toxicity.

A notable findings in this study was the increase in soil pH and base saturation following land use changes as revealed by the strongly positive correlation (up to $r = 0.97^{**}$) between soil pH and exchangeable cations (Table 4). The high base saturation (> 100%) under horticultural land uses (FH and IH) as compared to < 23% for the pine forest and tea plantation soils (Table 1) is associated with the presence of soluble salts (Ca, Mg and K) derived from lime, horse manure and K-fertilizer application. These soluble salts derived from the agricultural amendments are beneficial to soil fertility as they can be readily taken up by roots to meet plant nutrient requirements.

Conversion of pine forest (PF) to intensive horticultural crops (IH) resulted in the increase of nitrate content by 4–7 fold (from 5 to 22–35 mg NO₃-N kg⁻¹) (Fig. 4). This high concentration of nitrate is explained in part by mineralization of horse manure and urea $(150 \text{ kg ha}^{-1} \text{ season}^{-1})$ applications and the presence of positive charge on surfaces of nanocrystalline materials (e.g. allophane) to retain anions. According to Auxtero et al. (2004) the positive charge of subsurface allophane-rich horizons allowed Andisols to retain mobile anions such as nitrate, which is beneficial for crops. Further, the higher pH

Table 4

| Tuble 1 | | | | | | | | |
|-------------|--------|-------------|------|------------|----------|----|------|-------|
| Correlation | matrix | of selected | soil | properties | measured | in | this | study |

| Parameter | Silt | Clay | pН | С | Ν | D_b | P _{ret} | Ca | Mg | К | Fep | Al_p | Si _o | Fe _o | Al _o | W_{av} |
|-------------------|--------|---------|--------------|-------|-------|--------|------------------|--------------|--------|-------|-------|--------|-----------------|-----------------|-----------------|----------|
| Silt | 1.00 | | | | | | | | | | | | | | | |
| Clay | -0.50 | 1.00 | | | | | | | | | | | | | | |
| pН | -0.72* | 0.31 | 1.00 | | | | | | | | | | | | | |
| С | 0.49 | -0.66 | -0.03 | 1.00 | | | | | | | | | | | | |
| Ν | -0.21 | -0.13 | 0.72* | 0.64 | 1.00 | | | | | | | | | | | |
| D_b | -0.41 | -0.09 | 0.78* | 0.13 | 0.52 | 1.00 | | | | | | | | | | |
| P _{ret} | 0.51 | -0.19 | -0.88^{**} | 0.01 | -0.58 | -0.85* | 1.00 | | | | | | | | | |
| Ca | -0.62 | 0.33 | 0.97** | -0.05 | 0.68 | 0.83* | -0.92** | 1.00 | | | | | | | | |
| Mg | -0.51 | 0.33 | 0.92** | -0.08 | 0.60 | 0.82* | -0.95** | 0.94** | 1.00 | | | | | | | |
| К | -0.28 | 0.12 | 0.71* | 0.09 | 0.49 | 0.86* | -0.92** | 0.77* | 0.84* | 1.00 | | | | | | |
| Fep | 0.08 | -0.33 | -0.51 | -0.13 | -0.44 | -0.67 | 0.60 | -0.65 | -0.57 | -0.69 | 1.00 | | | | | |
| Alp | 0.61 | -0.87** | -0.52 | 0.72* | 0.02 | 0.02 | 0.40 | -0.53 | -0.57 | -0.20 | 0.19 | 1.00 | | | | |
| Sio | 0.07 | 0.80* | -0.16 | -0.38 | -0.27 | -0.49 | 0.14 | -0.10 | -0.01 | -0.11 | -0.18 | -0.57 | 1.00 | | | |
| Feo | 0.64 | -0.50 | -0.91^{**} | 0.11 | -0.67 | -0.54 | 0.70 | -0.92^{**} | -0.81* | -0.48 | 0.56 | 0.66 | -0.08 | 1.00 | | |
| Al _o | 0.18 | 0.56 | -0.34 | -0.25 | -0.29 | -0.51 | 0.47 | -0.24 | -0.36 | -0.50 | -0.19 | -0.29 | 0.71 | -0.07 | 1.00 | |
| W_{av} | -0.64 | 0.12 | 0.16 | -0.46 | -0.18 | -0.08 | 0.23 | -0.02 | -0.17 | -0.41 | 0.52 | -0.28 | -0.29 | -0.15 | -0.10 | 1.00 |

Notes: n = 8. *, ** significant correlation at (p < 0.05) and (p < 0.01), respectively; Fe_p and Al_p are organo-metal complexes (extracted by pyrophosphate); Si_o, Fe_o and Al_o are amorphous materials (extracted by acid oxalate); P_{ret} = phosphate retention, D_b = bulk density; W_{av} = water availability (water content at pF2.54 - pF4.2).

7 years showed appreciably lowering P retention (< 87%) in the upper 40 cm. The decrease in P retention and the increase of available P in the upper horizons of the IH profile were related to application of horse manure and inorganic SP36 fertilizer (160 kg ha⁻¹ yr⁻¹). These P dynamics could be associated with competition between organic functional groups derived from the horse manure and the applied P for sorption to the hydroxyl functional groups of the allophanic materials. Organic matter functional groups may block some reactive functional groups on allophanic materials, which in turn reduce P retention. In addition, the increase in pH from 4.5 in the PF soil to pH 6.1 in the topsoil of the IH soil may contribute to reduced P retention. This is supported by negative correlation coefficient between P retention and soil pH (Table 4). Maximum phosphate sorption in Andisols often occurs in the pH range of 3.0-4.5 and decreases with increasing soil pH (Nanzyo et al. 1993a). Thus, the application of animal manure and lime appears to be an effective nutrient management strategy to enhance P availability in these high P fixing Andisols.

Higher extractable S concentrations in the PF soil may be due to a combination of enhanced capture of H2S/H2SO4 emissions (from activity of Tangkuban Perahu volcano, 5 km away) by the canopy of the pine forest, low S uptake by the pine forest and/or low soluble PO₄ concentrations that could displace sorbed SO₄. The depth trend for extractable SO₄-S consisted of lower concentrations in the topsoil than the subsoil for pine forest and horticultural land uses. This is related to competition with P and organic matter and with the increase in soil pH for horticultural crops (pH 5.2-6.1). Previous workers have reported that sulfate and phosphate compete for the same anion-binding sites but P is adsorbed stronger than sulfate due to phosphate ions being able to form very strong inner-sphere complexes (Parfitt, 1990; Zhang and Sparks, 1990). In contrast, sulfate forms weaker inner-sphere and outersphere SO₄ sorption complexes on short-range ordered materials, with the former becoming more dominant with decreasing pH and increasing sulfate concentrations (Turner and Kramer, 1991; Sparks 1999; Vacca et al., 2003). Pigna and Violante (2003) reported phosphate sorption 2-5 times greater than sulfate in Andisols and by increasing pH, phosphate sorption slightly decreased, whereas sulfate retention decreased dramatically (at pH 5.5, sulfate sorption was usually very low or negligible). In addition organic matter competes more effectively with sulfate than with phosphate for sorption sites (Barreal et al., 2001), resulting in low S availability in the topsoil horizons with high organic matter in the present study.

Micronutrient availability is typically greater in more acidic soils due to higher metal solubility. In the present study, however, the micronutrient availability was higher in the horticultural soils having a higher pH (\sim 1 unit higher). In particular, the addition of horse manure appears to provide both a source of micronutrients as well as high dissolved and particulate organic matter concentrations to enhance metal solubility by complexation. Therefore, manure additions appear to provide a strong benefit with respect to micronutrient availability for agronomic crops.

4.3. Soil organic matter, microbial biomass, respiration rates and dissolved organic matter

The Andisols in this study contained much higher C stocks to a depth of 1 m $(25-29 \text{ kg C m}^{-2} \text{ for agriculture sites and 17 kg C m}^{-2} \text{ for pine forest})$ as compared to the global average for tropical Oxisols and Ultisols of 9.7 and 8.3 kg m⁻², respectively (Kimble et al., 1990). Further comparison to Oxisols and Ultisols from the Brazilian Amazon had C stocks from 8.5 to 10.5 kg m⁻² (Moraes et al., 1995), which were 2–3 time lower than the tropical Andisols in this study. These comparisons indicate that Andisols have substantially higher capacity than other mineral soils to preserve organic matter. These results are consistent with those of Torn et al. (1997) who concluded that Andisols contain about twice as much organic C per m² than Oxisols or any other soil orders, except for Histosols and Gelisols. Oxisols and Ultisols are

dominated by low activity clays that provide less active mineral surfaces for physical and chemical stabilization of soil organic C (Feller and Beare, 1997). In contrast, N stocks of our tropical Andisols $(1.0-2.3 \text{ kg N m}^{-2})$ were similar in magnitude to Oxisols and Ultisols in the Brazilian Amazon that varied from 0.71 to 2.3 kg N m^{-2} , but mostly from 0.7 to 1.3 kg N m^{-2} in the upper 100 cm (Moraes et al., 1995). Therefore, the Andisols of this study appeared to store organic matter with a higher C/N ratio than Amazonian Oxisols and Ultisols.

Overall, soil carbon and nitrogen stocks in the upper 1 m of soil profiles increased in agricultural soils (25–29 kg C m^{-2} ; 1.7 – 2.3 kg N m^{-2}) compared to the pine forest soil (17 kg C m⁻²; 1 kg N m^{-2} (Table 1). These data appear to suggest degradation of soil organic C and N in the topsoil following conversion to agriculture but compensation by the elevated C and N in subsoils. This condition results from pedon redistribution of organic C concentrations from topsoil to subsoil horizons. This redistribution may be attributed to a decrease in surface litter under agricultural land use with deeper incorporation of organic matter by tillage, and/or deeper rooting system of some horticultural plants. Alternatively, the appreciably higher bulk densities of the agricultural soils contributed to higher organic C stocks compared to the pine forest soil suggesting a role for compaction in increasing C stocks on volumetric basis. Finally, it is possible that periodic volcanic ash deposits have resulted in burial of organic-rich horizons, leading to the high organic matter in subsurface horizons. Importantly, in spite of intensive agricultural production for > 100 years, there was no appreciable loss of organic matter from these soils as has been documented in many soils following conversion of forest vegetation to agricultural purposes. Similarly, Panichini et al. (2017) reported that disturbance of Andisols in Chili by forest management did not alter carbon storage. They posited that organic matter was stabilized by amorphous materials and organo-mineral complex formation, and the humid climate protected soils from irreversible drying and potential carbon loss.

The ability of Andisols to strongly sequester and preserve organic C under various land-use/land management practices was demonstrated by the increase of organic matter in subsoil horizons of agricultural soils compared to the forest soil. In contrast, the lack of an organic matter build up in the topsoil and IH soil receiving horse manure for the last 7 years relative to the FH soil indicate that the added horse manure is quickly mineralized to provide nutrients to the horticultural crops. In addition, the increased N content from inorganic fertilizer may accelerate mineralization of organic C. On the other hand, the zero tillage in the FH soil compared to intensive cultivation in the IH soil. The strong correlation between organic C and Al_p and the lack of a significant correlation between organic C and Si_0 (a measure of allophane content) suggest that Al-organic complexes are more important than allophane in preserving organic matter in these tropical Andisols.

Microbial biomass C (MBC) trends showed a positive relationship with total C and extractable DOC. The most evident change with respect to land use was the large decrease in MBC in the topsoil upon conversion from pine forest to agricultural production (Fig. 6). Surprisingly, the lowest MBC values were found in the IH soil which received regular additions of horse manure for the past 7 years. Extractable DOC is considered an important carbon source to the microbial community and often correlates with microbial biomass. Extractable DOC represented 1.2–1.6% of total soil organic C for the PF and TP compared to < 1% for the IH and FH soils. This suggests that changes in vegetation possibly resulted in changes to the chemical nature of the organic matter affecting DOC solubility, which may affect substrate availability for the microbial community. Overall, agricultural practices had a strong impact in reducing microbial biomass C in topsoil horizons as compared to the pine forest.

The microbial-labile pool of organic C is revealed by C mineralization rates during the incubation period. The overall CO_2 mineralization rates followed PF > TP > IH > FH in both topsoil and subsoil horizons (Fig. 7). This agrees well with the highest DOC concentrations found in the PF soil and indicates more easily decomposable organic C substrates were available in PF soil than agricultural land uses. Interestingly, CO_2 emissions shifted to IH > PF > TP > FH after day 70 in the topsoil, indicating depletion of easily decomposable C in the PF and TP soils. The much lower C mineralization rates in the subsoil than topsoil horizons were accounted for in part by the higher amorphous material content in the former (Table 1). Chevallier et al. (2008) measured transformation of organic matter in volcanic soils by CO_2 respiration and showed that the decomposition decreased as the soil allophane content increased.

The low C mineralization rates for the FH profile (both topsoil and subsoil horizons) is likely due to depletion of the microbial labile C pool as new organic carbon inputs were minimal over the last 7 years due to fallowing of the soil. All land-use systems showed much higher C mineralization rates in the topsoil than subsoil horizons. This suggests that the topsoil contains more labile C substrate than subsoil horizons. According to Kavdir et al. (2005), the fresh litter contained labile and easily decomposed materials, which mainly consisted of O-alkyl C. Inputs of new organic matter will be preferentially incorporated into the topsoil horizons and organic matter in the subsoil horizons is likely more strongly stabilized by physical and chemical mechanisms. The formation of metal-humic complexes was shown by positive linear correlation between dissolved organic C with Al- and Fe- extracted by Na-pyrophosphate (Fig. 8). Determinant coefficients (R²) for Al and Fe were 0.84 and 0.80, respectively, suggesting that about 80% of dissolved organic C was bonded to the short-range ordered materials. The fraction of soil organic C bonded to Al and Fe (metal-humus complexes) varied from 25 to 50% with the magnitude following TP > FH > PF > IH in the topsoil and middle portions of the profiles (Fig. 9). In contrast, the organic carbon bonded to metals in the lower pedon followed: IH > TP ~ PF > FH. Previous studies on mineral control of carbon pool in Andisols in the Réunion Island (700 km east Madagascar) showed the largest proportion of organic matter (83%) occurred as organo-mineral complexes (Basile-Doelsch et al., 2007). The lower metal-humus complexes of Andisols in the present study as compared to Andisols from Réunion Island could be associated with the higher annual rainfall and temperature under tropical conditions (1902 mm and 20 °C vs 1700 mm and 13 °C) that accelerated organic matter decomposition. In our study the negative correlation between soil pH and Fe_p



Fig. 8. Correlation between organic C and Al and Fe as extracted by Na-pyrophosphate from Andisols of different land uses.



Fig. 9. Normalized distribution of organic C fraction bonded to Al- and Femetal (dissolved organic C in Na-pyrophosphate) within soil profiles for different land uses.

and Al_p was observed indicating favorable conditions for organo-metal complex formation under acidic conditions (Table 4). Tonneijck et al. (2010) suggested SOM stabilization in volcanic ash soils in natural Andean ecosystems of Ecuador is through organo-metallic (Al-humus) complex formation, low soil pH and toxic levels of Al, and physical protection of SOM in a very large micro-porosity.

5. Conclusions

The long-term (> 100 years) cultivation of tropical Andisols for agricultural crops in this study did not caused degradation to the soil physical properties. Tillage resulted in a small increase in bulk density and a small loss of macropores that was compensated for by the increase in meso/micropores that contributed to increased plant-available water holding capacity. Conversion of the pine forest to agricultural land use appears to result in an increase of soil carbon stocks on a pedon basis for the upper meter of soil (agricultural soils = 25–29 kg/m² vs pine forest = 17 kg/m²). Andisols used for horticultural crops had the lowest rates of carbon mineralization per unit soil carbon and lowest microbial biomass C as compared to pine forest indicating a strong ability to sequester additional C, thereby providing a positive impact on C mitigation.

The overall CO_2 mineralization rates followed pine forest > tea plantation > intensive horticulture > fallow of former horticultural use in both topsoil and subsoil horizons. Microbial biomass C (MBC) sharply decreased in the topsoil horizon due to land-use change from forest (330 mg kg⁻¹) to agricultural production (< 118 mg kg⁻¹). In subsoil horizons, MBC values were slightly higher in the tea plantation and pine forest soils (50–90 mg kg⁻¹) as opposed to the intensive horticultural soils (FH and IH; 15–60 mg kg⁻¹). In addition, the MBC sharply decreased from topsoil (330 mg kg⁻¹) to subsoil layers (80 mg kg⁻¹) in the pine forest land use, while the MBC tends to increase with soil depth in IH land use.

Extractable mineral NO₃-N concentrations in Andisols varied from 2 to 35 mg kg⁻¹ with the order of magnitude for land use following intensive horticulture > tea plantation > fallowed horticulture ~ pine forest. Horse manure additions reduced soil P retention and increased available P concentrations on the intensive horticultural land uses. Exchangeable base cations (Ca²⁺, Mg²⁺ and K⁺) and micronutrients (Zn, Mn and Cu) concentrations increased sharply under horticultural land uses compared to the pine forest and tea plantation soils. Soil pH values were also increased by more than one unit under horticultural

land use as compared to pine forest and tea plantation, which were both strongly acidic.

This study suggests that the tropical Andisols examined in this study are relatively resilient to long-term degradation resulting from conversion of rainforest to agronomic land use. These findings are consistent with Andisols in Indonesia having among the highest humancarrying capacities on Earth. Andisols with their unique properties and exceptionally high capability to sequester C with good management could play an important role in global C sequestration and reduce global warming, in addition to contributing to very productive agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

We would like to thank the Agency of Agricultural Research and Development, Ministry of Agriculture, Indonesia, for financial and technical support through SMARTD project. We acknowledge Mrs. Eviati (Centre for Agricultural Land Resource Research and Development) for her assistance in the laboratory work. We also thank the Director of the Indonesian Vegetable Research Institute for giving us permission to sample the soils from the experimental plots.

References

- Auxtero, E., Madeira, M., Sousa, E., 2004. Variable charge characteristics of selected Andisols from the Azores, Portugal. Catena 56, 111–125.
- Barreal, M.E., Arbestain, M.C., Macías, F., Fertitta, A.E., 2001. Phosphate and sulfate retention by nonvolcanic soils with andic properties. Soil Sci 166, 691–707.
- Basile-Doelsch, I., Amundson, R., Stone, W.E.E., Borschneck, D., Bottero, J.Y., Moustier, S., Masin, F., Colin, F., 2007. Mineral control of carbon pools in a volcanic soil horizon. Geoderma 137. 477–489.
- Batjes, N.H., 2014. Total carbon and nitrogen in the soils of the world. Eur. J. Soil Sci. 65, 4–21.
- Blakemore, L.C., Searle, R.L., Daly, B.K., 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Science. Report 80. New Zealand Society of Soil Science. Lower Hutt.
- Blake, G.R., 1986. Particle density. In: Klute, A. (Ed.), Methods of Soil Analysis, part I. Physical and Mineralogical methods: Agronomy Monograph no. 9 (2nd ed.), ASA SSSA., Madison, WI, pp. 363–375.
- Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed.), Methods of Soil Analysis, Part I. Physical and Mineralogical Methods: Agronomy Monograph no. 9 (2nd ed.), ASA SSSA., Madison, WI, pp. 377-382.
- Burns, D.A., Murdoch, P.S., 2005. Effects of clear cut on the net rates of nitrification and N mineralization in a northern hardwood forest, Catskill Mountains, New York, USA. Biogeochemistry 72, 123–146.
- Buytaert, W., Deckers, J., Wyseure, G., 2006. Description and classification of nonallophanic Andosols in south Ecuadorian alpine grasslands (páramo). Geomorphology 73, 207–221.
- Carlson, K.M., Curran, L.M., Ratnasari, D., Pittman, A.M., Soares-Filho, B.S., Asner, G.P., Trigg, S.N., Gaveau, D.A., Lawrence, D., Rodrigues, H.O., 2012. Committed carbon emissions, deforestation, and community land conversion from oil palm plantation expansion in West Kalimantan, Indonesia. Proc. Natl. Acad. Sci. USA 109, 7559–7564.
- Chartres, C.J., Van Reulert, H., 1985. Mineralogical changes with depth in a layered Andosol near Bandung, Java (Indonesia). J. Soil Sci. 36, 173–186.
- Cherubin, M.R., Franco, A.L.C., Cerri, C.E.P., da Silva Oliveira, D.M., Davies, C.A., Cerri, C.C., 2015. Sugarcane expansion in Brazilian tropical soils-Effects of land use change on soil chemical attributes. Agr. Ecosyst. Environ. 211, 173–184.
- Chevallier, T., Woignier, T., Toucet, J., Blanchart, E., Dieudonne, P., 2008. Fractal structure in natural gels: effect on carbon sequestration in volcanic soils. J. Sol-Gel Sci. Techn. 48, 231–238.
- Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. The nature, properties and management of volcanic soils. Adv. Agron. 82, 113–182.
- Deng, M., Kimura, S.D., Lee, J., Hojito, M., Yoh, M., 2011. Denitrification on Andosols in an intensive dairy farming region of central Japan. Agr. Ecosyst. Environ. 144, 330–337.
- Doane, T.A., Horwath, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36, 2713–2722.
- FAO, 2006.Global Forest Resources Assessment 2005: Progress Towards Sustainable Forest Management. FAO Forestry paper 147. Rome.

- FAO. 2016. State of the World's Forests 2016. Forests and agriculture: land-use challenges and opportunities. Rome. 126 p.
- Feller, C., Beare, M.H., 1997. Physical control of soil organic matter dynamics in the tropics. Geoderma 79, 69–116.
- Fierer, N., Strickland, M.S., Liptzin, D., Bradford, M.A., Cleveland, C.C., 2009. Global patterns in belowground communities. Ecol. Lett. 12, 1238–1249.
- Forster, J.C., 1995. Soil nitrogenMethods in Applied Soil Microbiology and Biochemistry. Academic Press, pp. 79–87.
- Horwath, W.R., Paul, E.A., 1994. Microbial biomassMethods of Soil Analysis. Soil Sci. Soc. Am, Madison, WI, pp. 753–773.
- Houghton, R.A., 2002. Temporal patterns of land-use change and carbon storage in China and tropical Asia. Sci. China Life Sci. 45, 10–17.
- Huygens, D., Boeckx, P., Templer, P., Paulino, L., Van Cleemput, O., Oyarzun, C., Müller, C., Godoy, R., 2008. Mechanisms for retention of bioavailable nitrogen in volcanic rainforest soils. Nat. Geosci. 1, 543–548.
- Kallenbach, C., Grandy, A.S., 2011. Controls over soil microbial biomass responses to carbon amendments in agricultural systems: a meta-analysis. Agr. Ecosyst. Environ. 144, 241–252.
- Katou, H., Chlotier, B.E., Green, S.A., 1996. Anion transport involving competitive adsorption during transient water flow in Andisol. Soil Sci. Soc. Am. J. 47, 1247–1251.
- Kavdir, Y., Ekinci, H., Yuksel, O., Mermut, A.R., 2005. Soil aggregate stability and ¹³C CP/ MAS-NMR assessment of organic matter in soils influenced by forest wildfires in Canakkale, Turkey. Geoderma 129, 219–229.
- Kimble, J.M., Swaran, H., Cook, T., 1990. Organic carbon on a volume basis in tropical and temperate soils. pp. 248-258. In Trans Int. Congr. Soil Sci 14th, Kyoto Japan. 12-18 Aug.1990. Vol. 5 ISSS, Wageningen, The Netherlands.
- Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42, 421–428.
- Ministry of Forestry., 2014. Ministry of Forestry Statistics 2013. Jakarta, Indonesia. Matus, F., Rumpel, C., Neculman, R., Panichini, M., Mora, M.L., 2014. Soil carbon storage and stabilisation in andic soils: A review. Catena 120, 102–110.
- Matus, F., Stock, S., Eschenbach, W., Dyckmans, J., Merino, C., Na'jera, F., Koster, M., Yakov Kuzyakov, Y., Dippold, M.A., 2019. Ferrous Wheel Hypothesis: Abiotic nitrate incorporation into dissolved organic matter. Geochim. Cosmochim. Acta 245, 514–524.
- Moraes, J.L., Cerri, C.C., Melillo, J.M., Kicklighter, D., Neill, C., Skole, D.L., Steudler, P.A., 1995. Soil carbon stocks of the Brazilian Amazon basin. Soil Sci. Soc. Am. J. 59, 244–247.
- Nanzyo, M., Dahlgren, R., Shoji, S., 1993a. Chemical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), Volcanic Ash Soils, Genesis, Properties and Utilization. Elsevier, Tokyo, Japan, pp. 145–187.
- Nanzyo, M., Dahlgren, R., Shoji, S., 1993b. Physical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), Volcanic Ash Soils, Genesis, Properties and Utilization. Elsevier, Tokyo, Japan, pp. 189–207.
- Olsen, S. R., Sommers, L. E., 1982. Phosphorus. In: Page, A. L. et al. (Eds.), Methods of soil analysis: Part 2. Chemical and microbiological properties. Agron. Mongr. 9. 2nd ed. ASA and SSSA, Madison, WI. pp. 403-430.
- Panichini, M., Neculman, R., Godoy, R., Arancibia-Mirandac, N., Matus, F., 2017. Understanding carbon storage in volcanic soils under selectively logged temperate rainforests. Geoderma 302, 76–88.

Parfitt, R.L., 1990. Allophane in New Zealand: a review. Aust. J. Soil Res. 28, 343–360. Parfitt, R.L., Wilson, A.D., 1985. Estimation of allophane and halloysite in three se-

- quences of volcanic soils. In: Fernandez-Cal-dos, E., Yaalon, D.H. (Eds.), Volcanic Soils, Weathering and Landscape Relationships of Soils on Tephra and Basalt. ISSS-AISS-IBG. Cremlingen, Catena. Suppl., vol. 7, pp. 1-8.
- Parfitt, R.L., Childs, C.W., 1988. Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Mossbauer methods. Aust. J. Soil Res. 26, 121–144.
- Pigna, M., Violante, A., 2003. Adsorption of sulfate and phosphate on Andisols. Commun. Soil Sci. Plant Anal. 34, 2099–2113.
- Prado, B., Duwig, C., Etchevers, J., Gaudet, J.P., Vauclin, M., 2011. Nitrate fate in a Mexican Andosol: is it affected by preferential flow? Agr. Water Manage. 98, 1441–1450.
- Ryan, M.C., Graham, G.R., Rudolph, D.L., 2001. Contrasting nitrate adsorption in Andisols of two coffee plantations in Costa Rica. J. Environ. Qual. 30, 1848–1852.
- Schulte, E.E., Eik, K., 1988. Recommended sulfate-sulfur test. W.C. Dahnke (Ed.), Recommended chemical soil test procedures for the North Central Region, North Central Region Publication no. 221, pp. 17-19.
- Scognamiglio, S., Basile, A., Calcaterra, D., Iamarino, M., Langella, G., Moretti, P., Vingiani, S., Terribile, F., 2019. Andic soils and flow-like landslides: Cause-effect evidence from Italy. Land Degrad. Dev. 30, 128–140.
- Shoji, S., Nanzyo, M., Dahlgren, R., 1993. Productivity and utilization of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds), Volcanic Ash Soils: Genesis, Properties and Utilization. Developments in Soil Science 21. Elsevier, Amsterdam. pp. 209–251.
- Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F., Rice, C., Scholes, B., Sirotenko, O., Howden, M., McAllister, T., Pan, G., Romanenkov, V., Schneider, U., Towprayoon, S., Wattenbach, M., Smith, J., 2008. Greenhouse gas mitigation in agriculture. Phil. Trans. R. Soc. B 363, 789–813.
- Soil Survey Laboratory Staff, 1992. Soil Survey Laboratory Methods Manual. Soil Survey Investigation Report No. 42, Version 2.0, USDA.
- Soil Survey Staff, 2014. Keys to Soil Taxonomy, 12th ed. USDA-Natural Resources. Conservation Service, Washington, DC.
- Sparks, D.L., 1999. Kinetics and mechanisms of chemical reactions at the soil mineral/ water interface. In: Sparks, D.L. (Ed.), Soil Physical Chemistry. CRC Press, Boca Raton, pp. 135–191.

- Tani, M., Okuten, T., Koike, M., Kuramochi, K., Kond, R., 2002. Nitrate adsorption in some Andisols developed under different moisture conditions. Soil Sci. Plant Nutr. 50, 439–446.
- Tonneijck, F.H., Jansena, B., Nierop, K.G.J., Verstratena, J.M., Sevink, J., De Lange, L., 2010. Towards understanding of carbon stocks and stabilization in volcanic ash soils in natural Andean ecosystems of northern Ecuador. Eur. J. Soil Sci. 61, 392–405. Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., Hendricks, D.M., 1997.
- Mineral control of soil organic C storage and turnover. Nature 389, 170–173. Tubiello, F.N., Salvatore, M., Rossi, M.S., Ferrara, A., Fitton, N., Smith, P., 2013. The
- FAOSTAT database of greenhouse gas emissions from agriculture. Environ. Res. Lett. 8, 1–10. Turner, L.J., Kramer, J.R., 1991. Sulfate ion binding on goethite and hematite. Soil Sci.
- 10rner, L.J., Kramer, J.R., 1991. Sulfate ion binding on goethite and nematite. Soil Sci. 152, 226–230.

Vacca, A., Adamo, P., Pigna, M., Violante, P., 2003. Genesis of tephra-derived soils from the Roccamonfina Volcano, Central-Southern Italy. Soil Sci. Soc. Am. J. 67, 198–207. Van Ranst, E., Utami, S.R., Shamshuddin, J., 2002. Andisols on volcanic ash from Java Island, Indonesia: physico-chemical properties and classification. Soil Sci. 167, 68–79.

- Voroney, R.P., Winter, J.P., Gregorich, E.G., 1991. Microbe/plant soil interactions. In: Coleman, D.C., Fry, B. (Eds.), Carbon Isotopes Techniques. Academic Press, New York, pp. 77–99.
- Wada, S.I., 1987a. Critical evaluation of 1M KCl- extraction method for determining exchangeable Al ions in variable charge soils. Soil Sci. Plant Nutr. 33, 153–160.
- Wada, S.I., 1987b. 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.
- Yanai, J., Omoto, T., Nakao, A., Koyama, K., Hartono, A., Anwar, S., 2014. Evaluation of nitrogen status of agricultural soils in Java. Indonesia. Soil Sci. Plant Nutr. 60, 188–195.
- Zhang, P.C., Sparks, D.L., 1990. Kinetics and mechanisms of sulfate adsorption/desorption on goethite using pressure-jump relaxation. Soil Sci. Soc. Am. J. 54, 1266–1273.