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Mineralogical and surface charge characteristics of Andosols experiencing long-term, land-use change in West Java, Indonesia

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ABSTRACT
Extensive areas of Andosols in tropical Indonesia have been subjected to long-term (>100 years) alterations from native forest to agricultural land use. This study assessed the mineralogical and surface charge characteristics of Andosols in West Java, Indonesia and assessed their resilience upon conversion from rainforest (PF1) to tea plantation (TP1) and horticultural practices. Soils developed in basaltic-andesite volcanic ash (<15,000 years B.P.) under an isothermal/peridic soil climate and were classified as Sialicic Andosols. The colloidal fraction of all soils was dominated by nanocrystalline/paracrystalline materials (e.g., allophane, imogolite, ferrihydrite) and Al/Fe-humic complexes. Crystalline minerals were a minor component of the clay fraction and followed kaolinite > hydroxy-Al interlayered vermiculite (HIV) ≈ gibbsite. The colloidal fraction appeared relatively resilient to changes in land use, except for the tea plantation in which allophanic material content decreased and Al–humus complexes increased due to strong soil acidification, and decreased ferrihydrite in the horticultural soils, possibly due to liming and increased organic matter. In spite of the abundance of allophanic materials, Fe (hydr)oxides and organic matter appeared to regulate surface charge characteristics of the colloidal fraction. Net soil charge in PF1 and TP1 soils was positive (pH<point of zero net charge; PZNC), while net surface charge in horticultural soils was negative (pH>PZNC). Horse manure and lime amendments to the horticultural soils lowered the PZNC, increased negative charge (CEC) and decreased positive charge (AEC). At ambient soil conditions, CEC increased from <1.2 cmol, kg⁻¹ in PF1 and TP1 soils to 6–20 cmol, kg⁻¹ in soils under horticultural management, while positive charge (AEC) was appreciably higher (0.7–4.3 cmol, kg⁻¹) in PF1 and TP1 soils than in horticultural soils (0.6 cmol, kg⁻¹). This study demonstrated that the colloidal fraction is relatively resilient to land-use change; however, charge characteristics of the variable-charged colloids can be readily altered by soil management practices.

1. Introduction
Tropical regions are experiencing wide-spread and rapid conversion of native vegetation to agricultural land uses, often resulting in severe soil degradation (FAO 2016; NYDF Assessment Partners 2019). Several studies document rapid degradation of selected soil properties, with a focus on processes affecting carbon cycling, soil fertility, and soil physical properties (e.g., Hattori et al. 2013; Tesfaye et al. 2016; Kassa et al. 2017; Tellen and Yerima 2018; Guillaume et al. 2018). However, few studies report on land-use changes to soil colloidal properties, such as mineralogical and surface charge characteristics. The few existing studies showed either no differences in clay mineralogy (Hashemi and Attaeian 2019; Rezaei, Roozitalab, and Ramezanpour 2012) or minimal clay mineral degradation (e.g., dissolution of the hydroxy-Al interlayers of vermiculite) with strong acidification resulting from long-term ammonium fertilizer application (Aleksseeva et al. 2011; Ross, Hoyt, and Neilsen 1985). In contrast to soil organic carbon and fertility characteristics, the soil colloidal fraction is generally more resilient to changes in land use and therefore any changes are difficult to detect in short-term studies. As a result, there is a distinct paucity of information regarding changes in soil mineralogical characteristic in response to land-use change, especially for tropical Andosols that represent >50% of global Andosol land area (IUSS Working Group WRB 2015).

Indonesia has 127 active volcanoes (~400 total volcanoes) resulting in wide distribution of Andosols. These Andosols support high agricultural productivity with some of the world’s highest human-carrying capacity being found on volcanic soils in Indonesia (Shoji, Nanzyo, and Dahlgren 1999a; Van Ranst et al. 2002). Andosols have several unique physical and chemical properties owing to a dominance of ‘active’ iron, aluminum and aluminosilicate materials (e.g., allophane, imogolite, ferrihydrite and metal-organo complexes) in their colloidal fraction. While volcanic soils have been extensively studied, there are relatively few studies examining the active Fe/Al fraction of tropical Andosols and their resilience to ecosystem perturbations, such as land-use change. It is expected that the active Fe/Al fraction will be more kinetically and thermodynamically susceptible to alteration from land-use conversion than crystalline clay minerals (Dahlgren and Saigusa 1994). As the active Fe/Al fraction imparts soil and ecosystem resiliency, it is important to document long-term changes in the soil colloidal fraction.
fraction in response to land-use change as this fraction has a strong effect on carbon cycling, soil fertility and nutrient leaching.

In Indonesia, land use/land cover of Andosols is primarily native rainforest, tea plantation, horticultural crops, paddy fields and other food crops. Land-use conversion from native rainforest to agriculture has taken place over long periods of time (>100 years) making assessments of long-term alteration to soil properties possible. Our previous assessment of changes in soil properties following conversion from rainforest to agronomic land use in Indonesia demonstrated strong resilience of soil physical properties, carbon stocks and fertility factors (Anda and Dahlgren 2020). For example, soils showed increased bulk density and meso/micro pores that contributed to increased plant-available water retention capacity; increased soil carbon and nitrogen stocks with a redistribution of organic matter from topsoil to subsoil horizons; and lower carbon mineralization and microbial biomass, especially in topsoil horizons. This study expands upon our previous work to examine changes in the mineralogical and surface charge characteristics of the soil colloidal fraction following conversion (>100 years) of native rainforest to tea plantation and horticultural crops. Results of this study inform strategic policy and management practices involving tropical forest conservation/reforestation and sustainable agricultural production in tropical Andosols.

2. Materials and methods

2.1. Site description

The study area is located in Lembang, West Java, Indonesia and lies between 6°46’25”–6°48’10” South latitude and 107°38’6”–107°38’54” East longitude with elevations ranging from 1236 to 1530 m above mean sea level. Native vegetation at all study sites was Merkus (or Sumatran) pine forest (Pinus merkusii), a pine native to much of Southeast Asia. Climate is tropical monsoon, with mean annual temperature and precipitation of 20°C and 1902 mm, respectively. A rainy season occurs between October and April accounting for ~79% of total annual rainfall. The soil temperature regime is isothermic and the soil moisture regime is perudic. Soils developed in basaltic-andesite tephra originating from Mt. Tangkuban Perahu eruptions. Tangkuban Perahu has produced ~43 distinct eruptions in the past 40,750 years (Kartadinata et al. 2002). Soils of this study formed in the Young Tangkuban Perahu tephra group composed of twelve tephra formations emplaced during the Holocene to Late Pleistocene. The tephra consists of unconsolidated pyroclastic deposits composed of particles with diameters ranging between 0.05 and 2 mm (Yatno and Zauyah 2008). Soils are dominantly classified as Hapludands and Melanudands in Soil Taxonomy (Soil Survey Staff 2014a). Soil age based on 14C dating of the buried IIIA (40–78 cm), IIIB (141–162 cm) and IVB (210–236 cm) horizons were 8,700 ± 200, 14,500 ± 300, and 17,700 ± 580 years B.P., respectively (Chartres and van Reuler 1985). As our study extended to a depth of 140 cm, the soil materials were a maximum of ~8,700 and ~14,500 years old in the upper and lower soil pedon, respectively.

We investigated four different current land-use/management types located within a 3-km radius: native pine forest (Pinus merkusii) (PF1), tea plantation (TP1; Camellia sinensis) and horticultural cropland (primarily vegetable crops) with either intensive cultivation (IH1) or intensive cultivation with recent bare fallow (HF1). Based on historical records, conversion of rainforest to agricultural production occurred more than 100 years ago and with agriculture adopting the evolving contemporary agronomic practices utilized over the time period. Seven years prior to sampling the horticultural site, a soil treatment that included horse manure amendment was initiated (IH1, plots – September 2006 to May 2013). Horse manure (20 Mg ha⁻¹ yr⁻¹) was annually incorporated to a depth of ~20 cm and compared to a previously cultivated plot receiving no horse manure (HF1 plot = horticulture-fallow). The HF1 plot located adjacent (4 m) to the IH1 plot was minimally tilled and received no manure or fertilizer additions for the 7 years prior to sampling to serve as a reference for comparison to manure amended soils (Anda and Dahlgren 2020).

2.2. Soil characterization analyses

Soil mapping and intensive field investigations of soil morphology suggested that soil properties were similar across all study sites prior to land-use change. We sampled soils from plots having similar landscape position (convex shoulder slopes), slope (5–8%) and aspect (southwest). We excavated a soil pedon with the dimensions of 150 × 200 × 110–140 cm (width × length × depth) at each of the four land-use/management sites. We collected a composite soil sample for each soil horizon from all sides of the pedon; the sample was thoroughly mixed prior to subsampling ~1 kg for analysis. Soils were air-dried, gently crushed, and passed through a 2-mm screen to remove coarse fragments and visible roots prior to laboratory analysis. Soil characterization methods followed Soil Survey Staff (2014b) standard methodologies unless otherwise noted. Selected physical (e.g., bulk density, pore size distribution, particle-size distribution, water-holding capacity), chemical (e.g., exchangeable cations, pH, P retention, total C/N and biological (e.g., microbial biomass and carbon mineralization rates) properties were previously reported (Anda and Dahlgren 2020).

2.3. Soil mineralogical analyses

We used non-sequential selective dissolution in Napyrophosphate, ammonium-oxalate and citrate-dithionite to characterize Fe, Al and Si in various pedogenic pools (Dahlgren 1994). The Fe and Al complexed with organic matter (Al₂o and Feo) were extracted with Na-pyrophosphate (Blakemore, Searle, and Daly 1987). Ammonium-oxalate extracted Al, Fe, and Si (Al₉o, Feo, and Si) from organic complexes, nanocrystalline Fe-(hydr)oxides (e.g., ferrhydrite) and nanocrystalline-paracrystalline aluminosilicates (e.g., allophane and imogolite) (Soil Survey Staff 2014b). Citrate-dithionite extraction (Fe₉ and Al₉) removed Fe from organic complexes and nanocrystalline to crystalline Fe-(hydr)oxide pools (Holmgren 1967). All extracts were treated with ‘Superfloc’ and centrifuged before quantification of Fe, Al and Si by ICP-AES.
The clay- (<2 μm) and silt-size (2–50 μm) fractions were isolated by sedimentation and sand fractions by sieving following sequential treatment with NaOCl (pH = 9.5), citrate-dithionite, ammonium oxalate and dilute sodium hexametaphosphate to enhance dispersion. The mineralogical composition of the 50–250 μm sand fraction was identified using a polarizing microscope (Carl Zeiss, Germany). We counted a total of 300 grains using line count transsects. X-ray diffraction (XRD) was performed on the clay, silt and fine-sand (50–250 μm) fractions using a Rigaku Ultima IV (Rigaku, Tokyo, Japan) producing Cu-Kα radiation generated with 40-kV accelerating potential and 40-mA tube current. Specimens were oriented on glass slides and subjected to standard treatments (Whittig and Allardice 1986): Mg-saturation, Mg-saturation plus glycerol solvation, K-saturation (25°C) and heat treatment of the K-saturated slides at 350°C and 500°C. Additionally, the Mg-saturated slide was treated with formamide to distinguish kaolinite from dehydrated halloysite based on a peak shift for dehydrated halloysite from 7 to 10 Å with formamide intercalation (Churchman et al. 1984).

We performed transmission electron microscopy (TEM) on the clay-size fraction following NaOCl (organic matter removal) and citrate-dithionite treatments. Dried clay specimens were dispersed in water and spotted onto carbon-coated collodion films for observation using a Hitachi-7650 (Hitachi High-Technologies Corp., Japan) operating at 100 kV. Total Fe, Al, Si, Ti and Zr concentrations in the <2-mm fraction were determined on pulverized (<125 μm) samples using a Thermo Scientific Xlt 600 XRF. Prior to and following sample analysis, calibration of the XRF was performed/verified with soil standard NCS DC 73,308 (Thermo #180-600).

2.4. Surface charge characterization

The point of zero charge (PZC) is defined as the pH value at which there are equal numbers of protonated and deprotonated sites on variable-charge surfaces (i.e., zero net electrical charge on the surface). We determined PZC using the method described by Gillman and Sumner (1987). Six 2 g aliquots of <2-mm, air-dried samples were weighed into 50 mL centrifuge tubes and saturated with 0.1 M CaCl₂, and subsequently washed (by centrifuging) and equilibrated with 0.002 M CaCl₂ to lower the ionic strength to approximate field conditions. Using HCl or Ca(OH)₂, the pH of the 0.002 M CaCl₂ suspension was adjusted to six relatively equally spaced values within the range of 3.5 to 6.5. The pH was adjusted daily until stable values were obtained (5 days in this study) and the equilibrated pH was recorded as pH0.002. Next, 0.5 mL of 2 M CaCl₂ was added to each tube, shaken and the pH was recorded after equilibration for the resulting 0.05 M CaCl₂ ionic strength as pH0.05. Using interpolation, the PZC was determined as the point where pH0.05 equaled pH0.002.

The point of zero net charge (PZNC) is defined as the pH where the number of cation exchange sites equals the number of anion exchange sites. After completion of PZC measurements, the 0.05 M CaCl₂ ionic strength soil suspensions (six tubes) were washed (by centrifuging) twice with 0.002 M CaCl₂ to lower the ionic strength (Gillman 2007). Then, the pH was adjusted to cover the desired pH range (3.5 to 6.0) until a stable pH reading was obtained (2 days in this study). Once the pH values were stable, the soil suspensions were centrifuged and supernatant retained for Ca²⁺, Al³⁺ and Cl⁻ analyses; tubes were weighed to estimate the volume of entrained solution. Next, 20 mL of 1 M NH₄NO₃ solution was added to each tube and shaken for 2 h to displace the adsorbed Ca²⁺, Al³⁺ and Cl⁻ from the soil. The soil suspension was centrifuged and filtered (0.2 μm membrane filter). Ca²⁺ and Al³⁺ concentrations were measured using ICP-AES and Cl⁻ by ion chromatography. Concentrations of Ca²⁺, Al³⁺ and Cl⁻ in the NH₄NO₃ solution were calculated and corrected for their concentrations in the entrained solution. Following Gillman and Sumner (1987), the adsorbed Ca²⁺ and Al³⁺ is a measure of the total negative charge (CEC) and Cl⁻ the total positive charge (AEC). Net charge (Ne,C) was calculated as the difference between positive and negative charges (i.e., AEC - CEC). PZNC was defined as the pH where CEC was equal to AEC. At pH < PZNC, the soil takes on an increasing net AEC; at pH > PZNC, the soil takes on increasing net CEC.

3. Results

3.1. General soil characterization

General soil characterization results for selected soil physical, chemical, and microbiological properties were previously published (Anda and Dahlgren 2020). Here we present a brief overview of salient properties to provide context for the mineralogical and surface charge properties presented in this study (Table 1). All soils were deeply weathered and well drained with A horizons (21–24 cm thick) overlying Bw horizons that extended to the depth of investigation (110–140 cm). Loamy soil textures were prevalent and no coarse fragments (>2 mm) were present. Soil pH values were strongly acidic in the pine forest (PF1; pH 4.4–4.5) and tea plantation (TP1; pH 4.7–4.9) while being moderately acidic in the horticultural plots with fallow (HF1; pH 5.2–5.6) and intensive cultivation/manure (IH1; pH 5.6–6.1). Potential for Al³⁺ toxicity was low given that exchangeable Al³⁺ concentrations were low (<0.4 cmolc kg⁻¹). Exchangeable Ca²⁺ and Mg²⁺ concentrations were very low for the PF1 and TP1 pedons (1.5 and 0.3 cmolc kg⁻¹, respectively), while the horticultural pedons that received recent horse manure and historic lime amendments had exchangeable Ca²⁺ and Mg²⁺ concentrations about an order of magnitude higher. Organic C concentrations in A horizons were highest in PF1 (80 g kg⁻¹) compared to 61 to 67 g kg⁻¹ under agricultural management. In contrast, organic C was lower in the subsoil of PF1 (32–35 g kg⁻¹), while the agricultural sites had elevated organic C concentrations (27–75 g kg⁻¹) in several subsoil horizons.

3.2. Mineralogical characteristics of sand and silt fractions

Mineralogical composition of the very fine/fine sand fraction was similar among pedons (Table S1) supporting the consistency of parent materials across study sites. The dominant minerals were labradorite, hornblende, augite and hypersthene. A notably contrast was found in the 2Bw3 horizon of the HF1
pedon that showed a sharp reduction in labradorite and corresponding increase in opaque minerals indicating a tephra-unit discontinuity. Volcanic glass was present at trace amounts (≤4%) throughout all profiles indicating rapid weathering of volcanic glass, the most weatherable component in tephra deposits.

In terms of chemical weathering, the Si/Al molar ratio based on total elemental analysis of the <2-mm fraction showed mean profile values ranging from 0.94 to 1.36 across the study sites (Table 2). These values indicate appreciable desilication based on a typical Si/Al ratio of ~2.9 for basaltic-andesite (SiO2 = 540 g kg⁻¹ and Al₂O₃ = 160 g kg⁻¹; Wilkinson 1986). Total Ti and Zr concentrations (considered conservative elements with respect to weathering) were markedly higher in the PF1 and TP1 pedons compared to the HF1 and IH1 pedons suggesting a higher degree of chemical weathering in the PF1 and TP1 pedons.

XRD analysis of the isolated sand fraction (50–250 μm) identified a small gibbsite (4.85 Å) peak in the PF1 and TP1 pedons (Fig. S1a and S1b) and a very strong gibbsite peak in the 2Bw3 horizon of the HF1 pedon (Fig. S1c). The silt-size fraction (2–50 μm) of the PF1 and TP1 pedons displayed a weak kaolinite peak (7.16 Å), but this peak was not observed in the HF1 and IH1 pedons (Fig. S3). A gibbsite peak (4.85 Å) appeared in the silt fraction and its intensity followed the order PF1 > TP1 > HF1 ≈ IH1. As in the sand fraction, the silt fraction of the 2Bw3 horizon in the HF1 pedon displayed a strong gibbsite peak.

### 3.3. Nanocrystalline and paracrystalline materials

Accumulation of highly reactive components (e.g., metal-organo complexes, nanocrystalline, and paracrystalline materials) is a primary reason for the unique physical and chemical properties of Andosols (Shoji and Fujiwara 1984; Wada 1985, 1986; Shoji, Nanzo, and Dahlgren 1993a). All soil horizons had acidic soil properties with active Al/Fe (Al₁+/2Fe₀⁺) concentrations ranging from 70 to 110 g kg⁻¹ (Table 3). There was a trend of higher Al₁+/2Fe₀⁺ in soil horizons below ~50-cm (older tephra deposits) and generally lower concentrations in horticultural pedons. All horizons classified as silicic (Al₂Si₂O₅-Al₂O₃) having Al₂Si₂O₅/Al₂O₃ ratios ranging from 0.04 to 0.15 (IUSS Working Group WRB 2015). Therefore, these soils are classified as allophanic Andosols as opposed to non-allophanic Andosols whose active Al/Fe fraction is dominated by Al/Fe humus complexes (Shoji et al. 1985). The mean (Al₂Si₂O₅-Al₂O₃)Si₂O₅ ratio was 2.05 (range 1.65 to 2.20) consistent with the presence of Al-rich allophane or imogolite. The presence of imogolite was verified by TEM that showed an abundance of tubular morphology (Fig. S2). Based on Si₂O₅ concentrations (Parfitt and Wilson 1985), estimated allophane/imogolite content ranged from 189 to 308 g kg⁻¹ of the fine-earth fraction (<2-mm). Among the four land-use types, the upper two horizons of the TP1 profile showed a distinctly lower allophane/imogolite content (190 g kg⁻¹) compared to the lower horizons (265–308 g kg⁻¹). The active Fe fraction (Fe₀) ranged from 21 to 53 g kg⁻¹ with distinctly higher concentrations (~2-fold) in the PF1 and TP1 pedons (44–53 g kg⁻¹) compared to the HF1 and IH1 pedons (21–38 g kg⁻¹). Ferric/hydride concentrations estimated from the formula 1.7 × Fe₀ (Childs, Matsue, and Yoshinaga 1991) ranged from 36 to 90 g kg⁻¹ of the fine-earth fraction. Total pedogenic iron (hydro)oxides (Fe₀) were generally lower in the HF1 and

### Table 3: Selected physical and chemical properties of soil profiles under different land use/management systems.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Profile</th>
<th>Soil depth (cm)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>pH</th>
<th>H₂O</th>
<th>C/N</th>
<th>Organic matter (g kg⁻¹)</th>
<th>Exchangable cations (μmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF1</td>
<td>Typic Hapludand under pine forest</td>
<td>0–24</td>
<td>56</td>
<td>0</td>
<td>44</td>
<td>4.5</td>
<td>60</td>
<td>80</td>
<td>0.2</td>
<td>Na = 101, K = 0.29, Ca = 0.3, Mg = 0.2</td>
</tr>
<tr>
<td>TP1</td>
<td>Typic Hapludand under tea plantation</td>
<td>24–40</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>4.5</td>
<td>60</td>
<td>80</td>
<td>0.2</td>
<td>Na = 101, K = 0.29, Ca = 0.3, Mg = 0.2</td>
</tr>
<tr>
<td>HF1</td>
<td>Typic Hapludand under wheat</td>
<td>40–60</td>
<td>45</td>
<td>45</td>
<td>10</td>
<td>4.5</td>
<td>60</td>
<td>80</td>
<td>0.2</td>
<td>Na = 101, K = 0.29, Ca = 0.3, Mg = 0.2</td>
</tr>
<tr>
<td>IH1</td>
<td>Typic Hapludand under tea plantation</td>
<td>60–100</td>
<td>45</td>
<td>45</td>
<td>10</td>
<td>4.5</td>
<td>60</td>
<td>80</td>
<td>0.2</td>
<td>Na = 101, K = 0.29, Ca = 0.3, Mg = 0.2</td>
</tr>
</tbody>
</table>

Note: Data were adapted from sequence publication Anda and Dahlgren (2020).
Table 2. Total elemental composition of <2-mm soil fraction and Si:Al molar ratio for soils under different land use/management systems.

<table>
<thead>
<tr>
<th>Profile/Height</th>
<th>Depth (cm)</th>
<th>Si (mg kg⁻¹)</th>
<th>Al (mg kg⁻¹)</th>
<th>Fe (mg kg⁻¹)</th>
<th>Zr (mg kg⁻¹)</th>
<th>Ti (mg kg⁻¹)</th>
<th>Si:Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF1 Typic Hapludand under pine forest</td>
<td>0–24</td>
<td>82</td>
<td>84</td>
<td>97</td>
<td>0.27</td>
<td>6.25</td>
<td>0.9</td>
</tr>
<tr>
<td>Bw1</td>
<td>24–60</td>
<td>78</td>
<td>86</td>
<td>97</td>
<td>0.27</td>
<td>6.70</td>
<td>0.9</td>
</tr>
<tr>
<td>Bw2</td>
<td>60–100</td>
<td>88</td>
<td>88</td>
<td>100</td>
<td>0.28</td>
<td>6.40</td>
<td>1.0</td>
</tr>
<tr>
<td>Bw3</td>
<td>100–140</td>
<td>88</td>
<td>85</td>
<td>96</td>
<td>0.26</td>
<td>6.54</td>
<td>1.0</td>
</tr>
<tr>
<td>TP1 Typic Hapludand under tea plantation</td>
<td>0–24</td>
<td>109</td>
<td>76</td>
<td>95</td>
<td>0.23</td>
<td>6.36</td>
<td>1.4</td>
</tr>
<tr>
<td>Bw1</td>
<td>24–54</td>
<td>112</td>
<td>75</td>
<td>97</td>
<td>0.23</td>
<td>6.50</td>
<td>1.4</td>
</tr>
<tr>
<td>Bw2</td>
<td>54–88</td>
<td>104</td>
<td>80</td>
<td>101</td>
<td>0.25</td>
<td>6.78</td>
<td>1.2</td>
</tr>
<tr>
<td>Bw3</td>
<td>88–130</td>
<td>84</td>
<td>92</td>
<td>105</td>
<td>0.26</td>
<td>6.75</td>
<td>0.9</td>
</tr>
<tr>
<td>HF1 Typic Melanudand under horticultural crops with fallow system</td>
<td>0–21</td>
<td>99</td>
<td>83</td>
<td>74</td>
<td>0.15</td>
<td>4.25</td>
<td>1.1</td>
</tr>
<tr>
<td>Bw1</td>
<td>21–48</td>
<td>111</td>
<td>86</td>
<td>65</td>
<td>0.12</td>
<td>3.65</td>
<td>1.2</td>
</tr>
<tr>
<td>Bw2</td>
<td>48–70</td>
<td>100</td>
<td>78</td>
<td>77</td>
<td>0.16</td>
<td>4.36</td>
<td>1.2</td>
</tr>
<tr>
<td>Bw3</td>
<td>70–110</td>
<td>58</td>
<td>112</td>
<td>129</td>
<td>0.31</td>
<td>7.58</td>
<td>0.5</td>
</tr>
<tr>
<td>IH1 Typic Melanudand under intensive horticultural crops with manure</td>
<td>0–21</td>
<td>124</td>
<td>82</td>
<td>69</td>
<td>0.13</td>
<td>3.74</td>
<td>1.5</td>
</tr>
<tr>
<td>Bw1</td>
<td>21–48</td>
<td>117</td>
<td>80</td>
<td>67</td>
<td>0.13</td>
<td>3.71</td>
<td>1.4</td>
</tr>
<tr>
<td>Bw2</td>
<td>48–70</td>
<td>121</td>
<td>87</td>
<td>76</td>
<td>0.16</td>
<td>4.15</td>
<td>1.3</td>
</tr>
<tr>
<td>Bw3</td>
<td>70–110</td>
<td>103</td>
<td>79</td>
<td>82</td>
<td>0.17</td>
<td>4.69</td>
<td>1.2</td>
</tr>
</tbody>
</table>

IH1 pedons (mean = 37 g kg⁻¹; range: 26–74 g kg⁻¹) compared to the PF1 and TP1 pedons (mean = 54 g kg⁻¹; range: 47–59 g kg⁻¹). The Fe₄O₇:Fe₅ ratio is a measure of iron (hydr)oxide crystallinity and was generally greater than 0.8 across all land-use/management types. An obvious exception was the 2Bw3 horizon of the HF1 profile that had the highest Fe₄O₇ (74 g kg⁻¹) and lowest Fe₄O₇:Fe₅ (0.5) value. As Fe₄O₇ concentrations reflect total pedogenic iron, the Fe₄ to total Fe ratio (Fe₄O₇:Fe₅) can be used as a relative measure of chemical weathering. Fe₄O₇:Fe₅ was generally higher in the lower soil horizons having older parent materials, and the mean ratios were higher in the PF1 (0.57) and TP1 (0.53) pedons than in the HF1 (0.48) and IH1 (0.42) pedons suggesting an apparently higher degree of chemical weathering in the PF1 and TP1 profiles.

3.4. Mineralogical characteristics of clay fraction
XRD diffractograms of the clay-size fraction without poorly-ordered materials removal by acid-ammonium oxalate treatment resulted in very broad, non-distinct peaks with a broad increase in the background intensity occurring between 20 and 30° 2θ, which is indicative of dominance by nanocrystalline/paracrystalline materials (Fig. S4). Following oxalate treatment,
XRD patterns for all four pedons showed generally well resolved peaks for a 2:1 mineral (14.25 Å, kaolinite (7.17 Å) and gibbsite (4.85 and 4.38 Å) (Figures 1 & 2). Further treatment with Mg and glycerol showed no appreciable change of the 14.25 Å peak excluding the presence of smectite. The K-saturated clays showed no appreciable peak change from the Mg-saturated slide, but heating of the K-saturated clay to 300 °C resulted in the collapse of the 14.25 Å peak to ~12.91 Å and further collapse to 10.10–10.20 Å with heating to 550 °C. These dynamics upon heating indicate the presence of hydroxy-Al interlayered vermiculite (HIV) (Whittig and Allardicce 1986). Based on formamide treatment, kaolinite rather than halloysite was the dominant kaolin mineral, except for the surface horizon of the PF1 pedon where the presence of halloysite was identified (formamide expansion to 10.49 Å).

Comparison of clay fractions among soils showed the PF1 and TP1 pedons contained similar clay minerals, which were dominated by kaolinite followed by HIV, gibbsite and some halloysite in the PF1 surface horizon. The HF1 and IH1 soils also showed similar clay minerals, but were dominated by HIV and kaolinite followed by gibbsite, except for the subsoil of the HF1 pedon that was dominated by gibbsite and lesser amounts of kaolinite.

3.5. Soil surface charge assessment

The mean (±std dev) PZC value across all soil samples was 4.66 ± 0.21 (range = 4.22–5.06), which compared to soil pH values of 4.88 ± 0.58 (range = 4.22–5.86) (Table 4 and Figure 3). PZC values were significantly correlated with Feₐ (r = 0.59; p = 0.015, Feₐ (r = 0.78; p < 0.001) and organic carbon (r = -0.63; p < 0.001). Notably, the highest PZC value (5.06) occurred in the lower horizon of the HF1 pedon that had an exceptionally high iron (hydr)oxide content (Feₐ = 74 g kg⁻¹).

The PZNC for equilibrated soil suspensions (pH range of 3.6 to 5.8) and the development of positive–negative-charge at various equilibrated pH values are shown in Figure 4. PZNC values were significantly correlated with Feₐ (r = 0.82; p = <0.001), Feₐ (r = 0.82; p < 0.001), allophanic materials (r = 0.63; p = 0.009), pH (r = -0.88; p < 0.001) and organic carbon (r = -0.61; p < 0.012). The lower PZNC values in the IH1 and HF1 soils were associated with higher organic matter and pH values, as well as lower Feₐ and Feₐ contents. With increasing soil pH, the negative charge of soil colloids increased while positive charge decreased. The increase in negative charge was much higher for the HF1 and IH1 pedons compared to PF1 and TP1 pedons. For the PF1 pedon, total negative charge increased from 0.10 to 0.36 cmolₖg⁻¹ at pH 3.7 to 5.0–8.0 cmolₖg⁻¹ at pH 5.8 (Figure 4(a)). In contrast, positive charge decreased from 2.8 to 5.0 cmolₖg⁻¹ at pH 3.7 to 0.2–0.3 cmolₖg⁻¹ at pH 5.8. The negative and positive charge development for the TP1 soils was similar to the PF1 pedon (Figure 4(b)). In contrast, negative charge development in the horticultural soils (HF1/IH1) increased remarkably from 0.05 to 2.0 cmolₖg⁻¹ at pH 3.6 to 14.0–19.5 cmolₖg⁻¹ at pH 5.8, while the positive charge sharply decreased from 2.0 to 4.5 cmolₖg⁻¹ at pH 3.6 to 0.02–0.32 cmolₖg⁻¹ at pH 5.8 (Figure 4(c,d)). This comparison indicates that horticultural practices (recent manure + historic lime amendments) increased the negative charge 2.4–2.8 times compared to the native pine forest.

At ambient soil conditions, the magnitude of negative surface charge changed appreciably only with conversion to horticultural land use (HF1/IH1) (Table 4). Total negative charge (CECₗ) was <1.2 cmolₖg⁻¹ throughout all horizons of the PF1 and TP1 pedons. In spite of the low pH for the PF1 and TP1 pedons (pH <4.5), the charge occupied by exchangeable acidity (CECₗ) was very low (<0.1 cmolₖg⁻¹). In contrast, the horticultural pedons (HF1/IH1) showed large increases in CECₗ under horticultural management (CECₗ HF1 6–14 vs IH1 10–20 cmolₖg⁻¹). This large increase in CECₗ values of horticultural soils is ascribed primarily to the higher pH (pH: PF1 = 4.2–4.4 vs HF1/IH1 = 5.0–5.9), and to perhaps a somewhat higher organic matter content that appeared more humified as reflected by its lower C/N ratio (PF1/TP1 = 17.5 ± 1.4 vs HF1/IH1 = 13.8 ± 3.0).

In contrast to CECₗ values, the positive charge (AEC) of the soil colloid fraction was appreciably higher (0.7–4.3 cmolₖg⁻¹) in the PF1 and TP1 pedons than the horticultural pedons (HF1/IH1 = <0.6 cmolₖg⁻¹; Table 4). Calculation of net charge (NₑC) on soil colloidal surfaces showed a distinct contrast between PF1 and TP1 pedons as compared to HF1 and IH1 pedons. In the PF1 and TP1 pedons, the NₑC was dominated by...
positive charge in all horizons, while the HF1/IH1 pedons were dominated by negative charge (Table 4). Overall, net surface charge was negatively correlated with pH ($r = -0.97; p < 0.001$) and positively correlated with $Fe_{o}$ ($r = 0.88; p < 0.001$) and $Fe_{d}$ ($r = 0.76; p < 0.001$). These charge characteristics are consistent with the relationship predicted from differences between pH and PZNC: net negative charge ($N_{wC}$) if soil pH > PZNC (as for HF1 and IH1) versus net positive charge ($N_{wC}$) if PZNC > pH (as for PF1 and TP1).

4. Discussion

4.1. Soil mineralogy and mineral transformations

4.1.1. Weathering of primary silicates and volcanic glass

Under the per udic/isothermal soil climatic regime in West Java, Indonesia, chemical weathering rates are expected to be very high. Weathering rates are further accelerated by several characteristics of the basaltic-andesite tephra, such as large surface area (silt & sand size grains), high permeability (promoting solid-solution interactions) and a glass fraction dominated by highly weatherable colored glass. Shoji et al. (1993b) measured rates of aluminum release from colored glass (basaltic-andesite composition) being 1.5 times greater than non-colored glass (rhyolite composition) and weathering rates increased ~1.5 times for each 10°C increase in temperature between 0 and 30°C. Thus, it is not unexpected that the volcanic glass fraction was largely depleted within the ~8,700 and ~14,500 years (upper and lower soil materials, respectively) since deposition. In particular, substantial desilication has occurred as indicated by the decrease in the Si:Al molar ratio from ~2.9 in a typical basaltic-andesite material to the range of 0.94 to 1.36 in the investigated soils. As the silica content of the soil becomes...
depleted, the clay-size mineralogy transforms from those materials requiring high silica activities (e.g., smectite, halloysite) to those stable at lower silica activities (e.g., allophane/imogolite, kaolinite, gibbsite) (e.g., Parfitt and Childs 1983; Parfitt and Wilson 1985; Wada 1989; Parfitt and Kimble 1989; Ugolini and Dahlgren 2003). Without periodic tephrta deposition to rejuvenate the weathering sequence, the intensity of the isothermic/peridic weathering environment would lead to severe desilicification and occurrence of Ultisols/Oxisols dominated by low activity clays in the humid tropics.

In terms of the land-use treatments, markedly higher weathering rates were suggested under PF1 and TP1 based on their higher total Ti and Zr concentrations that accumulate during chemical weathering/leaching (Young and Nesbitt 1998). For soil profiles developed from uniform parent materials, Ti and Zr concentrations decrease with increasing soil depth (Anda, Chittleborough, and Fitzpatrick 2009). However, in this study, Ti and Zr concentrations increased with increasing soil depth reflecting the older, more highly weathered soil materials at depth. Higher weathering rates in the PF1 and TP1 pedons are further supported by the higher Fe_D/Fe_T (PF1 = 0.57, TP1 = 0.53 vs. HF1 = 0.48, HI1 = 0.42) indicating a greater release of iron by chemical weathering.

We posit that higher apparent weathering rates may result from the lower pH (<1 unit lower) and higher DOC concentrations (organic acids/chelates) found in the PF1 and TP1 pedons (Anda and Dahlgren 2020). We acknowledge that subtle differences in the chemical composition of the tephrta deposits may contribute to differences among pedons. Therefore, it is difficult to assess whether the apparent differences in chemical weathering can be solely attributed to changes in land use over the ~100-yr period.

### 4.1.2. Nanocrystalline and paracrystalline materials

The dominance of poorly crystalline materials is likely associated with rapid weathering of the volcanic glass fraction. Rapid chemical weathering results in supersaturation of the soil solution, which kinetically favors formation of metastable nanocrystalline and paracrystalline precipitation products (Stumm 1992; Dahlgren, Saigusa, and Ugolini 2004). Further, the lack of a distinct dry season (i.e., peridic) hinders the crystallization process as Ostwald ripening (dissolution and reprecipitation) and dehydration are energetically and kinetically favored by prolonged periods of high temperature and desiccation (Takahashi, Dahlgren, and van Susteren 1993; Ziegler et al. 2003). These findings are similar to the weathering of tephrta deposits in mesic/udic climatic regimes, such as in northern Japan and New Zealand, which yields a prevalence of poorly crystalline materials with few crystalline minerals at a similar stage of weathering (<10,000 yr) (Parfitt and Childs 1983; Wada 1989; Shojo, Nanzyo, and Dahlgren 1993a).

Allophanic materials are the favored weathering product in humid, temperate climates under conditions of low organic matter concentrations and pH_{H2O} > 4.9 (Mizota and van Reeuwijk 1989; Shojo, Nanzyo, and Dahlgren 1993a). Soil genesis associated with the native pine forest, which was the dominant land use for the majority of time during soil formation at all sites, resulted in high organic matter (SOC >30 g kg⁻¹) and low pH values (<4.5) that might be expected to favor formation of Al-humus complexes as opposed to allophanic materials, thereby leading to formation of non-allophanic Andosols. However, another important factor controlling the fate of Al³⁺ in non-allophanic Andosols of northern Japan is elion inputs of 2:1 layer silicates from Asia, which incorporate Al³⁺ in their interlayer position rendering it unavailable for allophanic formation (Shoji and Fujiwara 1984; Shojo, Nanzyo, and Dahlgren 1993a). Elion inputs of 2:1 layer silicates in Indonesia are expected to be minor compared to northern Japan. Therefore, the release of Al³⁺ by chemical weathering appears to exceed the incorporation of Al³⁺ into organic complexes and 2:1 layer silicates leading to abundant formation of allophanic materials in this study.

In terms of land use, the TP1 topsoil displayed a distinctly lower allophanic content in the upper two horizons than the other land-use types. The lower allophanic concentrations may be due to dissolution of allophanic materials by soil acidification associated with high rates of ammonia-fertilizer application to tea plantations (Takahashi et al. 2008; Wang et al. 2010; Alekseeva et al. 2011). Dahlgren and Saigusa (1994) demonstrated rapid dissolution of allophanic materials under acidic conditions and dissolution rates showed a strong H⁺-dependence. This interpretation is consistent with Takahashi et al. (2008) who documented a decrease in allophanic materials with a concomitant increase in Al-humus complexes associated with strong acidification of tea plantations. Notably, the lower allophanic material concentrations in the upper two horizons of the TP1 pedon correspond to the highest Al-humus complex concentrations found in this study. While the PF1 profile also displayed strong acidification, its allophanic content was consistently high throughout the pedon compared to the other land-use types. We posit that biogenic cycling of silica by forest vegetation (Alexandre et al. 1997; Derry et al. 2005) coupled with higher evapotranspiration in the native forest, which lowers the leaching potential, may compensate for the strong natural acidity by maintaining higher silica activities to support the stability of allophanic materials.

The overall high Fe_D/Fe_T ratio (>0.8) across all soil profiles indicates the dominance of nanocrystalline iron (hydrido)oxides, such as ferrihydrite, whose formation is favored by high organic matter concentrations and high Al³⁺/silica activities that are posited to inhibit crystallization (Schwertmann 1988; Malucelli, Terribile, and Colombo 1999). Additionally, the peridic moisture regime prevents soil profile desication limiting Ostwald ripening and dehydration that promote crystallization. The 2Bv3 horizon of the HF1 profile was a notable exception to the overall iron (hydrido)oxide pattern having a very high Fe_d (74 g kg⁻¹) content and lower Fe_D/Fe_T (0.5). This horizon occurs at a tephrta-unit discontinuity and may represent a reoxy feature associated with imperfect vertical drainage (e.g., plagic horizon). We posit that reoxy cycling driven by alternating anaerobic/aerobic cycles leads to ferrolysis that contributes to intense proton generation and localized weathering leading to Fe (hydrido)oxides and gibbsite enrichment (Brinkman 1970).

Higher Fe_D concentrations in the PF1 and TP1 profiles may be associated with the appreciably lower pH values (<5.0) compared to the HF1/HI1 profiles (pH = 5.2-6.1). Historical application of lime raised the pH of the horticultural soils by
~1 unit compared to the PF1 and TP1 pedons resulting in a corresponding decrease in Al\(^{3+}\) activities. Higher Al\(^{3+}\) activities increase Al-substitution in Fe (hydr)oxides that hinders crystallization (Schwertmann et al. 1979). Additionally, the higher dissolved organic carbon concentrations associated with the PF1 and TP1 pedons (Anda and Dahlgren 2020) could inhibit crystallization due to its strong affinity to Fe (hydr)oxide surfaces, thereby blocking surface sites for continued crystal growth (Schwertmann 1985, 1988).

Accumulation of soil organic matter (SOM) is a characteristic property of Andosols. Across all soil horizons, Al\(^{3+}\) concentrations demonstrated a positive correlation with organic carbon (r = 0.70; p = 0.002). In contrast, allophanic materials (r = −0.62; p = 0.011) and active Al\(^{3+}\)/Fe\(^{2+}\) (r = −0.42; p = 0.102) demonstrated weak negative or no correlation with organic carbon concentrations. This suggests that organic matter bonding with allophanic and nanocrystalline iron (hydr)oxide materials is of lesser importance than Al-humus complexes in stabilizing organic matter (Percival, Parfitt, and Scott 2000).

### 4.1.3. Phyllosilicates

Consistent with previous studies, we found no obvious changes in crystalline clay mineral alterations resulting from changes in land use (Rezaei, Rozzitalab, and Ramezanpour 2012; Hashemi and Attaeian 2019) or strong soil acidification (Aleksseeva et al. 2011; Ross, Hoyt, and Neilsen 1985). Further, this study demonstrates that assessment of clay mineralogy in Andosols without acid oxalate pretreatment may lead to a serious misinterpretation of crystalline mineral abundance as their detection by XRD is strongly masked by nanocrystalline materials. The coexistence of allophanic materials with gibbsite and kaolinite were previously observed under peridic conditions and reflects the strong desilication/leaching environment (Nidayaragije and Delvaux 2003). Similarly, Van Ranst et al. (2008) found HIV, kaolinite, gibbsite and halloysite coexistence as the dominant clay mineral assemblage for Andosols in Dieng, Indonesia. The occurrence of kaolins and gibbsite in the fine sand and silt fractions of all soil invokes a pathway of pseudomorphic replacement of plagioclase by kaolin and gibbsite (Wilson 2004; Rasmussen, Dahlgren, and Southard 2010). Additionally, kaolins and gibbsite may be inherited as lithic fragments in the tephra deposits or formed by localized desilication of poorly crystalline materials (dissolution/reprecipitation) (Violante and Wilson 1983). Gibbsite was the dominant crystalline mineral in the 2Bw3 of the HF1 pedon and was associated with the previously discussed tephra-unit discontinuity that may impede soil profile drainage. The dominance of gibbsite is consistent with a localized intense weathering regime generated by ferrolysis (Brinkman 1970).

The prevalence of kaolinite and gibbsite rather than halloysite in this study reflects the strong desilication environment. However, the occurrence of halloysite in the upper horizon of the native pine forest pedon appears as a curious anomaly. As previously stated, biogenic silica cycling by the native pine forest though deposition of opal phytoliths in litter has previously been invoked to explain elevated Si concentrations in otherwise highly weathered tropical soils (Alexandre et al. 1997; Derry et al. 2005). However, additional research is necessary to verify the potential role of biogenic silica cycling in elevating silica activities in the native pine forests of West Java.

The origin of the precursor 2:1 mineral leading to formation of HIV may result from eolian deposition, inheritance of hydrothermal alteration products that were incorporated as lithic fragments in the tephra during the eruption, and/or neoformation in the pedogenic environment (e.g., Pevear, Dethier, and Frank 1982; Jongmans et al. 1994; Bautista-Tulin and Inoue 1997; Nidayaragije and Delvaux 2003). Regardless of the origin of the 2:1 component, the naturally acidic soil environment (pH 4.5–5) is highly conducive to hydroxy-Al-interlayering of the 2:1 layer silicate (Jackson 1963; Dahlgren, Saigusa, and Ugolini 2004). In the presence of high 2:1 layer silicates, the incorporation of Al\(^{3+}\) into the interlayer position may effectively compete for Al\(^{3+}\) released by weathering, thus hindering the formation of allophanic materials (anti-allophanic effect) and leading to formation of non-allophanic Andosols (Shoji, Nanzyo, and Dahlgren 1993a; Shoji 1985). In this study, 2:1 layer silicates are a minor component of the clay-size fraction, and therefore not an appreciable sink for Al\(^{3+}\) released by weathering.

### 4.1.4. Soil charge characteristics

The relatively low PZC/PZNC values (3.6–5.4) in this study reflect a colloidal fraction dominated by surface coatings consisting of humic substances, Al/Fe-humus complexes, allophanic materials, ferrhydrite and goethite/hematite. Across all soils, PZC/PZNC values were positively correlated with Fe (hydr)oxides (Fe\(_{\text{o}}\) & Fe\(_{\text{d}}\)) and negatively correlated with soil organic C. Additionally, PZC/PZNC values showed a weak positive correlation with allophanic materials, a dominant component (200–300 g kg\(^{-1}\)) of all soil horizons. In particular, humic substances have been reported to decrease PZNC values (Gillman 1985; Marcano-Martinez and McBride 1989; Van Ranst et al. 1998, 2002). This is consistent with PZNC values for all pedons being generally lower in surface horizons having higher organic matter content. However, even the subsoil PZC/PZNC values were lower than expected for crystalline Al/Fehydr(oxides) (ZPC = 7–9; Parks and de Bruyn 1962; Uehara and Gillman 1981), ferrhydrite (ZPC = 7.8–8.0; Karapinar 2016), and allophane/imogolite (Al/Si molar ratio of 2 - PZC/PZNC ~6.5; Parfitt 1980; Harsh et al. 1992).

Organic matter is responsible for lowering soil PZNC, while Fe (hydr)oxides are responsible for increasing soil PZNC (Sakurai, Ohdate, and Kyuma 1989; Marcano-Martinez and McBride 1989; Van Ranst et al. 1998). This relationship was demonstrated by Anda et al. (2008) showing that removal of organic matter increased the PZC of Oxisols from 3.9–5.7 to 5.3–6.7 and removal of SOM + iron oxides decreased PZC from 3.9–5.7 to 3.3–4.5. The relatively low PZNC values in this study suggest a strong influence of humic substances on surface charge characteristics, with a lesser influence by Fe (hydr)oxides and possibly allophanic materials. Given the strong sorption capacity of Fe (hydr)oxides and allophanic materials for humic substances, it is plausible that the surfaces of these constituents are strongly affected by sorbed humic substances, rendering humic substances the dominant control. Soil organic C concentrations exceeded ~30 g kg\(^{-1}\) in all soil horizons supporting the role of humic substances in regulating PZNC properties.
The Andosols in this study display low nutrient-holding capacity and require special management practices to maintain their productivity. The PF1/TP1 soils displayed acric properties (acrudivic in Soil Taxonomy & acroic in WRB) indicating a low capacity to retain exchangeable cations (<2.0 cmol, kg\(^{-1}\)) (Uehara and Gillman 1981). In contrast, the horticultural soils receiving recent organic matter amendments and long-term liming and phosphate fertilization have an appreciably high CEC (6–20 cmol, kg\(^{-1}\)). This enhanced CEC provides increased storage capacity for nutrient cations and reduces their losses by leaching. The added organic C from horse manure additions provides an important source of CEC associated with its carboxylic and phenolic functional groups, but also serves to reduce the PZNC value increasing the overall negative charge at the expense of positive charge. The upper two horizons of the pH1 treatment receiving horse manure had the lowest PZNC (3.6–3.8) among all soil horizons evaluated. The enhanced CEC and reduced AEC of the horticultural treatments reflect, in part, the role of organic matter as effective materials to manipulate surface charge properties of variable charged soils.

Phosphate sorption also serves to lower the PZC/PZNC of variable charged constituents, thereby increasing the surface negative charge (Uehara and Gillman 1981). Long-term phosphate fertilizer application to the horticultural soils was evident by reduced P retention (due to higher P-saturation), especially in the pH1 pedon (Anda and Dahlgren 2020). Wann and Uehara (1978) showed that the PZNC of an Oxisol was lower as more P was adsorbed resulting in an increase in negative charge and decreased cation leaching. Finally, liming soils with variable charge leads to an increase in their negative charge due to the increased pH. Thus, addition of organic matter, phosphate and liming materials enhanced retention of nutrient cations (Ca\(^{2+}\), Mg\(^2+\), K\(^+\), NH\(_4^+\)) and lower susceptible to cation leaching. However, there is a trade-off as the AEC (up to 4 cmol, kg\(^{-1}\)) was reduced by these soil amendments resulting in a higher susceptibility for leaching of mobile nutrient anions, especially NO\(_3^-\).

5. Conclusions

Andosols in the tropical region of Indonesia have experienced long-term (>100 years) land-use alterations from native vegetation to agriculture. In spite of the intense weathering environment, the colloidal fraction of all soils was dominated by metastable nanocrystalline/paracrystalline materials (e.g., allophone, imogolite, ferrihydrite) and Al-humic complexes, with only a minor component of crystalline minerals (kaolinite > hydroxyl-Al interlayered vermiculite (HIV = gibbsite). The composition of the colloidal fraction appeared relatively resilient to long-term changes in land use, except for tea plantation soils that demonstrated a decrease in allophamic materials and a corresponding increase in Al-humus complexes in the upper two horizons, and a decrease in ferrihydrite in the horticultural soils. Despite of the abundance of allophamic materials in the colloidal fraction, the Fe (hydroxide and organic matter fractions appeared to regulate the surface charge characteristics of the colloidal fraction. Net soil charge in pine forest and tea plantation soils was positive (pH>PZNC), while net surface charge in horticultural soils was negative (pH>PZNC). Horse manure and lime amendments to the horticultural soils lowered the PZNC, increased negative charge (CEC) and decreased positive charge (AEC) demonstrating the effectiveness of soil management practices in changing the surface charge characteristics. This study demonstrates that the composition of the colloidal fraction is relatively resilient to land-use change; however, the charge characteristics of these variable-charged colloids can be effectively altered by common soil management practices.

Note

1. Andosols is used in this paper to denote soils of volcanic origin meeting either Andosol (WRB) or Andisol (Soil Taxonomy) classification systems.

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