Tropical Andosol organic carbon quality and degradability in relation to soil geochemistry as affected by land use

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Abstract. Land use is recognized to impact soil geochemistry on the centennial to millennial time scale, with implications for the distribution and stability of soil organic carbon (SOC). Young ~~Juvenile~~ ~~v~~volcanic soils in tropical areas are subject to much faster pedogenesis, noticeable already on ~~with then also possibly a significant mediation by land use on much shorter~~ centennial or even decadal scale. As land use is recognized factor for soil formation, it is thus conceivable that even relatively recent land use conversion in such areas would already bear significant impact on the resulting formed soils., e.g. in terms of content of pedogenic oxides. Very scarce observational evidence exists and so such indirect implications of land use on SOC cycling are largely unknown. We here investigated SOC fractions, substrate specific mineralization (SOC or added plant residue), and net priming of SOC in function of forest or agricultural land use on Indonesian volcanic soils. ~~The~~ The content of oxalate-extracted Al (Al_o) ~~and exchangeable Ca~~ correlated well with OC associated with sand–sized aggregates, particularly in subsoil. ~~The concomitant more than tripling of T~~the proportion of SOC in sand-sized 400 J ml^{-1} ultrasonication resistant aggregates was also higher in agricultural ~~compared to~~than pine forest land use and a ~~and~~ likewise contrasts existed for ~~in~~ Al_o. These combined observations suggest that enhanced formation of Al-(hydr)oxides promoted aggregation and physical occlusion of OC. This was importantly also consistent with a relatively lesser degradability of SOC in the agricultural sites, though we found no likewise difference in degradability of added ^{13}C-labelled ryegrass or in native SOC priming between the pine forest and agricultural land uses. ~~the net priming of SOC and degradability of added ^{13}C-labelled ryegrass was not found to depend on land use.~~ We expected that amorphous Al content under agricultural land use would mainly have promoted mineral-association of SOC compared to under pine forest but found no indications for this. Improved small scale aggregation of tropical Andosols caused by conversion to agriculture and high carbon input via organic fertilizer may thus partially counter the otherwise expectable decline of SOC stocks following cultivation. Such indirect land use effects on the SOC balance appeared relevant for correct interpretation and prediction of the long-term C-balance of (agro)ecosystems with soil subject to intense development, like the here studied tropical Andosols.

1 Introduction

Storage of soil organic carbon (SOC) in terrestrial ecosystems can improve ecosystem services such as soil health, agricultural productivity, and climate change mitigation (Baldock, 2007; Lehmann and Kleber, 2015). The storage of SOC is influenced

30   by the interaction of ecological processes with net primary productivity and heterotrophic respiration usually being most important terms of the SOC balance. Land use determines the net-C input to soil and in doing so often bears an overriding control on the SOC balance, compared to other drivers of the C-cycle at ecosystem level. Forest ecosystems usually have relatively high net primary productivity compared to agricultural land use (Smith et al., 2014). The net result of cultivation then typically leads to a decline in SOC stock and increased human–induced CO_2 emission (Don et al., 2011; Wei et al., 2014).

35   The long-term SOC balance of ecosystems also depends on the capacity of soils to stabilize newly entering OC against microbial decomposition, resulting from heterotrophic respiration. Physical occlusion of OC at the microaggregate scale as well as binding of OC onto reactive mineral surfaces constitute two major mechanisms for stabilization of SOC (Matus et al., 2014). Soil characteristics such as content of poorly crystalline minerals, specific surface area, clay content and degree of soil micro-aggregation have all been linked to the capacity of soils to accumulate SOC (Hernández et al., 2012; Kleber et al., 2015;

40   Mikutta et al., 2006, 2009; Poirier et al., 2020). While soil mineralogy itself is thus a well-recognized controller of SOC stabilization (Basile-Doelsch et al., 2005; Hernández et al., 2012; Lyu et al., 2021; Tamrat et al., 2019), surprisingly little attention has gone into understanding how land use history, through its impact on soil geochemistry might in turn indirectly control stability of SOC and organic matter (OM) entering soil.

45   The geochemistry of the reactive mineral phase of a soil is the resultant of both the composition of its parent material and soil weathering status (Mikutta et al., 2009). Weathering status is crucially driven by the time since the onset of weathering, local climate and hydrologic conditions, resilience of minerals to weathering and vegetation cover (Doetterl et al., 2015). Land use, through its control on vegetation, can impact the weathering process by modifying the pH, influencing soil biological activity and nutrient levels, and releasing organic complexing compounds (Van Breemen et al., 1983; Cronan, 2018). On agricultural

50   lands, moreover fertilizer addition and soil disturbance caused by tillage have also been reported to significantly enhance weathering (Churchman and Lowe, 2012; Li et al., 2021; Taylor et al., 2016). While an extensive and still growing number of studies considered land use impacts on SOC stock, soil OM quality and its degradability (Covaleda et al., 2011; Cusack et al., 2013; Huygens et al., 2005), just very few ~~of~~ have considered the potential indirect impact of land use on SOC stability through its effect on the geochemical properties~~soil mineral phase~~. Moreover, the coverage remains limited for several soil groups,

55   including tropical Andosols. A recent study on the Gálápagos islands demonstrated that even after maximum of fifteen years conversion of native forest to cultivated land strikingly accelerated soil weathering (Gerzabek et al., 2019). In particular, formation of secondary minerals should impact SOC retention in volcanic soils as their high capacity to do so is acknowledged to emerge from abundantly present poorly crystalline Al and Fe oxides. Indeed, Asano and Wagai (2014) concluded the importance of short–range order minerals or organo–Al complexes for SOC stabilization in Andosols from correlations with

60   OC stock (Miyazawa et al., 2013), mean residence time (reviewed by Parfitt (2009)), and by chemical characterization of organo–mineral associations (Basile-Doelsch et al., 2007; Mikutta et al., 2009). Next to a large specific surface area, also microaggregation and occlusion therein of intra-microaggregate particulate OM (iPOM) is known to grant a degree of protection against its microbial decay (Six et al., 2000a), particularly in Andosols (Asano et al., 2018; Asano and Wagai, 2014).

Introduction of tillage and removal of permanent vegetative coverage usually adversely affect iPOM-induced physical
protection (Besnard et al., 1996). However, differences between untilled native vegetation or secondary forest on the one hand
and tilled cropland might not be significant for volcanic soils (Dörner et al., 2012; Huygens et al., 2005; Linlin et al., 2016) as
abundant nano sized organo–mineral composites overridingly act as binding agents in microaggregates in Andosols (Asano
and Wagai, 2015).

In Indonesia, the Sunda volcanic arc region (Mt. Tangkuban Perahu and Mt. Burangrang) in West Java, was covered by native
forest until only about two centuries back but has since then been largely replaced by secondary pine forest or agricultural land
use. The With differently aged volcanic deposits and co-occurrence of native forest, secondary forest and agriculturalcultivated
land use this region forms a useful means to understand how land use would influence geochemical properties and impact SOC
storage and stability in volcanic soils. Andosol development would impact SOC storage and stability. A first objective was to
further investigate how cultivation history in this region would have resulted in differential soil aggregation and levels of
iPOM, and mineral associated OM vs. free relatively unprotected OM. We did so by assessing soil OM fractions for a set of 6
Indonesian volcanic soil (Cambisols and Andosols) with native forest, secondary pine forest or agricultural land use. A second
goal was to infer how OM degradability in the topsoil of these tropical volcanic soils itself differs in function of forest vs.
agricultural land use. Assessing the indirect effect of land use on SOC degradability through its mediation of soil mineralogy
is, however, complicated by the fact that quality of native SOC itself is also function of land use. We therefore assessed the
degradability of a single model exogenous OM source (^{13}C-labelled ryegrass residues) to see how land use changes affect
stability of OC in soil. We hypothesize that the enhanced formation of pedogenic poorly crystalline Al under agricultural land
use, as we previously confirmed (Anindita et al., 2022), results in a relative stabilization of the exogenous OM as compared to
native forest or secondary forest. In doing so we take account for the well-known phenomenon that labile OC-inputs can
accelerate the decomposition of native SOC, a process called positive priming (Chen et al., 2014), or conversely restrain
decomposition of SOC and induce negative priming (Blagodatskaya et al., 2014; Qiao et al., 2014). By using a C-isotope
mixing model (Werth and Kuzyakov, 2010), mineralization of the exogenous OM (i.e., ryegrass) and native SOC are
distinguished in the soil incubation experiments.

2 Materials and methods

2.1 Site description and soil sampling

Our study covered soils from the Mount Tangkuban Perahu and Mount Burangrang regions that are part of the Sunda Volcanic
complex in West Java, Indonesia. Six sites were selected to represent the dominant land use types in the area, viz. primary
forest (NF-y), pine forest (PF-i and PF-o) and horticulture (AG-y, AG-i, and AG-o). The mean annual temperature in the study
sites is 19–21°C and mean annual precipitation ranges around 2000–3000 mm per year. Soils at sites NF-y and PF-i are andic
Cambisols and at the PF-o, AG-y, AG-i, AG-o sites aluandic Andosols (Anindita et al., 2022). All soils contain silicate minerals

(i.e. quartz, cristobalite, tridymite), gibbsite, albite, hornblende, 1:1 clay minerals, and non-crystalline materials (Anindita et al., 2022). The proportion of primary minerals is higher in the younger NF-y soil as it is closer (within 1.5 km) to the crater of Mt. Tangkuban Perahu and received ash more recently. The pine forest and agricultural sites were originally all under the primary forest vegetation. At PF-i and PF-o, secondary forests were planted in 1962 for restoration purposes, following earlier

100 deforestation. Agricultural land use at AG-y, AG-i, and AG-o dates back to just 30–50 years ago with mainly diverse horticultural crop rotations with crops potatoes (*Solanum tuberosum*), cabbage (*Brassica oleracea*), green bean (*Phaseolus vulgaris*), tomatoes (*Solanum lycopersicum*), and chayote (*Sechium edule*). Detailed information about land use history, and land management are given in (Anindita et al., 2022).

105 At every site, soil samples were taken at 0–20, 20–40, and 60–80 cm depth. At each depth, the bulk samples were mixed into composite ones, which were then dried to the air, homogenised and sieved (< 2 mm) until further analysis at the Dept. of Environment of Ghent University (Belgium). The pH H_2O was measured using a glass electrode pH meter in a 1:5 soil solution slurry. The estimated clay content was determined using the pipet method after full soil dispersion with Na^+–resin (Bartoli et al., 1991), after testing several other procedures for soil texture analysis that proved incompatible with the investigated set of

110 volcanic soils. The concentrations of total C and N were determined by dry combustion at 1100°C using a LECO 928 series CN-analyser. Aluminum extracted by 0.1 M pyrophosphate solution (Al_p) was taken as measure of complexed Al to OM (McKeague, 1967). Iron and aluminum extractable by ammonium oxalate (Al_o, Fe_o) were used as estimates of X-ray amorphous Al and Fe. We previously quantified crystalline minerals using X-ray diffraction analysis. The amount of amorphous materials undetectable by X-ray diffraction was semi-quantitatively estimated from the difference between the

115 obtained and the real amount of internal standard (Zincite 20%) after semi-quantification of crystalline minerals using BGMN Rietveld and Profex as user interface. Soil specific surface area (SSA) was assessed from adsorption-desorption of N_2 at 77°C following Brunauer–Emmett–Teller (BET) approach. Detailed methods and the results of geochemical analyses of the samples were documented in (Anindita et al., 2022) Selected physicochemical soil properties are given in Table 1. More detailed information of geochemical soil properties can be found in Supplement 1.

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Table 1. Physicochemical soil properties of 6 sampled soil profiles in the Sunda Volcanic complex in West Java, Indonesia (partly taken from Anindita et al. (2022))

Depth	pH H₂O	BD[a]	OC stock[a]	δ13C	C/N ratio	Clay	Exch. Ca	NH4-oxalate extractable		Al_p[a]	SSA[a]	Amorphous materials	Land use & estimated annual C-inputs[b]
								Al_o[a]	Fe_o[a]				
(cm)	(-)	(g cm⁻³)	Mg ha⁻¹	‰	-	%	cmol kg⁻¹	mg g⁻¹		mg g⁻¹	m² g⁻¹	g kg⁻¹	
Primary forest (NF-y)[c]													
0–20	4.1	0.77	56.9	-27.0	15.1	18.70	0.2	3.5	15.5	3.4	9	288	
20–40	4.4	0.78	43.1		20.2	19.81	0.1	2.3	25.4	3.5	27	254	

60–80	4.3	0.65	37.4		20.0	29.51	0.1	4.8	52.4	2.8	69	378	Natural vegetation (estimated plant C input: 6.7 – 12.2 Mg ha^{-1} yr^{-1})
Pine forest (PF-i)[c]													
0–20	4.5	0.64	30.4	-24.3	10.8	67.27	1.8	8.1	11.9	41.0	91	471	Pine forest
20–40	4.4	0.61	15.9		10.2	71.56	0.5	10.4	12.2	32.2	117	429	(estimated plant C input: 3.6 –
70–90	4.4	0.69	8.1		10.0	64.35	0.2	13.7	21.1	13.7	124	481	9.1 Mg ha^{-1} yr^{-1})
Pine forest (PF-o)[c]													
0–20	4.7	0.50	33.0	-24.2	12.6	55.48	0.7	28.5	17.5	10.1	107	497	Pine forest
20–40	4.9	0.56	20.4		12.2	46.43	0.4	27.7	17.2	9.8	145	506	(estimated plant C input: 3.6 –
60–80	4.4	0.60	18.8		11.9	48.82	0.4	25.9	17.5	9.4	127	447	9.1 Mg ha^{-1} yr^{-1})
Agriculture (AG-y)[c]													
0–20	5.1	0.67	40.2	-13.6	18.2	68.21	7.7	14.4	21.1	26.3	114	548	Intensive horticulture ± 50 years.
20–40	4.9	0.66	17.3		11.9	63.06	5.7	16.5	13.0	19.7	125	523	(estimated plant C input = 1.8
60–80	4.8	0.64	14.4		10.8	61.43	4.7	22.3	18.1	12.9	134	547	Mg ha^{-1} yr^{-1}, organic fertilizer C-input = 11.5 Mg ha^{-1} yr^{-1})
Agriculture (AG-i)[c]													
0–20	5.4	0.66	71.4	-15.4	14.7	27.24	6.6	31.4	12.3	7.6	48	623	Intensive horticulture ± 40 years
20–40	5.8	0.47	39.6		17.9	35.62	10.0	33.2	12.1	5.8	128	645	(estimated plant C input = 1.6
50–70	5.9	0.52	28.1		16.9	47.07	7.0	36.4	11.6	5.1	185	650	Mg ha^{-1} yr^{-1}, organic fertilizer C-input = 6.42 Mg ha^{-1} yr^{-1})
Agriculture (AG-o)[c]													
0–20	5.4	0.65	61.1	-24.0	10.5	54.91	10.5	17.1	9.7	9.0	74	531	Horticulture < 30 years
20–40	5.6	0.61	35.0		9.8	50.02	7.0	15.6	9.5	8.6	91	502	(estimated plant C input = 0.98
60–80	5.8	0.62	9.7		8.4	62.81	6.0	9.1	8.0	10.7	108	460	Mg ha^{-1} yr^{-1}, organic fertilizer C-input = 6.8 Mg ha$^{−1}$ yr$^{−1}$)

[a] BD = bulk density; OC = organic carbon; Al$_o$ = aluminum extracted by NH$_4$-oxalate; Fe$_o$ = iron extracted by NH$_4$-oxalate; Al$_p$ = aluminum extracted by Na-pyrophosphate; SSA = specific surface area

[b] C-inputs from vegetation (forest or annual crops) and organic amendments. Forest C-inputs estimated from studies on Indonesian pine forest (Bruijnzeel, 1985) and Indonesian tropical primary forest (Guillaume et al., 2018; Hertel et al., 2009). Crop C-inputs based on farmer interviews and SSB & UGhent (2008). C-inputs from organic amendments were based on farmer interviews and lab-analyses.

[c] History of land use can be referred to Anindita et al. (2022).

2.2 Soil organic matter fractionation

Soils were fractionated using size, density and chemical separation steps according to a modified version of a fractionation scheme proposed by Zimmermann et al. (2007) (Supplement 2, Fig. S1). This procedure separates SOC into five pools, namely into i) OC contained in soil aggregates and associated with sand (S+A), ii) in free particulate organic matter (POM), iii) in water dissolvable OC (DOC), iv) in oxidizable OC associated with the silt and clay (s+c – rSOC) fraction, and v) in a

135 chemically resistant SOC (rSOC) pool. Briefly, 30 g of equivalent dry soil (< 2 mm) was initially dispersed in water by a calibrated ultrasonic probe with an output energy of 22 J ml^{-1}. The resulting slurries were wet-sieved over a 63 µm sieve and rinsed with deionized water until the rinsing water became clear. In the original Zimmermann et al. (2007) method the > 63 µm fraction is further separated into S+A and POM based on density differences using sodium polytungstate at 1.8 g cm^{-3}. However, several samples could not be well separated into free OM on the one hand and predominantly mineral material of

140 the S+A fraction on the other. After pre-tests we instead used a 1.5 g cm^{-3} sodium polytungstate solution to separate free POM from the S+A soil fraction, as per Cerli et al. (2012)'s advise to per soil optimize density cut-off for best separation of free and occluded POM. A subsample of the < 63 µm suspension (±± 10 ml) derived from the wet sieving step was filtered through a 0.45 µm nylon membrane filter. The filtrate was analyzed for its dissolved OC concentration using a HT-I Formacs TOC-analyzer (Skalar, The Netherlands). The DOC pool was calculated by multiplying this OC concentration with the volume of

145 flush water used in the preceding wet sieving step. The < 63 µm suspension was dried at 40°C and weighted to constitute the overall silt+clay (s+c) fraction. A chemically inert share of the SOC (rSOC) was isolated by subjecting the s+c fraction to oxidation by 6 % NaOCl. To this end, one gram of s+c material was weighted inside a 65 ml Nalgene centrifuge tube and 50 ml 6 % NaOCl adjusted to pH 8 was added and allowed to react for 18 h at 25°C. After centrifugation, remnant NaOCl was discarded by decantation. This procedure was repeated three times, the pellet was washed three more times with deionized

150 water, transferred to a pre-weighted aluminum cup, dried at 40°C and weighted. The obtained S+A fraction remains composite as it contains silt+clay associated OC next to occluded POM. In addition to the original scheme proposed by Zimmermann et al. (2007) and Poeplau et al. (2013) a further fractionation of the S+A into s+c and POM and sand-associated OM was included: A 3 g subsample of the obtained S+A fraction was further dispersed by ultrasonication at 400 J ml^{-1} and then separated into two size fractions by passing the obtained slurries over a 63 µm sieve. The obtained < 63 µm fraction contains s+c OM and

155 the >63µm fraction primarily occluded POM and sand-bound OM contained in S+A as well as OM contained in > 63 µm aggregates resistant to dispersal at 400 J ml^{-1}. The S+A and s+c fraction was further on considered as to constitute a single joint OM fraction with s+c obtained after the first 22 J ml^{-1} and 63 µm sieving step. All fractions were analyzed for their C concentration using a LECO 928 series CN-analyzer.

2.3 Soil incubation experiment and isotopic signature measurements

160 Soils were incubated in a standardized way to compare degradability of a model plant-C substrate and SOC in the topsoil (0–20cm) of the 6 considered sites. Decomposition of either substrate was derived by regular measurement of the soil CO_2 efflux and inference of its $\delta^{13}C$ signature. Soil mesocosms were prepared by repacking approximately 150 g of soil (depending on bulk density) into PVC tubes (diameter: 6.8 cm, height: 7 cm) to reach a height of 6.2 cm and bulk density as encountered at the field sites. Soil moisture content was set to 50 % water–filled pore space by addition of deionized water. A ^{13}C-labelled

165 plant-substrate, i.e. pulse-labelled ryegrass (*Lolium perenne*) with $\delta^{13}C$ of +53.7 ‰, was applied at a dose of 1 g kg^{-1} of dry matter. The contrast in $\delta^{13}C$ with SOC (Table 1) allowed to distinguish emitted CO_2 into parts stemming from either native SOC or grass-C mineralization. The $\delta^{13}C$ of topsoil (expressed as $\delta^{13}C$ value (‰) vs. the international Vienna Pee Dee

Belemnite standard) was measured using a PDZ Europe ANCA-GSL elemental analyser, interfaced with a Sercon 20–22 IRMS with SysCon electronics (SetCon, Ceshire, UK).

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Soils were incubated at 20°C for 120 days. On days 1, 3, 5, 8, 12, 17, 24, 32, 38, 47, 59, 73, 87, 101, 111, 120 soil CO_2 emission was inferred by measuring CO_2 build-up in a cylindrical closed-chamber attached consecutively on top of each PVC tube for at least 10 min. The evolution of the headspace CO_2 concentration and its $\delta^{13}C$ was measured every 4 sec by connecting the closed-chamber with a cavity ring-down spectrometer (G2201-i CRDS isotopic CO_2 analyser, Picarro, USA) in a loop via

175 Teflon tubing. Soil CO_2 efflux rate in mg C kg^{-1} h^{-1} was calculated from the slope of the accumulating CO_2 concentration in function of time using the ideal gas law. The $\delta^{13}C$ of emitted CO_2 was estimated from the y-axis intercept of derived Keeling plots (Keeling, 1958). The fraction of CO_2 derived from grass was calculated using the following equations introduced by Werth and Kuzyakov (2010):

$$f_{grass-CO2} = \frac{\delta^{13}C_{total-CO2} - \delta^{13}C_{SOC-CO2}}{\delta^{13}C_{grass-CO2} - \delta^{13}C_{SOC-CO2}} \tag{1}$$

180 $$\delta^{13}C_{grass-CO2} = \delta^{13}C_{grass} - \varepsilon_{grass} \tag{2}$$

$$\delta^{13}C_{SOC-CO2} = \delta^{13}C_{SOC} - \varepsilon_{SOC} \tag{3}$$

with ε_{SOC} (in ‰) the net C-isotopic fractionation resulting from native SOC mineralization and diffusive CO_2 transport in soil until its efflux into the headspace air. The ε_{SOC} was obtained from CO_2-efflux monitoring parallel triplicate sets of control soils without grass added. A third parallel set of soils were amended with a very high dose of grass (viz. 6 g kg^{-1} added grass, i.e.

185 about 4 t C ha^{-1}) to estimate ε_{grass}. This value was operationally calculated by subtracting $\delta^{13}C_{grass}$ from the peak CO_2 emission δ^{13}C-CO_2 of soil with 6 g kg^{-1} grass under the assumption that virtually any emitted CO_2 was then derived from grass mineralization.

Using equations 1, 2 and 3 the fraction of emitted CO_2 derived from grass-C mineralization was calculated per soil and per

190 point in time. The rate of grass-C mineralization (C_{grass}-min, in mg C kg^{-1} h^{-1}) for each measurement day was calculated by multiplying the f_{grass} value with the total CO_2 emission. The rate of SOC mineralization (C_{SOC} min, in mg C kg^{-1} h^{-1}) was calculated by subtracting the rate of C_{grass}-min from the total CO_2-C emission rate. Cumulative CO_2 emissions derived from native SOC-C and grass-C were obtained by consecutively summing up $C_{SOC-CO2}$ and $C_{grass-CO2}$ respectively per time increment between flux measurements. The % of mineralized C_{SOC} was then derived from dividing $C_{SOC-CO2}$ by C_{SOC}.

195 **2.5 Statistics**

~~Independent samples t-tests~~Two-way ANOVA with depth increment and land use as fixed factors wa~~s~~ere used to compare soil properties and the distribution of OC over soil fractions. For individual increments (0 – 20, 20 – 40, and ± 60 – 80 cm) additional t-tests were used as well to test for specific differences between pine forest and agricultural land use. Total, ryegrass- and native SOC cumulative OC mineralization and net cumulative priming of native SOC were only assessed for the 0 – 20

200 cm depth increment and the comparison of means between the pine forest and agriculture land uses was made by independent sample t-tests. The primary forest was excluded from this comparison as it emerged that the parent material from which it developed differed from the other sites (Anindita et al., 2022). ~~both land uses (native and pine forest vs. agriculture, or alternatively agriculture vs. pine forests only) for the distribution of OC over soil fractions and for the cumulative amounts of grass C or native SOC mineralized.~~ Pearson correlation coefficients were used to investigate relations between soil ~~carbon~~

205 fraction SOC proportions, soil OC mineralization, and geochemical properties for the group of pine forest and agricultural soils. ~~The non-parametric test was used if the data were not normally distributed or if the condition of homoscedasticity was unmet.~~ Analyses were completed in IBM SPSS Statistics 27.

3 Results

3.1 Organic carbon in soil fractions

210 Across the studied soils a greater part of soil material ($\pm$ 70 %) was found as s+c fraction (Table 2). There were particularly large proportions of s+c in the PF-i, PF-o, and AG-o soils (> 80 %). Conversely, in the AG-i subsoil, the S+A fraction was the largest. The OC concentration of soil fractions decreased in the order: POM > s+c (including rSOC) > S+A > DOC and was generally higher in the topsoil than subsoil. The OC concentration of the S+A fraction was higher under agricultural than under forest land use ($p < 0.01$), particularly in topsoils of the sites under agricultural land use (30 ~~27~~ – 50 g C kg^{-1} fraction). No such

215 difference in OC concentration existed between SOC in the s+c, POM, DOC and rSOC fractions under agriculture compared to forest (i.e., including primary forest). ~~However,~~ The OC concentration of s+c and~~,~~ s+c – rSOC~~, and rSOC~~ fractions was generally higher ($p < 0.01$) in the agricultural when compared to the pine forest soils solely. The size of the DOC fraction was negligibly small ($\pm$ 0.002 g C kg^{-1} fraction) and is further disregarded. The mean total SOC content in all fractions was ~~not significantly different under forest (29.6 ± 15.1 g C kg^{-1} soil) and~~ higher in agricultural soils (29.6 $\pm$ 15.1 g C kg^{-1} soil) land

220 ~~use, but it was higher under agriculture~~ than pine forest (16.3 $\pm$ 7.7 g C kg^{-1} soil) ($P < 0.05$~~1~~).

Overall, the bulk of SOC was present in the s+c ($\pm$ 79 %) with higher proportion in~~-~~ rSOC ($\pm$ 44 %) than in the s+c - rSOC ($\pm$ 35 %) fraction, followed by S+A ($\pm$ 19 %) and POM ($\pm$ 1 %) fractions (Fig. 1). The distribution of SOC across soil fractions between both land uses. The mean~~amount of~~ OC content in the S+A fraction was higher in the agricultural (11.3 $\pm$

225 10.3 g C kg^{-1} soil) than pine forest (1.5~~2~~ $\pm$ 0.6~~1~~ g C kg^{-1} soil; though only p =~~<~~ 0.09~~1~~) soils. Likewise, its relative contribution to SOC was larger in the agricultural soils (32 % of SOC), both when compared to all three forest sites (8% of SOC) ~~(P < 0.01)~~ or to just the two pine forest sites (9% of SOC), (though only at p = 0.08). ~~(P < 0.01).~~ Particularly in ~~topsoil of~~ AG-y at depth 0 – 20 cm ~~(~~13 g C kg^{-1} soil) and in AG-~~i~~i at depth 0 – 20 and 20 – 40 cm (22 and 31 g C kg^{-1} soil, respectively), a large share of the SOC was in the S+A fraction. The s+c followed an opposite trend with a larger SOC proportion under forest (all three

230 (89.5 % of SOC) or just the two pine forests (89.8 % of SOC)) than under agricultural land-use (68 % of SOC) ($P < 0.08$~~5~~) (Fig. 1). Out of the s+c the resistant SOC (rSOC) fraction accounted for approximately a third to half of SOC and its proportion

(5244 % of SOC) was likewise higher under pine forest than agricultural land use (p < 0.05). Free POM contributed on average less than 5 % of SOC and constituted a larger share of SOC in topsoil compared to both subsoil depth layers (p < 0.05). The occasional low free POM C-concentrations (Table 2) indicate that some mineral matter was indicate that some mineral matter was left in the isolated POM fraction. However, given its very small mass proportion (median 0.1%) this artefact has negligible further impact on the overall distribution of SOC across soil fractions. The SOC proportion of free POM (% of SOC) was also higher under pine forest than agricultural land use (P < 0.01).

Table 2. Mass proportion, C concentration and total content of SOC contained in soil fractions isolated by a modified version of the Zimmermann et al. (2007) method

Depth (cm)	Soil mass proportion (%)			C concentration (g kg⁻¹ fraction)					Amount of C (g kg⁻¹ soil)				
	POM	S+A	s+c	POM	S+A	s+c		DOC	POM	S+A	s+c		Total SOC in bulk soil
						s+c - rSOC	rSOC				s+c -rSOC	rSOC	
Primary forest (NF-y)													
0–20	0.2	37.6	62.2	412.5	4.6	31.1	30.5	1.0	0.9	1.7	19.4	18.9	37.1
20–40	1.1	31.0	67.9	393.0	2.9	12.9	24.9	0.7	4.4	0.9	8.8	16.9	26.0
60–80	0.1	27.3	72.6	367.5	12.9	16.0	36.3	0.8	0.5	3.6	11.5	26.3	28.6
Pine forest (PF-i)													
0–20	0.1	9.2	90.7	227.0	11.5	12.2	9.8	1.9	0.3	1.1	11.1	8.9	23.6
20–40	0.1	16.5	83.5	162.0	11.6	5.6	7.1	1.0	0.1	1.9	4.7	6.0	13.0
70–90	0.0	7.1	92.9	103.6	3.6	2.9	4.1	0.4	0.1	0.3	2.7	3.8	5.9
Pine forest (PF-o)													
0–20	0.4	16.3	83.3	188.3	19.0	12.9	17.6	1.7	0.8	3.1	10.8	14.6	33.3
20–40	0.2	15.5	84.3	148.7	10.3	7.4	10.4	1.5	0.2	1.6	6.2	8.8	18.2
60–80	0.1	11.5	88.4	135.6	9.6	3.3	8.0	1.1	0.1	1.1	2.9	7.1	15.7
Agriculture (AG-y)													
0–20	0.1	39.6	60.3	206.0	32.2	12.7	17.8	1.5	0.1	12.8	7.7	10.7	29.9
20–40	0.04	34.8	65.2	63.7	15.5	6.6	9.5	0.3	0.02	5.4	4.3	6.2	13.0
60-80	0.04	30.5	69.4	15.6	12.2	5.8	7.6	0.4	0.01	3.7	4.0	5.2	11.2
Agriculture (AG-i)													
0–20	0.1	45.7	54.2	350.0	48.7	26.7	36.1	0.6	0.2	22.3	14.5	19.6	54.4
20–40	0.04	66.3	33.7	401.0	46.2	16.1	31.4	1.1	0.04	30.6	5.5	10.6	42.6
50–70	0.03	64.1	35.8	587.5	26.3	10.4	19.7	0.8	0.1	16.9	3.7	7.1	26.9
Agriculture (AG-o)													
0–20	0.2	9.2	90.6	420.7	29.6	21.7	17.2	1.8	0.8	2.7	19.7	15.6	47.0
20–40	0.2	8.2	91.6	311.3	19.0	14.4	12.5	1.3	0.5	1.6	13.2	11.5	28.8
60–80	0.04	4.6	95.4	92.6	7.1	7.0	3.0	1.2	0.1	0.3	6.7	2.8	7.8

60-80	0.1±0.1	11.5±2.2	88.4±2.2	135.6±48.9	9.6±0.8	3.3±0.9	8.0±0.3	1.1±0.0	0.1±0.0	1.1±0.2	2.9±0.8	7.1±0.4
Agriculture (AG-y)												
0-20	0.1±0.0	39.6±6.3	60.3±6.3	206.0±4.0	32.2±0.7	12.7±2.0	17.8±0.1	1.5±0.9	0.1±0.5	12.8±2.1	7.7±1.6	10.7±1.2
20-40	0.0±0.0	34.8±1.5	65.2±1.5	63.17±0.9	15.5±0.4	6.6±0.5	9.5±0.3	0.3±0.1	0.0±0.0	5.4±0.2	4.3±0.5	6.2±0.1
60-80	0.0±0.0	30.5±3.5	69.4±3.5	15.16±2.4	12.2±0.3	5.8±0.5	7.6±0.2	0.4±0.1	0.0±0.0	3.7±0.4	4.0±0.5	5.2±0.4
Agriculture (AG-i)												
0-20	0.1±0.0	45.7±1.0	54.2±1.1	3500.0±52.0	48.7±2.4	26.7±3.6	36.1±3.2	0.6±0.1	0.2±0.1	22.3±1.3	14.5±2.1	19.6±1.6
20-40	0.0±0.0	66.3±1.4	33.7±1.4	4010.0±88.0	46.2±0.3	16.1±2.3	31.4±1.8	1.1±0.7	0.0±0.4	30.6±0.8	5.5±1.0	10.6±2.6
50-70	0.0±0.0	64.1±1.8	35.8±1.8	5875±240	26.3±0.1	10.4±0.9	19.7±0.7	0.8±0.4	0.1±0.0	16.9±0.4	3.7±0.3	7.1±0.4
Agriculture (AG-o)												
0-20	0.2±0.0	9.2±0.3	90.6±0.3	420.7±88.3	29.6±2.6	21.7±5.4	17.2±0.8	1.8±0.4	0.8±0.3	2.7±0.3	19.7±5.0	15.6±0.7

Figure 1. The distribution of OC over soil fractions obtained by a modified version of the Zimmerman et al. (2007) procedure for 6 soil profiles sampled at 0 – 20, 20 – 40, ± (0-60 – 80 cm) soil profiles in the Sunda Volcanic complex in West Java, Indonesia. ErrorVertical bars indicate standard deviations for three lab-replicates (n = 3)

3.2 C:N ratio, amorphous aluminum and iron in the sand-aggregates (S+A) and silt-clay (s+c) fractions

The ratio of C:N ranged from 7.36 – 19.820 in S+A and 7.5 – 20.1 in s+c fractions (Table 3) and their mean values did not differ. The S+A C:N-ratio was higher in the agriculture than in the pine forest soils (p =< 0.075). The content of Al_o varied

between $1.7\overline{1.5}$ to $5\underline{6.67}$ g kg^{-1} and $3.\underline{2}\overline{2}$ to $4\underline{6.67}$ g kg^{-1} in the S+A and s+c fractions, respectively, whereas, ~~whereas~~ Fe$_o$ ranged from $9.6\overline{9.6}$ to $3\underline{4.3}\overline{0}$ g kg^{-1} and $7.6\overline{7.6}$ to $74.\underline{2}$ g kg^{-1} in the S+A and s+c fractions, respectively. A much lower Al$_o$ content in the NF-y site s+c and S+A fractions compared to all other soils was in line with its distinctive total elemental composition previously reported by Anindita et al. (2022). The ~~S+A~~ mean Al$_o$ content in S+A fraction at all depths was higher under agriculture ($28.9 \pm\overline{+} 20.8\overline{12}$ mg g^{-1}) than pine forest ($2\underline{0.9} \pm 12.4\overline{0}$ mg g^{-1}) (p = 0.09) ~~(p < 0.05) use~~. The Fe$_o$ contents in S+A and s+c fraction was generally higher under pine forest than agricultural soils, particularly at depth 20 – 40 and $\pm$ 60 – 80 cm, with no significant difference. ~~The s+c fraction Fe$_o$ content was higher under pine forest (21.6 ± 4.7 mg g^{-1}) than under agricultural land use (17 ± 7.2 mg g^{-1}) (p < 0.01).~~

Table 3. Ratio of C:N, oxalate extractable-aluminum (Al$_o$) and iron (Fe$_o$) in S+A and s+c fractions

~~Depth~~	~~S+A fraction~~			~~s+c fraction~~		
	~~C:N ratio~~	~~Al$_o$~~	~~Fe$_o$~~	~~C:N ratio~~	~~Al$_o$~~	~~Fe$_o$~~
		~~g kg^{-1}~~			~~g kg^{-1}~~	
~~Primary forest (NF-y)~~						
~~0-20~~	~~6.5 ± 2.9~~	~~1.7 ± 0.5~~	~~17.5 ± 1.6~~	~~15.5 ± 0.4~~	~~4.2 ± 0.6~~	~~26.6 ± 0.3~~
~~20-40~~	~~6.6 ± 1.6~~	~~1.7 ± 0.3~~	~~28.1 ± 4.0~~	~~19.8 ± 0.5~~	~~3.2 ± 0.6~~	~~39.3 ± 5.7~~
~~60-80~~	~~15 ± 2.2~~	~~1.5 ± 0.5~~	~~20.0 ± 7.6~~	~~20.1 ± 0.6~~	~~7.6 ± 0.4~~	~~74.2 ± 3.6~~
~~Pine forest (PF-i)~~						
~~0-20~~	~~9.5 ± 0.2~~	~~11.0 ± 0.6~~	~~19.9 ± 1.3~~	~~9.3 ± 0.7~~	~~11.1 ± 0.6~~	~~15.8 ± 0.7~~
~~20-40~~	~~9.1 ± 0.6~~	~~15.3 ± 0.2~~	~~21.1 ± 0.9~~	~~8.9 ± 0.2~~	~~15.3 ± 1.9~~	~~20.3 ± 5.2~~
~~70-90~~	~~7.3 ± 0.5~~	~~10.2 ± 0.2~~	~~28.5 ± 5.0~~	~~9.7 ± 2.8~~	~~16.7 ± 0.3~~	~~29.8 ± 1.1~~
~~Pine forest (PF-o)~~						
~~0-20~~	~~12.0 ± 0.5~~	~~34.6 ± 3.6~~	~~24.9 ± 3.5~~	~~11.2 ± 0.2~~	~~37.1 ± 0.8~~	~~21.6 ± 0.6~~
~~20-40~~	~~10.5 ± 0.3~~	~~28.5 ± 2.6~~	~~27.9 ± 1.5~~	~~10.7 ± 1.2~~	~~34.9 ± 1.1~~	~~20.2 ± 0.5~~
~~60-80~~	~~10.6 ± 0.3~~	~~10.6 ± 0.3~~	~~26.1 ± 1.9~~	~~10 ± 0.6~~	~~28.1 ± 2.8~~	~~21.9 ± 2.1~~
~~Agriculture (AG-y)~~						
~~0-20~~	~~18.7 ± 0.7~~	~~19.9 ± 0.3~~	~~30.1 ± 3.5~~	~~17.0 ± 0.8~~	~~18.6 ± 2.1~~	~~31.9 ± 4.2~~
~~20-40~~	~~12.1 ± 0.6~~	~~25.7 ± 1.5~~	~~24.0 ± 1.9~~	~~11.1 ± 0.6~~	~~19.3 ± 0.4~~	~~16.5 ± 1.5~~
~~60-80~~	~~11.0 0.8~~	~~29.4 ± 1.0~~	~~22.1 ± 2.8~~	~~10.6 0.3~~	~~26.5 ± 1.0~~	~~20.5 ± 2.5~~
~~Agriculture (AG-i)~~						
~~0-20~~	~~19.6 ± 0.3~~	~~44.8 ± 1.2~~	~~11.8 ± 1.1~~	~~11.7 ± 0.2~~	~~44.5 ± 1.5~~	~~13.7 ± 0.3~~
~~20-40~~	~~19.8 ± 0.4~~	~~53.0 ± 3.6~~	~~11.0 ± 1.8~~	~~15.6 ± 0.3~~	~~45.7 ± 0.5~~	~~10.2 ± 0.2~~
~~50-70~~	~~18.0 ± 0.9~~	~~56.6 ± 1.2~~	~~9.6 ± 0.5~~	~~16.2 ± 0.4~~	~~46.6 ± 2.2~~	~~7.6 ± 0.7~~
~~Agriculture (AG-o)~~						
~~0-20~~	~~12.6 ± 0.5~~	~~21.7 ± 2.5~~	~~27.4 ± 1.5~~	~~9.4 ± 0.9~~	~~22.0 ± 0.4~~	~~14.0 ± 0.9~~
~~20-40~~	~~9.5 ± 0.5~~	~~23.1 ± 1.6~~	~~34.3 ± 5.0~~	~~8.1 ± 0.2~~	~~21.6 ± 0.8~~	~~15.3 ± 1.7~~

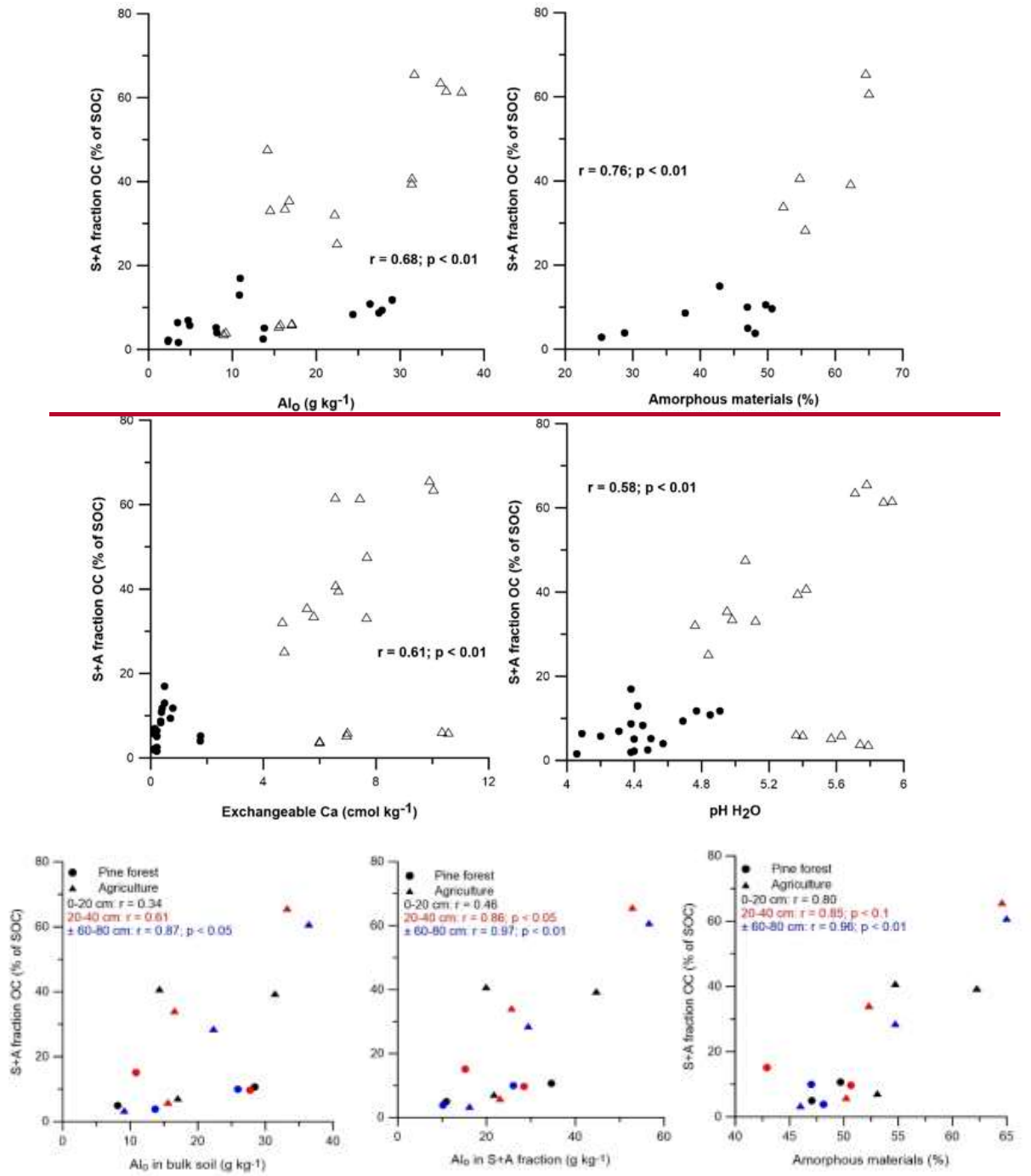
Depth	S+A fraction			s+c fraction		
	C:N ratio	Al_o	Fe_o	C:N ratio	Al_o	Fe_o
		g kg^{-1}				g kg^{-1}
~~60–80~~	~~7.5 ± 0.04~~	~~16.1 ± 1.0~~	~~33.5 ± 2.9~~	~~7.5 ± 0.6~~	~~14.5 ± 0.5~~	~~22.7 ± 1.2~~
Primary forest (NF-y)						
0 – 20	16.5	1.7	17.5	15.5	4.2	26.6
20 – 40	18.6	1.7	28.1	19.8	3.2	39.3
60 – 80	15.0	1.5	20.0	20.1	7.6	74.2
Pine forest (PF-i)						
0 – 20	9.5	11.0	19.9	9.3	11.1	15.8
20 – 40	9.1	15.3	21.1	8.9	15.3	20.3
70 – 90	7.3	10.2	28.5	9.7	16.7	29.8
Pine forest (PF-o)						
0 – 20	12.0	34.6	24.9	11.2	37.1	21.6
20 – 40	10.5	28.5	27.9	10.7	34.9	20.2
60 – 80	10.6	10.6	26.1	10.0	28.1	21.9
Agriculture (AG-y)						
0 – 20	18.7	19.9	30.1	17.0	18.6	31.9
20 – 40	12.1	25.7	24.0	11.1	19.3	16.5
60 – 80	11.0	29.4	22.1	10.6	26.5	20.5
Agriculture (AG-i)						
0 – 20	19.6	44.8	11.8	11.7	44.5	13.7
20 – 40	19.8	53.0	11.0	15.6	45.7	10.2
50 – 70	18.0	56.6	9.6	16.2	46.6	7.6
Agriculture (AG-o)						
0 – 20	12.6	21.7	27.4	9.4	22.0	14.0
20 – 40	9.5	23.1	34.3	8.1	21.6	15.3
60 – 80	7.5	16.1	33.5	7.5	14.5	22.7

3.3 Correlations between SOC fractions and selected chemical soil properties

The proportion of several of the isolated SOC fractions correlated to some of the geochemical soil properties (Fig. 2). ~~Across all land uses and depths~~By considering only pine forest and agricultural soils, the SOC proportion of the S+A fraction was

265 positively correlated with Al_o (in bulk soil as well as in the S+A fraction), ~~$Al_o+1/2Fe_o$, pH H_2O, exchangeable Ca,~~ C:N ratio of S+A fraction, and content of amorphous materials at all depths (p < 0.05~~1~~). These soil properties were also positively correlated with the amount of OC in S+A fraction (g C kg^{-1} soil) and OC concentration in S+A fraction (g C kg^{-1} fraction). ~~When considering only the pine forest and agricultural soils, SOC proportion of the S+A fraction was still positively correlated to those soil properties. The SOC proportion in s+c fraction was positively correlated with exchangeable Al and negatively~~

270 ~~correlated with pH H_2O (p < 0.01). When considering only pine forest and agriculture,~~ Ppositive correlations existed between SOC proportion in s+c fraction with the amount of Fe_o s+c fraction at depth of ± 60 – 80 cm (p < 0.05), but the amount of OC (g C kg^{-1} soil) and OC concentration (g C kg^{-1} fraction) in s+c fraction correlated negatively to Fe_o s+c fraction at all depths.

(p < 0.01). The proportion of rSOC in s+c fraction (i.e. rSOC / s+c x 100) correlated positively (pP < 0.05) to Al_o content at depth 60 – 80 cm (r = 0.967), SSA at 20 – 40 cm (r = 0.954), and the micropores volume at 0 – 20 and 20 – 40 cm (r = 0.66 and r = 0.86, respectively) and the Fe_o content (r = 0.52).

3.4 Carbon mineralization experiment

3.4.1 Gross soil carbon mineralization

Across all sites, C-mineralization (C-min) rates were highest for AG-i and AG-o and peaked already during the first day of incubation, while for the other soils rates peaked at day 3 or 5 only. After day 38, the C-min rates stabilized across time. The cumulative total CO_2-C emission and derived amount of C-mineralized (SOC + ryegrass) generally followed a sequence NF-y < AG-y < AG-i < PF-i < AG-o < PF-o. Pine forest soils displayed higher cumulative C mineralization than agricultural soils ($p < 0.05$). Overall, the 120-day cumulative C mineralization was 194–419 mg kg^{-1} higher in soil with grass added than without (Fig. 3).

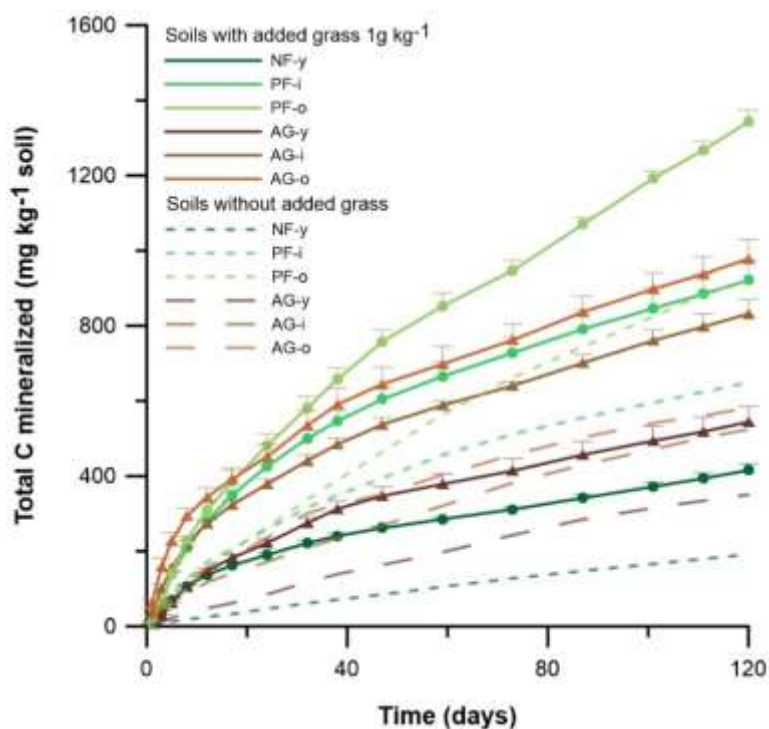



Figure 3. Gross cumulative amount of C mineralized in soil with and without 1 g C kg^{-1} ryegrass added. Vertical bars indicate standard deviations of three lab replicates (n = 3) and are presented for the grass amended soils only. Sites under forest and agriculture are indicated by ● and Δ, respectively.

3.4.2 Grass C-mineralization

The C_{grass}-min rates peaked within 12 days after the start of the incubation, and they dropped thereafter to just half to one third of the initial rates. The C_{grass} mineralization rate was conspicuously high on the first day of incubation in soils AG-i and AG-o, whereas for the other soils mineralization peaked on day 5 only. From day 38 onwards, the C_{grass}-min rate had become more or less similar in all six sites. By the end of the 120-days incubations, 22-38 % of the added ryegrass had been mineralized. The highest cumulative C_{grass}-min was found for PF-o (389 mg kg^{-1}), followed by AG-i > AG-o ≈ PF-i ≈ AG-y > NF-y. There were no significant differences in C_{grass}-min between the sets of agricultural and forest soils.

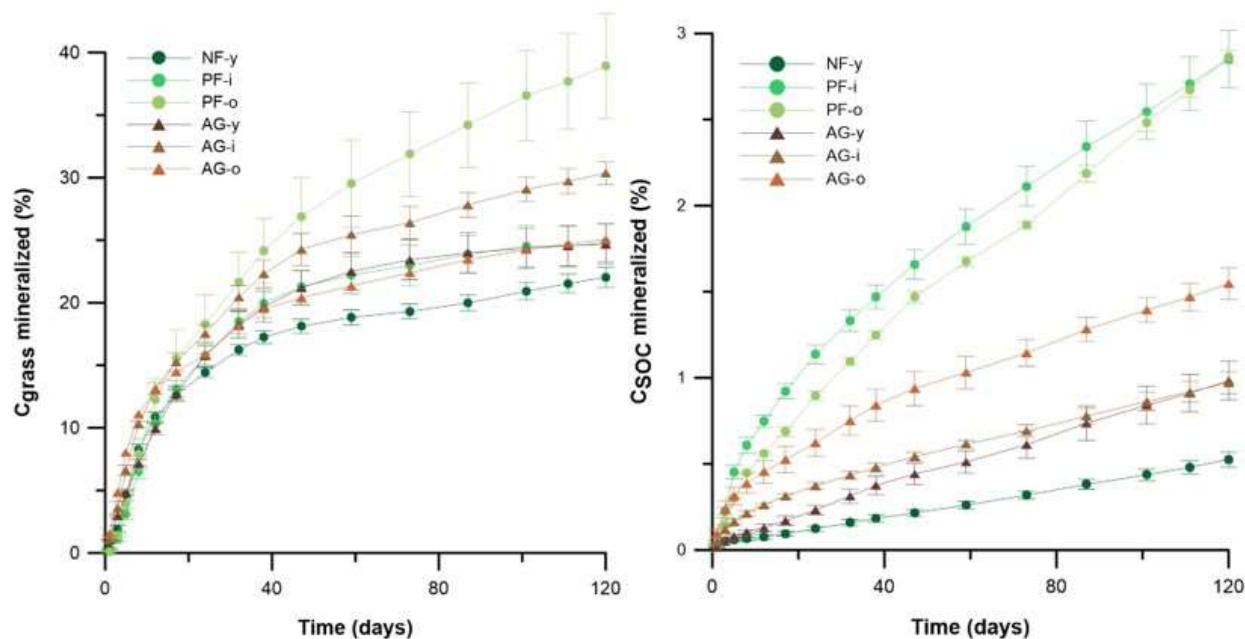



Figure 4. The percentage of C_{grass} (left) and C_{SOC} (right) mineralized during 120 days of incubation in soils with 1 g kg^{-1} grass or no grass added, respectively. Vertical bars indicate standard deviations of triplicate lab repetitions. Sites under forest and agriculture are indicated by ● and Δ, respectively.

3.4.3 Native SOC mineralization

Mineralization of SOC (C_{SOC} -min) contributed more to gross soil C mineralization than C_{grass} -min did. There were large differences in C_{SOC} -min between the 0-20 cm soil layers of the six sites. By the end of the incubation, the highest cumulative amount of SOC mineralized was found for PF-o (953 ±+ 13 mg kg^{-1}) while a fourfold lower amount was mineralized in case of NF-y (195 ±+ 17 mg kg^{-1}). Significantly less SOC was mineralized in the agricultural soils (517 ±+ 90 mg kg^{-1}) than in the pine forest soils (813 ±+ 156 mg kg^{-1}) (p < 0.01). Relatively, 0.5–2.9 % of the SOC had been mineralized within the 120 days incubations (Fig. 4). A larger relative share% of SOC was mineralized in the pine forest soils (2.9 % ±+ 0.1 % of SOC) than in the agricultural soils (1.2 % ±+ 0.3 % of SOC) (p < 0.01).

Priming of native SOC mineralization was assessed by comparing C_{SOC}-min between the soils with and without 1 g kg^{-1} grass added (Fig. 5). During the first week, grass addition tended to increase the C_{SOC}-min rate in most soils, i.e. there was positive priming of native SOC. Along the 120-days experiment, however, the direction and magnitude of the net cumulative priming effect varied strongly among soils. Little or no net priming of C_{SOC}-min occurred in the NF-y soil, as a result of initial positive priming until day 17 but negative priming afterwards. In the pine forest soils likewise periods of positive and negative priming alternated, with at the end of the 120-days period an alike limited net positive priming of SOC at both PF sites. Priming of SOC was diverse among the three agricultural soils. While strong positive priming throughout the 120-days period in the AG-o soil, while the opposite was true for AG-y and no net priming occurred in case of AG-i. On average, the net 120-days cumulative priming of SOC in forest (19.3 mg CO$_2$-C kg^{-1} day^{-1}) was lower than agricultural (31.2 mg CO$_2$-C kg^{-1} day^{-1}) land use, but due to wide variation between replicate sites this difference proved insignificant and moreover net priming rates were not significantly different from zero.

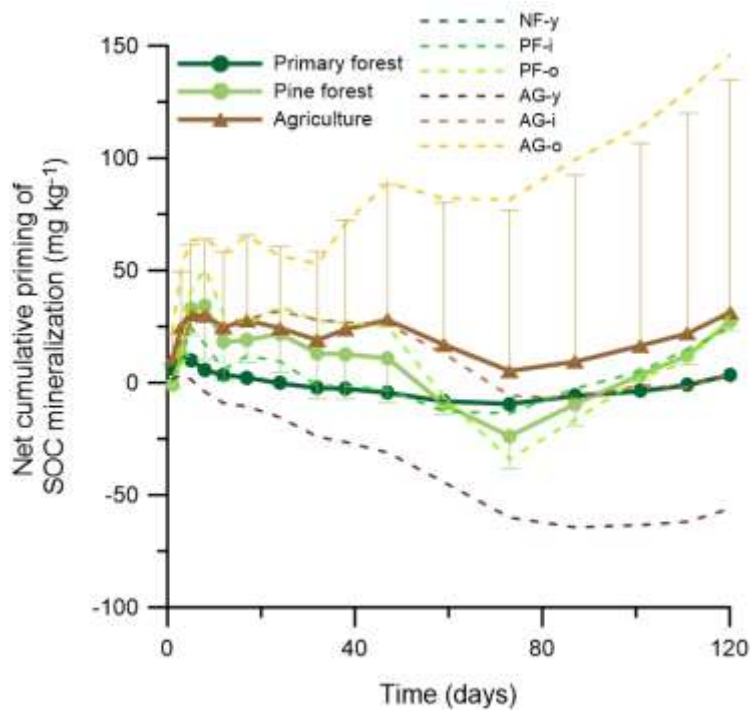
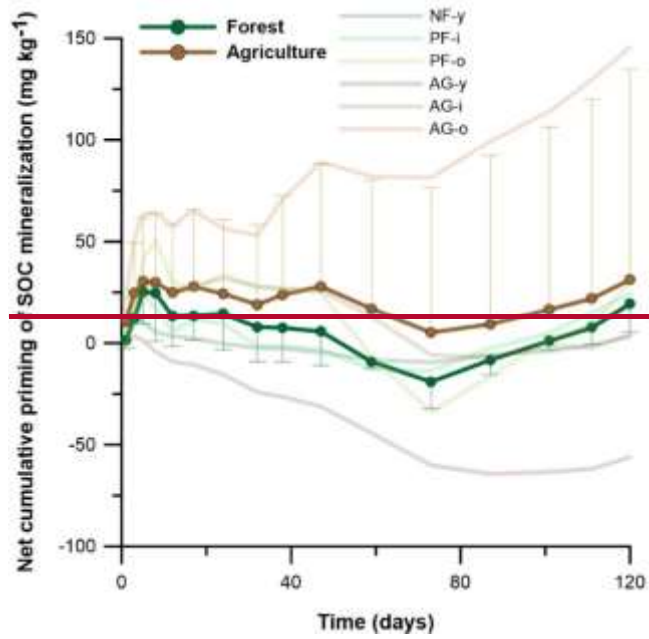



Figure 5. Net effect of grass addition (1 g kg^{-1}) on cumulative native SOC mineralization. Positive and negative figures denote net positive or net negative cumulative priming of SOC mineralization. Dotted lines present the temporal evolution of mean net cumulative priming effect for either forest or agricultural land use, with respectively only upper or lower error bars representing the standard deviations on the data.

4 Discussion

4.1 Land use effects on free and aggregate protected OC

335   Overall, the portion of S+A fraction material (i.e., > 63 µm 400 J ml^{-1} ultrasonication resistant aggregates and sand particles) was nearly double in the agricultural (34 ±+ 22 %) than pine forest sites (139 ±+ 310 %), and nearly double compared to all forest, including primary forest (though only at p =< 0.1, probably due to the small sample number). This indicated stronger soil aggregation and aggregate stability under agriculture. In line, a fourfold share of SOC resided in the S+A fraction under agriculture (32 + 22 %) than pine forest (87.7 + 4 %) (p =< 0.085). The important role of soil microaggregates for SOC storage

340   has been displayed by numerous studies (Dungait et al., 2012; Rabbi et al., 2016; Six et al., 2002). We expected a lesser share of SOC to be occluded inside aggregates in the tilled agricultural soils, as absence of tillage results in less disruption of macroaggregates with increased formation of microaggregates and occlusion of POM (Six et al., 2000b; Zheng et al., 2018). However, tillage is not the only determinant of soil aggregate formation and breakdown as aggregate stability also depends on presence of binding agents that cluster mineral and organic particles into aggregates as well as size and mineralogy of the less

345   reactive 'skeletal' particles. A further analysis of the soil mineralogy could prove useful to explain the observed variation in storage of OM in the S+A fraction between both land-uses. With respect to 'skeletal' particles, main identified constituents were from the quartz group (Tridymite, Quartz, Cristobalite) (7 – 14 %) and 1:1 clay minerals (5 – 35 %) (Anindita et al., 2022), which, because of their inherent low permanent negative charge may be considered as relatively unreactive as well. In addition, smaller shares of Hornblende, Andesine, Albite, and Rutile were present as well. Unsurprisingly, the XRD-estimated

350   levels of these primary minerals and 1:1 – clays did not correlate to the mass proportion of the S+A fraction, indeed suggesting that instead mainly other soil constituents acted as binding agents. Moreover, as contents of these relatively unreactive phases did not differ between the PF and AG soils, their variation could not explain the strong contrast in S+A contained OC between both land-uses.

355   Major binding agents considered to work at micron to submicron scales are instead poorly-crystalline minerals, redox-sensitive minerals and microbial products (detritus and metabolites) (Oades and Waters, 1991). Particularly XRD amorphous materials constituted the bulk of the mineral phase (up to 65 %). The limited oxalate extracted Si suggested allophane, imogolite, and volcanic glass levels to be minor (Anindita et al., 2022). Hence a large pool of unidentified Al and Fe (oxy-)(hydr-) oxides instead likely formed the chief part of the XRD amorphous mineral phase. Particularly, mineral associated with Al_o would

360   appear to be relevant colloids as bulk soil Al_o level correlated well with bulk soil micropores volume and specific surface area (Anindita et al., 2022). Wagai et al. (2018) indeed also found reactive metal phase to be important binding agents in Allophanic Andosols. As NH_4-oxalate extraction is not entirely selective toward poorly-crystalline minerals (Rennert et al., 2018), it is probable that Al_o partly derived from crystalline Gibbsite as well. The same goes for Fe and crystalline pedogenic Fe. All soils contained rather large proportions of XRD detectable Gibbsite (3 – 15 %) with the exception of AG-y also 1 – 3 % magnetite

365   (Anindita et al., 2022). However, with no consistent differences in their XRD-spectrum proportions between both land-uses,

and no correlation to the S+A fraction mass proportion, it is unlikely that variation in these secondary crystalline minerals led to contrasting soil aggregation and distribution of OC between the isolated S+A or s+c fractions between the PF and AG land-uses. Instead, the S+A mass proportion (in g kg^{-1} bulk soil) correlated to S+A concentrations (in g kg^{-1} S+A fraction) of both Al$_o$ (r = 0.86; p < 0.05) and OC (r = 0.73; p < 0.05). It is thus likely that the 'glue' between 'skeletal' mineral particles consisted of a mixture of OM and poorly crystalline non-allophane/imogolite Al-containing minerals. In turn, the SOC proportion of the S+A fraction correlated positively with contents of Al$_o$ and the % of X-ray amorphous materials, particularly at depths of 20 – 40 and ± 60 – 80 cm (r ± 0.8; p < 0.05). This indicates that higher levels of Al$_o$ as well as accumulation of SOC under agriculture and pine forest would have enhanced aggregation, and thus a larger share of SOC inside these aggregates. Furthermore, rRepeated addition of labile C via manure and compost amendments was shown to result in greater formation of macroaggregate (Du et al., 2014; Mikha and Rice, 2004; Yu et al., 2012) by increased production of microbial-derived binding agents. Manure and compost amendments to the AG sites were vast (Table 1), and so the enhanced addition of labile C as compared to the forest sites may have boosted aggregate formation with more SOC storage in the S+A fraction under agricultural land use. Nevertheless, it is long known that SOM can have an inhibiting effect on the crystallization process of Al-oxides, similar to the anti-gibbsitic effect, leading to polymerization rather than crystallization (Borggaard et al., 1990). Kang et al. (2009) as well argued that SOM can inhibit the crystallization of Al, resulting in less crystalline Al-oxides, which are in turn adsorbents of SOM. Particularly in a tropical climate where weathering and SOC decomposition occur fast, there may be important positive feedback between accumulation of SOM, induced by vast additions of exogenous OM and formation of poorly crystalline Al in Andosols that has not been looked into to date. Lastly, less free POM was found in the agricultural than forest soils likely as a logical consequence of more POM occlusion under agriculture. However, we cannot exclude that also a better degradability of crop-derived residues vs. pine or native forest litter co-explains these trends. It is well established that litter rich in cutin, waxes and lignin such as derived from pine forests is less degradable than plant litter richer in carbohydrates and organic N like most crop residues (Berg and McClaugherty, 2003).

Next to organic binding agents, Wagai et al. (2018) also found reactive metal phases to be important binding agents in Allophanic Andisols which was in line with the higher amount of Al$_o$ S+A in agricultural than forest soils (p < 0.05). With high to very high levels of Al$_o$ (up to 4% of the soil mass), it seems very likely that amorphous to poorly crystalline Al-containing minerals would have been prominent binding agents in our set of soils. The bulk soil and S+A fraction contents of Al$_o$ were also larger in the agricultural than in the forest soils (p < 0.05).. When comparing the agricultural sites and only the pine forest sites likewise differences existed. In other words the results were not biased by the deviating mineralogical composition and texture of the NF site. Other than aluminium oxides, the content of exchangeable Ca also correlated positively to S+A fraction mass proportion (r = 0.40) and the SOC proportion of the S+A fraction (r = 0.61; p < 0.01). Soil Ca is also well known for its positive effects on aggregation via formation of clay–polyvalent cation–OM complexes (de Kerchove and Elimelech, 2007; Six et al., 2004). This mechanism might have co-promoted aggregate occlusion of OC and its accumulation (Bertrand et al., 2007; Paul et al., 2003), but given the high Al$_o$ levels, likely Ca^{2+} would have played a smaller role. The higher

levels of exchangeable Ca under agriculture compared to forest (p < 0.05) evidently result from liming which increases the pH. The concomitant difference in Al_o, exchangeable Ca^{2+} and S+A OC content between agricultural and forest sites makes it impossible to derive the relative importance of these various binding agents in stimulation of aggregate OC occlusion under agricultural land use. Notwithstanding, when considering only pine forest and agricultural sites, the S+A SOC proportion sole best correlated to the S+A Al_o content (r = 0.80; p < 0.01), strengthening the view that to a substantial extent enhanced Al_o content under agriculture promoted storage of SOC inside stable aggregates. By expanding the Zimmerman et al. (2007) fractionation procedure with a stronger (400 J ml^{-1}) ultrasonic dispersion step we attempted to further isolate s+c associated OC from POM contained in the S+A fraction. The intermediate C:N ratio (mean: 12 ± 4.7) of the final 400 J ml^{-1} S+A fraction indicates that next to POM it still also contained other, likely mineral associated, OM, complicating further interpretation of mechanisms for S+A SOC storage in the agricultural sites. Nevertheless, the higher S+A fraction C:N ratio of the agricultural sites vs. the forests (P < 0.05) demonstrates that at least to some extent enhanced SOC storage in aggregates under agricultural land use resulted from extra occluded POM storage. Particularly for the 0 – 20 cm layer the contrast in the S+A C:N ratio (agriculture: 17.0 vs. forest: 9.3) supports this view. Lastly, less free POM was found in the agricultural than forest soils (p < 0.01), likely as a logical consequence of more POM occlusion under agriculture. However, we cannot exclude that also a better degradability of crop-derived residues vs. pine or native forest litter co-explains these trends. It is well established that litter rich in cutin, waxes and lignin such as derived from pine forests is less degradable than plant litter richer in carbohydrates and organic N like most crop residues (Berg and McClaugherty, 2003).

4.2 Effect of land use on SOC in the silt and clay fraction

Interaction of SOC with silt and clay provides long-term stabilization to SOC against decomposition and therefore forms a key mechanism for SOC sequestration (De Clercq et al., 2015). SOC sorbs to phyllosilicate clays, Al-, Fe- and Mn-oxides, poorly crystalline minerals, as well as polyvalent cations that form a bridge between minerals and organic constituents (Blanco-Canqui and Lal, 2004). However, for our soils we found that despite higher concentrations of Al_o under agriculture, a lesser share of the SOC was present in the s+c fraction (as % of SOC) compared to the pine forest soils (though only at p = 0.08)(p < 0.05). thus Aassociation of OC with Al_o–containing minerals could not explain the higher SOC proportion of OC in s+c under forest. As the amount of s+c OC (in g C kg^{-1} soil) was in fact similar between both land-uses, it appears that a lower s+c SOC contribution in the agricultural soils was instead simply mirroring trends in the S+A fraction. The s+c fraction proportion to SOC correlated negatively to soil pH and positively to exchangeable Al content but likewise these correlations probably do not point to a causal relationship but rather result from the higher SOC proportion of S+A OC under agriculture alongside liming-caused lifted soil pH and lowered exchangeable Al. A weak positive correlation between the s+c SOC proportion and Fe_o in s+c at ± 60 – 80 cm (r = 0.9345; p < 0.051) could indicate that association with poorly crystalline Fe stabilizes OM in the silt and clay fraction. But, again as s+c SOC content (g kg^{-1} soil) and OC concentration (g kg^{-1} fraction) did not differ betweencorrelated negatively at all measured depths with Fe_o in s+c fraction, the agricultural and the forest sites while Fe_o did, such land-use control on s+c Fe_o associated SOC seems unlikely. On the other hand, the higher SOC content (g C kg^{-1}

soil) in s+c fraction of NF-y than other soils, particularly at depth of ± 60 – 80 cm, might be due to the differences in mineralogy. At this depth, the amorphous Fe content (Fe$_o$ and Fe$_h$) in NF-y was very high compared to the other soils. The s+c

435   fraction was per the Zimmerman et al. (2007) fractionation procedure subdivided into oxidizable and resistant parts, expected to coincide roughly with SOC stabilized by mineral-association as opposed to its own biochemical inertness, respectively. Negative correlations existed between the share of s+c OC (% of s+c OC) that was oxidizable by 6% NaOCl (i.e. s+c - rSOC) with the contents of Al$_o$, the bulk soil of SSA, and micropores volume (Fig. 6). ~~Significant positive correlations existed between the share of s+c OC that was oxidizable by 6 % NaOCl (i.e., the rSOC / s+c x 100) with the contents of Al$_o$, the bulk soil SSA,~~

440   ~~and micropore volume (Fig. 6). Especially in subsoils the correlations with Al$_o$ was strong (Fig. 6).~~ These correlations suggest that the association of SOC with short-range order Al (hydr)oxides has been found to limit oxidation of SOC by 6% of NaOCl (Mikutta et al., 2006). It appears that geochemical properties influence the degree of mineral association of OC and its content in these Andosols. ~~These correlations suggest that the oxidizable s+c OC fraction indeed at least partially coincides with mineral-associated SOC, in spite that on the opposite association of SOC with Fe and Al (hydr)oxides has just as well before~~

445   ~~been found to limit oxidation of SOC by 6 % NaOCl (Mikutta et al., 2006).~~ As neither chemical inertness of the s+c OC (agriculture: 53 % of s+c vs. pine forest: 59% of s+c), nor the s+c Al$_o$, bulk soil SSA and micropore volume differed between both land uses, it appears that land-use history did not impact the degree of mineral association of OC and its content in these Andosols. This outcome further ~~-~~contradicts that more s+c OC would accumulate under forest because of a more biochemical inertness of the OC inputs compared to agriculture.

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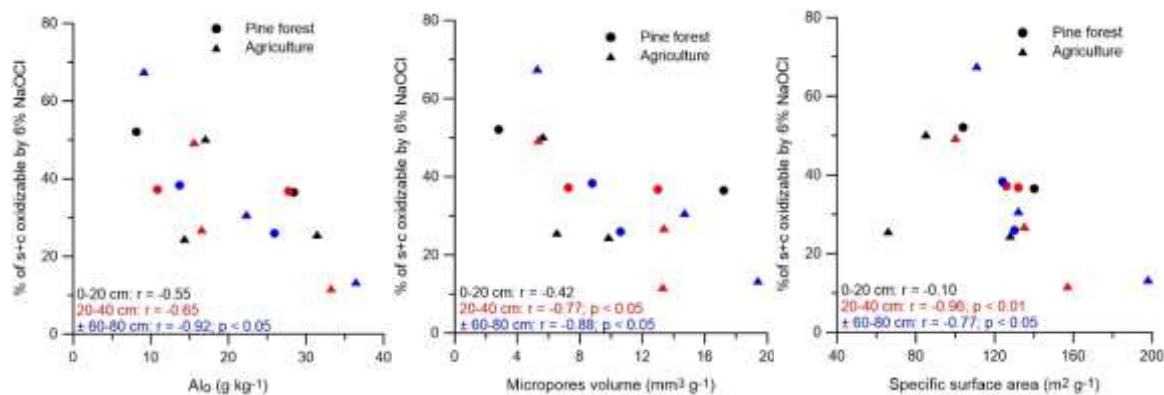
Figure. 6 Relation between the proportion of SOC that was oxidizable by 6% NaOCl~~rSOC of the s+c fraction~~ in the pine forest and agricultural soils with the soil Al$_o$, micropore volume, ~~(all dots jointly, n = 30)~~ and soil specific surface area (at each depth n = 5). ~~for the set of subsoil observations (in blue) specifically; and likewise relations with the soil specific surface area and the micropore volume (n = 15,~~

455   ~~SSA and micropore volume not replicated).~~ Sites under agriculture and pine forest are indicated by ▲~~A~~ and ●, respectively. Symbols and Pearson correlation coefficients in black and blue represent correlations ~~for the total dataset and for the set of subsoils, respectively.~~ at depths of 0 – 20, 20 – 40, and ± 60 – 80 cm, respectively.

4.3 Land use effects on native SOC degradability

460   The percentage of SOC mineralized after 120 days of incubation was less than half in the agricultural soils (1.2 %) than in the pine forest soils (2.9 %) (p < 0.01). This result was rather unexpected given the lower soil pH by 0.8 under pine forest, as acidic conditions are well known to retard SOC decomposition of SOC (Högberg et al., 2007; Malik et al., 2018) in line with Anda and Dahlgren (2020). To understand the apparent relative stabilization of SOC in the agricultural soils, we again consider the distribution of SOC across soil fractions. We (Anindita et al., 2022) previously hypothesized that the nearly doubled Al_o

465   content of the agricultural soils (21.8 g kg^{-1} on average) compared to the pine forest soils (13.9 g kg^{-1}) would partially explain the relatively elevated SOC stocks under agriculture for our study area due to enhanced organo–mineral association. Basile-Doelsch et al. (2005) likewise found that volcanic ash soil horizons containing much poorly crystalline material (proto–imogolite and proto–imogolite allophane) store large amounts of organic matter which turns over very slowly. But as no negative correlations existed between the amount or proportion of SOC mineralized and Al_o content, this hypothesis was not

470   confirmed. As mentioned above, we did find a higher % of SOC to be present in the rSOC fraction under forest but its content (g kg^{-1} soil) was not higher then under agricultural land use and again no correlation existed with SOC mineralization. Mikutta et al. (2006) indeed demonstrated that a larger chemical recalcitrance of SOC does not really translate into a larger biological stability. Once more, it appears that the larger SOC proportion of rSOC seems to simply result from less accumulation of SOC in the S+A fraction under forest.

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The proportion and concentration of the S+A fraction OC were higher under agriculture, so enhanced soil aggregation and occlusion of SOC might have significantly physically protected SOC against microbially mediated decomposition compared to pine forest land use. A study of Andosols in Colombia by Gijsman and Sanz (1998) also reported that aggregation holds considerable control on SOC decomposability as these authors observed a significant increase of CO_2 mineralization after

480   crushing large and small macroaggregates (> 53 µm). Indeed, we found that the amount of OC (g C kg^{-1} soil) in the S+A fraction negatively correlated to % SOC mineralized for the set of soils with agricultural and pine forest land use (r = -0.78; p < 0.05$\frac{}{1}$). It then appears that enhanced soil aggregation and occlusion of SOC under agricultural land use in part limited degradability of SOC, rather than enhanced association of SOC with soil minerals, including poorly crystalline or amorphous Al–containing minerals. As argued in 4.2, we can add to this that formation of amorphous materials and Al_o in the agricultural

485   soils most likely promoted soil aggregation. Hence, we hypothesize that enhanced pedogenesis forms a relevant indirect mechanism via which conversion to agricultural land use impacts the SOC balance of these relatively young tropical volcanic soils. However, since large amounts of exogenous OM are annually being applied to the in this study investigated agricultural fields (Table 1), we cannot unequivocally exclude that these instead explain the high SOC stocks and contribution of aggregate associated OC here and more observations on an expanded set of sites will be required to test this hypothesis.

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4.4 Land use effects of exogenous organic matter decomposition and net priming of SOC

In contrast to native SOC mineralization, added grass C mineralization did not differ between forest and agricultural soils. Therefore, apparently protection of ryegrass OC either by mineral association or occlusion inside aggregates must have been similar between both land uses and, in any case, did not impact its degradability in soil. Laboratory incubations with disturbed soils do not necessarily adequately reproduce field conditions in terms of soil structure, microclimate, and food webs. The observed similar degradability of ryegrass-C does not suggest a likewise enhanced storage of freshly added OM like for native SOC under agriculture than under forest. Possibly, such impact only emerges on the longer term when the added OM has been subject to sufficient diminution into smaller POM that could be occluded in microaggregates. Six et al. (2002) summarized that particularly 50 – 250µm scaled microaggregates grant sizable physical protection to POM, while the macroaggregate (> 250 µm) structure exerts little control on POM decomposability. Adding ryegrass to the 0–20 cm soils initially seemed to impact mineralization of native SOC with a general positive priming effect in first week of incubation, in line with many other studies, e.g. Liu et al. (2017). Thereafter, however, in four of the six studied soils net negative priming countered this initial stimulation of SOC mineralization. Such adverse impact of adding fresh OM on SOC mineralization could be due to a preferential utilization of the added substrate by microorganisms (Derrien et al., 2014). Regardless, the net result was that after 120 days SOC mineralization was not significantly stimulated (on average by 1.6 %). There was also no land use effect on the net priming of SOC after 120 days. Hence, in spite of differences in SOC quality under both land uses, as inferred from different SOC proportions of S+A and free POM, no differential stimulation of SOC mineralization by addition of a relatively labile plant-C substrate existed between agricultural or forest land use. These observations imply that no adverse effect is to be expected of the addition of generally relatively labile C (above ground crop residues, animal manure) on stability of the native SOC present under agricultural land use.

4.5 Importance of physical occlusion of POM for SOC stabilization

As an important side mark to the interpretation of the SOC fractionation data, it should be borne in mind that there is no guarantee that isolated SOM fractions coincide with distinct SOM pools, neither in terms of bioavailability nor intrinsic degradability. By expanding the Zimmerman et al. (2007) fractionation procedure with a strong (400 J ml^{-1}) ultrasonic dispersion step, we attempted to isolate s+c associated OC from POM contained in the S+A fraction. This ultrasonication step proved to result in incomplete disruption of the apparently very stable > 63 µm sized aggregates. With high levels of both OM as well as amorphous materials and poorly crystalline metal oxides, this is perhaps not surprising. The insignificant difference in C:N ratio between the S+A and s+c fractions suggests that while they obviously differ in their physical organization there is probably no strong contrast in the biochemical composition of the OM. Previous studies also found no clear difference of C composition from sand to clay fractions in Andosols (Baldock et al., 1992). Regardless, the here achieved subdivision of the SOM into OM present inside (S+A) or not (s+c) microaggregate structure would yet still appear relevant as the S+A SOC

proportion correlated negatively to SOC mineralization, suggesting indeed that such physical organization of soil grants 'physical protection' against microbial breakdown, thought to result from reduced accessibility of microbes, exo-enzymes, and/or e-acceptors (Keil and Mayer, 2014; Lehmann et al., 2007). The overall rather low C:N ratio of the S+A fraction (13.0 ± 4.2) indicates that it mainly contained mineral associated OM and probably little POM, complicating interpretation of mechanisms for a particular S+A SOC storage agricultural sites. Still, in the 0 – 20 cm layer, a higher S+A fraction C:N ratio of the agriculture (17.0) vs. pine forest (11.0) S+A fraction suggests that at least to some extent enhanced SOC storage in aggregates under agricultural land use might have resulted from extra occlusion of POM. However, our data do not provide unequivocal proof that the physical of SOM in the S+A fraction causes relatively protection against mineralization. In addition, the absence of any land use effect on protection of freshly added plant litter (see 4.4) leads to question this. Extra aggregation of OM into the S+A fraction in the agricultural soils might just be but a concomitant effect of the larger presence of tightly intermixed organo-metallic phases, while such smaller scaled structure themselves are instead zones of SOC stabilization. On the other hand, the fact that there was no negative correlation between Al_o or Fe_o and the relative SOC mineralization, while Al_o did positively relate to S+A SOC proportion would instead suggest that indeed the physical arrangement of OM into stable aggregates led to a relative stabilization of SOC. From the limited presence of POM in the S+A fraction, it logically emerges that mainly occlusion of smaller sized OM and its protection into aggregates was important. To further elucidate this, however, more detailed investigation of the formation organo-mineral phases and their organization into microstructure is required, building on the recently forwarded organo-metallic glue hypothesis and proposed methodologies by Wagai et al. (2020).

5 Conclusions

Following the fractionation of SOC by Zimmermann et al., (2007), the silt and clay associated OC forms the dominant SOC pool in tropical volcanic soils in Indonesia, regardless of land-use. But land-use strongly impacts SOC contained within 400 J m^{-1} ultrasonic dispersion resistant soil aggregates as its contribution to SOC rose from 9% of SOC in forest to as much as 32% of SOC several decades after conversion to agricultural use, with alongside also more OC stored in this fraction. The S+A SOC proportion was positively related to Al_o, $Al_o+1/2Fe_o$, exchangeable Ca, pH, and the % of amorphous materials. Our study thus indicates the larger of Al_o in agricultural soils promoted soil aggregation and physical occlusion of OC compared to pine forest. Our study thus indicates agricultural land use to stimulated development of poorly crystalline Al, which in turn promoted soil aggregation and physical occlusion of OC compared to forest land use. A negative correlation between relative decomposability of the SOC and the portion of SOC that is physically occluded further suggests that enhanced soil aggregation under cropland effectively stabilizes part of the SOC compared to under forest land use. Contrary to our hypothesis, however, we found no proof that stimulated formation of Al_o and amorphous minerals would have increased association of SOC with soil minerals under agriculture. Based on the present study we hypothesizepostulate that the enhanced formation of amorphous minerals and Al_o under agriculture with high OM inputs promoted development of stable soil aggregates and OC occlusion therein and this would in part counter otherwise expected losses of SOC compared to primary and secondary forest. However,

555 the contribution of large OM inputs vs. land-use conversion per sé could not be elucidated here and this will require study of other tropical Andosol forest-agricultural land use pairs with detailed inventory of OC inputs. Moreover, confirmation that agricultural land use promotes Al_o formation vs. forest will require time series analysis of such sites. To the least, our study points at the overall need to account for potential indirect land use effects on stability of SOC via its control on pedogenesis. Especially, this is so for pedoclimatic combinations where weathering can be very fast, like in tropical Andosols that have only 560 relatively recently been cultivated.

Appendix

No Appendix

Data availability

The data generated in this study are available from the corresponding author upon reasonable request

565 **Author contributions**

SS, PF, and SA conceptualized the study. SA conducted soil sampling and performed the experiment. SA prepared the manuscript with contributions from all the co-authors.

Competing interest

The authors declare that they have no conflict of interest

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