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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). Juvenile volcanic soils in tropical areas are subject to much faster pedogenesis, with then also possibly a significant mediation by land use on much shorter centennial or even decadal scale. 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 content of oxalate-extracted Al and exchangeable Ca correlated well with OC associated with sand–sized aggregates. The concomitant near doubling of the proportion of SOC in sand-sized aggregates compared to forest and likewise contrasts in Al and Ca suggest an enhanced formation of Al- (hydr)oxides and liming promoted aggregation and physical occlusion of OC. This was importantly also consistent with a relatively lesser degradability of SOC in the agricultural sites, though the net priming of SOC and degradability of added ^{13}C-labelled ryegrass was not found to depend on land use. We expected that the formation of amorphous Al after conversion of native forest to agriculture would mainly have promoted mineral-association of SOC compared to under pine forest but found no indications for this. Enhanced weathering but improved small scale aggregation of tropical Andosols caused by conversion to agriculture 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 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). 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; Mikutta et al., 2006, 2009; Poirier et al., 2020). While soil mineralogy itself is thus a well-recognized controller of SOC stabilization, 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.

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 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 soil mineral phase. Moreover, the coverage remains limited for several soil groups, including tropical Andosols. A recent study on the Gálápagos islands demonstrated that even within a few centuries to just several decades 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 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. 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. With differently aged volcanic deposits and co-occurrence of native forest, secondary forest and cultivated land this region forms a useful means to understand how 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., under review), 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, 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. The mean annual temperature in this region is 19–21°C and mean annual precipitation ranges around 2000–3000 mm per year. Six sites were selected to represent the dominant land use types in the area, viz. primary forest (NF), pine forest (PF1 and PF2) and horticulture (AG1, AG2, and AG3). Soils at sites NF and PF1 are andic Cambisols and at the PF2, AG1, AG2, AG3 sites aluandic Andosols (Anindita et al., under review). All soils contain silicate minerals (i.e. quartz, cristobalite, tridymite), gibbsite, albite, hornblende, 1:1 clay minerals, and non-crystalline materials (Anindita et al., under review). The proportion of primary minerals is higher in the younger NF 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 PF1 and PF2, secondary forests were planted in 1962 for restoration purposes, following earlier deforestation. Agricultural land use at AG1, AG2, and AG3 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. (under review).

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 H2O 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 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 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. (under review). Selected physicochemical soil properties are given in Table 1.

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. (under review))

Depth	pH H_2O	BD^{a}	OC^{a}	$\delta^{13}C$	C/N ratio	Clay	Exch. Ca	NH_4-oxalate extractable		Al_p^{a}	SSA^{a}	Amorphous materials	Land use
								Al_o^{a}	Fe_o^{a}				
(cm)	(-)	(g cm^{-3})	g kg^{-1}	‰		%	cmol kg^{-1}	mg g^{-1}			m^2 g^{-1}	g kg^{-1}	
Primary forest (NF)													
0–20	4.1	0.77	37.1	-27.0	15.1	18.7	0.2	3.5	15.5	3.4	9	288	Natural vegetation
20–40	4.4	0.78	26.0		20.2	19.81	0.1	2.3	25.4	3.5	27	254	
60–80	4.3	0.65	28.6		20.0	29.51	0.1	4.8	52.4	2.8	69	378	
Pine forest (PF1)													
0–20	4.5	0.64	23.6	-24.3	10.8	67.27	1.8	8.1	11.9	41.0	91	471	Pine forest
20–40	4.4	0.61	13.0		10.2	71.56	0.5	10.4	12.2	32.2	117	429	
70–90	4.4	0.69	5.9		10.0	64.35	0.2	13.7	21.1	13.7	124	481	
Pine forest (PF2)													
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	18.2		12.2	46.43	0.4	27.7	17.2	9.8	145	506	
60–80	4.4	0.60	15.7		11.9	48.82	0.4	25.9	17.5	9.4	127	447	
Agriculture (AG1)													
0–20	5.1	0.67	29.9	-13.6	18.2	68.21	7.7	14.4	21.1	26.3	114	548	Intensive horticulture ± 50
20–40	4.9	0.66	13.0		11.9	63.06	5.7	16.5	13.0	19.7	125	523	years; organic fertilizer
60–80	4.8	0.64	11.2		10.8	61.43	4.7	22.3	18.1	12.9	134	547	±76 Mg ha^{-1} year^{-1}
Agriculture (AG2)													
0–20	5.4	0.66	54.4	-15.4	14.7	27.24	6.6	31.4	12.3	7.6	48	623	Intensive horticulture ± 40
20–40	5.8	0.47	42.6		17.9	35.62	10.0	33.2	12.1	5.8	128	645	years; organic fertilizer
50–70	5.9	0.52	26.9		16.9	47.07	7.0	36.4	11.6	5.1	185	650	±20 Mg ha^{-1} year^{-1}
Agriculture (AG3)													
0–20	5.4	0.65	47.0	-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	28.8		9.8	50.02	7.0	15.6	9.5	8.6	91	502	organic fertilizer ± 18 Mg
60–80	5.8	0.62	7.8		8.4	62.81	6.0	9.1	8.0	10.7	108	460	ha^{-1} year^{-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

2.2 Soil organic matter fractionation

Soils were fractionated using size, density and chemical separation steps according to Zimmermann et al. (2007). 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 chemically resistant SOC (rSOC) pool. Briefly, 30 g of equivalent dry soil (< 2 mm) was 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 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 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

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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 water, transferred to a pre-weighted aluminum cup, dried at 40°C and weighted. All fractions were analyzed for their C concentration using a LECO 928 series CN-analyzer. Further details are given in Zimmermann et al. (2007) and Poeplau et al. (2013).

2.3 Soil incubation experiment and isotopic signature measurements

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 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).

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 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):

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

$$\delta^{13}C_{grass-CO2} = \delta^{13}\,C_{grass} - \varepsilon_{grass} \quad (2)$$

$$\delta^{13}C_{SOC-CO2} = \delta^{13}C_{SOC} - \varepsilon_{SOC} \quad (3)$$

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. about 4 t C ha^{-1}) to estimate ε_{grass}. This value was operationally calculated by subtracting $\delta^{13}C_{grass}$ from the

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peak CO_2 emission $\delta^{13}C$-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 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 $C_{SOC\text{-}CO2}$ and $C_{grass\text{-}CO2}$ respectively per time increment between flux measurements. The % of mineralized C_{SOC} was then derived from dividing $C_{SOC\text{-}CO2}$ by C_{SOC}.

2.5 Statistics

Independent samples t-tests were used to compare 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 fraction proportions and geochemical properties. 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

Across the studied soils a greater part of soil material ($\pm$ 55 %) was found as S+A fraction (Table 2). The highest S+A fraction occurred in the AG1, AG2, and topsoil PF1 soils (> 60 %). Conversely, in the PF2 and AG3 soils, the s+c fraction was largest. The OC concentration of soil fractions decreased in the order of 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 AG1 and AG3 (25–55 g C kg^{-1} fraction). No such 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 rSOC fraction was higher ($p < 0.01$) in the agricultural than pine forests sites. The size of the DOC fraction was negligibly small ($\pm$ 0.002 g C kg^{-1} fraction) and is further disregarded. Total SOC was not significantly different under forest (25.0 $\pm$ 12.4 g C kg^{-1} soil) and agricultural (30.6 $\pm$ 16.4 g C kg^{-1} soil) land use, but it was higher under agriculture than pine forest (18.4 $\pm$ 8.9 g C kg^{-1} soil).

Overall, the bulk of SOC was present in the S+A ($\pm$ 47%) fraction, then followed by the rSOC ($\pm$ 25 %), s+c - rSOC ($\pm$ 24 %), and POM (< 5 %) fractions (Fig. 1). The rSOC constituted 34-67 % of OC in s+c. The distribution of SOC across soil fractions varied to some extent between both land uses. The amount of OC in the S+A fraction was higher in the agricultural soils (19 ± 13 g C kg^{-1} soil) than under forest (8 ± 4 g C kg^{-1} soil; $p < 0.01$). Particularly in topsoil of AG1 (± 23 g C kg^{-1} soil) and AG2 (37 g C kg^{-1} soil) a larger share of the SOC was in the S+A fraction. In contrast, more C was contained in free POM and in the s+c fraction under forest than under agricultural land use ($p < 0.05$). The resistant SOC (rSOC) fraction accounted for approximately one quarter of SOC and its amount (in g C kg^{-1} soil) and proportion (% of SOC) was higher under forest than under agricultural land use ($p < 0.05$). Free POM constituted a significantly larger share of SOC in topsoil compared to both subsoil depth layers ($p < 0.05$), although this pool contributed on average less than 5 % of SOC.

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

Depth (cm)	**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**	
						s+c - rSOC	**rSOC**				**s+c -rSOC**	**rSOC**
Primary forest (NF)												
0–20	0.3 ± 0.1	52.8 ± 0.1	46.9 ± 0.1	412.5 ± 33.5	22.6 ± 6.8	32.2 ± 3.3	30.5 ± 3.3	1.0 ± 0.5	1.4 ± 0.3	11.9 ± 3.5	15.1 ± 1.6	14.3 ± 1.5
20–40	1.7 ± 0.4	46.7 ± 3.6	51.6 ± 3.7	393.0 ± 0.0	7.5 ± 2.0	16.9 ± 2.1	24.9 ± 2.2	0.7 ± 0.7	6.6 ± 1.6	3.6 ± 1.2	8.7 ± 1.2	12.9 ± 1.7
60–80	0.2 ± 0.1	50.0 ± 10.5	49.8 ± 10.4	367.5 ± 88.5	23.9 ± 5.5	18.8 ± 3.1	36.3 ± 1.5	0.8 ± 0.5	0.8 ± 0.6	12.1 ± 4.5	9.5 ± 3.4	17.9 ± 3.4
Pine forest (PF1)												
0–20	0.7 ± 0.5	59.0 ± 11	40.3 ± 11.5	227.0 ± 6.0	19.7 ± 1.7	12.1 ± 1.0	9.8 ± 1.0	1.9 ± 0.5	1.7 ± 1.2	11.6 ± 2.0	4.9 ± 1.6	3.9 ± 1.2
20–40	0.2 ± 0.1	61.4 ± 5.6	38.4 ± 5.8	162.0 ± 9.5	11.8 ± 0.2	6.8 ± 0.3	7.1 ± 0.3	1.0 ± 0.4	0.4 ± 0.2	7.2 ± 0.7	2.6 ± 0.4	2.7 ± 0.4
70–90	0.1 ± 0.1	29.9 ± 2.5	70.0 ± 2.6	103.6 ± 7.5	4.8 ± 0.1	3.4 ± 0.1	4.1 ± 0.2	0.4 ± 0.2	0.1 ± 0.07	1.4 ± 0.1	2.4 ± 0.0	2.9 ± 0.3
Pine forest (PF2)												
0–20	1.3 ±0.4	46.3 ± 5.5	52.5 ± 5.3	188.3 ± 43.2	26.7 ± 2.5	19.6 ± 1.8	17.6 ± 1.3	1.7 ± 0.6	2.2 ± 0.2	12.4 ± 2.6	10.4 ± 1.9	9.2 ± 0.8
20–40	0.4 ± 0.1	45.2 ± 5.6	54.3 ± 5.6	148.7 ± 47.3	14.3 ± 0.7	10.4 ± 0.1	10.4 ± 0.1	1.5 ± 0.4	0.6 ± 0.1	6.5 ± 1.1	5.7 ± 0.6	5.7 ± 0.5
60–80	0.2 ± 0.1	36.1 ± 4.7	63.7 ± 4.8	135.6 ± 48.9	16.0 ± 12.1	7.7 ± 0.7	8.0 ± 0.3	1.1 ± 0.0	0.2 ± 0.1	5.7 ± 4.3	5.0 ± 0.8	5.1 ± 0.2
Agriculture (AG1)												
0–20	0.1 ± 0.1	74.8 ± 6.7	25.1 ± 6.7	206.0 ± 4.0	31.3 ± 0.9	12.8 ± 0.2	17.8 ± 0.1	1.5 ± 0.9	0.2 ± 0.1	23.4 ± 1.6	3.2 ± 0.1	4.4 ± 1.1
20–40	0.1 ± 0.0	72.3 ± 2.8	27.7 ± 2.9	63.7 ± 0.9	14.8 ± 0.3	6.6 ± 0.4	9.5 ± 0.3	0.3 ± 0.1	0.03 ± 0.0	10.7 ± 0.2	1.8 ± 0.1	2.6 ± 0.3
60-80	0.1 ± 0.0	72.2 ± 3.3	27.7 ± 3.3	15.6 ± 2.4	12.2 ± 0.2	5.5 ± 0.1	7.6 ± 0.2	0.4 ± 0.1	0.01 ± 0.0	8.8 ± 0.3	1.5 ± 0.2	2.1 ± 0.2
Agriculture (AG2)												
0–20	0.1 ± 0.1	68.8 ± 1.6	31.3 ± 1.6	350.0 ± 52.0	54.1 ± 1.6	28.5 ± 3.4	36.1 ± 3.2	0.6 ± 0.1	0.3 ± 0.2	37.2 ± 1.6	8.9 ± 1.3	11.3 ± 1.0
20–40	0.0 ± 0.0	85.9 ± 0.8	14.1 ± 0.8	401.0 ± 88.0	46.5 ± 0.4	16.4 ± 2.4	31.4 ± 1.8	1.1 ± 0.7	0.04 ± 0.0	40 ± 0.1	2.3 ± 0.2	4.4 ± 0.5
50–70	0.0 ± 0.0	85.3 ± 1.2	14.7 ± 1.2	587.5 ± 240	28.3 ± 0.3	10.7 ± 1.3	19.7 ± 0.7	0.8 ± 0.4	0.08 ± 0.0	24.2 ± 0.4	1.6 ± 0.1	2.9 ± 0.3
Agriculture (AG3)												
0–20	0.7 ± 0.1	34.4 ± 6.7	64.9 ± 6.7	420.7 ± 88.3	38.3 ± 4.6	29.8 ± 1.9	17.2 ± 0.8	1.8 ± 0.4	2.9 ± 0.6	13.1 ± 2.5	19.5 ± 3.2	11.1 ± 1.0
20–40	0.8 ± 0.2	42.3 ± 8.7	56.9 ± 8.7	311.3 ± 39.9	23.0 ± 0.4	16.7 ± 0.7	12.5 ± 1.1	1.3 ± 0.4	2.4 ± 0.3	9.7 ± 1.8	9.6 ± 1.7	7.1 ± 0.6

60–80	0.1 ± 0.0	36.3 ± 4.3	63.6 ± 4.3	92.6 ± 19.2	8.3 ± 0.8	5.0 ± 0.2	3.0 ± 0.3	1.2 ± 0.9	0.1 ± 0.0	3.1 ± 0.6	3.1 ± 0.3	1.9 ± 0.3

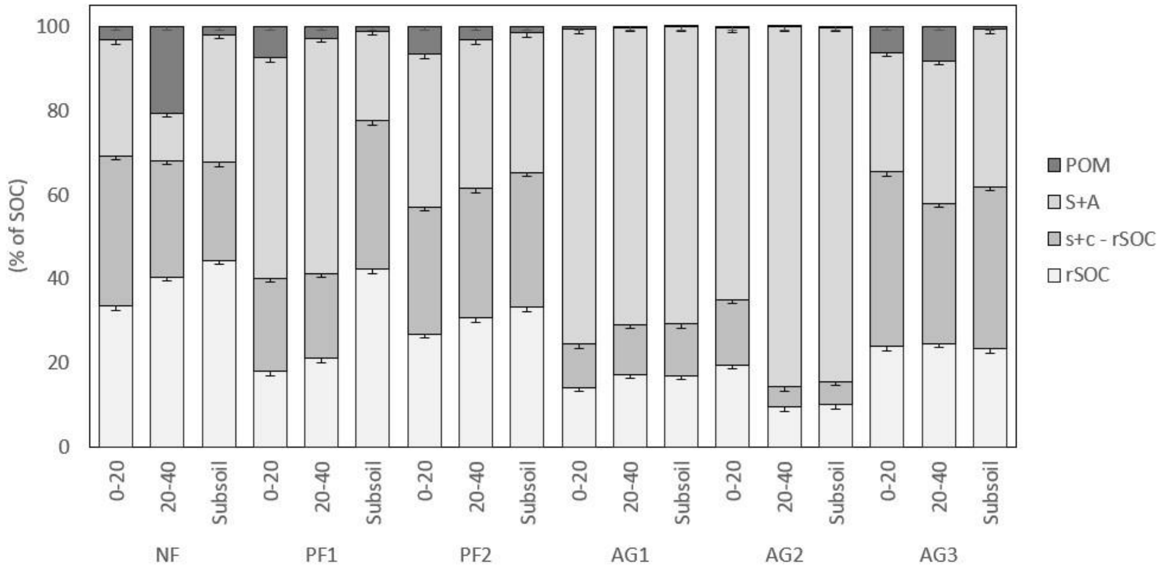

Figure 1. The distribution of OC over soil fractions obtained by the Zimmerman et al. (2007) procedure for 6 sampled (0-60cm) soil profiles in the Sunda Volcanic complex in West Java, Indonesia. Vertical bars indicate standard deviations for three lab-replicates (n = 3)

3.2 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, the SOC proportion of the S+A fraction was positively correlated with Al_o, Al_o+1/2Fe_o, pH H_2O, exchangeable Ca, and content of amorphous materials ($p < 0.01$). 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). There existed no significant correlations between the proportion of the other SOC fractions and any of the analyzed soil properties for the full dataset. But when considering only pine forest and agriculture, positive correlations existed between OC concentrations of the s+c and rSOC fractions (g C kg^{-1} fraction) with Al_o and Al_o+1/2Fe_o.

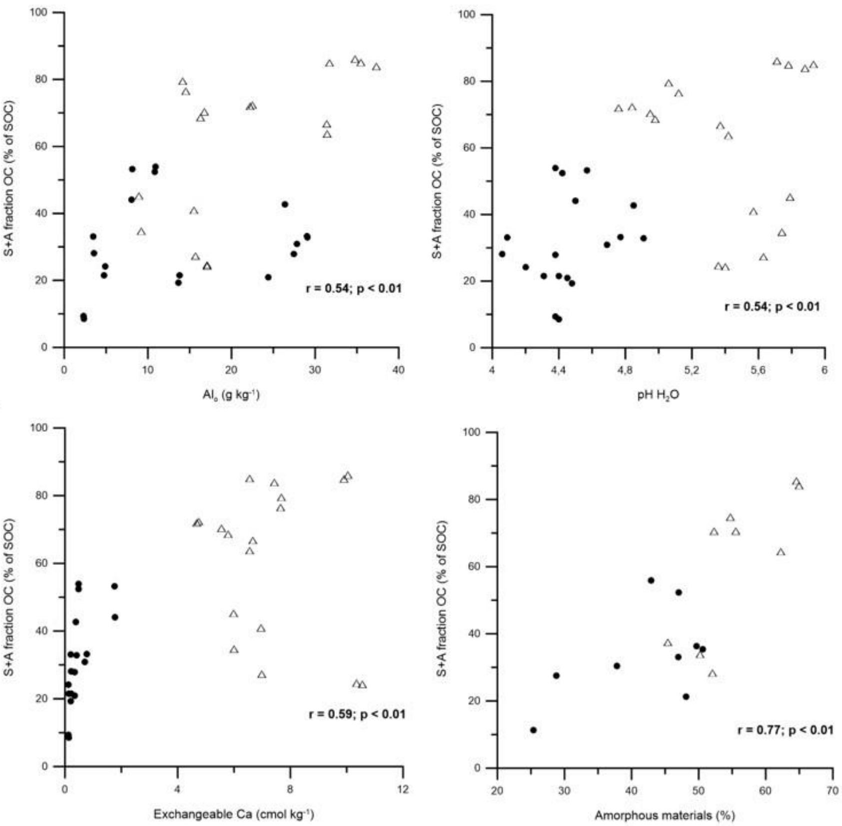

Figure 2. Scatter plots of the SOC proportion of the S+A fraction and selected chemical soil properties, with Pearson correlation coefficients and corresponding statistical significance level indicated. Sites under agriculture and forest are indicated by Δ and ● respectively.

3.3 Carbon mineralization experiment

3.3.1 Gross soil carbon mineralization

Across all sites, C-mineralization (C-min) rates were highest for AG2 and AG3 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 < AG1 < AG2 < PF1 < AG3 < PF2. Pine forest soils displayed higher cumulative C mineralization than agricultural soils ($p < 0.05$). Overall, 120-day cumulative C mineralization was 194–419 mg kg^{-1} higher in soil with grass added than without (Fig. 3).

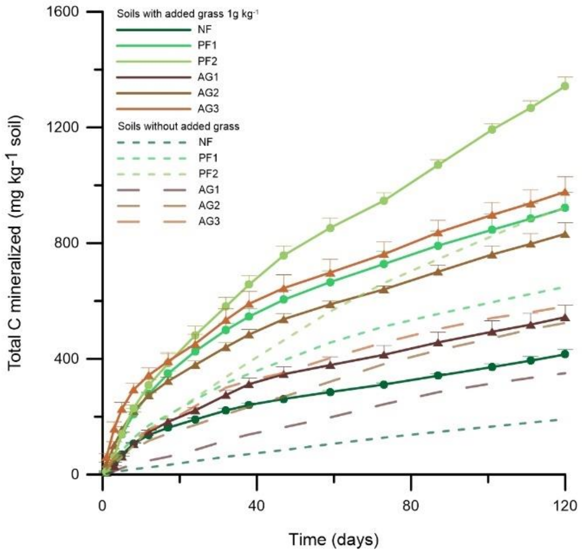

Figure 3. Gross cumulative amount of C mineralized in soil with and without 1 g C kg^{-1} ryegrass added. Vertical bars indicate standard deviations of three lab replicates (n = 3) and are presented for the grass amended soils only. Sites under forest and agriculture are indicated by ● and Δ, respectively.

3.3.2 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 AG2 and AG3, 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 PF2 (389 mg kg^{-1}), followed by AG2 > AG3 ≈ PF1 ≈ AG1 > NF. There were no significant differences in C_{grass}-min between the sets of agricultural and forest soils.

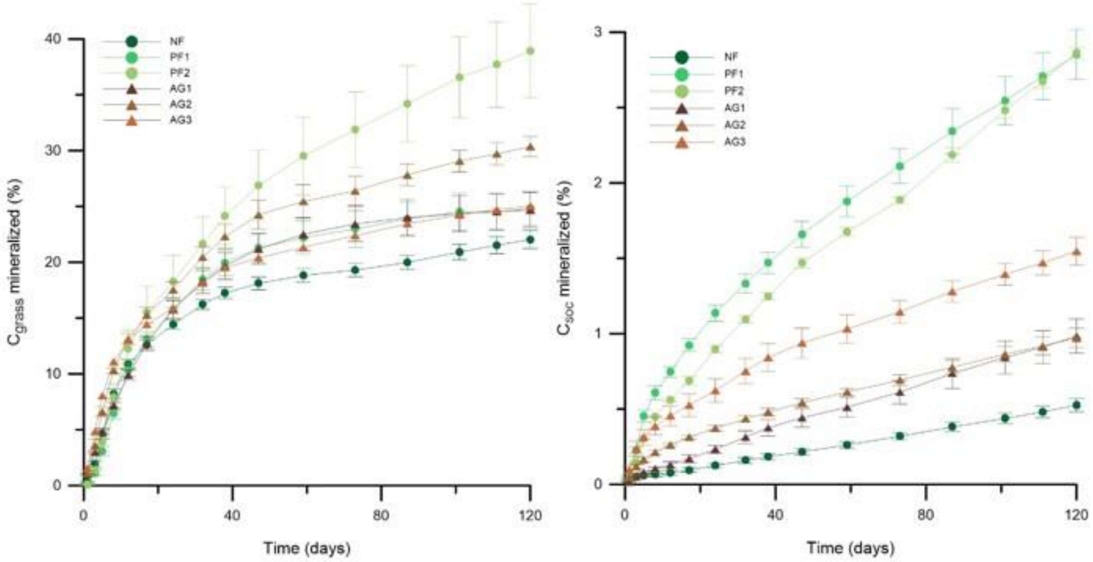

Figure 4. The percentage of C_{grass} (left) and C_{SOC} (right) mineralized during 120 days of incubation in soils with 1 g kg^{-1} grass or no grass added, respectively. Vertical bars indicate standard deviations of triplicate lab repetitions. Sites under forest and agriculture are indicated by ● and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

3.3.3 Native SOC C-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 PF2 (953 ± 13 mg kg^{-1}) while a fourfold lower amount was mineralized in case of NF (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 % of SOC was mineralized in the pine forest soils (2.9 % ± 0.1) than in the agricultural soils (1.2 % ± 0.3) ($p < 0.01$).

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 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 AG3 soil, while the opposite was true for AG1 and no net priming occurred in case of AG2. 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.

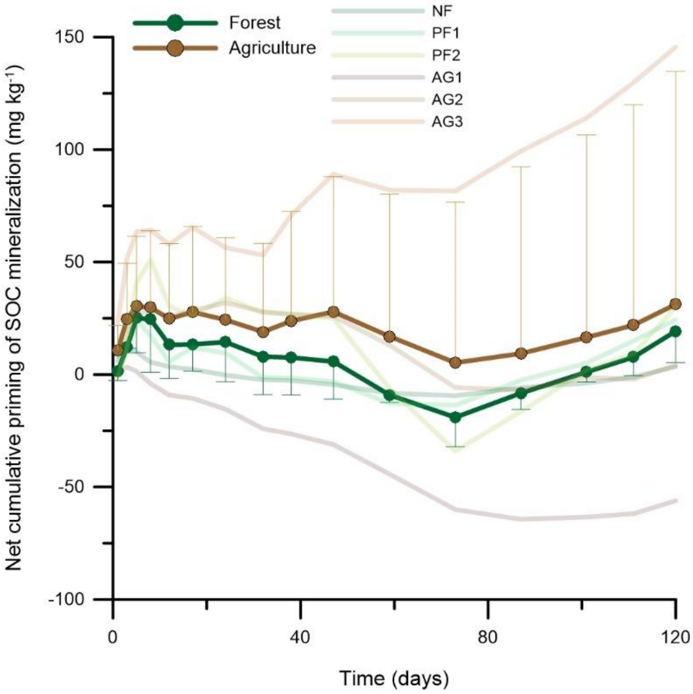

Figure 5. Net effect of grass addition (1 g kg^{-1}) on cumulative native SOC mineralization. Positive and negative figures denote net positive or net negative cumulative priming of SOC mineralization. Dotted lines present the temporal evolution of mean net cumulative priming effect for either forest 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

Overall, the portion of S+A fraction material (i.e. > 63µm aggregates and sand particles) was higher in the agricultural (64 ± 20 %) than forest sites (48 ± 11 %) ($p < 0.05$), indicating stronger soil aggregation under agriculture. In line, even a double share of SOC resided in the S+A fraction under agriculture (61 ± 21 %) than forest (34 ± 15 %) ($p < 0.05$). The important role of soil microaggregates for SOC storage 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, aggregate stability also depends on presence of binding agents that cluster mineral and organic particles into aggregates. Repeated 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. Next to organic binding agents, Wagai et al. (2018) also found reactive metal phases to be important binding agents in Allophanic Andisols. 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 SOC proportion of the S+A fraction and its OC concentration (g C kg^{-1} S+A fraction) correlated positively with contents of Al_o and Al_o+1/2Fe_o, and with the % of X-ray amorphous materials. This indicates that higher levels of Al_o under agriculture than forest would have enhanced aggregation, and in doing so occluded a larger share of SOC inside these aggregates. Other than aluminium oxides, the content of exchangeable Ca also correlated positively to S+A fraction mass proportion ($r = 0.45$) and SOC proportion of the S+A fraction ($r = 0.59$) ($p < 0.01$). 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, thus having higher capacity to bind Ca^{2+}. 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. Lastly, less free POM was found in the agricultural than forest soils ($p < 0.05$), 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, 2014).

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 forest soils ($p < 0.05$). The content of s+c OC (in g C kg^{-1} soil) displayed likewise trends. Particularly, the all-depth layers at the NF site had high s+c content and proportion of SOC, but this was in fact accompanied with a larger contribution of younger less-weathered minerals present, low Al_o level and smaller share of amorphous minerals (Anindita et al., under review). Hence association of OC with Al_o–containing minerals could not explain the higher SOC proportion and amount of OC in s+c under forest. Most likely a larger s+c proportion of SOC under forest simply mirrors trends in the S+A fraction, although it cannot be ruled out that other factors such as a lower soil nutrient availability, lower soil pH, and likely wetter microclimate and more biochemically inert OC inputs would have caused relative storage of OC in the s+c fraction under forest. Our experimental design did not allow to infer unambiguously if such soil and environmental factors alternatively caused the larger SOC proportions in s+c. Significant positive correlations existed between the share of s+c OC that was oxidizable by 6 % NaOCl (i.e. rSOC / s+c x 100) with content of Al_o, % of amorphous materials and the SSA, especially in subsoils where such correlations were strong (Fig. 6). Association of SOC with Fe and Al (hydr)oxides has indeed before been confirmed to limit oxidation of SOC by 6 % NaOCl (Mikutta et al., 2006). Since we also found that agricultural land use had higher Al_o by 14% compared to pine forest (Table 1), these results at first sight might suggest that the enhanced mineral weathering under agricultural land use lowered the chemical oxidizability of s+c OC. However, the difference in the chemical inertness of the s+c OC appeared insignificant between both land uses (agriculture: 53 % of s+c vs. pine forest: 49 % of s+c). This outcome then at least contradicts that more s+c OC would accumulate under forest because of a more biochemical inertness of the OC inputs compared to agriculture.

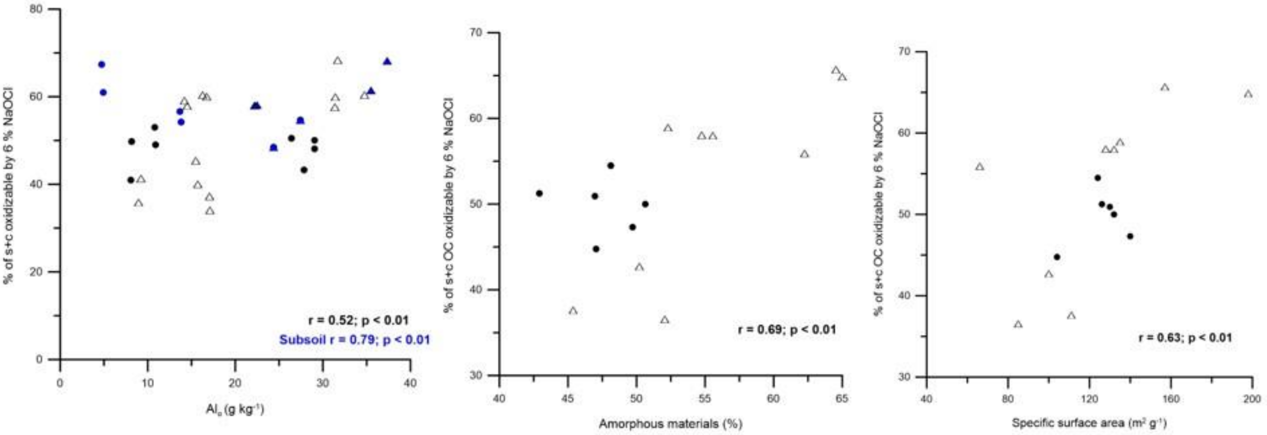

Figure. 6 Relation between the proportion of rSOC of the s+c fraction in the pine forest and agricultural soils with the soil Al_o (all dots jointly, n = 30) and for the set of subsoil observations (in blue) specifically; and likewise relations with the % of amorphous materials, and the soil specific surface area (n = 15, SSA and X-ray diffraction not replicated). Sites under agriculture and pine forest are indicated by Δ and ●, respectively. Pearson correlation coefficients in black and blue represent correlations for the total dataset and for the set of subsoils, respectively.

4.3 Land use effects on native SOC degradability

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 considered distribution of SOC across soil fractions. We (Anindita et al., under review) previously hypothesized that the nearly doubled Al_o content of the agricultural soils (21.8 g kg^{-1} on average) compared to the pine forest soils (13.9 g kg^{-1}) would explain 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 confirmed. As mentioned above, we did find a higher % of SOC to be present in the rSOC fraction under forest but 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 lability. Moreover, the share of SOC in rSOC was actually lower (but not significantly) under forest than under agriculture and so as argued above, the larger SOC proportion of rSOC seems to simply result from less accumulation of SOC in the S+A fraction under forest.

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 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 ($r = -0.75$; $p < 0.01$). 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. Formation of amorphous materials and Al_o in the agricultural soils most likely promoted soil aggregation. Hence, we provisionally conclude 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.

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.

5 Conclusions

Following the fractionation of SOC by Zimmermann et al., (2007), the sand–aggregates fraction in general was a dominant SOC pool in our soils, accounting for 47 % of total SOC in all soil fractions, and was positively associated to Al_o, Al_o+1/2Fe_o, exchangeable Ca, pH, and amorphous materials. Our study thus indicates that higher levels of poorly crystalline Al, more amorphous materials and under agricultural land use stimulate soil aggregation and physical occlusion of OC compared to forest land use. The negative correlation between the portion of SOC that is physically occluded on the one hand and to lower relative decomposability of the SOC on the other, suggest that enhanced soil aggregation under cropland indeed effectively stabilizes part of the SOC compared to under forest land use. Contrary to our hypothesis 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 do postulate that faster pedogenesis under agriculture would counter otherwise expected loss of SOC compared to secondary forest, but further study of more tropical Andosol land use pairs with detailed inventory of OC inputs is now needed to affirm this. 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 relatively recently been cultivated.

Appendix

No Appendix

Data availability

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

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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