

Massive carbon addition to an organic-rich Andosol increased the subsoil but not the topsoil carbon stock.

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Dear associate editor Yakov Kuzyakov, dear reviewers,

we would like to thank all reviewers for taking the time to provide us with your feedback on our manuscript. We have carefully considered your comments. Our responses and suggestions for possible changes are given below each comment.

5 Implementing these changes based on the comments of the reviewers has improved our manuscript. The reviewer comments have led us to clarify the abstract, the bulk density measurements, results of the bulk organic carbon and the data analysis. We included a paragraph about organic carbon stocks in section 4.3. Furthermore we improved the discussion on organic carbon response to the sawdust input. We feel that our suggested revisions will improve our manuscript beyond the level necessary to be published in Biogeo-sciences.

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Reviewer 2

The authors have revised the manuscript very well. I have only some minor comments.

1) In the Abstract, please revise it in a concise way. For example, the main result is in the line 15, only a sentence.

15 *Author response: We summarised the main result in one sentence at the end of the abstract.*

2) Please give the full name of 'WRB' in page 4 Line22.

Author response: We provided the full soil names according to the World Reference Base for Soil Resources (2015) in the Materials section.

20

3) In the Table 1, please give full information of 'Xox' in the table title in Page 5. Second, what is the unit for Alox and other mineral, g kg⁻¹ dry soil? or g kg⁻¹ organic C?

Author response: We gave full reference to Al_{ox} , Si_{ox} and Fe_{ox} in the table title instead of referring to X_{ox} . The oxalate-extractable metals are presented as $g\ kg^{-1}$ mineral part (or inorganic part) of the dry soil. We used this unit in order to evaluate the amount of oxalate-extractable metals in relation to total mineral constituents. The large and strongly varying concentrations of organic matter with depth masks the actual proportion of oxalate extractable minerals. For better comparability, we normalized the oxalate-extractable metals to the mineral soil component instead of to dry soil. For clarification, we added explanations to section "2.5. Acid oxalate extraction..." and the table titles.

4) The similar description as above mentioned for Table 2 in Page 9.

Author response: see above (3).

10

5) In the result section, '3.2 sequential density fractionation' in Page 13 and Page 14, the description is not clear, please revise it in a concise way.

Author response: We assume that you find section 3.2.1 (p. 13 line 3 to p. 14 line 2) not clear. We added additional information on the purpose of the data for each of the three paragraphs.

15

6) In the figure 2, I am wondering why the sampling depths at the two sites are different?

Author response: We sampled in the middle of each horizon. Horizon thickness varied slightly between profiles, which is a common feature of forest soils. In result also the sampling depths for the profiles selected for density fractionation were not identical.

20

7) In Page 18, the methods and calculation description need to put in the material section? I am wondering why.

Author response: We put the calculation description in the discussion, because we developed this new calculation method for evaluating the prevailing short range-ordered phases. The formulas used are based on well known formulas and assumptions. The assumptions result from the data of the oxalate-extraction. The idea to calculate the proportion of imogolite-type on short range-ordered on the basis of solely aluminium is new. We revised section "4.2 Mineral composition..." to point this out.

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Reviewer 3

The manuscript brings interesting conclusions about the carbon storage capacity of andosols. The analyzes are well documented and lead to the description of interesting mechanisms to explain an important carbon storage capacity in the subsoil when the topsoil binding capacities are exhausted.

30

The manuscript would need a thorough English proofreading.

Author response: A professional English proofreading was carried out.

1) The authors could reformulate the title to state the positive result first (C storage in subsoils).

Author response: We changed the title to “Massive carbon addition to an organic-rich Andosol increased the subsoil but not the topsoil carbon stock.”

5 2) Page 2, L.3: “Soil holds more organic carbon (OC) than there is carbon in the global vegetation and atmosphere combined”: the authors should provide reference(s) from scientific literature.

Author response: We provided the reference: Lehmann, Johannes, and Markus Kleber. “The Contentious Nature of Soil Organic Matter.” Nature 528, no. 7580 (Dezember 2015): 60–68. <https://doi.org/10.1038/nature16069>.

10 3) Page 2, L. 12: “the main factor”: the authors should be more specific (of what?).

Author response: We changed the sentence to: “Paustian et al. (1997) consider the OC stocks to increase linearly and limitless with increasing organic input.”

15 4)Page 4, L. 9-10: the authors could discuss the fact that higher vegetation in the sawdust site may have consequences on carbon intakes from the soil. Could the fact that vegetation is higher be due to sawdust additions?

Author response: Unfortunately, we have no data of possible differences in plant biomass and plant community composition. We calculated a worst case scenario to exclude possible differences in C input with litter between the sites. The scenario shows, that differences in input of plant-derived C between sites are insignificant relative to the sawdust input. We clarified the purpose of the scenario calculation in the manuscript.

20

5) Page 4, L. 16-19: a schema or photo of a soil profile would help to understand how horizons were delimited. It could be added as an appendix.

Author response: We provided a picture of the soil profile in the Appendix.

25 6) Page 5, Table 1: For each element presented in the table, the number of data that were pooled to calculate the mean value could be specified in the table (eg :“BD, g.cm-3, n=2” or “C/N, n=5). Standard deviations (rather than standard errors) should probably be used in tables. In column BD, why isn’t the standard error/deviation specified?

30 *Author response: We added a row in the Table 1 showing the number of data that were pooled. We added the standard error of BD. According to Altman and Bland (2005) and Reinhart (2015), the standard deviation (SD) is a measure of variability and describes the spread of individual data points. The standard error (SE = SD/sqrt(n)) is a type of standard derivation, which describes how far the average for this sample might be from the true average. As we are more interested in the latter, we choose the standard error.*

Altman, Douglas G, and J Martin Bland. "Standard Deviations and Standard Errors." *British Medical Journal* 331, no. 7521 (October 15, 2005): 903.

Reinhart, Alex. *Statistics Done Wrong: The Woefully Complete Guide*. No Starch Press, 2015.

5 7) Page 9, Table 2 / Page 11, L.7: How was the "representative" profile chosen?

Author response: The representative soil profiles were selected to meet the following criteria: five horizons within the upper 1 m, largest OC concentration in the topmost horizon, similar amounts of acid oxalate-extractable Al, Fe, and Si, and having different bulk OC concentrations in the third horizon. This was already lined out in section "2.7 Data analysis". We moved the
10 *decision basis to the caption of Table 2.*

8) Page 13, L. 3 / Page 14, L.5: The authors should explain how values can exceed 100 wt%.

Author response: We added the following sentence to section "3.2.1 Organic matter".: "Values exceeding 100 wt% are probably caused by random errors of measurements and some sodium polytungstate not entirely removed by sample washing."

15 9) Page 13, L. 5-6 / Page 14, L.6: Could the authors explain why normalizations were performed?

Author response: The amount of OC of the density fractionation are normalized to the mass of the fraction or the mass of the bulk soil representing either the OC concentration "in the fraction" or "with the fraction".

20 10) Paragraph 4.4: The authors should emphasize more on the fact that the very low number of data used for comparing the sites may also be responsible for the absence of significant differences.

Author response: We agree with you and included the calculation of statistical power and its results to the manuscripts discussion and Appendix.

25 11) Page 23,L.30: The authors could add a sentence on the potential of mineral phases for carbon storage.

Author response: We calculated the carbon stock potential for the case, that the Andosols upper horizon will one day stretch down to 100 cm and added a sentence in the conclusion accordingly.

30 12) Page 24, L. 5-7: the absence of significant difference could also be due to the fact that the number of data was too small to detect it.

Author response: We emphasized this accordingly in the Discussion section 4.4 and the Conclusion.

Reviewer 4

The manuscript answers the specific question of how much organic carbon (OC) can be stored in a specific type of soil (Andosol), giving experimental support to the theory of a finite OC accumulation potential of soils due to the limited binding capacities of minerals. I found the manuscript well written and well organized. Even though the experimental site was not designed from the beginning for this trial, I agree with the authors saying that it is rare to have such a long history of treatments, and this is particularly valuable when studying carbon dynamics in soil. My bigger concern regards the bulk density (BD) values reported in table 1 and the way they were assessed. As reported in equation 1, BD is of a pivotal importance in assessing the total amount of OC in the soil (Mg/ha), so I think it should be specified with more details how the sampling was carried out, which volume of soil was considered, which corer and so on. Ten sampling points don't represent a huge number, but for BD just 2 were used, which is really low for such a big area.

Author response: We agree that the BD is of pivotal importance. We added the standard error in Table 1. The bulk density was determined at two profiles per site (all horizons). For each horizon, five replicates were sampled with 100 cm³ corers, oven-dried at 105 °C for 24 hours and weighted. We think that the number of bulk density measurements are sufficient, because the standard error was small (with <0.05 g cm⁻³). We added those details in the revised manuscript.

This observation arises because the BD values reported in table one are really low even for andosols (<0.4 Mg m⁻³), which causes a relatively low amount of OC per hectare considering the relevant percentage that OC reaches in that soil (up to 21%). For instance, 315 Mg ha⁻¹ found in this study (considering 1 m soil depth) are obtainable with a 2.6% of OC in a soil with BD = 1.2 Mg m⁻³, very typical in mineral soils. Thus, besides improving the description of the sampling methodology, I suggest adding some reference supporting such low BD values.

Author response: We added some references supporting BD values below 0.5 g cm⁻³ in Andosols. Especially aluandic Andosols feature often such low BD values. We also added some sentences to Section 4.3 to compare the OC stock of this Andosol with values from other soils.

Basile-Doelsch, I., R. Amundson, W.E.E. Stone, D. Borschneck, J. Y. Bottero, S. Moustier, F. Masin, and F. Colin. "Mineral Control of Carbon Pools in a Volcanic Soil Horizon." Geoderma 137, no. 3-4 (2007): 477-489.

<https://doi.org/10.1016/j.geoderma.2006.10.006>.

Marin-Spiotta, Erika, Oliver A. Chadwick, Marc Kramer, and Mariah S. Carbone. "Carbon Delivery to Deep Mineral Horizons in Hawaiian Rain Forest Soils." Journal of Geophysical Research: Biogeosciences 116, no. 63 (2011):

<https://doi.org/10.1029/2010JG001587>.

Tonneijck, Femke H., B. Jansen, K. G. J. Nierop, Jacobus M. Verstraten, Jan Sevink, and L. de Lange. "Towards Understanding of Carbon Stocks and Stabilization in Volcanic Ash Soils in Natural Andean Ecosystems of Northern Ecuador." *European Journal of Soil Science* 61, no. 3 (2010): 392-405. <https://doi.org/10.1111/j.13652389.2010.01241.x>.

5 I would also stress this fact more in the discussion chapter, section 4.4: the low BD is likely due to a low content of minerals, which can be "easily" saturated with OC at least in the upper layers. Please provide also some more info about the way in which sawdust was distributed over the years, specifying to which degree can the soil treated with sawdust considered homogeneous within the 3 hectares of the trial.

10 *Author response: Yes, the smaller content of mineral phases in the topsoil might cause the smaller sorption capacity but probably the smaller mineral content itself is just a result of the strong sorption of organic matter by highly reactive mineral phases. The sawdust was distributed approximately evenly over the site by hand. We added this information to the Materials and Methods section 2.1.*

15 Some technical notes:

P1-L3: please add a reference at the end of the first sentence (storage of organic carbon in soils)

P4-L11: please use the same decimals (1-16 or 0.9-16.0 Mg ha⁻¹ year⁻¹)

P6-L9: standard deviation (not derivation)

Author response: Thank you for pointing this out. We changed the manuscript accordingly.

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With kind regards

Antonia Zieger on behalf of all of the co-authors

Massive carbon addition to an organic-rich Andosol ~~did not increase~~ increased the topsoil-subsoil but not the subsoil-topsoil carbon stock.

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Abstract. Andosols are among the most carbon rich soils, with an average of 254 Mg ha⁻¹ organic carbon (OC) in the upper 100 cm. A current theory proposes an upper limit for OC stocks independent of increasing carbon input. ~~This is assigned to~~ because of finite binding capacities ~~for organic matter (OM)~~ of the soil mineral phase. We tested the possible limits in OC stocks for Andosols with already large OC concentrations and stocks (212 g kg⁻¹ in the first horizon; 301 Mg ha⁻¹ in the upper 100 cm). The soils received large inputs of 1800 Mg OC ha⁻¹ as sawdust within a time period of 20 years. Adjacent soils without sawdust application served as controls. We determined total OC stocks as well as the storage forms of ~~OM-organic matter (OM)~~ of five horizons down to 100 cm depth. Storage forms considered were pyrogenic carbon, OM of < 1.6 g cm⁻³ density and with no to little interaction with the mineral phase, strongly mineral-bonded OM forming particles of densities between 1.6 and 2.0 g cm⁻³ or > 2.0 g cm⁻³. The two fractions > 1.6 g cm⁻³ were also analyzed for Al-organic matter complexes (Al-OM-Al-OM complexes) and imogolite-type phases using ammonium oxalate-oxalic acid extraction and X-ray diffraction (XRD).

Pyrogenic organic carbon represented only up to 5 wt% of OC, and thus, contributed little to soil OM. In the two topsoil horizons, the fraction between >1.6 and 2.0 g cm⁻³ had 65-86 wt% of bulk soil OC and were dominated by Al-OM-Al-OM complexes. In deeper horizons, the fraction > 2.0 g cm⁻³ contained 80-97 wt% of the bulk soil's total OC and was characterized by a mixture of Al-OM-Al-OM complexes and imogolite-type phases, with proportions of imogolite-type phases increasing with depth. In response to the sawdust application, only the OC stock ~~in at~~ at 25-50 cm depth increased significantly ($P=0.05$ alpha = 0.05, $1 - \beta = 0.8$). The increase was entirely due to increased OC in the two fractions > 1.6 g cm⁻³. However, there was no significant increase in the total OC stocks within the upper 100 cm.

~~We assume, the topsoil is saturated in terms of OC concentrations, and thus, added OC partly migrates downwards, where it becomes retained by OC-undersaturated minerals. This indicates the possibility to sustainably increase already large OC stocks further, given that the subsoil still has binding capacity and OC transport into deeper horizons is facilitated. The results suggest that long-term large OC inputs cannot be taken up by the obviously OC-saturated topsoil but induce downward migration and gradually increasing storage of OC in subsurface soil layers.~~ The little additional OC accumulation despite the extremely large

OC input over 20 years, however, shows that long time periods of high input are needed to promote the downward movement and deep soil storage of OC.

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1 Introduction

5 Soil holds more organic carbon (OC) than there is carbon in the global vegetation and atmosphere combined ~~Moreover soil~~
([Lehmann and Kleber, 2015](#)). Soil organic matter (OM) improves plant growth and protects water quality by retaining nutrients
as well as pollutants in the soil (Lal, 2004). Thus, understanding the soil OC dynamics is crucial for developing strategies to
mitigate the increase of atmospheric CO₂ concentrations and [to increase soil fertility](#) (Stewart et al., 2007). The ~~large dynamic~~
[nature of the soil carbon reservoir](#) ~~however is not steady. It results from a~~ [is the result of the](#) dynamic equilibrium between
10 organic and inorganic material entering and leaving the soil (Schrumpf et al., 2011).

There are ~~contradictory views on~~ [contradicting views at](#) soil carbon storage capacities. According to Lal (2004), the OC
stock to 1 m depth ranges from 30 in arid climates to 800 Mg ha⁻¹ in organic soils in cold regions; the predominant range is
50 to 150 Mg ha⁻¹. Paustian et al. (1997) consider the carbon input rate as the main factor ~~and state that the~~ [for influencing](#)
15 [carbon stocks. The authors state that](#) OC stocks increase linearly with increasing organic input without having an upper limit.
Most current OC models ~~which use~~ [using](#) this linear relationship, perform reasonably well across a diversity of soils and
land use changes (Campbell and Paustian, 2015). On the contrary, Campbell et al. (1991) published data, where soils rich
in OC show little or no increase in soil OC despite a two to ~~three-fold~~ [three-fold](#) increase in carbon input. This motivated
Six et al. (2002) and Stewart et al. (2007) to propose that [the](#) OC accumulation potentials of soils are limited independent of
20 increasing carbon input. ~~The authors attribute~~ [They attributed](#) this to the limited binding capacities of minerals. This concept
is reflected by the model of Schmidt et al. (2011), in which the OC input is stepwise mineralized, surpassing the form of large
biopolymers, small biopolymers with less than 600 Da and monomers. At each step the possibility of interaction with mineral
phases increases, leading to different OC storage forms with differing turnover times and degree of interaction with the mineral
phase. ~~Overall the~~ [The](#) predominant proportion of OM in soils is associated with the mineral phase (e.g. Schrumpf et al., 2013).
25 Minerals have finite reactive surface areas ~~and consequently~~ [and consequently](#), finite OM binding capacities. The size of the
surface area depends on the type of mineral, and so, the differences in OC stocks among soils are due to different types and
amounts of the contained minerals. Thus, the OC input rate is only crucial as long as the mineral OC storage capacities are not
exhausted. However, the concept of limited storage capacity has hardly been experimentally tested so far.

30 Allophane and imogolite-type phases are, besides Al and Fe oxides, the most effective minerals to bind OM (Kögel-Knabner
et al., 2008; Huang et al., 2011a). They dominate the mineral assemblage of Andosols, making them the most carbon-rich min-

eral soil (Huang et al., 2011a; WRB, 2006; Basile-Doelsch et al., 2007)(Huang et al., 2011a; IUSS Working Group WRB, 2015; Basile-Doelsch et al., 2007). Andosols are subdivided in silandic and aluandic subgroups. Silandic Andosols have 80-120 g OC kg⁻¹ soil, whereas aluandic Andosols can contain up to 300 g OC kg⁻¹ soil (Huang et al., 2011a). Differences in OC concentrations among both subgroups are explained by differing carbon storage mechanisms. Organic matter in silandic Andosols is mainly bound to allophanes, imogolites and protoimogolites (grouped as imogolite-type phases Levard et al. (2012)). The OM in aluandic Andosols is mainly stored ~~with~~ within aluminium-organic complexes (~~Al-OM-Al-OM~~ complexes). The Al in these complexes can be either monomeric Al³⁺ ions, but also hydroxylated Al species (Huang et al., 2011a; Colombo et al., 2004; Masion et al., 1994). ~~Independent of the type of Andosol, the main OM stabilizing mechanisms are organic-mineral interactions.~~ Andosols with extremely high OC concentrations likely present OM-saturated mineral phases, at least in the topsoil, and should respond with no change in OC concentrations to increasing carbon input.

In order to test the concept of limited OC storage capacity in soils we took the opportunity of a unique setting in the Ecuadorian rainforest, where a carbon-rich Andosol (301 Mg OC ha⁻¹ within the first 100 cm) received an extra 1800 Mg OC ha⁻¹ input as sawdust during a period of 20 years. Adjacent soils without sawdust application served as controls.

We tested the following hypotheses: i) The additional OC input did not result in increased OC in the topsoil, but in the subsoil, because the mineral binding capacities for OM in the topsoil are exhausted and mobile OM is transported into the subsoil and retained there; ii) the increase of OC in the subsoil is due to OM binding to the mineral phase; and iii) the total OC stock of the soil increased significantly.

We determined total OC stocks as well as the storage forms of OM and the mineral composition down to 100 cm depth. For determining different OM storage forms we used the sequential density fractionation method ~~to obtain fractions yielding OM~~ with yielding OM fractions of different degrees of mineral interaction. We also determined pyrogenic organic carbon (PyC) ; because of its significant contribution to ~~the~~ OC stocks in some regions of the Amazon basin (e.g. Glaser et al., 2000)). We used ammonium ~~oxalate-oxalic~~ oxalate-oxalic acid extraction and X-ray diffraction for characterizing the prevalent mineral species in ~~the~~ density fractions containing organic-mineral associations.

2 Materials and methods

2.1 Soil sample source and handling

The study site is located in Ecuador, within the *Centro de Rescate de la Flora Amazónica* (CERFA) 3 km south of Puyo (1°30'50" S, 77°58'50" E, 950 AMSL). Puyo, located in the transition zone between the Andes and the western Amazon basin, lies in the center of ~~an alluvial fan affected by deposition of a largely homogeneous alluvial fan composed of re-deposited~~ Pleistocene volcanic debris ~~called of~~ the Mera formation (~~Sauer, 1971~~)(Sauer, 1971; Mortimer et al., 1980). The deposited material belongs to the andesite-plagidacite series or the andesite andesitedacite-rhyolite series ~~. Later on additional thick layers of~~

volcanic ash from eruptions were deposited (Hörmann and Pichler, 1982). Today fresh ash is deposited only infrequently from the volcanoes Tungaraghua and Sangay (Le Pennee et al., 2012). Tungaraghua ash composition ranges from basic andesites to dacites (Hall et al., 1999). (Hörmann and Pichler, 1982). The climate is diurnal tropical with mean annual temperatures of 20.8 °C and annual precipitation of 4403 mm (Schwarz, 2015). The vegetation cover is tropical rainforest and pasture (Tello, 2014).

5 . (Tello, 2014)

Before 1980 the sampling area ~~has undergone~~ was first used for traditional shifting cultivation ~~and later on, and then,~~ pasture dairy farming. Since 1980 ~~of the~~ 5 ha of pasture were reforested by ~~the individual~~ Nelson Omar Tello Benalcázar. On 3 ha, within this area, he applied 1800 t OC ha⁻¹ additional litter in form of sawdust until the year 2000 (sawdust site). About 10 m³ of sawdust where applied ~~manually approximately evenly over the site by hand every day~~ on 5 days a week for 20 years. The sawdust was collected on a daily basis from a local sawmill. ~~Nowadays the are covered by about old~~ The 5 ha reforested area is now covered by a 37 years-old secondary rainforest. (Tello, 2014)

~~We got in contact with this interesting project in 2013.~~ As the site was originally not designed for experimental purposes ~~it does not reflect our research plots are not arranged in~~ a randomized plot design. Nevertheless, we think that it can be scientifically ~~evaluated useful~~ because the plot ~~area on which we sampled is areas are fairly~~ large (2-3 ha at each site) and essential conditions like exposition, inclination, climate ~~, weather conditions~~ and geology are ~~comparable between the same for~~ the treated and untreated areas. No information about changes in tree species over time and possible differences ~~between in~~ species due to the sawdust input ~~were available. Instead we estimated additional litter input at the sawdust site due to higher vegetation biomass productivity based on the literature. Clark et al. (2001) reported fine litterfall biomasses of for tropical forest all over the world. If the sawdust site would have been covered with a tropical forest for the whole 37 years and the adjacent site (contorl site) not, litter biomass would have been additionally added since 1980. This litter carbon represents less than are available. Therefore, no precise information on differences in carbon input due to litterfall are available. Using the litterfall biomass of 0.9-6.0 Mg ha⁻¹ year⁻¹ carbon reported by Clark et al. (2001) for tropical forests across the world, we estimated the litter input since 1980 at the study site to 33-222 Mg ha⁻¹ . This means the maximum carbon input with litter represents 2-12 % of the total sawdust carbon input and is therefore insignificant. In order to eliminate estimate the belowground biomass as the dominating a possible soil organic carbon source, we measured the gravimetric root intensity. The results show We found no significant difference between the sites (for data see the appendix). A1).~~

30 We classified the soil as an alusilandic Andosol, based on the IUSS Working Group WRB (2015) (for selected properties see Table 1, for profile example see Figure A1). Few prominent X-ray diffraction reflexes indicate simple mineral composition. The crystalline primary minerals are amphibole, chlorite, quartz and plagioclase. Kaolinite and other secondary clay minerals are not present. Contents of crystalline Fe oxides and gibbsite are little. Oxalate extractions indicate large amounts of short range-ordered and nano- or micro-crystalline mineral phases.

35

The soil samples for this study were taken in 2014 from the upper 100 cm at five profiles at each the secondary rainforest with sawdust application (sawdust site) and the adjacent forest where no sawdust was applied (control site). The ~~position~~ positions of the ten profiles were randomly selected and ~~had each a profile~~ each profile had a width of 1 m. We define horizon one and two as the topsoil and horizon three to five as the subsoil. Samples were oven dried at 40 °C in Ecuador at the Universidad
5 Estatal Amazónica, before ~~transporting them to the German laboratory and sieving them~~ transport to the laboratory in Germany and sieving to <2 mm.

~~We classified the soil as an alusilandic Andosol, based on the WRB (2006). All analyses, except for X-ray diffraction, which was carried out with no replicate, were carried out in duplicates. Results are presented as means of replicates. Sequential density fractionation, subsequent mineralogical analyses and PyC analyses were carried out for one representative profile per site (for~~
10 ~~selected properties~~ soil data see Table 1). ~~Few prominent X-ray diffraction reflexes indicate simple mineral composition. The crystalline primary minerals are amphibole, chlorite, quartz and plagioclase. Kaolinite and other secondary clay minerals are completely missing. Contents of crystalline Fe minerals and gibbsite are little. Oxalate extractions indicate large amounts of short range-ordered and nano- or micro-crystalline mineral phases.~~ 2). The soil profiles for these analyses were selected on the basis of having five horizons within the upper 1 m, largest bulk OC concentration in horizon one, similar amount of acid
15 oxalate-extractable elements and having different bulk OC concentrations in the third horizon. All calculations and graphs were processed with R version 3.4.3 (The R Foundation for Statistical Computing, 2017).

Table 1. Selected bulk properties of the studied Andosol. Soil ~~layer thickness~~ horizon thicknesses, pH values, bulk densities (BD), bulk organic carbon ~~concentration~~ concentrations (OC) and carbon nitrogen ratios (C/N) are given as ~~the mean and where convenient along means~~ with the standard error ~~of data from five profiles~~. Bulk density (BD) is given as the mean of data from two profiles ~~where appropriate~~. ~~X~~The ~~Al_{ox} is the concentration of~~, ~~Si_{ox} and Fe_{ox} represent~~ ammonium ~~oxalate-oxalic-oxalate-oxalic~~ acid extractable ~~elements~~ aluminium, silicon and iron and are given as the mean ~~of data from three profiles~~ concentrations and standard error. Fe_d is ~~the concentration of~~ dithionite-extractable iron ~~performed-analyzed~~ with samples from only one profile per site. The concentrations of Al, Si and Fe are normalized to the mineral ~~portion-part (or inorganic part) of the dry soil~~ assuming that the mass of OM is two times the mass of OC (Sollins et al., 2006). ~~Parenthesis represent standard deviation~~ The row marked with n represents the number of sample parallels profiles analyzed per site.

| horizon | layer <u>horizon</u> thickness [‡] | pH _{C_aCl₂} | BD [‡] | OC [‡] | C/N | Al _{ox} | Si _{ox} | Al _{ox} /Si _{ox} | Fe _{ox} | Fe _d |
|--------------|--|---|--------------------------------------|----------------------|----------|--------------------|--------------------|------------------------------------|--------------------|--------------------|
| | cm | - | g cm ⁻³ | g kg ⁻¹ | - | g kg ⁻¹ | g kg ⁻¹ | molar ratio | g kg ⁻¹ | g kg ⁻¹ |
| <u>n</u> | <u>5</u> | <u>5</u> | <u>2</u> | <u>5</u> | <u>5</u> | <u>3</u> | <u>3</u> | <u>3</u> | <u>3</u> | <u>1</u> |
| control site | | | | | | | | | | |
| H1 | 10 (±1) | 4.1 | 0.26 <u>0.27 (± 0.00)</u> | 212 (±16) | 12 | 55 (±2) | 12 (±2) | 4.7 (±0.8) | 21 (±3) | 20 |
| H2 | 13 (±5) | 4.6 | 0.38 <u>0.37 (± 0.01)</u> | 128 (±9) | 11 | 67 (±7) | 23 (±8) | 3.1 (±0.7) | 20 (±2) | 20 |
| H3 | 24 (±4) | 4.8 | 0.38 <u>0.39 (± 0.00)</u> | 75 (±0) [*] | 11 | 85 (±3) | 35 (±4) | 2.5 (±0.2) | 22 (±2) | 24 |
| H4 | 31 (±6) | 5.0 | 0.32 <u>0.37 (± 0.05)</u> | 76 (±1) | 12 | 95 (±7) | 42 (±4) | 2.3 (±0.0) | 20 (±5) | 22 |
| H5 | 35 (±3) | 5.1 | 0.31 <u>0.32 (± 0.01)</u> | 66 (±1) | 12 | 121 (±4) | 53 (±1) | 2.3 (±0.1) | 20 (±9) | 20 |
| sawdust site | | | | | | | | | | |
| H1 | 12 (±1) | 4.5 | 0.26 <u>0.30 (± 0.04)</u> | 214 (±18) | 13 | 56 (±4) | 13 (±2) | 4.3 (±0.6) | 25 (±1) | 25 |
| H2 | 16 (±6) | 4.8 | 0.26 <u>0.31 (± 0.05)</u> | 143 (±14) | 13 | 70 (±9) | 22 (±6) | 3.2 (±0.6) | 25 (±1) | 28 |
| H3 | 20 (±3) | 5.4 | 0.32 <u>0.36 (± 0.03)</u> | 89 (±4) [*] | 12 | 76 (±6) | 29 (±5) | 2.7 (±0.3) | 28 (±2) | 26 |
| H4 | 29 (±3) | 5.6 | 0.38 <u>0.39 (± 0.01)</u> | 77 (±4) | 12 | 84 (±20) | 35 (±9) | 2.4 (±0.1) | 28 (±7) | 24 |
| H5 | 28 (±9) | 5.6 | 0.32 (<u>± 0.00</u>) | 67 (±3) | 12 | 92 (±13) | 39 (±3) | 2.4 (±0.2) | 31 (±8) | 33 |

2.2 Bulk organic carbon concentration and stock

~~Aliquots of all bulk samples were grounded, oven dried at for prior to OC and nitrogen (N) determination with an Elementar Vario EL III CNS analyzer.~~

Organic carbon stocks were calculated based on soil volume to the fixed soil depth of 1 m. ~~We found~~ The equivalent soil mass approach propagated by Schrumpf et al. (2011) and Wendt and Hauser (2013) was not applied, because i) bulk density did not vary much between sites for the same horizons, ii) the studied site was no cropland and iii) the approach increases uncertainties of OC stocks of undisturbed soils (Schrumpf et al., 2011).

We distinguished up to five soil layers-horizons per profile and determined bulk density, layer-horizon thickness and OC concentrations (Eq. (1)). Horizon thickness and OC concentrations were measured-recorded at all five profiles per site. The bulk density was only ~~Aliquots of all bulk samples were grounded and oven dried at 105 ° C for 24 h prior to OC and nitrogen (N) determination with an Elementar Vario EL III CNS analyzer. The bulk densities were determined at two profiles per site (all horizons)and the mean-. At each horizon five replicates were sampled with 100 cm³ corers, oven-dried at 105 ° C for 24 hours and weighted. For calculating the OC stock of horizons in all five profiles per site (horizon_i) the mean of bulk densities (meanBD) was used for calculations. Thus (Eq. 1). The OC stock of each profile is the sum of the respective horizons' OC stocks. The OC stocks are presented as their mean and range, instead of standard derivationthe means with their 95 % confidence interval. As the soils contained only minimal amounts of material-no material > 2 mm, the soil particles < 2 mm represents-represent the total soil mass.~~

$$OC\ stock_i [Mgha^{-1}] = OC_i [gkg^{-1}] \cdot horizon\ thickness_i [dm] \cdot meanBD [kg\ dm^{-3}] \quad (1)$$

For comparing OC stocks at different depths, we also cumulated the OC stocks of each horizon proportionally. We choose the ~~depth depths~~ 0-25, 25-50and 50-100 cm-, 50-75 and 75-100 cm in order to represent the topsoil, horizon three (25-50 cm) and the subsoil below horizon three. We performed ~~the 'Welch two sample t-test' of means (p=0.05, non-paired) two sample t-tests of means~~ for comparing bulk OC stocks -

$$OC\ stock [Mgha^{-1}] = OC [gkg^{-1}] \cdot meanBD [kg\ dm^{-3}] \cdot layer\ thickness [dm]$$

~~The equivalent soil mass approach propagated by Schrumpf et al. (2011); Wendt and Hauser (2013) was not applied, as i) bulk density was not detected temporarily and did not vary much between sites for the same horizons, ii) the studied site was no cropland and iii) and OC concentrations between sites. The two sample t-tests were performed unpaired, one sided, at the significance level $\alpha = 0.05$ and the approach increases uncertainties of OC stocks of undisturbed soils (Schrumpf et al., 2011) power of $1 - \beta = 0.8$. The OC concentration and OC stocks at the sawdust site were considered significantly larger, if the t-test's confidence interval did not contain zero and the sampling number was sufficient. We calculated the minimum sample number (n_{min}) and power ($power_{th}$) for the difference we wish to detect (Δ th) between the sites to evaluate the power of our data. The Δ th is either the mean difference or assumed to be 10 % of the mean at the control site.~~

2.3 Pyrogenic carbon analyses

Analysis of pyrogenic carbon (PyC) was ~~performed by the staff of~~ carried out in the department of soil science at Rheinische Friedrich-Wilhelms-Universität Bonn. It ~~was carried out following~~ followed the revised protocol of Brodowski et al. (2005). For quantifying the benzene polycarboxylic acids (BPCA), 10 mg of dried and ground soil material was treated with 10 ml
5 4 M $\text{CF}_3\text{CO}_2\text{H}$ (99%, Sigma Aldrich, Taufkirchen, Germany) to remove polyvalent cations. The PyC was then oxidized with HNO_3 (8 h, 170 °C) and converted to BPCAs. After ~~cleanup via~~ removal of metal ions with a cation exchange column (Dowex 50 W X 8, 200-400 mesh, Fluka, Steinheim, Germany), the BPCAs were silylated and determined using gas chromatography with flame ionization detection (GC-FID; Agilent 6890 gas chromatograph; Optima-5 column; 30 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco, Steinheim, Germany). Two internal standards citric acid and biphenyl dicarboxylic acid were used.
10 Carefully monitoring the pH avoided decomposition of citric acid during sample processing as criticized by Schneider et al. (2010). The recovery of internal standard 1 (citric acid) ranged between 78 and 98 %. Carbon content of BPCA (BPCA-C) was converted to PyC ~~with~~ using the conversion factor 2.3 (Brodowski et al., 2005). The analyses showed good repeatability, with differences between two measurement parallels being <4.2 g PyC kg⁻¹OC, except for the second horizon at the control site were the parallels differed by 12.5 g PyC kg⁻¹OC.

15 2.4 Sequential density fractionation of OM

We modified the sequential density fractionation procedure (Fig. 1) described by Cerli et al. (2012) in order to separate four different fractions. The first light fraction F1 contains ~~mainly~~ OM basically not interacting with the mineral phase often ~~called~~ labeled free particulate OM. The second light fraction (F2) contains mainly particulate OM being incorporated into aggregates thus having little interaction with the mineral phase. The third and fourth fraction (F3, F4) are heavy fractions mainly containing
20 OM strongly ~~interacting with~~ bound to the mineral phase, ~~which are often called organic-mineral associations~~.

Fifteen gram of dried (40 °C) and sieved (<2 mm) soil were mixed with 75 ml of sodium polytungstate solution (SPT, TC-Tungsten Compounds) with a density of 1.6 g cm⁻³ in 200 ml PE bottles. To obtain F1, the bottles were gently shaken a few times, and then the suspensions were allowed to settle for 1 h and subsequently centrifuged at 4500 g for 30 min (Sorvall RC-5B). The supernatant was siphoned with a water jet pump and the F1 fraction was collected on a pre-rinsed 1.2 μm
25 cellulose-nitrate membrane filter. After rinsing with deionized water until the conductivity of the filtrate was <50 μS cm⁻¹, F1 was ~~carefully~~ transferred into a 50 ml PE bottle and subsequently freeze dried (Christ alpha 2-4 and 1-4 LCS).

The residue was re-suspended with re-collected SPT solution and refilled with fresh SPT solution (1.6 g cm⁻³) until the
30 original ~~bottle-sample~~ sample bottle mass was maintained. In order to release F2, the ~~aggregates~~ samples were dispersed by sonication (~~energy input~~ with 10-mm pole head sonotrode, submersed to 15 mm depth, oscillation period 50/60 Hz, amplitude 2 AMP; Branson Sonifier 250) ~~according to the calibration of~~ The energy input was 300 J ml⁻¹ , calibrated according to Schmidt et al. (1999). The appropriate energy input was determined in a preliminary experiment as ~~the~~ that energy which

released the largest amount of largely pure OM, following Cerli et al. (2012) (Cerli et al., 2012). Temperature was kept < 40 °C using an ice bath to avoid thermal sample alteration. Thereafter, the sample was centrifuge at 4500 g for 30 min and floating material was separated, washed and dried as described above for F1.

5 In order to further separate the residual ~~fraction into Al-OM~~ >1.6 g cm⁻³ fraction into Al-OM complexes and imogolite-type phases we introduced an additional density cut off. This is sensible because the overall density of ~~an~~ organic-mineral ~~association~~ associations depends on OM density, mineral density, and OM load (Kaiser and Guggenberger, 2007; Chenu and Plante, 2006). The densities of pure imogolite-type mineral phases and ~~Al-OM complexes are very~~ Al-OM complexes are similar (Huang et al., 2011c), but Boudot (1992) and Kaiser and Guggenberger (2007) showed that ~~Al-OM~~ Al-OM complexes
10 have a higher OM load than imogolite-type phases. The second density cut off ~~was set at~~ 2.0 g cm⁻³, ~~which was determined in a preliminary experiment on the basis of~~ was selected based on OC concentrations, XRD spectra and oxalate-extractable Al, Si and Fe concentrations determined in a preliminary experiment. The fraction with a density between 1.6. and 2.0 g cm⁻³ was found to be enriched in ~~Al-OM~~ Al-OM complexes (F3), while that >2.0 g cm⁻³ (F4) was rich in imogolite-type phases.

15 For obtaining F3, the residue of the previous separation step was re-suspended in 75 ml fresh SPT solution (density of 2.0 g cm⁻³), dispersed at 30 J ml⁻¹ to ensure ~~complete soil wetting with new SPT solution~~ dispersion, centrifuged, separated, washed and dried as described above for F1. The final residue of > 2.0 g cm⁻³ density (F4) ~~, mainly containing imogolite-type phases and crystalline minerals,~~ was rinsed with deionized water until the conductivity of the supernatant was <50 μS cm⁻¹ and subsequently freeze-dried.

20

Aliquots of all fraction samples were oven dried at 105 °C for 24 h prior to OC and N determination with an Elementar Vario EL III CNS analyzer.

25 To test if the separation of particles with F3 and F4 is caused by either variations in mineral density or OM loading we calculated the overall soil particle densities $\rho_{soil\ particle}$ in F3 using Eq. (2) (Chenu and Plante, 2006). We assume the minerals to have densities (ρ_M) of about 2.7 g cm⁻³ (Huang et al., 2011c) and OM (x_{OM} as 2 × OC) to have an average density (ρ_{OM}) of 1.4 g cm⁻³ (Mayer et al., 2004).

$$\rho_{soil\ particle} = \frac{a}{x_{OM} + b} \quad \text{with} \quad b = \frac{\rho_{OM}}{\rho_M - \rho_{OM}} \quad \text{and} \quad a = \rho_M \cdot b \quad (2)$$

Table 2. Selected ~~bulk~~ properties of ~~bulk~~ samples used in the sequential density fractionation. The soil profiles were selected on the basis of having five horizons within the upper 1 m, largest OC concentration in horizon one, similar amount of acid oxalate-extractable elements and having different bulk OC concentrations in the third horizon. Presented are bulk organic carbon (OC) concentrations, ~~carbon-nitrogen~~ carbon-to-nitrogen ratios (C/N) and pyrogenic carbon (PyC) ~~as proportion of contents normalized to bulk soil OC.~~ ~~XAl_{ox} is-, Si_{ox} and Fe_{ox} are the concentration concentrations of ammonium oxalate-oxalic oxalate-oxalic acid extractable elements~~ aluminium, silicon and iron. The concentrations of Al~~and~~, Si ~~and~~ Fe are normalized to the mineral ~~portion-part (or inorganic part) of the dry soil~~ assuming that the mass of OM is two times the mass of OC (Sollins et al., 2006).

| horizon | depth cm | pH _{C_αCl₂} - | OC g kg ⁻¹ soil | C/N - | PyC g kg ⁻¹ OC | Al _{ox} g kg ⁻¹ | Si _{ox} g kg ⁻¹ | Al _{ox} /Si _{ox} molar ratio |
|--------------|-------------|--|-------------------------------|----------|------------------------------|--|--|---|
| control site | | | | | | | | |
| H1 | 0-8 | 4.0 | 252 | 12 | 46 | 57 | 11 | 5.1 |
| H2 | 8-15 | 4.4 | 137 | 11 | 65 | 59 | 18 | 3.2 |
| H3 | 15-35 | 5.1 | 75 | 11 | 67 | 87 | 36 | 2.4 |
| H4 | 35-70 | 5.1 | 72 | 12 | 95 | 104 | 47 | 2.2 |
| H5 | 70-100 | 5.1 | 64 | 12 | 60 | 119 | 54 | 2.2 |
| sawdust site | | | | | | | | |
| H1 | 0-15 | 4.1 | 256 | 13 | 47 | 52 | 11 | 4.9 |
| H2 | 15-28 | 4.4 | 170 | 12 | 65 | 60 | 15 | 3.9 |
| H3 | 28-50 | 4.8 | 102 | 12 | 42 | 69 | 23 | 3.0 |
| H4 | 50-76 | 5.1 | 63 | 11 | 147 | 63 | 26 | 2.4 |
| H5 | 76-100 | 5.1 | 76 | 12 | 50 | 83 | 37 | 2.2 |

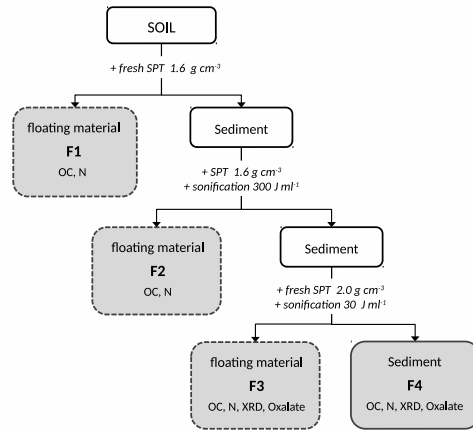


Figure 1. Sequential density fractionation scheme. SPT: sodium-polytungstate solution, F1: fraction ~~which comprises material with predominately organic matter of~~ densities $<1.6 \text{ g cm}^{-3}$, ~~in theory organic matter~~ with basically no interaction with the mineral phase, F2: fraction ~~which comprises material with predominately organic matter of~~ densities $<1.6 \text{ g cm}^{-3}$ and ~~limited interaction weakly associated~~ with the mineral phase, F3: ~~comprises material strongly interacting with mineral phases and overall~~ soil ~~partiele materials of~~ densities between 1.6 and 2.0 g cm^{-3} . ~~F4: comprises material and holding organic matter strongly interacting with bound to mineral phases and overall~~, F4: soil ~~partiele materials of~~ densities $> 2.0 \text{ g cm}^{-3}$ ~~and holding organic matter strongly bound to mineral phases~~. Below the fraction labeling subsequent ~~analysis analyses~~ are ~~named listed~~. OC: total organic carbon concentration, N: nitrogen concentration, XRD: X-ray diffraction, Oxalate: ammonium ~~oxalate-oxalic~~ ~~oxalate-oxalic~~ acid extraction

2.5 Acid oxalate extraction of F3 and F4

Aluminium (Al) and silicon (Si) of short range-ordered phases were extracted using the ammonium oxalate–oxalic acid reagent proposed by Schwertmann (1964). Either 0.1 or 0.5 g of oven dried ($105 \text{ }^\circ\text{C}$) and grounded F3 and F4 material, were suspended in 0.2 M ammonium oxalate–oxalic acid at pH 3 at a soil-to-solution ratio of 1 g:100 ml and shaken for two hours in the dark.

- 5 The suspension was decanted over ~~MUNKEL-MUNKTELL~~ 131 paper filters, with the first turbid ~~effluent-effluent~~ being discarded. Clear solutions were stored in the dark and at room temperature for no more than one day. Aluminium and silicon concentrations were determined by ICP-OES (Thermo Scientific iCAP 6000 series). The ~~Fe-iron (Fe)~~ concentrations were measured but results are not presented here since very low compared to ~~other soils like Ferrasols those of Al and Si~~ ($<30 \text{ g kg}^{-1}$, Table 1). The recovery rates are calculated as the sum of the elements' amount quantified in F3 and F4 normalized to ~~bulk~~
- 10 ~~oxalate-extracted-oxalate extractable~~ amounts of the element ~~-The results are normalized in bulk samples. Since the large and strongly with depth varying concentrations of organic matter masks the actual contribution of oxalate extractable minerals to total mineral constituents, we normalized the oxalate-extractable metals to the mineral portion of the fraction assuming that soil component (or inorganic part) instead of to dry soil. We calculated the mineral proportion of the samples assuming the~~

mass of OM ~~is being~~ two times the mass of OC (Sollins et al., 2006).

2.6 X-ray diffraction of F3 and F4

X-ray diffraction (XRD) spectra were obtained on each one F3 and F4 sample per horizon of the samples from the sawdust site.

- 5 Samples were grounded with a ball mill and oven dried at 105 °C for 24 h. The random oriented powders were analyzed using a PANalytical EMPYREAN X-ray diffractometer with theta/theta-geometry, 1 D-PIXcell detector, Cu-K α radiation at 40 kV and 40 mA, at an angle range of 5-65 °2 θ with 378 s counting time per 0.013 ° 2 θ step and automatically acting diaphragm. Evaluation was performed ~~with using the~~ X'Pert HighScore Plus V 3.0 (PANalytical) software.

10 2.7 ~~Data analysis~~

~~All analyses, except for X-ray diffraction, which was carried out with no replicate, were carried out in duplicates. Bulk analyses are carried out with samples from five profiles per site. Sequential density fractionation and subsequent mineralogical analyses and PyC analyses were carried out for one representative profile per site (for selected soil data see Table 2 soil profiles for these analyses were chosen on the basis of having five horizons within the upper, largest OC concentration in horizon one, similar amount of acid oxalate-extractable elements and having different bulk OC concentrations in the third horizon. Results are presented as means of replicates. All calculations and graphs were processed with R version 3.1.0 (2014 The R Foundation for Statistical Computing).~~

3 Results

3.1 Bulk organic carbon

- 20 The bulk OC concentrations are largest in the first horizon with around 212 g kg⁻¹, declining continuously with depth to around 66 g kg⁻¹ (Table 1 and A3). The first two horizons show large variances, being slightly larger at the sawdust site. The subsoil horizons have low variances and have also, except for horizon three with a difference of 14 g kg⁻¹, very low differences in their means between sites. The PyC proportion on bulk OC range between 42 and 147 g PyC kg⁻¹ OC (Table 2) and vary with depth in a non-regular pattern.

25

The total OC stocks ~~are between 277 and 352 with a mean of~~ at the sawdust site has a mean of 343 Mg ha⁻¹ with a 95 % confidence interval of [288, 399]. At the control site ~~total OC stocks range between 256 and 313 the confidence interval is [277, 324]~~ with a mean of at the control site (Table ??) 301 Mg ha⁻¹ (Figure 2). The ~~total OC stocks did not significant~~ 0-25 cm segment contributes most to the total OC stock and their confidence intervals have also the largest range. Both mean and the

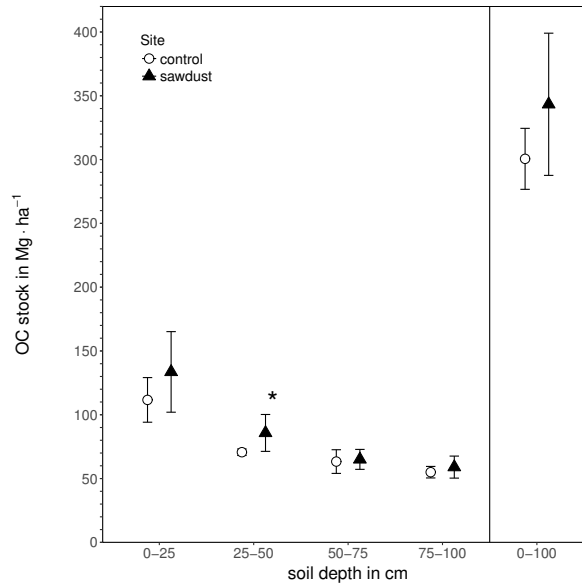


Figure 2. The organic carbon (OC) stocks of the sawdust and the control site. Presented are the entire profile (0-100) and the four selected depth increments 0-25, 25-50, 50-75 and 75-100 cm as the mean and the 95 % confidence interval.

* the OC stock at the sawdust site is significantly ($\alpha = 0.05$, $\beta = 0.8$) larger compared to the control site.

ranges of the confidence intervals decrease with depth at both sites.

The total OC stock does not significantly differ between the two sites. But out of the chosen depth sections the section of, although the t-test confidence interval was close to be positive (Appendix Table A2). Additionally a sample number larger than 9 would have been necessary to reach the test power of 0.8. Out of the selected depth increments the 25-50 cm segment, which comprises mostly the third horizon showed significant differences between the two sites (Table ??). In the third horizon the showed significant larger OC stocks at the sawdust site and the collected sample number was sufficient (Appendix Table A2). The bulk OC concentrations showed significant differences, whereas the layer thickness and the bulk density did not of horizon three at the sawdust site was significantly larger (Table 4).

The PyC proportion on bulk OC range between (Table 2) and vary with depth in a non-regular pattern (A3). The OC concentrations at all other horizons did not show significant differences between sites.

Organic carbon (OC) stocks are presented as mean along with standard error (n=5). † 'Welch two sample t-test' conducted with a p value of 0.05 provides evidence that OC stocks differ significantly at the two sites only for the depth - depth cm control site sawdust site 0-25 111 (± 7) 116 (± 8) 25-50 66 (± 2) * 78 (± 4) * 50-100 113 (± 5) 120 (± 5) total 289 (± 9) 315 (± 15)

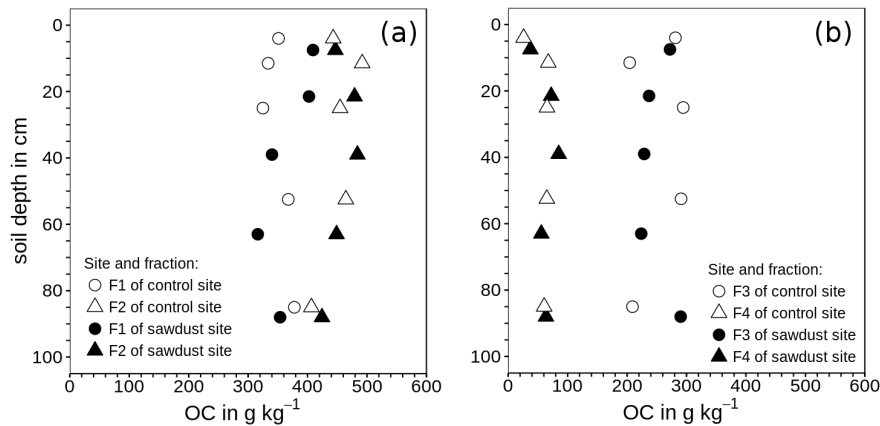


Figure 3. Mean of organic carbon (OC) concentration of concentrations in density fractions one to four normalized related to the mass of the respective fraction instead of the bulk soil mass. (a) Fractions 1 and 2 contain material (aF1), which was contains material released directly; fraction 2 (F1F2) and represents material released after applying 300 J ml^{-1} sonication energy. (F2b) Fraction Fractions 3 and 4 (b) comprise material organic matter strongly interacting with bound to mineral phases and overall in soil particles particles of densities between $1.6\text{-}2.0$ (F3) and $>2.0 \text{ g cm}^{-3}$ (F4) respectively.

3.2 Sequential density fractionation

3.2.1 Organic matter analysis

The performance of the density fractionation was evaluated using the recovery of mass and OC and at the OC concentration patterns within the fractions (Fig. 3). The recoveries of the soil mass range between 98 and 102 wt%. The OC recoveries are on average 95 and always larger than 89 wt%. Thus despite the numerous fractionation steps and extensive rinsing the overall high recoveries suggest very little losses of material due to dissolution and dispersion during the fractionation. Values exceeding 100 wt% are probably caused by random errors of measurements and some sodium polytungstate not entirely removed by sample washing.

- 10 The OC concentrations increase in the order $F4 < F3 < F1 < F2$ at all depths and all sites (Fig. 3). The OC concentrations are normalized related to the respective fraction mass. The two light fractions (F1, F2) are rich in OC with $285\text{-}422$ and $371\text{-}501 \text{ g kg}^{-1}$. Fraction three shows has also large OC concentrations, which vary slightly over depth between 204 and 294 g kg^{-1} changing in no particular pattern with depth, showing no regular depth patterns. In F4 the OC concentrations only increase within are much lower. They are the smallest in the first 10 cm from and then remain constant for lower horizons (30 g kg^{-1}) and remain at the similar but slightly higher level of (65 g kg^{-1}) deeper down the profile.
- 15

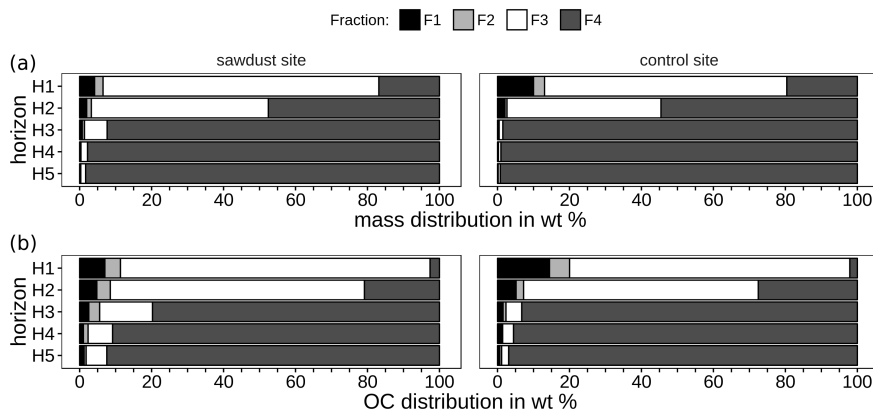


Figure 4. Mass (a) and organic carbon (OC, b) distribution in over density fractions in percent, given as percentages of cumulated masses of fractions. Fraction 1 and 2 contain material either, which was released directly released (F1) and/or after applying 300 J ml⁻¹ sonication energy (F2). Fractions 3 and 4 comprise material organic matter strongly interacting with bound to mineral phases and overall in soil particles of densities between 1.6-2.0 (F3) and/or >2.0 g cm⁻³ (F4) respectively.

To evaluate the OC storage forms, we evaluated the contribution of individual fractions to bulk sample OC (Fig. 4). Fractions one and two account for less than 11 wt% of bulk sample OC at the sawdust site and 20 wt% at the control site (Fig. 4, b). Their proportions decrease rapidly with depth to 2 and 1 wt% in horizon five. In general, the proportions of OC in the OC with F3 decrease drastically from >65 wt% in the topsoil to <7 wt% in the subsoils at both sites.

- 5 The proportion of OC in OC with F4 increase strongly from <27 wt% in the topsoil to >91 wt% in the subsoils at both sites.

Figure 5, shows the analysis of OC concentrations of F3 and F4 normalized to bulk soil mass (g kg⁻¹ bulk soil) figure 5) may give explanations for differences in OC concentrations between sites. The F3 of the second horizon at the sawdust site contains 29 g kg⁻¹ soil more OC than F3 at the control site, which. This represents 91 wt% of the differences in bulk OC concentration in the second horizon. In the third horizon, F3 and F4 at the sawdust site contain 11 and 14 g kg⁻¹ more OC than the respective fractions at the control site; combined they represent 93 wt% of the differences in the horizon's bulk OC concentrations of the third horizon. In the fourth and fifth horizon the OC concentration differences, the differences in OC concentrations of the fractions between the two sites are <3 g OC kg⁻¹ soil and, and thus, not significant.

15

3.2.2 Acid oxalate extraction of F3 and F4

The recoveries of Al are on average 101 wt% and for Si systematically lower for Si, ranging between 87 and 96-96 wt%. The concentrations of oxalate-extractable Al are normalized to the mineral portion, assuming that the mass of

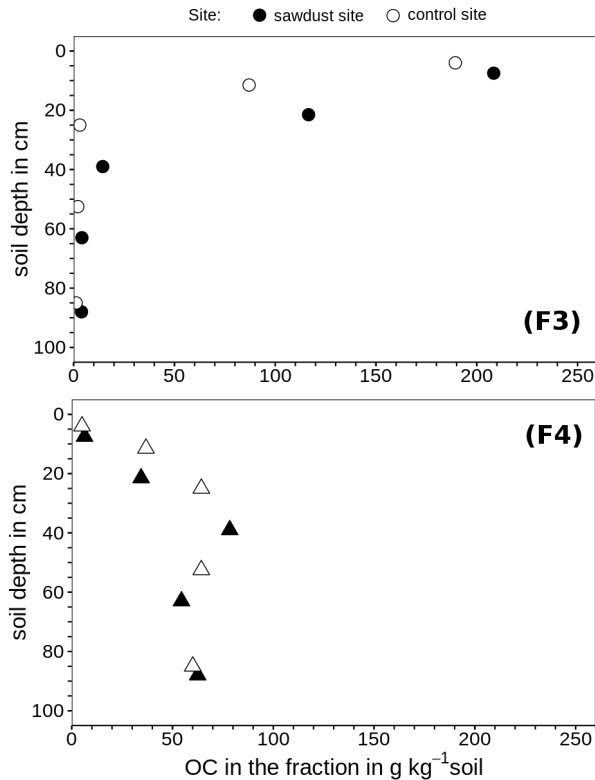


Figure 5. Organic carbon concentrations of fraction three and four normalized-related to the bulk soil mass. The-These fractions comprise material-organic matter strongly interacting-with-bound to mineral phases and-overall-in soil partiele-particles of densities between 1.6-2.0 (F3) and-or $>2.0 \text{ g cm}^{-3}$ (F4) respectively.

OM is two times the mass of OC (Sollins et al., 2006) soil components (see section 2.5). The concentrations of Al in F3 range between 63 and 227 g kg^{-1} and are 2.1-6.7 times larger than those of F4, which range only between 5 and 128 g kg^{-1} (Fig. 6). For both sites, the Al concentrations increase with increasing soil depth. The mineral-portion-normalized-Si concentrations show in general the same depth trend as the respective Al concentrations for all fractions and sites with-depth. They range between 11-61 g kg^{-1} for F3 and 1-51 g kg^{-1} for F4. The Al/Si molar ratios are always larger than two and are distributed in a concave function with depth, similar to bulk soil ratios (see-Table 2 for data). Only the Al/Si molar ratio in F4 of the uppermost horizon at the sawdust site is very low. At all sites, the Al/Si molar ratios in F3 are larger than the Al/Si molar ratios in F4 throughout the profiles.

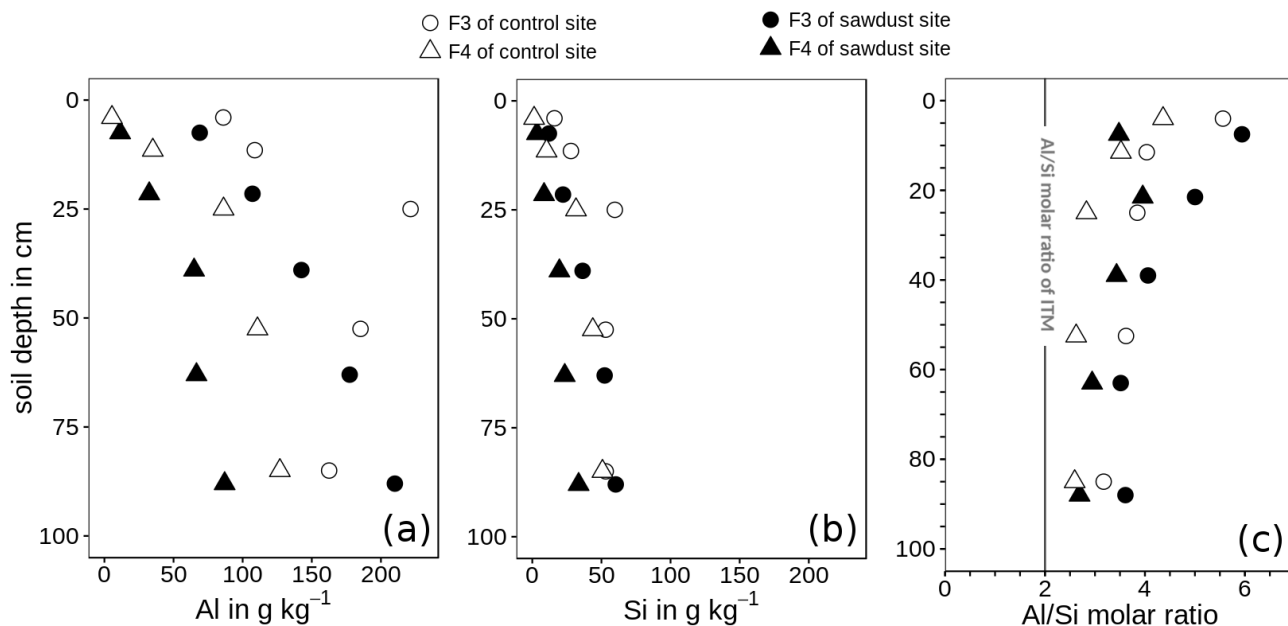


Figure 6. Concentration of acid oxalate-extractable aluminium (Al, a) and silica (Si, b) and Al/Si molar ratios (Al/Si, c) of the density fractions, which comprise material strongly interacting with mineral phases and overall soil particle of densities between 1.6-2.0 (F3) and $>2.0 \text{ g cm}^{-3}$ (F4), respectively. The metal concentrations are normalized to the mineral portion of the fraction, assuming that the mass of OM is two times the mass of OC (Sollins et al., 2006). ITM: imogolite-type mineral phases.

3.2.3 X-ray diffractograms of F3 and F4

Differential X-ray spectra of F3 and F4 show similar main reflexes as the spectra of the bulk samples. The overall signal intensities in F4, are higher than for F3 spectra (Fig. 7). Moreover the F4 spectra show hardly any broad reflexions, while the F3 spectra have broad reflexions at 6-8, 20-30 and $40^\circ 2\theta$. These characteristics features reflect low crystallinity material and are assigned to such as imogolite-type mineral phases (Yoshinaga and Aomine, 1962; Basile-Doelsch et al., 2007). In contrast, the F4 spectra indicate larger amounts of crystalline minerals. Spectra of both fractions show increases in broad reflexions at 6-8 and $20\text{-}30^\circ 2\theta$ with increasing soil depth.

4 Discussion

4.1 Sequential density fractionation and oxalate extraction performance

10 Despite the numerous fractionation steps and extensive rinsing the overall high recoveries suggest very little losses of material due to dissolution and dispersion during the fractionation.

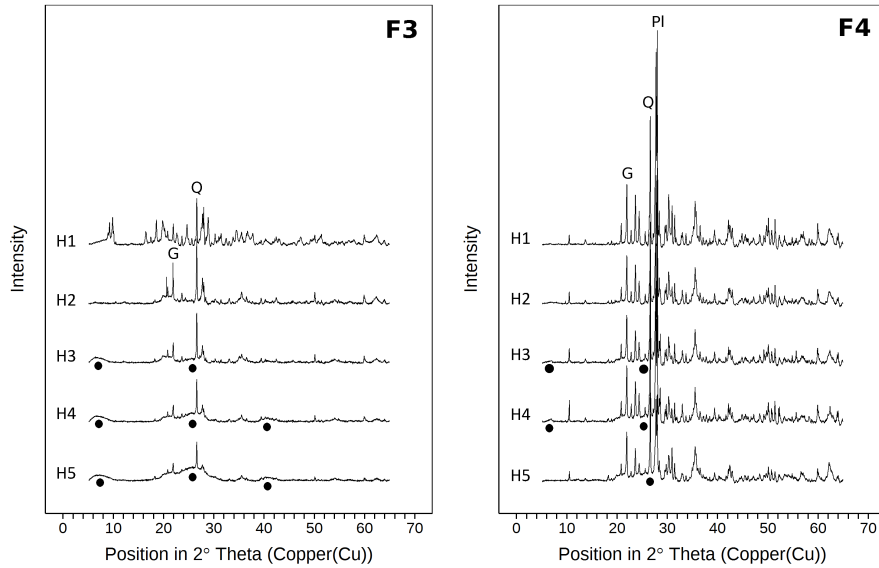


Figure 7. X-ray diffractograms (Cu-K α radiation) of the heavy fractions for all horizons of samples from the sawdust site. Fraction 3 and 4 comprise ~~material strongly interacting with mineral phases and overall soil particle~~ particles of densities between 1.6-2.0 (F3) and >2.0 g cm $^{-3}$ (F4), ~~respectively~~. All diffractograms are normalized to the same vertical scale. Circles indicate poorly crystalline material. Q marks the main quartz reflex. PI marks the main plagioclase reflex. G marks the main gibbsite reflex.

The OC concentrations in F2 (Fig. 3 a) are within the range of 400-500 g kg $^{-1}$, which ~~Cerli et al. (2012) determined as almost suggests~~ pure organic matter. Thus, the applied sonication energy of 300 J ml $^{-1}$ did not ~~produce artefacts through cause~~ redistribution of mineral phases over light fractions (Cerli et al., 2012). However, there is also no evidence for complete dispersion of aggregates, which Chenu and Plante (2006) state as impossible. The OC concentrations of F2 are larger than those of F1. This may be caused by sonication, which strips off basically all adhering mineral materials (Cerli et al., 2012). This „cleaning effect“ leads to purer OM fractions in F2 than in F1. In consequence, the OC concentrations in F1 range ~~only~~ between 300-400 g kg $^{-1}$. The ~~weight proportions of OM (x_{OM} as $2 \times OC$) in F3 range between . We assume that the average mineral densities (ρ_M) in F3 are about (Huang et al., 2011c) and that OM is evenly distributed among the minerals with an average density (ρ_{OM}) calculated (Equation (2)) particle densities of (Mayer et al., 2004). The resulting overall soil particle densities ~~$\rho_{soil\ particle}$ calculated with Eq. (2) (Chenu and Plante, 2006) F3~~ are between 1.7 and 2.0 g cm $^{-3}$, which is ~~as expected from the density fractionation method. This is in line with the nominal density range of F3. This also~~ indicates that the overall soil particle density ~~in this Andosol is likely of the studied Andosol is largely~~ due to OM loadings and not caused by variations in mineral density. This contrasts the results of Basile-Doelsch et al. (2007).~~

$$\rho_{soil\ particle} = \frac{a}{x_{OM} + b} \quad \text{with} \quad b = \frac{\rho_{OM}}{\rho_M - \rho_{OM}} \quad \text{and} \quad a = \rho_M \cdot b$$

The recoveries of acid oxalate-extractable Al and Si were large. The lower recovery of Si could be due to Si being present as silicic acid or ~~silicic acid~~ sorbed to ferrihydrite and other poorly crystalline phases (Childs, 1992), and may become ~~desorbed~~ released during the sequential density fractionation.

4.2 Mineral composition of F3 and F4

5 Peak intensities of XRD spectra in F4 are up to 2.5 times larger than in F3. This indicates enrichment in crystalline minerals in F4 as compared to F3 and vice versa enrichment in short range-ordered phases in F3. ~~The later enrichment~~ This enrichment in short range-ordered phases is supported by the 2-7 times larger amount of oxalate-extractable Al in F3 than in F4. The broad signals in XRD spectra of F3 and F4 in deeper horizons suggest the presence of imogolite-type phases. ~~The~~ These broad signals are less prominent ~~for in~~ F4, because ~~they are overlaid~~ overlain by signals of crystalline minerals. ~~On one hand,~~ Despite the largely similar XRD patterns the Al/Si molar ratios of F3 are larger than ~~the ratios~~ those of F4 in all horizons. Also, the C/Al molar ratios of F3 are larger than those of F4 throughout the profile, meaning that the organic-mineral associations in F3 have more OC. We conclude that F3 is ~~enriched in Al-OM complexes compared to~~ more enriched in Al-OM complexes than F4. ~~On the other hand, we detected no differences in the assemblage of short range-ordered phases between fractions in the XRD spectra when comparing each horizon.~~ Additionally, F4 of the topsoil has Al/Si molar ratios of 4, which means ~~Al-OM-Al-OM~~ complexes have to be present in addition to imogolite-type phases. Thus, ~~a complete separation of Al-OM complexes and OM-loaded Al-OM complexes and OM-loaded~~ imogolite-type phases was not achieved by our density fractionation method. We think that ~~Al-OM-Al-OM~~ complexes and imogolite-type phases either form into continuous phases or that the density ranges of the two phases may overlap. Moreover, we think that quartz and other minerals could also be present in those fractions, because ~~in the topsoil~~ the XRD spectra of the topsoil F3 show reflexes for primary minerals. This is also ~~supported by the extremely low mineral-portion-normalized-Al and Si concentrations in F3 of the topsoil samples.~~

The Al/Si molar ratios decrease with depth, which indicates changes in the assemblage of short range-ordered phases. This allows for identifying those phases predominating the two ~~heavy fractions of fractions~~ $>1.6 \text{ g cm}^{-3}$ in the different horizons. Many authors such as Yagasaki et al. (2006) use $(\text{Al}-\text{Al}_{py})/\text{Si}$ molar ratios, with Si and Al being oxalate-extractable Al and ~~Si~~ Si respectively, and Al_{py} being pyrophosphate-extractable Al. Pyrophosphate is supposed to extract Al from ~~Al-OM-Al-OM~~ complexes (Parfitt and Childs, 1988). We did not follow this approach, because the reliability of ~~pyrophosphate-extraction~~ pyrophosphate-extraction has been questioned (Kaiser and Zech, 1996; Thompson et al., 2011). Kaiser and Zech (1996) attribute this to high pH of the extractant, which can result in dissolution of Al-containing mineral phases.

30 According to Amonette et al. (1994), oxalate-extractable Si originates almost exclusively from imogolite-type phases. The results of ~~our oxalate-extraction show, that this Andosol is~~ the oxalate-extraction indicate the studied Andosol to be poor in ~~Si concentration~~, and therefore, only imogolite-type phases with the minimum silicon content should be present. Instead of ~~the pyrophosphate-extraction we proceeded as follows: We used the assumptions listed below and adapted the formula proposed by Parfitt et al. (1985) and Mizota and Recuwijk (1989) with a fixed Al/Si molar ratio of 2 for Si-poor imogolite-type phases. With~~

this it is possible to estimate relying on the pyrophosphate-extraction we developed a formula to determine the prevailing short range-ordered species in the density fractions. We estimated imogolite-type phases, Al in Al-OM complexes Al-OM complexes, and their molar portion in contribution to short range-ordered phases using the Eq. (3) to Eq. (5) (Table 3). These equations are based on the formula proposed by Parfitt et al. (1985), Mizota and Reeuwijk (1989) and the assumptions listed below. The proportion of imogolite-type phases on short range-ordered phases are given in mol%, because the exact composition of Al-OM complexes are unknown.

- oxalate-extractable Al (Al) is only incorporated in Al-OM-Al-OM complexes (Al_{AOC}) and imogolite-type phases (Al_{ITP})
- Al-OM-Al-OM complexes comprise compounds which contain mainly Al-O-C bonds and scarcely any Al-O-Al bonds, because OM concentrations are high. Therefore we assume that Al-OM-Al-OM complexes contain on average 1.1 mol Al per 1 mol Al-OM-Al-OM complexes.
- oxalate-extractable Si is only incorporated in imogolite-type phases (= Si_{ITP})
- Al_{ITP}/Si_{ITP} molar ratio is 2
- ITP_{cal} calculated concentration of imogolite-type phases

$$ITP_{cal} = 7.5 \cdot Si_{ITP} \quad (3)$$

$$Al_{AOC} = Al - 2 \cdot Si_{ITP} \quad (4)$$

$$ITP_{proportion} = \frac{1/2 \cdot Al_{ITP}}{1/2 \cdot Al_{ITP} + 1/1.1 \cdot Al_{AOC}} \cdot 100 \quad \text{with Si and Al in } mol \cdot kg^{-1} \quad (5)$$

We used the $ITP_{proportion}$ data from Table 3 to evaluate the prevailing short range-ordered species in each horizon. The results are compiled in Table 4 along with the abundance of short range-ordered phases with F3 and F4 on total mineral masses. The results show that in the topsoil short range-ordered phases are mostly present in F3 and in the subsoils they are mostly present in F4. The prevailing short range-ordered species in topsoils are Al-OM complexes, since dominating F3. In the subsoil, the presence of imogolite-type phases and Al-OM complexes is more balanced in F4, with increasing portions of imogolite-type phases with depth.

Table 3. ~~Concentration~~ Concentrations of imogolite-type ~~phase-phases~~ (ITP_{cal}), Al in ~~Al-OM-Al-OM~~ complexes (Al_{AOC}) and ~~imogolite-type phase~~ molar ~~portions on the assemblage proportions~~ of imogolite-type phases on short range-ordered phases (~~SROITP~~ proportion) ~~for in~~ F3 and F4, as calculated with Eq. (3) to Eq. (5). Data is presented as ~~the mean means~~ and ranges in parenthesis.

| horizon | depth cm | ITP_{cal} g kg ⁻¹ | | Al_{AOC} g kg ⁻¹ | | $ITP_{proportion}$ mol % | |
|--------------|-------------|-----------------------------------|----------|----------------------------------|---------|-----------------------------|----|
| | | F3 | F4 | F3 | F4 | F3 | F4 |
| control site | | | | | | | |
| H1 | 4 | 122 (±2) | 10 (±1) | 55 (±0) | 3 (±0) | 24 | 32 |
| H2 | 12 | 212 (±23) | 78 (±0) | 55 (±6) | 15 (±1) | 35 | 42 |
| H3 | 25 | 452 (±11) | 239 (±3) | 106 (±3) | 25 (±0) | 37 | 57 |
| H4 | 52 | 402 (±0) | 332 (±4) | 83 (±0) | 26 (±0) | 40 | 63 |
| H5 | 85 | 402 (±0) | 384 (±3) | 60 (±0) | 29 (±0) | 48 | 65 |
| sawdust site | | | | | | | |
| H1 | 8 | 91 (±5) | 26 (±4) | 46 (±5) | 5 (±1) | 22 | 42 |
| H2 | 22 | 168 (±3) | 64 (±3) | 64 (±1) | 16 (±1) | 27 | 36 |
| H3 | 39 | 276 (±2) | 149 (±0) | 72 (±1) | 27 (±1) | 35 | 43 |
| H4 | 63 | 396 (±5) | 178 (±0) | 77 (±4) | 21 (±1) | 42 | 54 |
| H5 | 88 | 457 (±4) | 254 (±2) | 94 (±2) | 22 (±1) | 40 | 61 |

We estimated the weight proportion of short range-ordered phases from F3 and F4 on the bulk mineral mass and divided them into the groups "very abundant", "abundant", "low" and "traces" by using Al and Si mass distributions in the different fractions (Table 4). Results show that in the topsoil short range-ordered phases are mostly present in F3 and in the subsoil they are mostly present in F4. On the basis of the calculated imogolite-type phase molar portions we decided on the prevalent species of the short range-ordered phase assemblages (Table 4). In the topsoil, Al-OM complexes prevail, because imogolite-type phases contribute only with to short range-ordered phases of F3. In the subsoil, the presence of imogolite-type phases and Al-OM complexes is more balanced in F4, with increasing portions of imogolite-type phases with depth.

The characteristic broad signals indicating imogolite-type phases in the X-ray diffractograms appear in the subsoil, but not in the topsoil (Fig. 7). Imogolite-type phases dissolve at pH values below 4.8 (Huang et al., 2011b). The pH values in the subsoil are equal or above 4.8, whereas pH values in the topsoil are below 4.8 (Table 1). Thus, the X-ray diffractograms and pH values support our suggestion and explain are well in line with the estimated distribution of short range-ordered species, suggesting the presence of imogolite-type phases in the subsoil and their absence in the topsoil. We conclude that the studied Andosol shows aluandic properties in the topsoil and silandic properties in the subsoil.

4.3 Organic carbon stock and storage forms

~~In comparison~~ The OC stocks within the first 100 cm of the studied soil are above the mean OC stocks for Andosols (254 Mg ha⁻¹, Huang et al. (2011a)) and similar to the 375 ± 83 Mg ha⁻¹ found in an aluandic Andosol under tropical rainforest on Hawaii (Marin-Spiotta et al., 2011). The observed low bulk densities, resulting from large OC accumulation, are a common feature of aluandic Andosols (Marin-Spiotta et al., 2011; Basile-Doelsch et al., 2005).

The studied Andosol has medium to high PyC concentrations compared to Amazonian Oxisols (1-3 g PyC kg⁻¹ soil, 140 g PyC kg⁻¹ OC, Glaser et al. (2000)) and Terra Preta soils (4-20 g PyC kg⁻¹ soil, 350 g PyC kg⁻¹ OC, Glaser et al. (2000)); ~~the studied Andosol has medium to high PyC concentrations. However, PyC plays only a marginal role for the accumulation of total OM because it.~~ The PyC, however, contributes only up to 5 wt% to the OC concentration. ~~We consider the later conclusion true, although the conversion factor of 2.3 is criticized by Schneider et al. (2010) as inaccurate~~ total OC concentration, thus plays only a marginal role for the accumulation of total OM.

Only up to 20 wt% of OM in the topsoil and 2 wt% in the subsoil is not bound to mineral phases. The low proportions of OC in the light fractions ~~is~~ are in line with data published by Paul et al. (2008) for topsoils of Andosols under tropical rainforest (20 wt% for of material with densities <1.6 g cm⁻³). ~~This is caused by rapid mineralization of particulate OM and the strong interaction of minerals with OM in Andosols (Basile-Doelsch et al., 2007; Huang et al., 2011a).~~ Thus, the mineral phase plays the dominant role in stabilizing OM in this Andosol, which is in agreement with numerous previous studies (e.g. Basile-Doelsch et al., 2007; Huang et al., 2011a).

We used ~~OC mass distributions in the different fractions for dividing OC from the~~ data from Figure 4 to estimate the abundances of OC with F3 and F4 ~~into the groups "very abundant", "abundant", "low" and "traces" on total OC and correlate it with the abundance and prevalent species of the short range-ordered phases~~ (Table 4). The OC ~~abundance~~ abundances clearly correlates with the ~~distribution~~ respective abundance of mineral phases in ~~both the two~~ fractions. In the topsoil, OC is mainly associated with ~~Al-OM-Al-OM~~ complexes, whereas the OC in the subsoil is mainly bonded to imogolite-type phases. ~~Based on the results~~ As explained in section 4.2 we suggest that ~~Al-OM-Al-OM~~ complexes are in close contact to imogolite-type phases i.e. g. precipitate on the they precipitate on their surfaces.

Table 4. Mineralogical control-Mass contribution of organic carbon (OC) stabilization in fraction three and four. The mass proportions in the different fractions for OC and short range-ordered and nano- or micro-crystalline-phases (SRO) range to fractions three (F3) and four (F4). The grouping ranges from "+++" (very abundant, > 75 wt%), "++" (abundant, 75-30 wt%), "+" (low, 30-3 wt%) to "tr" (traces, < 3 wt%). The prevalent short range-ordered species are defined **by according to the imogolite-type phase** molar proportion **of imogolite-type phases** on the short range-ordered **phase phases (ITP proportion of** Table 3). For the mean molar proportions of **both sites** < 33 wt% **Al-OM-Al-OM** complexes (AOC) prevail. For molar proportions between 33 and 67 wt% **Al-OM-complexes-AOC** and imogolite-type phases (ITP) are largely balanced, with the **first mentioned short range-ordered** species **listed first** being **present in** slightly larger portion than the other **more abundant**. For molar proportions > 67 wt% **imogolite-type phases prevail. ITP : imogolite-type phases prevail. AOC: Al-OM-complexes**

| horizon | F3 | | | F4 | | |
|---------|---------------|----------------|-----------------------|------------------|----------------|-----------------------|
| | OC proportion | SRO proportion | prevalent SRO species | OM-OC proportion | SRO proportion | prevalent SRO species |
| H1 | +++ | +++ | AOC | tr | tr | AOC, ITP |
| H2 | ++ | ++ | AOC | + | + | AOC, ITP |
| H3 | + | + | AOC, ITP | +++ | +++ | AOC, ITP |
| H4 | tr | tr | AOC, ITP | +++ | +++ | ITP, AOC |
| H5 | tr | tr | AOC, ITP | +++ | +++ | ITP, AOC |

4.4 Organic carbon response to sawdust input

No sawdust was optically visible neither in the soil profile nor in the light density fractions prior to grounding. Seemingly, the period since the last sawdust application was long enough to allow for complete decay. Chambers et al. (2000) report that wood density and bole diameter were significantly and inversely correlated with the decomposition rate ~~constants~~ for dead trees in tropical forests of the central Amazon. For the smallest bole diameter (10 cm) the authors calculated 0.26 year^{-1} as the lowest rate ~~constant~~. A dead tree with such a diameter would then be decomposed to 99 % after 17 years. Additionally Powers et al. (2009) showed that in tropical soils the decomposition rate increases ~~linearly with the~~ linearly with precipitation. With sawdust being much finer in texture than a dead tree trunk and the precipitation at the CERFA site being twice as high as at the site of Chambers et al. (2000), we expect a much faster decomposition ~~than~~. Moreover, the phosphorus concentrations, determined in an aqua regia solution for samples taken from the first 20 cm (data not shown) are significantly larger at the sawdust site than at the control site. The additional phosphorus at the sawdust site matches the phosphorus input via sawdust. Additionally, the C/N ratios of all fractions in the upper two horizons are below 20, showing no difference between the two sites. From all this we conclude that the added sawdust, which has a C/N mass ratio of around 110, was completely decomposed on-site.

~~The sawdust did not significantly increase the~~ In the first horizon the differences between both sites in bulk OC concentrations ~~in the upper two horizons. We also found no indications of~~ are, with around 2 g kg^{-1} OC, extremely small. Additionally, the observed variances in these forest topsoils are large. This makes it impossible to find a significant increase in the bulk OC concentration, even with larger sample numbers. We conclude that the OC concentration of the first horizon did not change upon sawdust input. In the second horizon the difference between OC concentrations are larger than in the first horizon, but are not significant due to a large variance. For the second horizon, a larger sample number may have revealed a significant OC increase at the sawdust site. The results of the sequential density fractionation show no indications for additional inclusion of OM into macro-aggregates. This holds true despite the fact that the sample of the second horizon used for the sequential density fractionation at the sawdust site has a larger OC concentration than the sample at the control site. Those results ~~have~~ need to be interpreted with some caution in terms of site comparison, because we conducted the fractionation ~~experiment~~ only with one profile per site. The sequential density fractionation also revealed that over 80-89 wt% of OC are strongly associated with minerals. We therefore conclude that the ~~topsoil is mineral phase of the topsoil, especially the first horizon, is completely saturated with OC and not even small parts of~~ so despite the massive carbon input ~~can be additionally stored. We assign this to limited and saturated storage capacities of the mineral phase~~ not even the faintest additional storage occurred.

Kaiser and Kalbitz (2012) state that in soils, where percolating water controls transport processes, a steady input of surface-reactive ~~plant-derived compounds force~~ compounds from overlying soil layers forces less strongly binding compounds to move further down. ~~Thus, OM migrates downwards in form of dissolved OM if the~~ With OM storage capacities in the top ~~layer are exhausted~~ layers being exhausted, increasing amounts of OM become displaced and start migrating downwards. When reaching soil horizons with free storage capacity ~~the dissolved these~~ OM compounds are retained and the respective horizon's OC con-

centration increases. This process would explain the significantly larger OC concentration in the third horizon at the sawdust site. As long as the third horizon has free storage capacities, the OC concentration in horizon four and five will not increase, which is in line with our results. Over 90 wt% of the additional OM in the third horizon are recovered in F3 and F4 together. Thus, the increase in bulk OC concentration in the third horizon is due to OM strongly interacting with the mineral phase and
5 ~~thus of long-term stability~~likely becoming long-term stabilized.

The increase in OC concentration in the third horizon~~in response to the added sawdust could, with respect to the mechanisms, be either, however, is probably not only~~ due to undersaturated ~~sorption complexes or a change in carbon storage mechanisms towards mechanisms with higher carbon storage capacities. It is noticeable, that the larger OC bulk mineral phases. The~~
10 increased OC concentration in the bulk sample of the third horizon of the sawdust site used in the fractionation experiment ~~of the sawdust site~~ correlates with a larger proportion of F3 and slightly lower pH values ~~compared to than those of~~ the third horizon at the control site. ~~The lower pH values are not the result of the mineralization of~~ Since not affecting the overlying horizons, the lower pH in the third horizon at the sawdust site was unlikely due to mineralization of the 18 Mg ha⁻¹ nitrogen ~~, which were added along added~~ with the sawdust, ~~because the decomposition of sawdust was complete and therefore basic cations were also released. Those basic cations buffer the released protons from the nitrification reaction (Breemen et al., 1983). This result suggest that the percolating DOM solution also influences the short range-ordered phase composition via reactions with protons. This implies that previously formed.~~ More likely, the acidification was caused by the downward movement of organic acids formed during the decomposition of sawdust. These acids may promote the weathering of imogolite-type phases may be in situ transformed into Al-OM complexes in response to changes in pH and OM input and subsequent formation of Al-OM
15 complexes.
20 complexes.

The OC stock increased significantly at the sawdust site for the ~~depth section of~~ 25-50 cm segment, which belongs to the subsoil and comprises mostly the third horizon. ~~We found that this difference was~~ This difference was basically due to the increase in OC concentration ~~and not caused by neither layer thickness, nor bulk density variations.~~ Despite this increased ~~in~~
25 OC stock in parts of the subsoil, we found no evidence ~~that the added sawdust increased the total OC stock significantly for~~ increased total soil OC stocks. We think that this is not due to ~~smaller numbers~~ the small number of bulk density measurements ~~compared to all other parameters, because,~~ because the standard error was very low with $\leq 0.05 \text{ g cm}^{-3}$ (see Table 1). Moreover, Schrumpf et al. (2011) found that the contribution of bulk density to the OC stock variability was lower ~~and decreased with soil depth~~ than the contribution of OC concentration and ~~layer thickness~~ horizon thickness and decreased with
30 soil depth. We rather think, that the large variability of OC concentrations in the topsoil overlay the effect of the larger OC concentration in the subsoil at the sawdust site. Therefore we recommend for topsoils an increased number of samples in order to detect significant differences.

To evaluate the OC accumulation ~~, we calculated~~ in response to the sawdust application, we referred to the increase in
35 OC stock within the ~~depth section~~ 25-50 cm segment (Tab ~~??~~A2). The resulting additional OC stock ~~at the sawdust sites is~~

is 15 Mg ha^{-1} , which represents only 0.8 wt% of the originally added $1800 \text{ Mg OC ha}^{-1}$. Thus, the ~~studied Andosol has an extremely low~~ OC accumulation rate. ~~Six et al. (2002)~~ is extremely low. That is in line with Six et al. (2002), who postulate in their saturation concept that soils, which are close to their maximum OC storage capacity have low accumulation rates.

5 Conclusions

- 5 The massive OC input did not increase the OC concentrations in the topsoil but in the subsoil, which also resulted in significantly larger OC stocks for the subsoil. ~~Thus, the~~ The OC-rich Andosol topsoils are not capable of storing additional carbon, likely because of limited binding capacities of their mineral phases. Seemingly, some of the additional OC migrates downwards with the percolating water until reaching layers/horizons where free binding sites are available. The studied soils, hence, are saturated with OC when only considering the topsoils but still have large some capacity to host more OC in their deeper
- 10 layers/horizons. Leaving the time and input aspect aside and imagining that the Andosols upper horizon will one day stretch down to 100 cm, the OC stock would have increased by 260 Mg ha^{-1} compared to the control site.

The OC increase in the subsoil was exclusively due to binding to mineral phases. Since binding to mineral phases promotes retarded mineralization, i.e., longer turnover times, stabilization, and thus, long-term storage of the additional OC can be expected.

15

The additional OC was likely stored within ~~Al-OM~~ Al-OM complexes and by binding to imogolite-type phases. There are indications that the input of additional OC into the subsoils induced dissolution of the imogolite-type mineral phases and subsequent formation of ~~Al-OM~~ Al-OM complexes. This transition from a predominately silandic to a more aluandic mineral

20 assemblage would increase the subsoils storage capacity for OC. ~~It also~~ We suggest that silandic Andosols can gradually become aluandic.

Despite the increase in subsoil OC, there was no significant change in total OC stocks in response to the massive OC inputs over a period of 20 years. This was basically because of spatial variations that demand for larger sample numbers or larger

25 changes than the observed ones to become significantly different.

The results clearly show that accumulation efficiency of the added OC was very low. Increasing the OC stock in soils already rich in OC requires comparably large inputs over long time periods to induce OC transport into the deeper soil layers/horizons. This contrasts the situation in young soils where OC stocks build up rapidly in surface-near layers/horizons.

30 *Code availability.* TEXT



Figure A1. [Profile of the studied Andosol](#)

Data availability. TEXT

Code and data availability. TEXT

Appendix A

A1

Table A1. ~~gravimetric~~ Gravimetric determined rooting intensity, measured ~~at 5 soil cores~~ with five 2.7 dm³ corers at each site

| depth | mean | standard deviation | standard error |
|--------------|---------------------|---------------------------|-----------------------|
| cm | Mg ha ⁻¹ | Mg ha ⁻¹ | Mg ha ⁻¹ |
| control site | | | |
| 0-20 | 3.8 | 1.3 | 0.3 |
| 20-40 | 0.7 | 0.7 | 0.1 |
| sawdust site | | | |
| 0-20 | 5.5 | 2.6 | 0.5 |
| 20-40 | 0.4 | 0.3 | 0.1 |

Table A2. The means of the OC stocks ($\bar{x}(sawdust)$, $\bar{x}(control)$), their differences ($\Delta\bar{x}$) and their pooled standard deviation (SD) are presented. The confidence interval (CI) is calculated from a t-test (one sided, significance level $\alpha = 0.05$, power $1 - \beta = 0.8$, sample size 5, unpaired) to answer the alternative hypothesis that $x(sawdust) - x(control)$ is larger than zero. The difference is significantly larger if the CI is > 0 . We also calculated the minimum sample size (n_{min}) and power ($power_{th}$) for a theoretical difference (Δth) between the sites to evaluate the power of our data. The Δth is either taken from $\Delta\bar{x}$ or assumed to be 10% of $\bar{x}(control)$.

| <u>depth</u> | <u>$\bar{x}(sawdust)$</u> | <u>$\bar{x}(control)$</u> | <u>$\Delta\bar{x}$</u> | <u>SD</u> | <u>CI</u> | <u>Δth</u> | <u>n_{min}</u> | <u>$power_{th}$</u> |
|---------------|--------------------------------------|--------------------------------------|-----------------------------------|---------------------------|------------------------------------|-------------------------------|-----------------------------|--------------------------------|
| <u>cm</u> | <u>Mg ha⁻¹</u> | <u>Mg ha⁻¹</u> | <u>Mg ha⁻¹</u> | <u>Mg ha⁻¹</u> | <u>Mg ha⁻¹</u> | <u>Mg ha⁻¹</u> | <u>-</u> | <u>-</u> |
| <u>0-25</u> | <u>134</u> | <u>112</u> | <u>22</u> | <u>21</u> | <u>$[-3.2, \infty)$</u> | <u>22</u> | <u>12</u> | <u>0.46</u> |
| <u>25-50</u> | <u>86</u> | <u>71</u> | <u>15</u> | <u>8</u> | <u>$[+4.0, \infty)$</u> | <u>15</u> | <u>5</u> | <u>0.83</u> |
| <u>50-75</u> | <u>65</u> | <u>63</u> | <u>2</u> | <u>7</u> | <u>$[-6.4, \infty)$</u> | <u>6</u> | <u>18</u> | <u>0.35</u> |
| <u>75-100</u> | <u>59</u> | <u>55</u> | <u>4</u> | <u>6</u> | <u>$[-2.8, \infty)$</u> | <u>5</u> | <u>16</u> | <u>0.37</u> |
| <u>total</u> | <u>343</u> | <u>301</u> | <u>43</u> | <u>35</u> | <u>$[-0.5, \infty)$</u> | <u>43</u> | <u>9</u> | <u>0.56</u> |

Table A3. The means of the OC concentrations ($\bar{x}(sawdust)$, $\bar{x}(control)$), their differences ($\Delta\bar{x}$) and their pooled standard deviation (SD) are presented. The confidence interval (CI) is calculated from a t-test (one sided, significance level $\alpha = 0.05$, power $1 - \beta = 0.8$, sample size 5, unpaired) to answer the alternative hypothesis that $x(sawdust) - x(control)$ is larger than zero. The difference is significantly larger if the CI is > 0 . We also calculated the minimum sample size (n_{min}) and power ($power_{th}$) for a theoretical difference (Δth) between the sites to evaluate the power of our data. The Δth is either taken from $\Delta\bar{x}$ or assumed to be 10% of $\bar{x}(control)$.

| <u>depth</u> | <u>$\bar{x}(sawdust)$</u> | <u>$\bar{x}(control)$</u> | <u>$\Delta\bar{x}$</u> | <u>SD</u> | <u>CI</u> | <u>Δth</u> | <u>n_{min}</u> | <u>$power_{th}$</u> |
|--------------|--------------------------------------|--------------------------------------|-----------------------------------|--------------------------------|-------------------------------------|--------------------------------|-----------------------------|--------------------------------|
| <u>-</u> | <u>$g\ kg^{-1}$</u> | <u>$g\ kg^{-1}$</u> | <u>$g\ kg^{-1}$</u> | <u>$g\ kg^{-1}$</u> | <u>$g\ kg^{-1}$</u> | <u>$g\ kg^{-1}$</u> | <u>-</u> | <u>-</u> |
| <u>H1</u> | <u>214</u> | <u>212</u> | <u>2</u> | <u>37</u> | <u>$[-41.7, \infty)$</u> | <u>21</u> | <u>40</u> | <u>0.20</u> |
| <u>H2</u> | <u>143</u> | <u>128</u> | <u>15</u> | <u>24</u> | <u>$[-18.8, \infty)$</u> | <u>15</u> | <u>33</u> | <u>0.23</u> |
| <u>H3</u> | <u>89</u> | <u>75</u> | <u>14</u> | <u>5</u> | <u>$[+6.6, \infty)$</u> | <u>14</u> | <u>3</u> | <u>0.98</u> |
| <u>H4</u> | <u>77</u> | <u>76</u> | <u>1</u> | <u>6</u> | <u>$[-7.4, \infty)$</u> | <u>8</u> | <u>9</u> | <u>0.56</u> |
| <u>H5</u> | <u>67</u> | <u>66</u> | <u>1</u> | <u>5</u> | <u>$[-5.5, \infty)$</u> | <u>7</u> | <u>8</u> | <u>0.64</u> |

Author contributions. TEXT

Competing interests. The authors declare that they have no conflict of interest.

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Acknowledgements. The authors acknowledge the financial support of the *Technische Universität Berlin*. The pyrogenic carbon analysis
5 were conducted by Arne Kappenberg at the department of soil science at the *Rheinische Friedrich-Wilhelms-Universität Bonn*, for which we
are grateful. We also acknowledge Nelson Omar Tello Benalcázar and Josue Tenorio for providing the study sites and assisting during the
field work.

References

- Amonette, J. E., Zelazny, L. W., and Dahlgren, R. A.: Quantification of Allophane and Imogolite, in: Quantitative Methods in Soil Mineralogy, ACSESS publications, Soil Science Society of America, 1994.
- Basile-Doelsch, I., Amundson, R., Stone, W., Masiello, C. A., Bottero, J. Y., Colin, F., Masin, F., Borschneck, D., and Meunier, J. D.:
5 Mineralogical control of organic carbon dynamics in a volcanic ash soil on La Réunion, *European Journal of Soil Science*, 56, 689–703, <https://doi.org/10.1111/j.1365-2389.2005.00703.x>, <http://dx.doi.org/10.1111/j.1365-2389.2005.00703.x>, gelesen, 2005.
- Basile-Doelsch, I., Amundson, R., Stone, W., Borschneck, D., Bottero, J. Y., Moustier, S., Masin, F., and Colin, F.: Mineral control of carbon pools in a volcanic soil horizon, *Geoderma*, 137, 477–489, <https://doi.org/10.1016/j.geoderma.2006.10.006>, gelesen, 2007.
- Boudot, J.-P.: Relative efficiency of complexed aluminum noncrystalline Al hydroxide, allophane and imogolite in retarding the biodegradation of citric acid, *Geoderma*, 52, 29–39, [https://doi.org/10.1016/0016-7061\(92\)90073-G](https://doi.org/10.1016/0016-7061(92)90073-G), <http://www.sciencedirect.com/science/article/pii/001670619290073G>, 1992.
10
- Breemen, N. v., Mulder, J., and Driscoll, C. T.: Acidification and alkalization of soils, *Plant and Soil*, 75, 283–308, <https://doi.org/10.1007/BF02369968>, <https://link.springer.com/article/10.1007/BF02369968>, 1983.
- Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., and Amelung, W.: Revised black carbon assessment using benzene polycarboxylic acids, *Organic Geochemistry*, 36, 1299–1310, <https://doi.org/10.1016/j.orggeochem.2005.03.011>, 2005.
15
- Campbell, C. A., Zentner, R. P., Bowren, K. E., Townley-Smith, L., and Schnitzer, M.: Effect of crop rotations and fertilization on soil organic matter and some biochemical properties of a thick Black Chernozem, *Canadian Journal of Soil Science*, 71, 377–387, <https://doi.org/10.4141/cjss91-036>, <http://www.nrcresearchpress.com/doi/abs/10.4141/cjss91-036>, 1991.
- Campbell, E. E. and Paustian, K.: Current developments in soil organic matter modeling and the expansion of model applications: a review, *Environmental Research Letters*, 10, 123 004, <https://doi.org/10.1088/1748-9326/10/12/123004>, <http://stacks.iop.org/1748-9326/10/i=12/a=123004>, 2015.
20
- Cerli, C., Celi, L., Kalbitz, K., Guggenberger, G., and Kaiser, K.: Separation of light and heavy organic matter fractions in soil — Testing for proper density cut-off and dispersion level, *Geoderma*, 170, 403–416, <https://doi.org/10.1016/j.geoderma.2011.10.009>, 2012.
- Chambers, J. Q., Higuchi, N., Schimel, J. P., Ferreira, L. V., and Melack, J. M.: Decomposition and carbon cycling of dead trees in tropical forests of the central Amazon, *Oecologia*, 122, 380–388, <https://doi.org/10.1007/s004420050044>, <https://link.springer.com/article/10.1007/s004420050044>, 2000.
25
- Chenu, C. and Plante, A. F.: Clay-sized organo-mineral complexes in a cultivation chronosequence: revisiting the concept of the ‘primary organo-mineral complex’, *European Journal of Soil Science*, 57, 596–607, <https://doi.org/10.1111/j.1365-2389.2006.00834.x>, 2006.
- Childs, C. W.: Ferrihydrite: A review of structure, properties and occurrence in relation to soils, *Zeitschrift für Pflanzenernährung und Bodenkunde*, 155, 441–448, <https://doi.org/10.1002/jpln.19921550515>, <http://dx.doi.org/10.1002/jpln.19921550515>, 1992.
30
- Clark, D. A., Brown, S., Kicklighter, D. W., Chambers, J. Q., Thomlinson, J. R., Ni, J., and Holland, E. A.: Net Primary Production in Tropical Forests: An Evaluation and Synthesis of Existing Field Data, *Ecological Applications*, 11, 371–384, [https://doi.org/10.1890/1051-0761\(2001\)011\[0371:NPPITF\]2.0.CO;2](https://doi.org/10.1890/1051-0761(2001)011[0371:NPPITF]2.0.CO;2), [http://onlinelibrary.wiley.com/doi/10.1890/1051-0761\(2001\)011\[0371:NPPITF\]2.0.CO;2/abstract](http://onlinelibrary.wiley.com/doi/10.1890/1051-0761(2001)011[0371:NPPITF]2.0.CO;2/abstract), 2001.
- Colombo, C., Ricciardella, M., Cerce, A. D., Maiuro, L., and Violante, A.: Effect of Tannate, pH, sample preparation, ageing and temperature on the formation and nature of Al oxyhydroxides, *Clays and Clay Minerals*, 52, 721–733, <https://doi.org/10.1346/CCMN.2004.0520607>, <http://ccm.geoscienceworld.org/content/52/6/721>, 2004.
35

- Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G., and Zech, W.: Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region, *Organic Geochemistry*, 31, 669–678, [https://doi.org/10.1016/S0146-6380\(00\)00044-9](https://doi.org/10.1016/S0146-6380(00)00044-9), <http://www.sciencedirect.com/science/article/pii/S0146638000000449>, 2000.
- Hall, M. L., Claude, R., Bernardo, B., Mothes, P., and Monzier, M.: Tungurahua Volcano, Ecuador: structure, eruptive history and hazards. *J Volcanol Geotherm Res, Journal of Volcanology and Geothermal Research*, 91, 1–21, [https://doi.org/10.1016/S0377-0273\(99\)00047-5](https://doi.org/10.1016/S0377-0273(99)00047-5), 1999.
- Huang, P. M., Li, M., and Sumner, M., eds.: *Handbook of Soil Sciences: Resource Management and Environmental Impacts Volume II: chapter 7 Mineralogical, Physicochemical, and Microbiological Controls on Soil Organic Matter Stabilization and Turnover*, CRC Press Inc, [s.l.], 2 auf. edn., 2011a.
- 10 Huang, P. M., Li, Y., and Sumner, M. E., eds.: *Handbook of Soil Sciences: Properties and Processes, Second Edition: Chapter 20 Alteration, Formation, Occurrence of Minerals in Soils*, Taylor & Francis, <https://books.google.de/books?id=9BJIVxJLNO8C>, 2011b.
- Huang, P. M., Li, Y., and Sumner, M. E., eds.: *Handbook of Soil Sciences: Properties and Processes, Second Edition: Chapter 33.3 Andisols*, Taylor & Francis, <https://books.google.de/books?id=9BJIVxJLNO8C>, 2011c.
- Hörmann, P. K. and Pichler, H.: Geochemistry, petrology and origin of the Cenozoic volcanic rocks of the Northern Andes in Ecuador, *Journal of Volcanology and Geothermal Research*, 12, 259–282, [https://doi.org/10.1016/0377-0273\(82\)90029-4](https://doi.org/10.1016/0377-0273(82)90029-4), 1982.
- 15 IUSS Working Group WRB: World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps., no. 106 in *World Soil Resources Reports*, Food and Agriculture Organization of the United Nations, 2015.
- Kaiser, K. and Guggenberger, G.: Distribution of hydrous aluminium and iron over density fractions depends on organic matter load and ultrasonic dispersion, *Geoderma*, 140, 140–146, <https://doi.org/10.1016/j.geoderma.2007.03.018>, 2007.
- 20 Kaiser, K. and Kalbitz, K.: Cycling downwards – dissolved organic matter in soils, *Soil Biology and Biochemistry*, 52, 29–32, <https://doi.org/10.1016/j.soilbio.2012.04.002>, <http://www.sciencedirect.com/science/article/pii/S0038071712001381>, 2012.
- Kaiser, K. and Zech, W.: Defects in estimation of aluminium in humus complexes of podzolic soils by pyrophosphate extraction, *Soil Science*, 161, 452–458, <https://doi.org/10.1097/00010694-199607000-00005>, 1996.
- 25 Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., and Leinweber, P.: Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry, *Journal of Plant Nutrition and Soil Science*, 171, 61–82, <https://doi.org/10.1002/jpln.200700048>, <http://onlinelibrary.wiley.com/doi/10.1002/jpln.200700048/abstract>, 2008.
- Lal, R.: Soil Carbon Sequestration Impacts on Global Climate Change and Food Security, *Science*, 304, 1623–1627, <https://doi.org/10.1126/science.1097396>, <http://science.sciencemag.org/content/304/5677/1623>, 2004.
- 30 Le Pennec, J.-L., Ruiz, G. A., Ramón, P., Palacios, E., Mothes, P., and Yepes, H.: Impact of tephra falls on Andean communities: The influences of eruption size and weather conditions during the 1999–2001 activity of Tungurahua volcano, Ecuador, *Journal of Volcanology and Geothermal Research*, 217–218, 91–103, <https://doi.org/10.1016/j.jvolgeores.2011.06.011>, 2012.
- Lehmann, J. and Kleber, M.: The contentious nature of soil organic matter, *Nature*, 528, 60–68, <https://doi.org/10.1038/nature16069>, <http://www.nature.com/nature/journal/v528/n7580/abs/nature16069.html>, 2015.
- 35 Levard, C., Doelsch, E., Basile-Doelsch, I., Abidin, Z., Miche, H., Masion, A., Rose, J., Borschneck, D., and Bottero, J. Y.: Structure and distribution of allophanes, imogolite and proto-imogolite in volcanic soils, *Geoderma*, 183–184, 100–108, <https://doi.org/10.1016/j.geoderma.2012.03.015>, <http://www.sciencedirect.com/science/article/pii/S0016706112001280>, 2012.

- Marin-Spiotta, E., Chadwick, O. A., Kramer, M., and Carbone, M. S.: Carbon delivery to deep mineral horizons in Hawaiian rain forest soils, *Journal of Geophysical Research: Biogeosciences*, 116, n/a–n/a, <https://doi.org/10.1029/2010JG001587>, <http://dx.doi.org/10.1029/2010JG001587>, 2011.
- Masion, A., Thomas, F., Bottero, J.-Y., Tchoubar, D., and Tekely, P.: Formation of amorphous precipitates from aluminum-organic ligands solutions: macroscopic and molecular study, *Journal of Non-Crystalline Solids*, 171, 191–200, [https://doi.org/10.1016/0022-3093\(94\)90355-7](https://doi.org/10.1016/0022-3093(94)90355-7), <http://www.sciencedirect.com/science/article/pii/0022309394903557>, 1994.
- Mayer, L. M., Schick, L. L., Hardy, K. R., Wagai, R., and McCarthy, J.: Organic matter in small mesopores in sediments and soils, *Geochimica et Cosmochimica Acta*, 68, 3863–3872, <https://doi.org/10.1016/j.gca.2004.03.019>, <http://www.sciencedirect.com/science/article/pii/S0016703704002443>, 2004.
- 10 Mizota, C. and Reeuwijk, L. P. v.: Clay mineralogy and chemistry of soils formed in volcanic material in diverse climatic regions, vol. 2 of *Soil monograph*, International Soil Reference and Information Centre, Wageningen, the Netherlands, 1989.
- Mortimer, C., Huacho, J., and Almeida, C.: Mapa Geologico del Ecuador - El Puyo, https://www.geoinvestigacion.gob.ec/mapas/100K_r/HOJAS_GEOLOGICAS_100k/EL_PUYO_PSAD56_Z17S.compressed.pdf, 1980.
- Parfitt, R. L. and Childs, C. W.: Estimation of forms of Fe and Al - a review, and analysis of contrasting soils by dissolution and Mossbauer methods, *Soil Research*, 26, 121–144, <https://doi.org/10.1071/sr9880121>, <http://www.publish.csiro.au/sr/SR9880121>, 1988.
- 15 Parfitt, R. L., Wilson, A. D., and Hutt, L.: Estimation of allophane and halloysite in three sequences of volcanic soils new zealand, *Volcanic Soils Catena Supplement*, 1985.
- Paul, S., Veldkamp, E., and Flessa, H.: Soil organic carbon in density fractions of tropical soils under forest – pasture – secondary forest land use changes, *European Journal of Soil Science*, 59, 359–371, <https://doi.org/10.1111/j.1365-2389.2007.01010.x>, <http://dx.doi.org/10.1111/j.1365-2389.2007.01010.x>, 2008.
- 20 Paustian, K., Andrén, O., Janzen, H. H., Lal, R., Smith, P., Tian, G., Tiessen, H., Van Noordwijk, M., and Woomer, P. L.: Agricultural soils as a sink to mitigate CO₂ emissions, *Soil Use and Management*, 13, 230–244, <https://doi.org/10.1111/j.1475-2743.1997.tb00594.x>, <http://onlinelibrary.wiley.com/doi/10.1111/j.1475-2743.1997.tb00594.x/abstract>, 1997.
- Powers, J. S., Montgomery, R. A., Adair, E. C., Brearley, F. Q., DeWalt, S. J., Castanho, C. T., Chave, J., Deinert, E., Ganzhorn, J. U., Gilbert, M. E., González-Iturbe, J. A., Bunyavejchewin, S., Grau, H. R., Harms, K. E., Hiremath, A., Iriarte-Vivar, S., Manzane, E., De Oliveira, A. A., Poorter, L., Ramanamanjato, J.-B., Salk, C., Varela, A., Weiblen, G. D., and Lerda, M. T.: Decomposition in tropical forests: a pan-tropical study of the effects of litter type, litter placement and mesofaunal exclusion across a precipitation gradient, *Journal of Ecology*, 97, 801–811, <https://doi.org/10.1111/j.1365-2745.2009.01515.x>, <http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2745.2009.01515.x/abstract>, 2009.
- 25 Sauer, W.: *Geologie von Ecuador*, vol. 11, Gebruder Borntraeger, Berlin, Stuttgart, 1971.
- Schmidt, M. W. I., Rumpel, C., and Kögel-Knabner, I.: Evaluation of an ultrasonic dispersion procedure to isolate primary organomineral complexes from soils, *European Journal of Soil Science*, 50, 87–94, <https://doi.org/10.1046/j.1365-2389.1999.00211.x>, 1999.
- Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Weiner, S., and Trumbore, S. E.: Persistence of soil organic matter as an ecosystem property, *Nature*, 478, 49–56, <https://doi.org/10.1038/nature10386>, <http://www.nature.com/nature/journal/v478/n7367/full/nature10386.html>, 2011.
- 30 Schneider, M. P., Hilf, M., Vogt, U. F., and Schmidt, M. W.: The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C, *Organic Geochemistry*, 41, 1082–1088, <https://doi.org/10.1016/j.orggeochem.2010.07.001>, 2010.

- Schrumpf, M., Schulze, E. D., Kaiser, K., and Schumacher, J.: How accurately can soil organic carbon stocks and stock changes be quantified by soil inventories?, *Biogeosciences*, 8, 1193–1212, <https://doi.org/10.5194/bg-8-1193-2011>, <http://www.biogeosciences.net/8/1193/2011/>, 2011.
- Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I., and Schulze, E.-D.: Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and attachment to minerals, *Biogeosciences*, 10, 1675–1691, <https://doi.org/10.5194/bg-10-1675-2013>, druck vorhanden, 2013.
- Schwarz, T.: Klima: Puyo, <http://de.climate-data.org/location/2971/>, 2015.
- Schwertmann, U.: Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung, *Zeitschrift für Pflanzenernährung, Düngung, Bodenkunde*, 105, 194–202, <https://doi.org/10.1002/jpln.3591050303>, 1964.
- 10 Six, J., Conant, R. T., Paul, E. A., and Paustian, K.: Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils, *Plant and Soil*, 241, 155–176, <https://doi.org/10.1023/A:1016125726789>, <http://link.springer.com/article/10.1023%2FA%3A1016125726789>, 2002.
- Sollins, P., Swanston, C., Kleber, M., Filley, T., Kramer, M., Crow, S., Caldwell, B. A., Lajtha, K., and Bowden, R.: Organic C and N stabilization in a forest soil: Evidence from sequential density fractionation, *Soil Biology and Biochemistry*, 38, 3313–3324, 15 <https://doi.org/10.1016/j.soilbio.2006.04.014>, 2006.
- Stewart, C. E., Paustian, K., Conant, R. T., Plante, A. F., and Six, J.: Soil carbon saturation: concept, evidence and evaluation, *Biogeochemistry*, 86, 19–31, <https://doi.org/10.1007/s10533-007-9140-0>, <http://link.springer.com/article/10.1007/s10533-007-9140-0>, 2007.
- Tello, O.: History of the region around CEFRA: verbal, 2014.
- Thompson, A., Rancourt, D. G., Chadwick, O. A., and Chorover, J.: Iron solid-phase differentiation along a redox gradient in basaltic soils, 20 *Geochimica et Cosmochimica Acta*, 75, 119–133, <https://doi.org/10.1016/j.gca.2010.10.005>, <https://www.sciencedirect.com/science/article/pii/S0016703710005740>, 2011.
- Wendt, J. W. and Hauser, S.: An equivalent soil mass procedure for monitoring soil organic carbon in multiple soil layers, *European Journal of Soil Science*, 64, 58–65, <https://doi.org/10.1111/ejss.12002>, <http://onlinelibrary.wiley.com/doi/10.1111/ejss.12002/abstract>, 2013.
- WRB: World reference base for soil resources, 2006: A framework for international classification, correlation and communication, vol. 103 25 of *World soil resources reports*, Food and Agriculture Organization of the United Nations, Rome, 2006 ed. edn., 2006.
- Yagasaki, Y., Mulder, J., and Okazaki, M.: The role of soil organic matter and short-range ordered aluminosilicates in controlling the activity of aluminum in soil solutions of volcanic ash soils, *Geoderma*, 137, 40–57, <https://doi.org/10.1016/j.geoderma.2006.07.001>, 2006.
- Yoshinaga, N. and Aomine, S.: Allophane in Some Ando Soils, *Soil Science and Plant Nutrition*, 8, 6–13, <https://doi.org/10.1080/00380768.1962.10430983>, <http://dx.doi.org/10.1080/00380768.1962.10430983>, 1962.