

Interactive comment on “Soil andic properties as powerful factors explaining deep soil organic carbon stocks distribution: the case of a coffee agroforestry plantation on Andosols in Costa Rica” by Tiphaine Chevallier et al.

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Comment 1 Parts of the manuscript are below standard. Unfortunately, important parts of the manuscript are below standard. In the abstract, there is no information on the results of the study. This is unacceptable. The introduction should present the state of knowledge, open questions, hypotheses and objectives. The authors present two hypotheses which are related to MIRS. One might get the idea that MIRS is the core of the paper. However, half of the introduction (the first three paragraphs) does not deal with MIRS and the remaining part of the introduction does not give specific information

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on known and open issues with MIRS in the context of the study (which are the known absorption bands, how good was the estimation accuracy in different studies?). Since there are two hypotheses, one would expect two objectives. In fact, there are three objectives, but only one objective deals with MIRS. In summary, there is a need for a major improvement.

Answers 1/We agreed with the inconsistency of the abstract. The results were in the short abstract and were deleted to the main abstract. We wrote another abstract to underline the need of 598 soil samples (69 soil profiles), the use of MIRS and to give the results of the study.

Here is the new Abstract. Soil organic carbon (SOC) constitutes the largest terrestrial C stock, particularly in the Andosols of volcanic areas. Quantitative information on distribution of SOC stocks is needed to construct a baseline for studying temporal changes in SOC. The spatial variation of soil short-range-order constituents such as allophane usually explains the variability of topsoil SOC contents, but SOC data for deeper soil layers are needed. We found that within a 1-km² Costa Rican basin covered by coffee agroforestry, SOC stocks in the upper 200 cm of soil were highly variable (24 to 72 kgC m⁻²). Topsoil SOC stocks were not correlated with SOC stocks present in deeper layers. Diffuse-reflectance mid-infrared (MIR) spectroscopy made possible the analysis of a large number of samples (69 soil profiles, i.e. 598 soil samples) for ammonium-oxalate and sodium-pyrophosphate extractable forms of Al, Fe and Si, as well as SOC content and bulk density. The MIR spectra identified two different soil materials, which occurred one on top of the other in some soil profiles. Andic soil properties and the thickness of a young andic A horizon explained the high variability of SOC. This study illustrates that knowledge of topography and pedogenesis are needed to understand and extrapolate the distribution of SOC stocks at landscape scales.

Short summary. Soil organic carbon (SOC) is the largest terrestrial C stock. Andosols of volcanic areas hold particularly large stocks. E.g. from 24 to 72 kgC m⁻² in the upper 2 m of soil, as determined via MIR spectrometry, at our Costa Rican study site:

a 1 km² basin covered by coffee agroforestry. Andic soil properties explained this high variability, which did not correlate with stocks in the upper 20 cm of soil. Topography and pedogenesis are needed to understand the SOC stocks at landscape scales.

2/ The introduction was rewritten to underline the main objective of our research which was not MIRS but the variability of soil material (andic soil material and halloysite soil material) and then of SOC contents and stocks. Our main objective was to underline that surface SOC stocks does not always give a good image of the SOC stocks in deeper soil horizons in volcanic areas. You need to know about soil pedogenesis if you want to estimate accurately soil carbon stocks in this young volcanic environment. MIRS was an useful tool to analyse a lot of soil samples for andic properties. The only new result in our study about MIRS is to show that MIRS spectra could be used to classify andic material from non andic material.

Here is the new introduction. Soil organic carbon (SOC) not only contributes importantly to soil fertility and productivity, but is a larger pool of C than the world's vegetation and atmosphere combined (Lal, 2004). Those facts suggest that SOC is a potential sink for atmospheric CO₂, especially in soils whose formerly high levels of SOC have become depleted through land use. Therefore, many benefits may accrue from quantitative research on spatial patterns of SOC stocks at scales ranging from landscapes down to individual experimental plots. Among the many factors that affect those patterns are soil type, climate, topography, and vegetation biomass (Batjes, 2014; Jobbagy and Jackson, 2000). High spatial variations in SOC content can occur even at small scale (m) due to soil topography (Gessler et al., 2000) or to changes in land use (Chevallier et al., 2000). Such variations increase the uncertainty of comparisons among SOC stocks under different land-management practices (Costa Junior et al., 2013). For example, as when evaluating the effectiveness of different soil-conservation measures for restoring SOC in depleted soils. Attempting to decrease experimental uncertainty by testing SOC at smaller spatial intervals can be impractical because of the time and expense of standard SOC analyses. Therefore, development of accurate, low-

cost techniques for quantifying SOC contents at the necessary spatial scales may help researchers carry out experiments that would provide more definitive results. As a soil type on which to test those techniques, Andosols have three attractive traits: they store a disproportionate amount of soil carbon; their SOC patterns are spatially complex both vertically and horizontally (Mora et al., 2014); and the soil constituents (short-range-order constituents, e.g. allophane) associated with SOC in Andosols might be used as proxies for quantifying SOC contents via diffuse-reflectance mid-infrared spectroscopy (MIRS) (Kinoshita et al. 2016). We will discuss each of those traits of Andosols in turn, using the standard nomenclature in which the symbols Alo, Feo and Sio represent ammonium-oxalate-extractable forms of Al, Fe, and Si, and Alp and Fep represent the sodium-pyrophosphate-extractable forms of Al and Fe. Although Andosols represent only about 0.84% of the terrestrial soils, they store approximately 5% of the global soil C (Matus et al. 2014). Derived from volcanic material, they have high levels of short range order (SRO) constituents, i.e. Allophane or imogolite; high SOC concentrations (Batjes, 2014; Feller et al., 2001; Torn et al., 1997); high water retention; and low bulk densities (Shoji et al. 1996). They can store up to three times as much SOC as non-Andosols. Clear correlations have been found between SOC content and Allophane content (Basile-Doelsch et al., 2005) or Aluminium humus complexes (Alp) (Percival et al., 2000; Shen et al., 2018). As explanations for the high SOC contents, most authors have posited that SOC in Andosols is stabilized against decomposition by some combination of (i) acidic condition; (ii) Al toxicity; (iii) SOC adsorption on the mineral surfaces (Mayer and Xing, 2001); (iv) complexation, precipitation, and formation of organo-metal (Al/Fe) complexes, also called Al/Fe humus complexes (Percival et al., 2000; Scheel et al., 2007; Torn et al., 1997); and (v) entrapment in the mesoporosity (Mayer, 1994) with a particular network structure (Chevallier et al., 2010; Mayer et al., 2004; McCarthy et al., 2008). SOC in the deeper levels of Andosols has not been studied extensively. Most calculations of global-level C-budgets have not taken deep SOC into account because SOC at those levels is not considered to contribute much to the exchange of C between soil and the atmosphere. However, authors are now paying increased

attention to dynamics and estimated storage capacities of deep SOC that underlies different ecosystems (Bounouara et al., 2017; Cardinael et al., 2015; Mathieu et al., 2015; Rasse et al., 2006; Shi et al., 2013). In a global review for tropical regions, Batjes (2014) estimated SOC stocks in the 0-200 cm depth range at 616 to 640 PgC, versus 384-403 PgC in the 0-100 cm range. Volcanic regions with high percentages of Andosols (compared to the other soil types) showed some of the lowest degrees of vertical stratification of SOC stocks, but with a high degree of uncertainty. For Andosols, the ratio of SOC stocks at 0-30 cm those at 0-100 cm has been evaluated as 0.48, with a coefficient of variation of 29% (Batjes 2014). According to Churchman et al. (2016), the SRO distribution in volcanic regions can be complex both vertically and horizontally in areas where (i) an active volcano produces thin, intermittent ash deposits, (ii) soil erosion causes movement of soil materials (Zehetner et al., 2003), and (iii) the ash weathers in humid climates on slopes in which zones from which Si is leached away (thereby enabling SRO constituents to form and persist) alternate with zones in which Si accumulates (thereby causing those constituents to crystallize into aluminosilicates like halloysite). Factors (ii) and (iii), especially, can combine to produce terrains in which older, SRO-depleted soils become overlain by newer, SRO-rich topsoils. Previous work (Kinoshita et al., 2016) at the study site described in this article (a 1 km² volcanic micro-watershed) showed that spatial variations in Alp and allophane contents explained the high spatial variation of SOC contents of topsoils. Those same spatial variations in SOC (from 48 to 172 gC kg⁻¹soil at 0-5 cm depth) were not explained by topographic or vegetation covariates. Kinoshita et al. did not sample deeper layers of soil at the site. However, Kinoshita et al.'s correlations between SRO and SOC, together with Mora et al.'s (2014) data on the potentially complex distributions of SRO components in volcanic soils, suggested that deep-soil SOC stocks may be not related to topsoil SOC stocks. More generally, we hypothesized that SOC stocks would be highly variable along soil profiles. Testing those hypotheses required the analysis of hundreds of soil samples from soil profiles at widely distributed locations within the site. The results provided a large database with which to test an additional hypothesis:

that signatures of SRO components in MIR spectra of soil samples would be useful proxies for SRO constituents, type of soil material (Andic vs Halloysitic soil material), SOC and bulk density (Bd). Several authors have shown that diffuse-reflectance MIR spectroscopy is a time- and cost-effective analysis to quantify SOC contents. Therefore, MIR spectroscopy has become increasingly popular for spatial mapping of SOC (Ben-Dor et al., 2009; Clairotte et al., 2016; Nocita et al., 2015; Visacarra Rossel et al., 2016). Especially in the MIR region, each of a soil's mineral constituents affects spectra in a characteristic way. For example, absorbance peaks of Allophane and imogolite two SRO constituents that are specific to Andosols are near 1000 cm⁻¹. In contrast, the absorbance peaks of polymerized silicates are near 350 cm⁻¹ (Parfitt, 2009). As SRO constituents control soil Bd (Shoji et al. 1996) and SOC content (Torn et al., 1997), SRO signatures in MIRS spectra may be useful proxies for soil Bd and SOC. Therefore, MIR spectra might contain enough information to predict Bd as well as SOC stocks. Therefore, MIR spectroscopic analysis could replace soil extractions for some purposes (Janik et al., 1998). Those purposes include the spatial mapping of SROs and SOC in volcanic areas where soil age, type, and andic properties vary. If true, then MIRS could be appropriate for classifying soil samples as Andosols or non-Andosols. Based upon those classifications, researchers could build different prediction models for SOC contents for a large number of soil samples. In summary, then, the three hypotheses that we tested in the work reported here were that 1. Spatial distribution of SOC stocks at depths down to 200 cm depth can vary dramatically volcanic areas, even within a small watershed; 2. Surface SOC stocks in volcanic areas are not reliable predictors of stocks that might exist down to depths of 200 cm; and 3. MIRS is an effective and reliable technique for classifying soil materials according to some characteristics of andic soils associated with contents of SRO constituents (e.g., Alo, Alp, Sio, Feo, Alo+0.5 Feo, Allophane, (Alo-Alp)/Sio).

Comment 2 The core of the study is not sufficiently clear to me. Unfortunately, the core of the study is not sufficiently clear to me. A main focus is on MIRS for which 98 spectra were scanned and where there are also wet-chemical results. In total, however, there

are 598 soils and I do not see that the difference (598 - 98, the 500 soils) is really required for this study.

Answer: The core of the study and the need of 598 soil samples were specified in the abstract and the introduction, see answer and modifications in the Ms in our answer to comment 1.

Comment 3 The chemometric modelling is not exciting. The authors carried out a LOO-cross-validation for a modified PLS regression using a mixture of replicates and pseudoreplicates (soils from the same profile at different depths). This is not really exciting. More exciting would have been an independent validation, where one makes sure that soils from a profile are kept together in the calibration or validation sample.

Answer: The 10 soil samples of the soil profile sampling were not considered as pseudo-replicates, neither the 69 soil samples of a same depth but from a different soil profile. However, we agree they are not independent, they are spatially linked and were especially used for understanding the vertical and horizontal variability of allophane and carbon contents. We have thus proceeded to independent validations of the prediction models for all Alo, Sio, Feo and Alp, and the global model for SOC content. The models of prediction were built on 7 soil profiles (n=69). Validation was performed on 3 other soils profiles (n= 29.) It was not possible to do it for the other models (Bd, SOC by clusters) as we did not have enough conventionally measured soil samples to constitute two groups. Table 1 and material and method were modified. In this study, the new result is not the model building but the classification of 2 soil materials from the MIR spectra whatever the soil depth of the soil sampling. We underline this information in the introduction (third hypotheses) and it was also discussed in §3.1.2. Clustering according to soil type based upon MIR spectra, versus conventional analyses.

Here are the changes in the text, in Material and Method section (§2.5.1): From the data sets for MIRS (Sect. 2.3) and laboratory analyses (Sect. 2.4.1), we developed predictive models for contents of Alo, Alp, Sio, Feo, and SOC. One model was devel-

oped for each constituent, for a total of five models. All of the models were based upon 69 samples, from seven soil profiles, that were common to both data sets. The other 29 samples that were common to both data sets were used for validating the models, as described below. The models were developed by fitting the samples' MIR absorbance spectra to the samples' measured contents of each of the five constituents. Except as noted in Sect. 2.3, the spectra were not given mathematical pre-treatments. Fitting was done via modified partial least-squares regressions. The accuracy of each prediction model was determined by external validation using laboratory analyses and MIRS spectra of the above-mentioned 29 samples, which were from three different soil profiles. The accuracy was quantified by computing (i) the coefficient of determination (R^2), (ii) the root mean square error (RMSE) between predicted and measured values, and (iii) the ratio (denoted as RPD) of the standard deviation of the value set to RMSE.

Please see below the new Table 1

Comment 4 The anova modelling is not convincing. As above, there are problems with pseudo replication. In anova, independent data are required. Data from different depths are not independent from each other. Repeated measures anova or a mixed effects model is required.

Answer : We agreed with the reviewer. As repeated anova was not possible because all the soil profiles were not complete (10 soil depths), linear mixed models were used to analyse our data. Changes were made in the Ms, Changes were also made in table 2, 3, 7 and 8.

Changes in Material and methods §2.6.2: Effects of spectral cluster and soil depth on andic properties, SOC contents, Bd, and SOC stocks were analysed with linear mixed models that considered soil profile a random effect. The T-test was used to assess the effect of spectral cluster on the variable to be explained for each depth. A random forest regression model was used to evaluate and order the importance of andic properties, spectral cluster, and soil depth on SOC contents. Random forest is a machine-learning

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technique based on randomly built decision trees. At each node, a subset of covariates is also randomly chosen. Random forest was used instead of multiple-linear-regression methods because it allows use of both categorical and numeric covariates, collinearity between covariates, and non-linear relationships between covariates and the variable to be explained. %IncMSE was used to assess the relative importance of covariates in explaining variability of SOC content. For a given covariate, %IncMSE is the difference between mean standard error (MSE) of the model with permutation of this covariate, and model without that permutation. The larger the %IncMSE, the more important this covariate in predicting SOC content. We used R software (R Core Team, 2018) for the statistical analyses.

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Table 1. Validation statistics of modified partial least square (mPLS) regression for the models used to predict SOC and extractable Al, Si, and Fe contents from MIR spectra.

		n	n outliers	Mean	Sd	RMSE	R ²	RPD
Al _e	Calibration	69	0	2.18	1.72	0.4	0.94	4.9
Al _e	External validation	29		2.85	2.15	0.8	0.85	2.6
Si _e	Calibration	69	3	0.88	0.53	0.14	0.93	3.9
Si _e	External validation	29		1.06	0.64	0.19	0.91	3.4
Fe _e	Calibration	69	0	1.0	0.5	0.2	0.81	2
Fe _e	External validation	29		1.1	0.5	0.5	0.19	1
Al _p	Calibration	69	1	0.26	0.17	0.07	0.85	2.4
Al _p	External validation	29		0.24	0.12	0.06	0.72	2
SOC	Calibration	69	2	39.7	26.1	3.6	0.97	7.3
SOC	External validation	29		39.7	21.3	9.4	0.86	2.3

n: number of soil samples for calibration. Mean and Standard deviation (Sd) of the measured Al_e, Si_e, Fe_e, Al_p population (in g 100 g⁻¹ soil) and SOC content (g kg⁻¹) used for model calibration RMSE: Root Mean Square Error, R²: cross-validation determination coefficient, RPD: ratio of Sd to RMSE, Sd: Standard deviation.

Fig. 1. Table 1: Validation statistics of modified partial least square (mPLS) regression for the models used to predict SOC and extractable Al, Si, and Fe contents from MIR spectra.