



- 1 Is the content and potential preservation of soil organic
- 2 carbon reflected by cation exchange capacity? A case study
- **in Swiss forest soils**
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- 5 Emily F. Solly¹, Valentino Weber¹, Stephan Zimmermann², Lorenz Walthert², Frank
- 6 Hagedorn², Michael W. I. Schmidt¹
- 7

8 ¹ University of Zurich, Department of Geography, Winterthurerstrasse 190, 8057 Zürich,

9 Switzerland.

² Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Zürcherstrasse 111,

- 11 8903 Birmensdorf, Switzerland.
- 12 Correspondence to: E. Solly (<u>emily.solly@geo.uzh.ch</u>)
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14 Abstract

15 The content of organic carbon (C) in soils is not stable, but depends on a number of 16 environmental variables and biogeochemical processes that actively regulate its balance. An improved identification of the environmental variables that can be used as predictors of soil 17 organic C (SOC) content is needed to reduce uncertainties of how the soil C reservoir will 18 19 respond to environmental change. Although several simulations rely on the amount of clay to reproduce changes in the balance of SOC, recent efforts have suggested that other soil 20 physicochemical properties may serve as better predictors. Here we tested whether the effective 21 cation exchange capacity (CEC eff.), may be a more suitable predictor of the content and 22 23 potential preservation of SOC as compared to the mere quantification of clay-size particles. We further assessed how various climatic, vegetation and edaphic variables explain the variance of 24 25 SOC content across different soil depths and soil pH classes. A set of more than 1000 forest





26 sites across Switzerland, spanning a unique gradient of mean annual precipitation (636-2484 27 mm), altitude (277-2207 m a.s.l), pH (2.8-8.1) and representing different geologies and soil 28 orders was used as a case study for this linear model analysis. Our results showed that CEC eff. has the largest explanatory potential of SOC content (35 % of response variance in the complete 29 30 mineral soil profile) as compared to the amount of clay (which only explained 7 % of the response variance in the complete mineral soil profile) and other environmental variables. CEC 31 eff. is strongly linked to SOC especially in the top mineral soil (0-30 cm depth) with the larger 32 33 presence of organic matter. At deeper soil depths most of the variance in SOC is instead explained by climate, which in Switzerland is related to a greater weathering activity and 34 35 translocation of organic C through leaching with increasing mean annual precipitation. We further observed soil pH to have a complex influence on SOC content, with CEC eff. being a 36 37 dominant variable controlling SOC content at pH > 4.5 in the upper mineral soil and pH > 6 in 38 the subsoil. Since CEC eff. is an edaphic property which is intimately associated to both the 39 conditions that shaped the soil and the current edaphic physicochemical conditions, these findings indicate that considering CEC eff. as an integrative proxy for the potential preservation 40 of SOC and its alteration could improve future predictions of how the soil C reservoir will feed 41 42 back to environmental change.

43

44 **1 Introduction**

Large uncertainties in our understanding and predictions of how the terrestrial carbon (C) cycle interacts with alterations in the environment exist about the effects on the content of soil organic C (SOC) and its stabilization or destabilization (Jobbágy and Jackson, 2000; Friedlingstein et al., 2014; Jackson et al., 2017; Todd-Brown et al., 2013). To assess the impacts not only of the occurring but also of the forecasted global changes, it is desirable to identify environmental predictors of SOC dynamics (Bailey et al., 2018; Rasmussen et al., 2018; Harden et al., 2018), that match the recent shifts in paradigm of SOC (de)stabilization (Lehmann and Kleber, 2015;





Schmidt et al., 2011). Measuring and predicting the content and potential preservation of SOC is elaborate due to the large spatial and temporal scales that are needed to detect changes (Harden et al., 2018; van der Voort et al., 2016). However, the exchange of knowledge between empirical research and simulation models offers great promise to facilitate innovations in C management and programs to reach climate-change mitigation goals, e.g. the '4 per mille Soils for Food Security and Climate' international research program (Minasny et al., 2017).

Advances in soil science have demonstrated that the content and preservation of SOC is 58 not controlled by the chemical composition of organic matter alone but is rather predominantly 59 60 driven by environmental and biological variables (Schmidt et al., 2011; Marschner et al., 2008; 61 Kleber and Johnson, 2010). In this context, the effects of climatic, biotic, and geogenic controls of SOC dynamics have been extensively studied for different spatial and temporal scales 62 63 (Davidson and Janssens, 2006; Hicks Pries et al., 2017; Jobbágy and Jackson, 2000; Falloon et al., 2011; Liang et al., 2017; Doetterl et al., 2015). Climatic variables generally appear to exert 64 65 a major control of SOC dynamics and consequently a significant feedback of the terrestrial-C cycle to climate change is expected (Carvalhais et al., 2014; Chen et al., 2013). Biotic activity 66 (plant and microbial) and soil physicochemical variables are additionally contributing to 67 explain the large uncertainties covering the fate of SOC (Doetterl et al., 2015; Schmidt et al., 68 2011; Rasmussen et al., 2018; Torn et al., 1997). 69

70 Despite this improved understanding, model frameworks aimed at assessing how SOC 71 responds to environmental change still necessitate the use of proxy variables that represent soil 72 characteristics that cannot be measured (correlative proxies), or that aggregate information about multiple soil characteristics (integrative proxies) (Bailey et al., 2018). To improve 73 74 projections of the largest actively cycling terrestrial C reservoir to environmental change, recent efforts have hence been focusing on identifying new sets of variables that can be used to 75 determine the content of SOC. For instance, although several biogeochemical models rely on 76 77 the amount of clay to simulate mineral protection of SOC (Coleman and Jenkinson, 1996;





78 Wieder et al., 2015), Rasmussen et al. (2018) recently suggested that other soil physicochemical 79 properties, such as exchangeable Ca or Fe, and Al oxyhydroxides, can be used as better 80 predictors depending on the local soil pH. Soil pH reflects the chemical state of soil systems, e.g. protonation, controlled by geological and mineralogical properties, and dictates some of 81 82 the main driving processes of SOC (de)stabilization (Deng and Dixon, 2002; Oades, 1988). Such processes include organo-mineral complexation, solubility and organism activity, which 83 vary with depth across soil profiles (as reviewed by Sollins et al., 1996; Six et al., 2004; 84 85 Trumbore, 2009).

The amount of clay, that is the soil mineral fraction $<2 \,\mu m$ in size, influences the content 86 87 of SOC by promoting the adsorption of organic molecules to its surfaces primarily by the interaction with pedogenic oxides and the aggregation within clay structures (Lützow et al., 88 2006; Oades, 1988; Eusterhues et al., 2003). Through its control on soil hydrology, oxygen 89 90 availability as well as soil microbial community, the amount of clay can further indirectly alter 91 SOC preservation (Andrews et al., 2011; Fierer and Schimel, 2002). Due to these properties, the amount of clay is often used as a proxy for sorption on mineral surfaces and aggregation of 92 93 SOC, especially by more generalized larger scale models (Bailey et al., 2018). Several recent studies, however, did not find the amount of clay to be a predominant physicochemical predictor 94 of SOC content and preservation (e.g. Schrumpf et al., 2013; Rasmussen et al., 2018; Doetterl 95 et al., 2015). A reason for this is likely that the amount of clay merely represents a size class of 96 97 soil particles rather an equivalent indication of available surface area or aggregate formation. It 98 follows that other soil properties that represent an indication of available soil surfaces may be more appropriate to estimate SOC than clay. 99

An example of a soil property representing an indication of available soil surfaces is the effective cation exchange capacity (CEC eff.). CEC eff. is an edaphic property reflecting geology, mineralogical composition, organic matter and the pH that shapes the soil and its current physicochemical conditions. The CEC eff. of a soil represents the total amount of





exchangeable cations such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Al³⁺, Fe²⁺, H⁺ that can be retained 104 105 through electrostatic adsorption on soil particle surfaces. Soil particles exhibit negative and 106 positive charges that can adsorb oppositely charged ions from the soil solution. In most soils, CEC eff. increases with soil pH. At low pH, it is mainly the permanent charges of the 2:1 type 107 clays that adsorb exchangeable cations, while at higher pH values the negative charges on some 108 109 1:1-type clays, allophane, Fe- and Al- oxides, and soil organic matter increase, thereby increasing CEC eff. (Weil and Brady, 2016). There are several reasons why CEC eff. may be a 110 111 better integrative proxy for the content and potential preservation of SOC than others. Quantifying the amount of clay is time-consuming. Determining clay mineralogy is expensive 112 113 and requires specialized equipment, and quantification can be challenging. The key variables 114 for soil organic matter protection are short range order minerals, Al- and Fe- oxyhydroxides, 115 and Al-, Fe- organo-metal complexes (Rasmussen et al., 2018), which cannot be thoroughly identified and quantified for large sample sets with analytical techniques available today. Soil 116 117 surface area that has been calculated by using gas adsorption as a proxy for the protective potential of soil and sediment, cannot be measured routinely on large sample sets. On the other 118 hand, CEC eff. is measured routinely to assess soil fertility for agricultural and forest use. 119

Here we ask the question whether CEC eff. can serve as a new integrative proxy of SOC content and its potential preservation, integrating effects of soil surfaces of different clay types, short-range order mineral phases and organic matter at the actual soil pH. Moreover, we are interested in understanding how the variance of SOC content is explained by various environmental variables across different soil depths and soil pH classes. We test this by using a set of more than 1000 forest soil profiles across Switzerland spanning a strong gradient of climate, altitude, geology, soil pH and soil orders (Gosheva et al., 2017).

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128 2 Materials and Methods

129 2.1 Study area and dataset





130 The study area covers the complete country of Switzerland (~ 45-47° N, 6-10° E), situated in 131 the centre of Europe. Switzerland offers a wide and intricate range of geology and topography 132 which vary abruptly often within short distances, leading to very diverse soil orders (Walthert et al., 2013; Gosheva et al., 2017). About 30 % of the country (~ 12.000 km²) is covered by 133 forest, and half of this area is located above 1000 m a.s.l. Forest management is mainly practiced 134 135 at low elevations, where no large-scale clear-cutting is applied and natural regeneration is often fostered by silvicultural management (Brassel and Brändli, 1999). Forest soil fertilization and 136 137 liming was always forbidden in Switzerland.

The dataset analyzed in this study originates from a database of the Swiss Federal Institute for Forest, Snow and Landscape Research (WSL) containing data on 1204 forest sites across Switzerland (for more details see Walthert et al., 2013; and Walthert and Meier, 2017). More than 80% of these sites have been covered for at least 150 years with forests (Gosheva et al., 2017).

The variables which we evaluated included SOC content (g kg⁻¹) and other soil physicochemical properties (pH in CaCl₂, CEC eff. (mmolc kg⁻¹) and soil texture) as well as climatic, topographic and vegetation data. In this study we report weighted means of SOC content over fixed depths rather than SOC stocks. This is because SOC content represents a direct measure of SOC after a single correction for the amount of fine earth in pedogenic horizons, while SOC stock estimates required multiple imponderable corrections (Gosheva et al., 2017).

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151 2.2 Soil chemical and physical properties

In each forest site a soil profile was sampled by pedogenetic horizons down to a profile depth of 120 cm if possible, otherwise down to parent rock, with six samples per pit on average. Soil samples were dried at 40-60° C and sieved at 2 mm for chemical analyses. SOC content was measured in milled subsamples by dry combustion using a C/N analyser (NC 2500, Carlo Erba





156 Instruments, Italy). Inorganic C was removed in samples with a pH above 6.0 by fumigating 157 with HCl vapour prior to analysis (Walthert et al., 2010). Soil pH was measured 158 potentiometrically in 0.01 M CaCl₂ with a soil - extract ratio of 1:2 after 30 min of equilibration. 159 Exchangeable cations were extracted in an unbuffered solution of 1 M NH₄Cl for 1 h on an endover-end shaker using a soil - extract ratio of 1:10. The elemental concentrations were 160 subsequently measured with an ICP-AES (Optima 3000, Perkin-Elmer). For soil samples with 161 a pH (CaCl₂) <6.5 concentrations of exchangeable protons were calculated as the difference 162 between the total and the Al-induced exchangeable acidity with the KCl method (Thomas, 163 1982). For soil samples with a higher pH, concentrations of exchangeable protons were 164 assumed to be negligible. The effective cation exchange capacity (CEC eff.) was finally 165 calculated by summing the charge equivalents of exchangeable Na, K, Mg, Ca, Mn, Al, Fe and 166 167 H. Grain size distribution was measured with the sedimentation method according to Gee and Bauder (1986) for 750 soil profiles. For the remaining soil profiles, we used the field estimates 168 based on ten texture classes from Walthert et al. (2004). We focused on the following soil-depth 169 intervals: 0-30 cm of the mineral soil profile (topsoil), 30-120 cm of the mineral soil profile 170 (subsoil) and for a comprehensive interpretation of the data we also considered the complete 171 mineral soil profile at 0-120 cm. We calculated the mean average content of all the above 172 mentioned soil properties for 0-30 cm, 30-120 cm and 0-120 cm by weighting the averages of 173 the content with the amount of fine earth determined in the pedogenetic horizons of those fixed 174 175 depth increments, as described in Walthert et al. (2013). Soil type was classified according to the World Reference Base from 2007 (IWG, 2007). 176

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178 **2.3 Climatic, topographic and vegetation data**

The soil data of each forest site was paired with climatic and vegetation data. Climatic data was
based on the Swiss metereological network (MeteoSwiss), combined with suitable interpolation
algorithms (Walthert et al., 2013). Specifically, mean annual precipitation (MAP) and mean





annual temperature (MAT) were provided by Meteotest (https://meteotest.ch/en/) for the period
1981-2010 (for details see Remund et al., 2014). The altitude of the forest sites was extracted
from a 25 m digital elevation model (DEM) of the Federal Geo-Information centre swisstopo.
For each forest site, the local Leaf Area Index (LAI) a common measure of canopy foliage
acting as a control over primary production (Asner et al., 2003), was further estimated according
to Schleppi et al. (2011) based on data from a vegetation survey using the Braun-Blanquet cover
abundance scale (Braun-Blanquet, 1964; Mueller-Dombois and Ellenberg, 1974).

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190 2.4 Statistical analysis

191 To identify which environmental variable of interest had the greatest prediction power on SOC content in the complete mineral soil profiles (0-120 cm), topsoils (0-30 cm) and subsoils (30-192 193 120 cm), we applied linear model analysis. CEC eff., percentage of clay, LAI, MAT and, MAP were treated as explanatory variables while SOC content was treated as main response variable. 194 195 To meet the normality assumptions of the applied statistical tests and standardize the variation among variables, we transformed the continuous variables to normal distributions applying log-196 197 transformations when required, and subsequently standardized them to a mean of 0 and standard 198 deviation of 1. The linear models were checked for multicollinearity using the variance inflation factor (VIF). The value of VIF >4 was set as a threshold for evidence of multicollinearity. We 199 checked the model assumptions using the diagnostic plot functions in R (Crawley, 2012), and 200 201 the normality of the residuals was tested using histograms. The explanatory power of the 202 variables included in the linear models was computed as the standardized regression coefficient. The more positive or negative the coefficient is, the higher is its relative power in predicting 203 204 the response variable SOC. We then partitioned the contribution of each of the explanatory variables to the explained variance in SOC employing hierarchical variance partitioning. For 205 this, we used the 'lmg' metric in the R package 'relaimpo' (Groemping and Matthias, 2006), 206 207 which decomposes R squares into non-negative contributions that automatically sum to the total





208 R squared of the linear model and takes care of the dependence on orderings by averaging over 209 orderings (Grömping, 2006). The contribution of the environmental variables in explaining the 210 variance of SOC was additionally normalized to sum to 100 %, i.e. in place of the total R squared (Groemping and Matthias, 2006). We further performed a linear model analysis of the 211 relative importance of climatic, vegetation and edaphic variables to predict SOC across pH 212 classes at 0-120 cm, 0-30 and 30-120 cm soil depth. Specifically, soil-pH data was grouped into 213 nine consecutive pH ranges: (pH: <4, 4-4.5, 4.5-5, 5-5.5, 5.5-6, 6-6.5, 6.5-7, 7-7.5, >7.5 see 214 215 Table 1 for the complete pH ranges at the three different depths). The relation between SOC 216 content and all explanatory variables, parsed among different soil depths and pH classes, was 217 also tested using Spearman's correlation coefficient. Significance was evaluated based on Bonferroni's corrected p-values to account for Type I errors. For each statistical test P < 0.05218 219 was considered to be statistically significant. All analyses were performed with the R statistical 220 software version 3.5.0 (R Core Team, 2018), and the packages 'vegan', 'MASS', 'dplyr', 221 'plyr', 'car', 'quantPsyc', 'caret', 'relaimpo', 'Psych'.

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223 3 Results

224 3.1 Environmental characteristics of the forest sites

The Swiss forest sites where the soils were sampled are distributed between 277 and 2207 m 225 226 a.s.l. They are characterized by a mean annual precipitation (MAP) ranging between 636 and 2484 mm, and mean annual temperatures (MAT) ranging between 0.1 and 12.0 ° C. MAT and 227 228 altitude are strongly negatively correlated (r = -0.97). The predominant soil types are classified 229 as Cambisols (n = 365), Luvisols (n = 127) and Gleysols (n = 89). About half of the sites are covered by broadleaf tree species while the rest are coniferous forests (Gosheva et al., 2017), 230 with LAI values varying between 2 to 7.2. pH values range from 2.8 to 8.1 and the percentage 231 232 of clay varies between 0.8 and 75.6 % (for details about specific ranges in topsoils and in the subsoils see Table 1). The parent material of the north of Switzerland is dominated by a 233 9





calcareous bedrock and sediments, from which alkaline soils have developed. The most acidic soils are instead found in the Southern Alps and parts of the Swiss plateau, in the center of Switzerland (Figure S2). The content of SOC varies between 6 and 376.8 g kg⁻¹ in topsoils (upper 0-30 cm of the mineral soil) and between 0 (lower than detection limit) and 229 g kg⁻¹ in subsoils (30-120 cm depth). CEC eff. ranges between 20.4 and 1046.4 mmolc kg⁻¹ in topsoils and between 6.2 and 727.9 mmolc kg⁻¹ in subsoils.

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241 **3.2 Predictors of soil organic carbon (complete pH range)**

All of the explanatory variables except MAT in the topsoil have a significant effect on SOC 242 243 content when considering the complete pH range (Table 2). The standardized regression coefficients indicate that throughout Switzerland the SOC content increases with increasing 244 245 CEC eff. and MAP, while decreases with greater MAT, LAI and percentage of clay. The signs of these relations are overall coherent with the sign of significant Pearson's correlations 246 247 coefficients, with the exception of the correlation between SOC and CEC eff. in the pH range 4.5-5 in the subsoil (Fig. 1). The assessment of the relative contribution of the explanatory 248 variables to the explained variance in SOC shows that within the complete mineral soil profile 249 CEC eff. explains most of the response variance in SOC content (35 %), followed by MAP (26 250 %), and smaller significant contributions of explained variance by LAI and MAT (Table 2). 251 Within the topsoil CEC eff. also has the overall strongest influence on SOC accounting for 60 252 253 % of its variance (Table 2). In subsoils, climatic variables (MAP and MAT) are instead the 254 predominant variables controlling the variance in SOC content (31 and 28 % respectively) 255 (Table 2).

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257 3.3 Soil organic carbon across pH classes

SOC content is greater in more alkaline soils with pH > 5.5 (Fig. S1). The relative contribution of the explanatory variables to the explained variance in SOC is dependent upon pH (Fig. 1,





260	Fig. 2). For lower pH classes, MAP explains the largest portion of the response variance of
261	SOC content, while CEC eff. explains the greatest portion of variance in more alkaline soils
262	Fig. 3 presents the normalized contribution of MAP, MAT, LAI, percent clay and CEC eff. in
263	explaining the variance of SOC content. The total amount of variance explained (R squared) by
264	each independent linear model across pH classes ranges between 0.76 (0-30cm depth, pH 6-
265	6.5) and 0.11 (30-120 cm depth, pH 5.5-6) (Fig. 4). On average, each pH class contains 125 ± 94
266	(mean \pm SD) forest sites that we could analyze with independent linear models (Fig. 4). The
267	total amount of variance explained by the linear model runs is independent from the number of
268	forest sites included in the models.

269

270 4 Discussion

271

4.1 Can the effective cation exchange capacity be used as a proxy for soil organic carbon content?

274 Our linear model analysis indicates that throughout 1204 Swiss forest sites, encompassing a 275 pronounced gradient of climate, geology, soil pH and soil orders, CEC eff. has the largest explanatory potential of SOC content (35 % of response variance in the complete mineral soil 276 277 profile) as compared to other environmental variables (Table 2). Since CEC eff. is an edaphic property which is intimately associated to both the conditions that shaped the soil and the 278 279 current physicochemical conditions in the soil, the significant link between CEC eff. and SOC hints towards a potential of this edaphic property to be used as an integrative proxy of the 280 281 present and future content of SOC. In our evaluation we included a range of climatic, vegetation and edaphic properties, as these variables are commonly regarded as primary controls of SOC 282 283 (Torn et al., 2009). However, we cannot rule out that our analysis could be biased by the lack of available information on the activity by soil organisms (microbial communities and soil 284 285 macro- and meso- fauna) (Jackson et al., 2017). The weak relationship between the vegetation





286 property we adopted as an indication of plant primary production (the LAI) and SOC content 287 strongly suggests that the quantity of litter inputs is less important for SOC than 288 physicochemical properties. This is in agreement with mechanistic studies employing isotopic tracers, as well as spectroscopic and molecular techniques (Hagedorn et al., 2003; Marschner 289 290 et al., 2008; Schmidt et al., 2011). The weak relationship may however also result from the lack of information on the growth of belowground plant biomass as well as on differing 291 decomposition rates of above and belowground plant debris before incorporation into the soil 292 293 (Hobbie et al., 2010). Nevertheless, the results of our analysis clearly demonstrate that CEC eff. explains a larger portion of the variance in SOC content than the percentage of clay - on which 294 295 many biogeochemical models rely as a proxy of SOC. Such pattern might be partly related to the contribution of variably charged functional groups of organic matter to CEC eff. but it also 296 297 corroborates the emerging conceptual understanding that other soil physicochemical properties 298 predict the content and potential persistence of SOC better than the amount of clay (e.g. 299 Rasmussen et al., 2018).

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4.2 How is the variance of soil organic carbon content explained by environmental variables at different soil depths?

In agreement with vast ranging observations showing that SOC content decreases with soil 303 depth (e.g. Jobbágy and Jackson, 2000; Rumpel and Kögel-Knabner, 2011), we observed a 304 305 higher SOC content in the upper 30 cm of the mineral soil as compared to that found at lower 306 depths (Table 2). This pattern is commonly related to a decline in the inputs of plant-derived organic matter with depth because litterfall from leaves, needles and twigs occurs on the soil 307 308 surface, and this material is only partially translocated to the subsoil in dissolved form or via bioturbation. Moreover, plant root densities are commonly smaller in subsoils than in topsoils 309 (Jackson et al., 1997). Microbial communities involved in the breakdown of organic matter also 310 311 vary across depth profiles (e. g. Lindahl et al., 2007). Our linear model analysis demonstrates





312 that CEC eff. is the strongest predictor of SOC in topsoils (explaining 60 % of the total variance 313 in SOC content) while climatic variables (MAT and MAP) are stronger predictors of SOC in subsoils (Table 2). The primary influence of CEC eff. on SOC content in topsoils as compared 314 to deeper soil depths can be attributed to the overall larger presence of organic matter that 315 316 contributes markedly to a higher number of available negative charges in soils to which cations 317 can bind. The dominant control of climate on the content of SOC in subsoils is instead connected to a significant transport of fresh C to deeper soil depths through leaching of 318 dissolved organic matter (Kaiser and Guggenberger, 2000), which increases with increasing 319 precipitation and a greater accumulation of organic horizons, especially under cool and humid 320 321 climatic conditions (Gosheva et al., 2017). Analyses of the content of SOC in the soil solution and in the organic debris residing inside and outside aggregates and bound to minerals would 322 323 be necessary to test these mechanisms across complete soil profiles in Swiss forest sites.

324

4.3 How does soil pH influence the variance of soil organic carbon content explained by different environmental variables?

327 Overall, we observed a significant and complex influence of soil pH on the content of SOC confirming results from previous studies (Rasmussen et al., 2018; Newcomb et al., 2017). Our 328 study provided a unique soil pH gradient (spanning from 2.8 to 8.1, Fig. S2) which largely 329 resulted from the complex topography and orogeny of the territory of Switzerland 330 331 encompassing various types of parent material, made up of sedimentary, crystalline or 332 metamorphic rocks with highly variable mineralogical compositions (Gosheva et al., 2017). We found that SOC content is higher in more alkaline soils with pH >5.5 (Fig. S1). However, it has 333 334 to be noted that SOC stocks in Swiss forests are generally not higher in calcareous than acidic soils (Gosheva et al., 2017), indicating that acidic soils e.g. in the South of Switzerland (Fig. 335 S2), have a lower SOC content but are generally deeper. Moreover, our analysis revealed that 336 337 the relative control of climatic, vegetation and edaphic variables on SOC evolves as a function





of soil pH. MAP explained most of the variance in SOC content at low pH (pH <5.5), while
CEC eff. was the dominant variable at higher pH values (pH >4.5 in topsoils and pH >6 in
subsoils) (Fig. 2).

The strong influence of MAP on SOC that we observed at low pH is likely primarily 341 related to the reaction of organic ligands with aluminium cations (Al³⁺) that often occurs in 342 many soils of regions with a high MAP and thus high water availabilities (Chadwick and 343 Chorover, 2001; Torn et al., 1997; Blaser et al., 1997; Blaser and Sposito, 1987; Eckmeier et 344 al., 2010). Firstly, in acid soils the presence of Al^{3+} cations is commonly associated to the 345 production of organo-metal complexes during the process of weathering. Secondly, a strong 346 chelation of Al³⁺ by organic acids in Swiss forest soils characterized by a high MAP and acid 347 soils, is pointed out by the high levels of exchangeable aluminium (Al^{3+}) found at low pH 348 classes (Fig. S1), and by the observation of the highest MAP regimes in regions with the most 349 350 acidic soils (Fig. S2, S3). These patterns corroborate previous results showing that the relatively 351 humid climate of the Southern Alps promotes both the formation of pedogenic oxides and the leaching of dissolved organic C from the organic layer to the mineral soil, where organic matter 352 353 i.e. tannins and other polyphenols forms organo-metal complexes (Eckmeier et al., 2010). The peak in the explanatory power of MAP on the content of SOC at pH 4.5-5 (Fig. 3) is probably 354 related to the greater occurrence of Luvisols and Podzols in this pH range (Fig. S4). These soil 355 orders are characterized by translocation of clay and organic matter. 356

The dominant contribution of CEC eff. in explaining the variance of SOC in higher pH classes can be explained by the established knowledge that the amount of available negative charges to which cations can be bound on organic matter - together as on allophane and some 1:1-type clays - increase with rising pH (Weil and Brady, 2016). In particular, the deprotonation of carboxyl and hydroxyl groups present in organic matter has often been observed to contribute markedly to the greater number of available negative charges in soils, and more so at higher pH values (Krishnaswamy and Richter, 2002; Tate and Theng, 1980; Sullivan et al., 2006).





Furthermore at pH levels higher than 6 the charges of 2:1-type clays have been observed to increase due to a deprotonation of exposed hydroxyl functional groups (Tournassat et al., 2016).

367 5 Conclusions

In conclusion, our study of Swiss forest soils provides a first indication that CEC eff. could be 368 369 used as an integrative proxy of SOC content and its potential preservation. Determining whether CEC eff. is an effective proxy for the content of SOC also in non-forested ecosystems and in 370 other geographical locations would be a further step forward to test its broad applicability in 371 Earth System models. This information could be compiled starting from available soil profile 372 samples, soil surveys and monitoring programs at the country, continental or climatic zone level 373 374 (e.g. http://icp-forests.net/, http://ncsslabdatamart.sc.egov.usda.gov/). Some global gridded 375 data about CEC. eff has also already been derived (Hengl et al., 2017) by the international soil reference and information center ISRIC. We observed that CEC eff and SOC are closely linked 376 especially in the top mineral soil (0-30 cm depth) as compared to deeper depths. This is due to 377 378 the overall larger presence of organic matter contributing to a higher number of available negative charges in topsoils. In subsoils most of the variance in SOC is instead explained by 379 380 climate, which in our study is potentially related to increasing weathering and transport of fresh 381 C to greater soil depths through leaching of dissolved organic matter with increasing MAP. Soil 382 pH strongly affects the explanatory power of CEC eff. on the content of SOC in Swiss forest 383 soils, with CEC eff. being the dominant variable at pH > 4.5 in topsoils and pH > 6 in subsoils. 384 Since 73% of the land surface is covered by soils with pH > 5.5 (area calculated according to 385 the global pH dataset IGBP-DIS (1998)) the consideration of CEC eff. as an integrative proxy for the potential alterations of SOC content could strengthen our ability to predict future 386 changes in the belowground C reservoir. 387





389 Author contributions

- 390 MWIS, SZ, FH conceived the idea of this analysis, SZ and LW provided and quality checked
- 391 the data, EFS developed the ideas for this manuscript and considering the preliminary analyses
- by VW defined the final statistical approach. EFS prepared and wrote the manuscript withcontributions from all co-authors.
- 394

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405

406 **Competing interests**

407 The authors declare no competing interests.

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Figures:

Fig. 1: Pearson's correlations between the content of SOC and explanatory variables for (a) complete mineral soil profiles (0-120 cm depth), (b) topsoils (0-30 cm depth), (c) subsoils (30-120 cm depth). MAP, mean annual precipitation (mm), MAT, mean annual temperature (°C), LAI, leaf area index, clay, percentage of clay (%), CEC, effective cation exchange capacity (mmolc kg⁻¹). Those correlations with P >0.05 are considered not significant (NS) based on Bonferroni's correction.

Fig. 2: Amount of explained variance by climatic, vegetation and edaphic variables in predicting the content of SOC (g kg⁻¹) across pH classes for (a) complete mineral soil profiles (0-120 cm depth), (b) topsoils (0-30 cm depth), (c) subsoils (30-120 cm depth). Horizontal bars show the amount of variance explained by each variable (R squared) in the linear models as calculated using the 'lmg' metric in the R package 'relaimpo'. Significant variables (p-value <0.05) are marked by an asterisk (*). MAP, mean annual precipitation (mm), MAT, mean annual temperature (°C), LAI, leaf area index, clay, percentage of clay (%), CEC, effective cation exchange capacity (mmolc kg⁻¹). The total amount of variance explained (R squared) by each independent linear model is presented in Fig. 4 together with the number of samples used. **Fig. 3:** Relative contribution (percentage of R squared) of climatic, vegetation and edaphic variables in predicting the content of SOC across pH classes, for (a) complete mineral soil profiles (0-120 cm depth), (b) topsoils (0-30 cm depth), (c) subsoils (30-120 cm depth). The response variance explained by each environmental variable was normalized to sum to 100 %. MAP, mean annual precipitation (mm), MAT, mean annual temperature (°C), LAI, leaf area index, clay, percentage of clay (%), CEC, effective cation exchange capacity (mmolc kg⁻¹).

Fig. 4: (a) Number of samples and (b) total variance explained (R squared) by each independent linear model as presented in Fig. 1.





Fig. 1:

(a) Complete mineral soil profile 0 – 120 cm depth										
pН	<4	4-4.5	4.5-5	5-5.5	5.5-6	6-6.5	6.5-7	7-7.5	>7.5	All pH
MAP	0.27	0.53	NS	NS	NS	NS	NS	NS	NS	0.21
MAT	-0.21	NS	NS	-0.52	NS	NS	NS	NS	NS	-0.13
LAI	-0.22	NS	NS	-0.20						
Clay	-0.23	-0.25	NS	NS	NS	NS	NS	NS	NS	NS
CEC	0.19	NS	NS	NS	NS	0.78	0.86	0.84	0.62	0.51
(b) Topsoil 0-30 cm depth										
pН	<4	4-4.5	4.5-5	5-5.5	5.5-6	6-6.5	6.5-7	7-7.5	>7.5	All pH
MAP	0.39	0.52	NS	NS	NS	0.52	NS	0.29	NS	0.22
MAT	-0.12	NS	-0.40	NS	NS	NS	NS	NS	NS	-0.14
LAI	-0.19	NS	NS	NS	NS	NS	NS	-0.27	NS	-0.20
Clay	-0.16	NS	NS	0.16						
CEC	0.23	NS	0.57	0.73	0.88	0.87	0.84	0.88	0.80	0.60
(c) Subsoil 30-120 cm depth										
pН	<4	4-4.5	4.5-5	5-5.5	5.5-6	6-6.5	6.5-7	7-7.5	>7.5	All pH
MAP	NS	0.42	0.43	NS	NS	NS	NS	0.29	0.21	0.21
MAT	-0.45	NS	NS	-NS						
LAI	-0.29	NS	NS	NS	NS	NS	NS	-0.31	NS	-0.16
Clay	-0.26	-0.23	-0.43	NS	NS	NS	NS	0.37	NS	NS
CEC	NS	NS	-0.47	NS	NS	0.68	NS	0.79	0.73	0.73













Fig. 3:











Fig. 4:









Table 1: Range of climatic, vegetation and edaphic variables for complete mineral soil profiles (0-120 cm depth), topsoils (0-30 cm depth) and subsoils (30-120 cm depth). MAP, mean annual precipitation; MAT, mean annual temperature; LAI, leaf area index; SOC, soil organic carbon content, CEC eff., effective cation exchange capacity.

Soil depth	0-120 cm	0-30 cm	30-120 cm		
MAP (mm)	636-2484				
MAT (°C)	0.1-12.0				
Elevation (m a.s.l.)		277-2207			
LAI	2-7.2				
SOC (g kg ⁻¹)	1.3-376.8	6.0-376.8	0-229.0		
CEC eff. (mmolc kg ⁻¹)	11.4-753.2	20.4-1046.4	6.2-727.9		
Clay (%)	1.2-74.7	1.5-74.6	0.8-75.6		
рН	3.0-8.0	2.8-8.0	3.0-8.1		





Table 2: (a) Standardized coefficients indicating explanatory power of climatic, vegetation and edaphic variables in predicting the content of SOC, and (b) amount of variance (% of R squared) explained by the explanatory variables for complete mineral soil profiles (0-120 cm depth), topsoils (0-30 cm depth) and subsoils (30-120 cm depth). The R squared of metrics is normalized to sum to 100 %. MAP, mean annual precipitation; MAT, mean annual temperature; LAI, leaf area index; CEC eff., effective cation exchange capacity; n., number of samples; NS, non significant.

	Complete pH	range				
Depth (cm)	0-120	0-30	30-120			
(a) Standardized regression coefficients in predicting SOC (g kg ⁻¹)						
MAP (mm)	0.31	0.30	0.26			
MAT (°C)	-0.14	NS	-0.18			
LAI	-0.16	-0.13	-0.11			
Clay (%)	-0.26	-0.26	-0.23			
CEC eff. (mmolc kg ⁻¹)	0.48	0.66	0.32			
R squared	0.26	0.39	0.17			
n.	1138	1146	1099			
(b) Relative importance (% of R squared) in predicting SOC (g kg ⁻¹)						
MAP (mm)	26	18	31			
MAT (°C)	15	4	28			
LAI	17	9	7			
Clay (%)	7	9	17			
CEC eff. (mmolc kg ⁻¹)	35	60	17			