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1 **Liquid and plastic limits of clayey, organic C-rich mountain soils: role of organic matter and mineralogy.**

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8

9 **Abstract**

10 The soil liquid (LL) and plastic limit (PL), and their difference PI (plasticity index) are physical properties
11 related with the soil mechanical behavior, determined on the <0.425 mm soil fraction, and used in different
12 fields of earth and soil sciences. They are known to depend on soil organic matter (SOM) and/or clay
13 content, but these soil properties are generally determined on the <2 mm fraction (fine earth).
14 Furthermore, these dependencies can be affected by many qualitative aspects, such as the specific surface
15 area (SSA) and the equivalent basal spacing (EBS) of clay minerals, and clay aggregation. The aims of our
16 research were therefore i) to investigate the role of clay and SOM contents in a set of clay- and organic C-
17 rich mountain soils, considering both the <2 mm and <0.425 mm fractions; ii) to assess the effect of the
18 mineralogical composition (type of minerals, EBS and SSA) and clay aggregation in the <0.425 mm fraction.
19 The relationships observed between Atterberg limits and the clay and organic C amounts evidenced the
20 importance of considering the <0.425 mm soil fraction instead of the fine earth. The relative role of clay
21 and organic C contents in the <0.425 mm fraction was comparable for LL, while in the case of PL the most
22 relevant variable was TOC. Therefore, in a first stage of increasing water content, the role of SOM is
23 fundamental (i.e. in the semisolid state and plastic interval), then the interactions among clay particles
24 dominate. No clear relationship was instead observed with the mineralogical composition, although SSA
25 and EBS were both correlated positively with LL and PI. The aggregated clay amount was positively related
26 with LL and PI, and EBS. This, together with the relationships with EBS and SSA, evidenced that a role of clay
27 exists in determining the soil mechanical behavior, but it seems to be more related to the interactions
28 among clay particles occurring in the soil, than to the simple mineralogical composition. The findings
29 suggested that, while PL seems to be more controlled by the organic fraction, LL and PI are more influenced
30 by SOM and clay minerals and their interactions.

31

32 **Keywords:** Atterberg, specific surface area, soil mineralogy, equivalent basal spacing, Ligurian Alps

33 **List of abbreviations:** LL (liquid limit), PL (plastic limit), PI (plasticity index), SOM (soil organic matter), MIF
34 (mineral intensity factor), SSA (specific surface area), EBS (equivalent basal spacing), BS (base saturation) TC
35 (total C), TOC (Total organic C), SEE (standard error of the estimate), VIF (variance inflationary factor).

36 1. Introduction

37 In earth sciences, the plastic limit (PL) and liquid limit (LL) were defined by Atterberg (1911) as the soil
38 gravimetric water contents (%) needed for the transition of the < 0.425 mm fraction from the solid to
39 plastic state, and from the plastic to liquid state, respectively. The detailed methods description is provided
40 by ASTM and BSI standard methods (BSI, 1990; ASTM D 4318–10e1, 2010), and by McBride (2002).

41 Atterberg limits are relevant for a wide range of purposes such as soil classification in engineering
42 (Atterberg, 1911; Casagrande, 1932), soil mechanics (Haigh 2012; Haigh et al., 2013; Zbik et al., 2015),
43 agricultural soil management and plant growth (Keller and Dexter, 2012; Abbaspour-Gilandeh and Sedghi,
44 2015, Zolfaghari et al., 2015a), and natural hazard assessment (Yalcin, 2007; Ramezanpour et al., 2010;
45 Diaz-Hernandez et al., 2015), with a particular focus on sloping areas (Summa et al., 2010; Stanchi et al.,
46 2013, 2015).

47 In agricultural and forest soils, LL and PL have been often related with soil organic matter (SOM) and clay
48 contents (e.g. De La Rosa, 1979; De Jong et al., 1990; Mbagwu and Abeh, 1998; Schmitz et al., 2004).
49 However, as pointed out by Blanco-Canqui et al. (2006) and Zolfaghari (2015b), the studies on Atterberg
50 limits and related soil properties often gave contrasting results; dependencies were not always observed
51 and, when present, they could be affected by a large number of additional characteristics such as SOM
52 type, hence land use, and soil mineralogy. Moreover, soil databases normally report the chemical
53 properties of the fine earth fraction (i.e. <2 mm), which is the standard fraction for analytical purposes (e.g.
54 van Reeuwijk, 2002; Soil Survey Staff, 2014a).

55 Stanchi et al. (2015) found no correlation between LL, PL and the clay fraction content, while they observed
56 a positive relationship with organic C on a dataset of mountain forest soils in the Aosta Valley (N-W Italy),
57 particularly in SOM-enriched soil horizons such as A, Bs, and Bh. They therefore concluded that SOM was
58 the dominating property controlling LL and PL in the mountain topsoils of the study area, and that its effect
59 in deeper soil horizons was visible only when the organic C amount was above a certain threshold (around
60 20 g kg⁻¹). This predominance of SOM seems reasonable, considering that the clay fraction of the studied
61 soils was relatively scarce (always less than 20%), as often observed for alpine soils and it showed a small
62 inter-sample variation. Keller and Dexter (2012) found that LL and PL were well related with both SOM and
63 texture in a dataset of agricultural topsoils (i.e. tilled layer) from EU and USA, where the correlation with
64 clay was stronger for LL than PL, even if the reasons were not clear. In addition, they concluded that PL was
65 not affected by clay contents lower than 35%, confirming that a linear correlation cannot always be
66 foreseen.

67 Mineralogical characteristics may play some role in determining the soil mechanical properties. Depending
68 on the charge density of exchangeable cations that provide strong hydrophilic sites for solvent sorption
69 (Schoonheydt and Johnston, 2006), several water layers may be incorporated in the interlayer of
70 phyllosilicates with low layer charge, such as smectites. When instead the layer charge is higher, as in illites,

71 or the interlayer is occupied by Mg-octahedral sheets or stable Al polymers, as in lithogenic or pedogenic
72 chlorites (Tolpeshta et al., 2010), the amount of water that can be sorbed is much lower. As layer charge
73 affects the interlayer distance, an index that may help understanding the effects of mineralogy on soil
74 mechanical properties is the equivalent basal spacing (EBS), a global evaluation of the interlayer distance
75 suggested by Schmitz et al. (2004). Badia et al. (2015) studied the relationships between Atterberg limits
76 and soil mineralogy in illite-rich soils using either semi-quantitative mineralogical analysis or EBS, and found
77 that the least plastic soils had abundant quartz and carbonates. Hajjaji et al. (2010) observed a good
78 correlation between LL, PL and EBS for sediments taken from stratigraphic sequences in Tunisia.
79 Furthermore, different clay minerals have a different specific surface area (SSA), which may vary depending
80 on the formation pathway and environment, globally affecting the colloidal behavior and the water
81 sorption capacity. Dolinar (2012) observed a direct relationship between the Atterberg limits (LL, PL) and
82 the SSA. Keller and Dexter (2012) speculated that the mechanical behavior of soils at water contents higher
83 than the liquid limit might be more controlled by SSA than the one in the plastic range. Among the
84 qualitative aspects related with the clay fraction, Keller and Dexter (2012) highlighted the role of the
85 aggregated clay particles that can actually behave as silt-sized grains in soils, hence reducing its plasticity.
86 Some indirect effect of soil aggregation was observed also by Blanco-Canqui (2006), who explained
87 differences in soil consistency with variations in SOM amount and the effects it had on structure. Also
88 Zolfaghari et al. (2015b) remarked that clay aggregation and SOM quality might need further investigation
89 with respect to Atterberg limits, and this might be particularly true for the surface soil horizons where the
90 influence of the organic component is more pronounced.

91 Therefore, despite some general consensus on the influence of the clay fraction and organic matter on the
92 soil liquid and plastic limits, some points still need to be addressed by research. First, while LL and PL are
93 determined on the <0.425 mm soil fraction, the other soil properties (e.g. texture, SOM content) generally
94 refer to the fine earth soil fraction (i.e. <2 mm). In addition, the role of clay mineralogy in organic matter-
95 rich soil horizons such as non-agricultural soils (e.g. mountain forest topsoils), potentially prone to natural
96 hazards, is still poorly studied, as a large part of the research focuses on agricultural soils, sediments or
97 stratigraphic sections.

98 In particular, little is known about mid-altitude mountain soils located in geographical regions where even
99 small changes in temperature and precipitation largely affect snowfall frequency and amount, thus altering
100 the precipitation regime (Terzago et al., 2013) with potential effects on natural hazards frequencies. We
101 therefore investigated a set of forest soils (Ligurian Alps, NW Italy), that are relatively rich in both the clay
102 fraction and SOM, with the aim of evaluating the relationships among LL, PL, and these soil properties from
103 both the quantitative and the qualitative point of view. In particular we investigated:

- 104 1) the relative effect of clay and organic matter. We hypothesized that LL and PL might be better
105 correlated with the properties of the <0.425 mm soil fraction than those of the fine earth;

106 2) the relationships between the mineralogical composition and aggregation of the clay fraction, and
107 LL and PL in the <0.425 mm size range.

108 **2. Materials and Methods**

109 *2.1. Description of the study area*

110 The study area is located in the Ligurian Alps (NW-Italy, Figure 1) at elevation ranging from 800 to 1600 m
111 a.s.l., at the boundary between Piemonte and Liguria Regions, 30 km far from the Mediterranean Sea. It is
112 particularly interesting for the combination of environmental factors, as it is located at the convergence of
113 the Mediterranean, European, and Alpine biogeographic regions (Cornara et al., 2014).

114 The average annual temperature ranges between 4 and 7.5 °C, decreasing with altitude and with local
115 variability with slope aspect. The annual precipitation is around 1000-1200 mm, with spring and fall
116 maxima, and summer minima (Biancotti et al., 1998). The soil moisture regime is always udic, while the
117 temperature regime varies from mesic (below 1300 m a.s.l.) to frigid (above 1300 m a.s.l.). Forests cover a
118 large part of the territory and are dominated by beech (*Fagus sylvatica* L.), chestnut (*Castanea sativa* Mill.),
119 larch (*Larix decidua* L.), fir (*Abies alba* Mill.), and Scots pine (*Pinus sylvestris* L.). The soils of the area develop
120 on a wide range of parent materials, from pelitic and metapelitic sedimentary (or weakly metamorphosed)
121 rocks to hard and coarse grained quartzite. Pelitic and metapelitic rocks allow the development of relatively
122 clay-rich soils that are therefore characterized by both high SOM contents, which are typical of forest soils,
123 and fine texture (with both lithogenic and pedogenic layer silicates). Quartzite instead supports the
124 development of coarser textured soils. A detailed description of soils, vegetation cover, and geology of the
125 area is provided by Catoni et al. (2016). We selected 11 soil samples on varying parent material (Table 1): 2
126 were on quartzite or metamorphic porphiroids, 3 on limestone-dolostone, and 6 on the Helminthoides
127 Flysch unit formed by both calcareous and non-calcareous weakly metamorphosed siltstones and
128 claystones discontinuously interbedded by sandstones. Topsoils (0-10 cm) were collected, then air dried
129 and sieved at 2 mm (fine earth fraction).

130 *2.2. Chemical and physical analyses*

131 On the <2 mm fraction, the total C (TC) contents were determined by dry combustion with an elemental
132 analyzer (NA2100 CE Instruments, Rodano, Italy). The content of inorganic C was measured with the TIC-
133 solid module of a TOC analyzer (Vario TOC132 Elementar, Hanau, Germany). The total organic C (TOC)
134 content was computed as the difference between C measured by dry combustion and carbonate-C. Soil
135 particle distribution was determined by the pipette method with Na-hexametaphosphate after pre-
136 treatment for SOM oxidation with H₂O₂ (Gee and Bauder, 1986). As TOC is linearly related to SOM, it was
137 considered as an indicator for SOM content in further statistical analyses. The exchangeable amounts of
138 elements (Ca, Mg, K and Na) were determined by AAS after extraction with NH₄⁺-acetate at pH 7.0 and the
139 CEC was determined spectrophotometrically after back-exchange of NH₄⁺ with NaCl (Soil Survey Staff,

140 2014a). Only the base saturation (BS, sum of measured exchangeable cations/CEC*100) and the
141 exchangeable Ca²⁺ contents are reported.

142 The fine earth fraction was then dry-sieved at 0.425 mm and we determined LL and PL according to the
143 standard methods (ASTMD 4318–10e1, 2010), i.e. the automatic cone penetrometer (cone angle 30°, total
144 mass 80 g, penetration depth 20 mm) and the thread rolling method. The plastic index (PI) was computed
145 as the difference between LL and PL. TOC content was determined on the <0.425 mm fraction as already
146 done for the <2 mm fraction. We plotted all our samples on the plasticity chart, ideated by Casagrande
147 (1932; and then modified by Howard, 1984). The meaning of the chart has been deeply discussed by
148 Polidori (2003) and Polidori et al. (2004). It is the scatterplot of PI vs. LL, used in geotechnical engineering to
149 represent graphically the mechanic behavior of clays. In particular, the A-line in the chart allows separating
150 materials with different mechanical behavior, i.e. a different relationship between PI and LL. The U-line
151 instead represents an upper envelope for most of the world soils (Zolfaghari et al., 2015b).

152 The clay of the <0.425 mm size fraction, to be used for mineralogical analyses, was separated with two
153 dispersion methods, i.e. only water dispersion (clay_{<0.425mmw}) and Na-hexametaphosphate dispersion after
154 H₂O₂ pre-treatment (clay_{<0.425mmPER}) as reported in Stanchi et al. (2008). The difference between the two clay
155 contents in each soil sample (clay_{<0.425mmPER} - clay_{<0.425mmw}) was computed, and interpreted as a measure of
156 the amount of aggregated clay present in the <0.425 mm size range.

157 The SSA of the clay separated from <0.425 mm soil fraction was estimated using the methylene blue
158 absorption method (spot test) as described in ASTM (1984), which allows to consider both the external and
159 internal surface areas of the clay minerals.

160 The soil specific surface area (SSA, expressed in m² g⁻¹) was computed as:

$$161 \quad SSA = \left(\frac{1}{320}\right) \left(\frac{10}{1000}\right) (vol) Av \left(\frac{A_{mb}}{m}\right) \quad (1)$$

162 where 320 g mol⁻¹ is the molar weight of methylene blue, 10/1000 is the concentration of the methylene
163 blue solution (10 g l⁻¹), vol is the amount of methylene blue solution added (ml), Av is Avogadro number
164 (molecules mol⁻¹), A_{mb} is the covering area of methylene blue (130·10⁻²⁰ m² molecule⁻¹), m is the mass of dry
165 soil (g). The methylene blue determination was first carried out for water-dispersed clay (W) and then
166 repeated on H₂O₂-pretreated samples (PER).

167 All chemical and physical analyses were made in duplicate and then averaged.

168 2.3. Mineralogical analyses

169 The mineralogical composition (<0.425 mm fraction) was evaluated through X-ray diffraction using a
170 PW1810 diffractometer (40 kV and 20 mA, Co K α , graphite monochromator) on the clay fraction (both after
171 water dispersion and after Na-hexametaphosphate dispersion plus SOM oxidation). The clay fraction was
172 saturated with MgCl₂ and analyzed as air-dried (AD), ethylene glycol solvated (EG), and heated (550°C)
173 oriented mounts. Scans were made from 3 to 35 °2 θ at a speed of 1 °2 θ min⁻¹.

174 Chlorite was identified by the presence of a 1.4-nm peak after 550°C heating, illite by the 1.0-nm peak in

175 the AD diffraction pattern, swelling clay minerals by the presence of a peak or shoulder at 1.6–1.7 nm after
176 EG treatment. Interstratified minerals were recognized by the presence of a diffraction peak or band
177 exhibiting a behavior intermediate to that of the single components. Associated minerals (i.e. quartz,
178 feldspars) were identified by peak positions according to the data reported by Brown (1980).

179 A semi-quantitative evaluation of mineral abundance was performed by taking into account the areas of
180 the peaks and the MIFs (mineral intensity factors) reported by Islam and Lotse (1986). For the analysis, the
181 background was subtracted and the peak intensities and positions were calculated using the second
182 derivative option of the PowderX software (Dong, 1999).

183 EBS (Equivalent basal spacing) was computed as in Schmitz et al. (2004) as:

$$184 \quad EBS = TCF \sum (Cf_i \times BS_i^{(001EG)}) \quad (2)$$

185 where TCF is the total amount of phyllosilicate clay in the sample (% weight fraction) and Cf_i is the
186 percentage abundance of the i^{th} mineral; Bs_i is the average basal spacing in nm (001 or 002) referred to the
187 ethylene glycol treatment, thus the highest is the index the highest the content of smectite and other
188 swelling minerals (e.g. swelling mixed layers or low charge vermiculite). Because of the abundance of
189 chlorite whose interlayer is filled with a brucitic or gibbsitic sheet that cannot sorb water, the EBS was
190 modified by attributing to chlorite a basal spacing of 0.7 nm (instead of 1.4 nm) that is equivalent to that of
191 kaolinite. EBS was computed both for water-extracted clay (EBS_W) and pre-treated clay (EBS_{PER}).

192 2.4. Data treatment

193 All the statistical analyses were carried out with SPSS software version 20.0. Multiple regression analysis
194 was performed in order to quantify the relative clay and SOM contribution to LL, PL and PI.

195 3. Results

196 The $TOC_{<2mm}$ content ranged from 18.5 to 84.3 g kg⁻¹ (Table 1) and was positively correlated with $TOC_{<0.425mm}$
197 ($r=0.78$, $p<0.01$, Table 2). The studied soils had a varied clay content (Table 1) with values between 124 and
198 434 g kg⁻¹ for the <2 mm fraction. The clay fraction contents of the <0.425 mm fraction were in the range
199 21-118 g kg⁻¹ for $clay_{<0.425mmw}$ and 134-332 for $clay_{<0.425mmPER}$. These values were highly variable after each
200 extraction method, giving rise to differences in the range 61-272 g kg⁻¹ (Table 1), and no correlation was
201 found between clay content in the two soil fractions (i.e., <2 and <0.425 mm) or between the two methods
202 of extraction in the <0.425 mm soil fraction (Table 2). Ca²⁺ always dominated among basic cations and the
203 base saturation was extremely variable depending on parent material (average 51%).

204 Soil LL (Table 1) ranged from 42% to 85%; PL ranged from 31 to 61% and could not be determined for
205 sample 7. LL and PL were significantly correlated with each other ($r=0.87$, $p<0.01$, Table 2).

206 PI ranged from 5 to 24% (Table 1), i.e. soils ranged from slightly to moderately plastic according to the
207 ASTM D 4318–10e1 (2010) classification. Considering Casagrande's chart plotted in Figure 2, all samples fell
208 below the U-line, and also fell on or below the A-line (mostly in the area representing "inorganic silts with
209 high compressibility and organic clays").

210 LL and $\text{TOC}_{<2\text{mm}}$ were not significantly correlated (Table 2), while a positive correlation was present between
211 PL and $\text{TOC}_{<2\text{mm}}$ ($r=0.69$, $p<0.05$). Both LL and PL were better correlated with $\text{TOC}_{<0.425\text{mm}}$ ($r=0.71$, $p<0.01$;
212 $r=0.85$, $p<0.01$, respectively). LL and PL were not correlated with $\text{clay}_{<2\text{mmPER}}$. No relationship was present
213 with $\text{clay}_{<0.425\text{mmW}}$, while a positive correlation was visible between LL and $\text{clay}_{<0.425\text{mmPER}}$ ($r=0.64$, $p<0.05$), as
214 well as between PI and $\text{clay}_{<0.425\text{mmPER}}$ ($r=0.72$, $p<0.01$). The difference between $\text{clay}_{<0.425\text{mmPER}}$ and
215 $\text{clay}_{<0.425\text{mmW}}$ contents showed a strong relationship with LL ($p=0.73$, $p<0.05$) and PI ($r=0.84$, $p<0.01$), as
216 reported in Table 2. No relationship of Atterberg limits with base saturation and exchangeable Ca contents
217 was observed (data not shown).

218 Stepwise multiple regression including clay and TOC contents was significant and evidenced a similar
219 contribution of clay and TOC to the variability of LL (equation 3), while the determination coefficient was
220 lower for PL and the only significant variable was TOC (equation 4).

$$221 \text{ LL} = 0.687 \text{ TOC}_{<0.425\text{mm}} + 0.615 \text{ Clay}_{<0.425\text{mmPER}} \quad \text{adjR}^2=0.85, \text{ SEE} = 4.4 \quad (3)$$

$$222 \text{ PL} = 0.847 \text{ TOC}_{<0.425\text{mm}} \quad \text{adjR}^2=0.68, \text{ SEE} = 4.7 \quad (4)$$

223 VIF (i.e. variance inflation factors), used as indicators of the goodness of the regression, were always
224 around 1, so that a strong multicollinearity between variables could be excluded. Both regressions were
225 significant ($p<0.01$).

226 The mineralogical composition of the clay fraction showed a complex suite of minerals, present both as
227 single and mixed layer phases (Figure 3). The clay mineralogical composition of the studied samples
228 (considering always the $<0.425\text{mm}$ fraction, two dispersion methods) is detailed in Table 3 and depended
229 on the clay dispersion method. Illite was detected in all samples (range 16-50% for W, 8-87% for PER).
230 Smectite in W dispersion was observed, though in limited amounts, only in samples 6 and 16, while traces
231 were present in sample 17. Among PER samples, 1-4-7-16, and 17 showed some amount of the mineral, but
232 in most cases the relative proportion was $\leq 2\%$. Chlorite was present in all W-dispersed samples in variable
233 amounts (1-28%); in PER samples a comparable range was observed. Vermiculite was always present, and
234 exceeded 50% in samples 1, 4, 12 (W). After PER pre-treatment, it was present in all samples except 17, and
235 ranged from 10 to 49%. Interstratified minerals were sporadically present, even if in some cases they
236 accounted for a relevant proportion of the total (e.g. W samples 7, 9, 11, 16, 17 Table 3). In PER samples
237 the amount of interstratified minerals generally decreased, with the exception of illite-vermiculite in
238 samples 7, 9, 11, 12. In the clay fraction, the amount of quartz was always $<3\%$ and feldspars were always
239 below 10%. EBS never exceeded 0.145 nm for water dispersible clay minerals (W; Table 3) and increased
240 after the removal of SOM (EBS for PER ranged from 0.158 to 0.388 nm). The SSA of the $<0.425\text{mm}$ soil
241 fraction differed between treatments only for sample 17. The global range of SSA_w was 12.2-85.6 m^2g^{-1} ,
242 without any clear trend with mineralogy.

243 No significant relationship was visible between Atterberg limits and EBS_w (Fig. 4a), nor mineral abundances,
244 but EBS_{PER} was related to LL (Fig. 4b). EBS_{PER} was also strongly correlated with $clay_{<0.425mmPER} - clay_{<0.425mmW}$
245 ($r=0.843$, $p<0.01$, data not shown). SSA_w was related with LL and PI as visible in Figure 4c.

246

247 4. Discussion

248 LL and PL values (Table 1) were in the range reported for Italian mountain soils (e.g. Stanchi et al., 2012,
249 2015). However, the averages were slightly higher than reported from a similar number of topsoil samples
250 from previous studies (e.g. Stanchi et al., 2012, PL=38, LL=49). This was likely due to the different
251 environmental characteristics of this study area, i.e. often finer soil textures and higher organic matter
252 contents, and was confirmed by higher PI values (average 16% vs. 10% of the previous research). The
253 relatively high organic matter content was related with the good development of organic horizons in these
254 forest soils, as described by Catoni et al (2016). High $clay_{<2mmPER}$ content was always measured, too, even if
255 we excluded from this study the paleosols which are also abundant in the area (D'Amico et al., 2016).

256 In the <2 mm fraction a positive correlation was present only between $TOC_{<2mm}$ and PL. According to Keller
257 and Dexter (2012) the plastic limit in topsoils is positively related to SOM, but in our dataset, the use of TOC
258 and clay fraction contents determined on the <0.425 mm fraction considerably improved the relationship
259 (Table 2) highlighting the importance of the fraction choice to properly understand the soil mechanical
260 behavior. This suggests that the contrasting results previously reported in literature about the variables
261 controlling LL and PL can be partially related to methodological issues, as the amounts of clay fraction in the
262 <2 mm and <0.425 mm are not proportional.

263 Equation (3) and (4) obtained by regression of TOC and/or clay fraction contents in the finer fraction
264 (<0.425 mm) showed a good predictability of LL and PL from these properties in terms of significance and
265 R^2 . While for LL the two considered factors showed a similar relevance (eq. (3)), only $TOC_{<0.425mm}$ was
266 retained in the model for PL prediction and explained a relevant part of the variability, as visible from eq.
267 (4). The importance of the considered factors was further confirmed by the correlation observed between
268 the amount of aggregated clays in the <0.425 mm fraction (i.e. $(clay_{<0.425mmPER} - clay_{<0.425mmW})$) and both LL
269 and PI. As visible from the correlations reported in Table 2, the amount of aggregated clays was strongly
270 related with the plastic index of the soils in the study area, i.e. soils with a wider range of plastic behavior,
271 together with higher LL, also showed higher amounts of aggregated clays in the <0.425 mm fraction. This
272 suggests that, in the studied environment, PL seemed to be more controlled by the amount of organic C,
273 while LL seemed to be controlled by the clay fraction in terms of abundance and degree of aggregation
274 promoted by SOM.

275 The conceptual stages of the clay/water interactions taking place for increasing water content can explain
276 these findings. First, water fills the soil pores (at the solid/semisolid state). Once pores are filled, water is
277 retained by SOM due to its intrinsic hydrophilic behavior (e.g. Yang et al., 2014); in such conditions the soil
278 is at the semisolid or plastic state. Then water is adsorbed by clay minerals (transition from plastic towards

279 liquid state). For increasing water contents above the liquid state, the specific soil volume further increases
280 and the clay particles are dispersed. At the liquid state the separation distances between clay particles or
281 clay-sized aggregates are in equilibrium with the inter-particle forces (Pandian and Nagaraj, 1990).
282 Therefore, in a first stage of increasing water content, the role of SOM is fundamental (in particular, in the
283 semisolid state and plastic interval), then the interactions among clay particles become more relevant, up
284 to full colloidal repulsion (i.e. above LL).

285 Keller and Dexter (2012) speculated that the mechanical behavior of soils with water content exceeding LL
286 might be more controlled by SSA than the one in the plastic range. It is also generally assumed that SSA in
287 fine grained soils mainly depends on clays (Dolinar, 2012). However previous research (e.g Dolinar, 2012)
288 quantified SSA by N₂ adsorption, which allows to measure only the external surface area of minerals and is
289 little sensitive to the SSA of SOM (Catoni et al., 2014). Despite the differences in SSA determination
290 methods, our findings seem to support this hypothesis, as the soil SSA_w was positively related with LL and
291 PI but not PL, which instead seemed to be more controlled by SOM, as also showed by the regressions
292 obtained. Some role of SOM was however evidenced by the methylene blue spot test for sample 17
293 (chestnut stand on quartzite), displaying a reduction of SSA after SOM oxidation (Table 2). This specific
294 behavior suggested a strong contribution of SOM to available surfaces, in line with forest environments
295 with SOM-rich topsoil. Some general considerations can be made on the base of soil profile morphology
296 and description. Sample 17 showed a loose structure, suggesting a weaker degree of organo-mineral
297 interactions. Moreover, this sample had a much higher C/N ratio than the others with the same vegetation
298 used in this work (17.3 vs an average of 13.7, data not shown), thus indicating a lower degree of
299 transformation of organic matter. Upon destruction of SOM, new mineral surfaces and pores become
300 available in case of mineral-organic interactions (Echeverría et al., 1999), while if organic matter and
301 minerals were present as poorly transformed separated phases, SOM oxidation would simply result in area
302 subtraction. No clear relationship was visible between LL, PL and mineralogy, i.e. no correlation was
303 present between LL, PL and the abundance of specific minerals, or with subsets of minerals (e.g.
304 interstratified or expandable). The positive relationship between EBS_{PER} and LL (Fig. 4) indicates that soils
305 with high EBS_{PER} require higher amounts of water to pass from plastic to liquid state, i.e. EBS somehow
306 affects clay-water interactions. This is in agreement with the positive correlation we found between
307 aggregated clay and EBS_{PER}, suggesting that the clay fraction tends to be more aggregated when it contains
308 higher amounts of 1.6 and 1.4 nm phyllosilicates (i.e. smectites and vermiculites), whose interlayer may
309 incorporate water molecules. A general trend towards a greater aggregation of more highly charged
310 minerals (such as, e.g., vermiculite vs illite) can be expected, but the aggregation phenomena in soils are
311 complicated by the presence of organic matter and by the charge of sand particles on which clay particles
312 react (Falsone et al., 2007, 2016). Another factor that may affect clay aggregation is the presence of
313 divalent cations, such as Ca²⁺, on the cation exchange complex (e.g. Wuddivira and Camps-Roach, 2007)

314 that may act as a bridge between negatively charged components such as SOM and layer silicates. Despite
315 the variability in exchangeable Ca contents of the soils, we did not find any correlation between Ca^{2+} and
316 Atterberg limits or clay aggregation. The lack of correlation with PL may be related to the dominant effect
317 of SOM, while in the case of LL, the high amounts of water added may induce clay dispersion even in the
318 presence of flocculating cations with large hydration shell such as Ca^{2+} (Sposito, 1989). These complex
319 interactions may justify the absence of a clear trend in increase or decrease of single specific minerals in
320 the aggregated clay (Table 3) and the lack of correlations between limits and mineralogy that are often
321 assumed to be present.

322

323 **5. Conclusions**

324 We investigated the relationship between the Atterberg limits (LL, PL) and clay fraction, and organic matter
325 contents in forest topsoils from the Ligurian Alps. While LL did not show any correlation with TOC content
326 of the <2 mm fraction, and PL only a weak one, strong positive correlations were instead visible between
327 both Atterberg limits and the TOC content of the <0.425 mm fraction, i.e. the one used for Atterberg limits
328 determination according to international standard methods. We also observed a relationship between LL
329 and clay_{<0.425mmPER}. Therefore, we can conclude that the observed relationships are more evident when the
330 <0.425 mm fraction is considered, as hypothesized in the aims, and contrasting results about the role of
331 these variables in previous research might be partly due to methodological issues.

332 The role of the clay fraction and SOM in the <0.425 mm size fraction was investigated through regression
333 analysis, evidencing a similar relevance of the two soil variables in the case of LL, while for PL only the TOC
334 content was retained. This suggested that PL is more controlled by SOM while LL seems to be affected by
335 both SOM and clay fraction. In addition, the amount of aggregated clay in the <0.425 mm fraction strongly
336 affected LL and PI, i.e. the interval of soil plastic behavior, in the studied environment.

337 The semi-quantitative mineralogical composition did not add relevant information. However, the
338 relationships between SSA, EBS and the Atterberg limits provided further insight on the mechanisms
339 explaining the soil behavior in the plastic interval, again evidencing a qualitative role of clay fraction and its
340 aggregation.

341 The findings helped a deeper understanding of the mechanical properties of the studied soils, with
342 potential insights in soil protection and hazard prevention, i.e. soil resistance to large water inputs due to
343 intense rainfall. This might be particularly relevant as mid-elevation areas at intermediate latitudes, such as
344 the study sites, are very sensitive to climate change, and variations in the rainfall pattern might affect the
345 topsoil degradation.

346

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349

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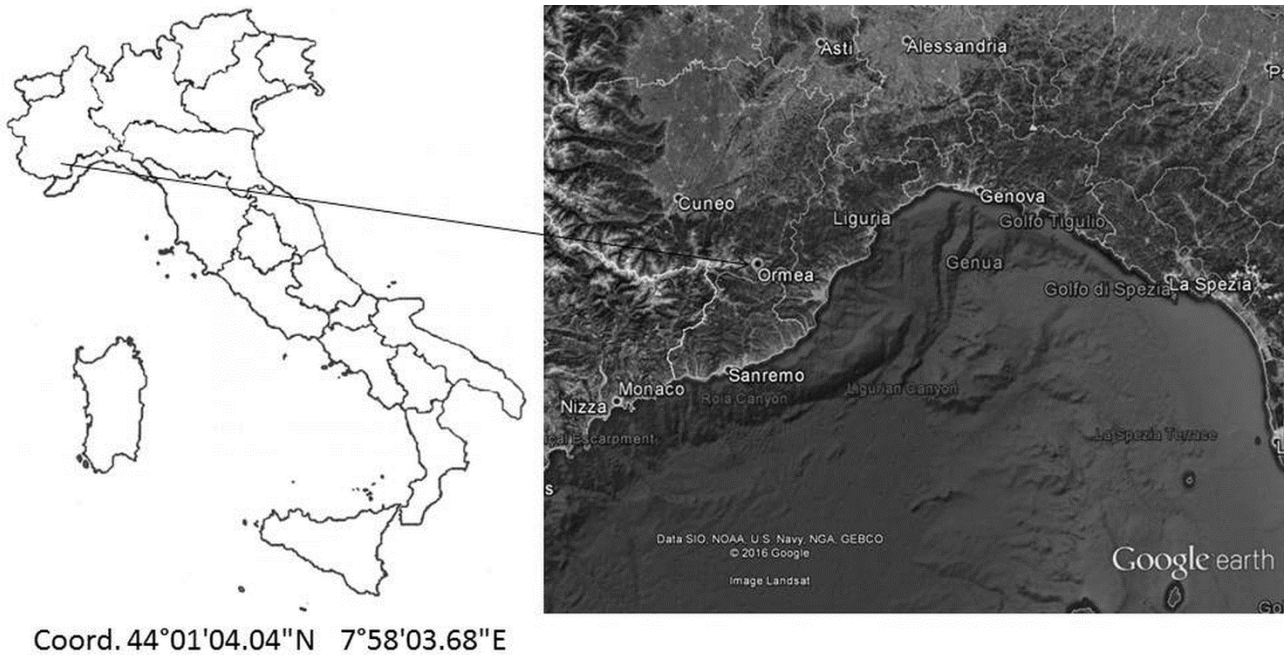
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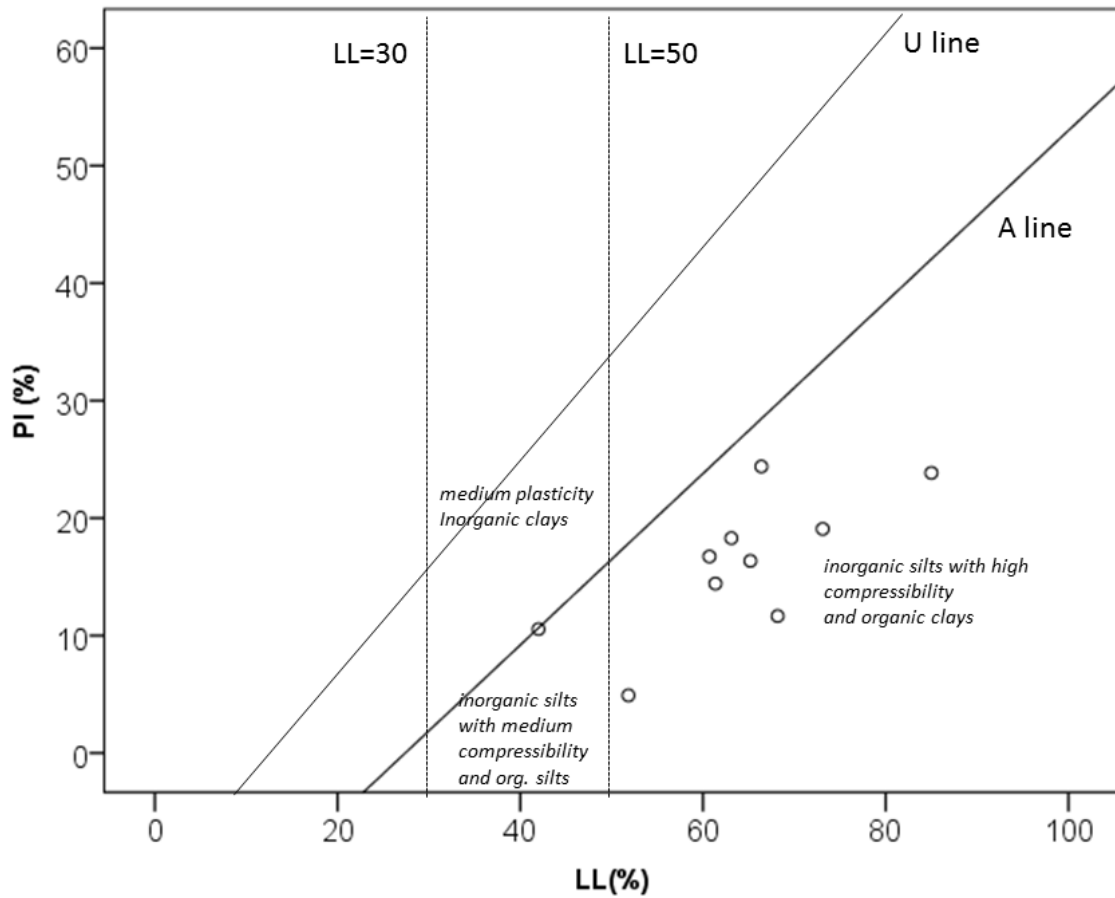
467 **Figure captions**

468 **Figure 1: The study area. Coordinates refer to the town of Ormea, located at the centre of the study area.**



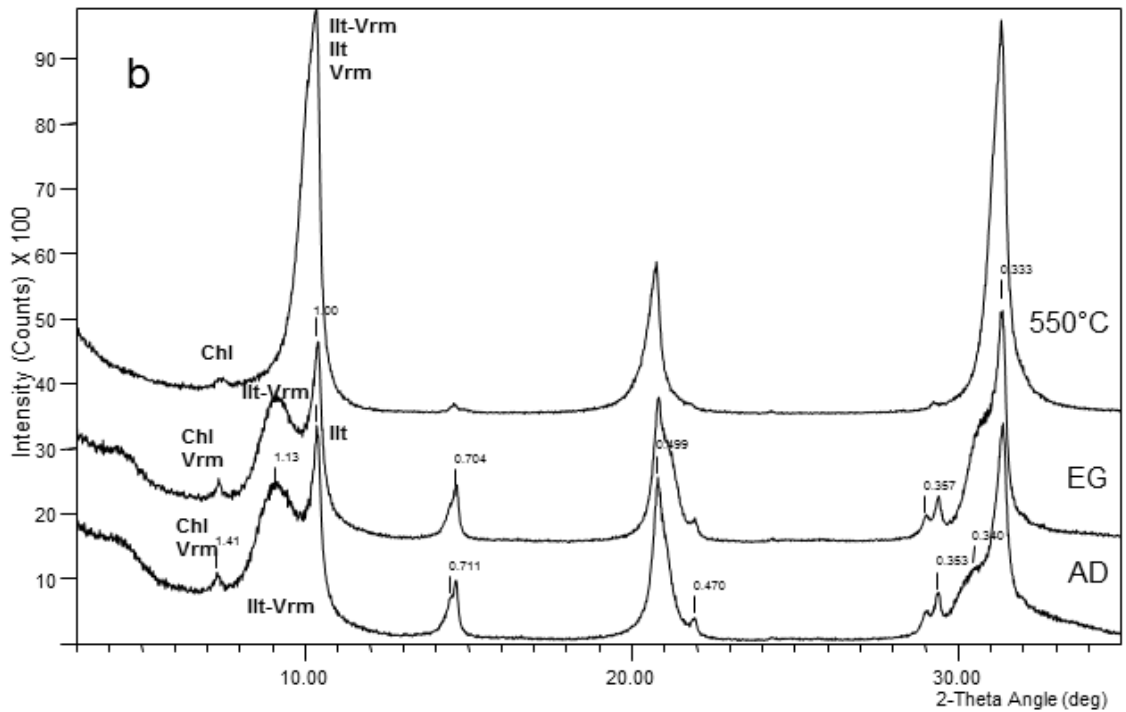
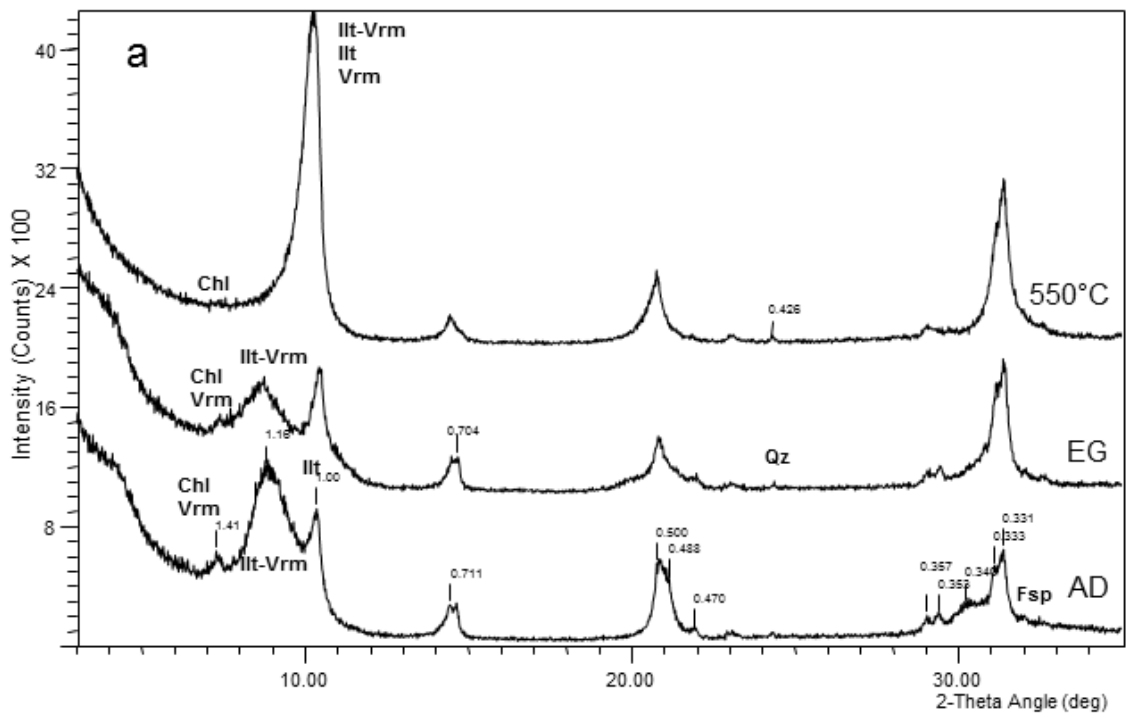
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470 **Figure 2: Casagrande plasticity chart displaying the A-line and the U-line.**

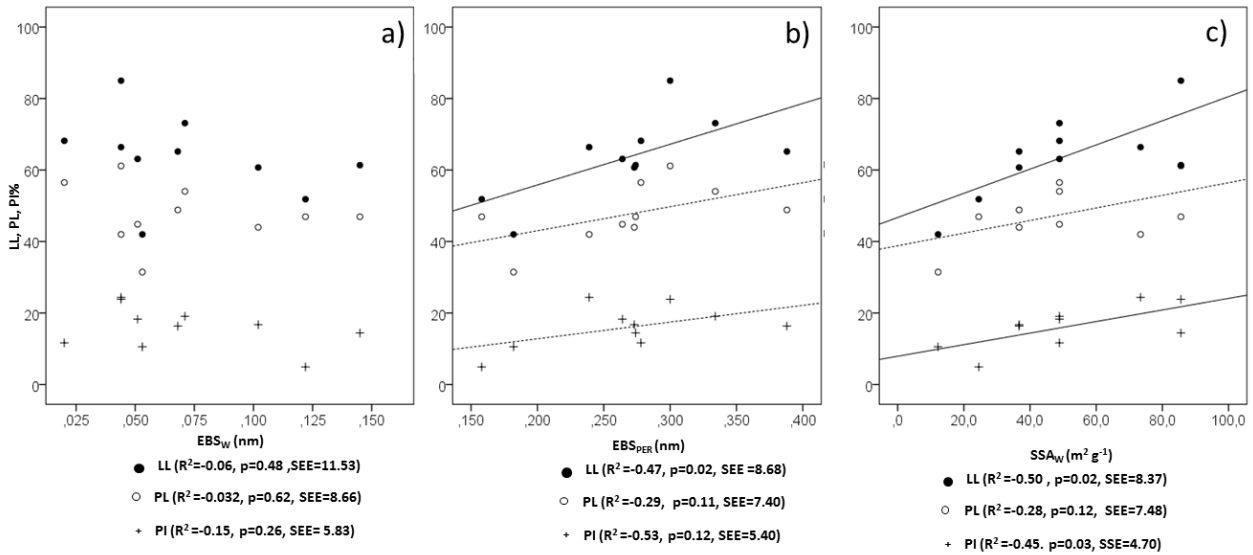


471

472 **Figure 3: XRD patterns of the clay of sample 9 after water extraction (clay_{<0.425mmW}, a) and peroxide**
 473 **oxidation followed by hexametaphosphate dispersion (clay_{<0.425mmPER}, b). AD, EG and 550°C indicate air-**
 474 **dried, ethylene glycol solvated and heated sample, respectively. Peak marks are in nm and the minerals**
 475 **contributing to the peaks are also reported Abbreviations for minerals are reported after Withney and**
 476 **Evans (2010) (Illt (illite), Sme (smectite), Vrm (vermiculite), Chl (chlorite), Qz (quartz), Fsp (feldspars).)**



478 **Figure 4: Relationship between LL, PL, PI and EBS (a,b), SSA_w (c). Significant relationships are represented**
 479 **by a continuous line. The number of samples was 11 for LL, 10 for PL and PI.**



480
 481 **Table 1: Selected chemical and physical properties of the two soil fractions.**
 482

WRB classification	Altitude (m asl)	PM	TOC _{<2mm} (g kg ⁻¹)	Clay _{<2mmPER} (g kg ⁻¹)	pH	TOC _{<0.425mm} (g kg ⁻¹)	BS (%)	Ca _{exc} (cmol _c kg ⁻¹)	LL (%)	PL (%)	PI (%)	Clay _{<0.425mmw} (g kg ⁻¹)	Clay _{<0.425mm} (g kg ⁻¹)
Skeletal Alisol (Loamic, cutanic, Differentic, leptic, Loaminovic), udalf, clayey-skeletal, mixed,	1321	FLY	32.7	132	5.0	21.5	35.7	3.13	52	47	5	99	160
tic Colluvic Protic Eutric (loamic)	1609	FLY	32.0	315	7.0	30.6	90.2	15.93	61	47	14	118	258
orthent, fine-loamy, mixed, acid, frigid	838	LIM	63.2	180	8.1	72.3	100	26.10	68	57	12	21	139
letic Chernozem (Loamic, hyperhumic)													
udoll, loamy-skeletal, mesic													
orthoskeletal Luvisol (Clayic, typereutric, Hyperhumic,	1230	LIM	81.6	434	7.4	55.2	99.0	26.0	55	nd	nd	28	134

apludalf, clayey, mixed, e, nonacid, mesic.														
olluvic Protic Orthodystric (Loamic, Humic)	1666	FLY	49.9	217	5.6	42.6	40.5	6.1	63	45	18	46	256	
rthent, sandy-skeletal, mixed, igid														
yperdystric Cambisol (Humic)	1234	QTZ	32.5	170	4.7	21.7	29.0	2.56	42	31	11	46	146	
rudept, sandy-skeletal, d, mesic														
c Orthoeutric Regosol (Humic)	1021	FLY	84.3	306	5.9	56.2	51.7	11.85	73	54	19	62	290	
rthent, fine-loamy, mixed, e, nonacid, mesic														
etic Protic Hyperdystric (Loamic, Humic)	1032	FLY	18.5	273	4.8	17.9	4.50	0.30	61	44	17	89	274	
rthent, fine-loamy, mixed, d, mesic														
odystric Regosol (Loamic, Humic, Transportic)	875	FLY	20.1	247	5.5	26.0	25.1	3.49	66	42	24	41	251	
rthent, fine-loamy, mixed, e, acid, mesic														
ypereutric Cambisol (Loamic, Humic)	1411	LIM	58.6	370	6.3	36.1	57.2	15.11	65	49	16	59	332	
rudept, fine-loamy, mixed, e, nonacid, frigid														
etic Hyperdystric Cambisol (Lithic, Humic) over Skeletic dystric Regosol (Loamic)	970	QTZ	62.6	124	4.5	81.1	25.7	2.50	85	61	24	49	302	
rudept, loamy-skeletal, eractive, acid, frigid														
			48.7 (23.2)	252 (99)	5.9 (1.2)	41.9 (21.6)	50.7 (32.5)	10.3 (9.4)	63 (11)	48 (8)	16 (6)	60 (30)	231 (72)	

483 *The horizons sequence does not include organic horizons.

484

485 nd: not determined

486 WRB classification (IUSS Working Group WRB, 2014); USDA classification (Soil Survey Staff, 2014b)

487 PM is the soil parent material (FLY: Helminthoides Flysch units; LIM: limestone; QTZ: quartzite)

488 LL: liquid limit; PL: plastic limit; PI: plastic index; for clay fraction subscript indicates the investigated soil

489 fraction (< 2mm or <0.425 mm) and the clay dispersion method (simple water dispersion, W; pre-treatment

490 for SOM oxidation with hydrogen peroxide, PER)

491 BS is the base saturation

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Table 2: Correlation matrix for relevant soil properties. In brackets the p values.

LL (%)	PL (%)	PI (%)	TOC _{<2 mm} (g kg ⁻¹)	TOC _{<0.425 mm} (g kg ⁻¹)	Clay _{<2mm,PER} (g kg ⁻¹)	Clay _{<0.42mm5,w} (g kg ⁻¹)	Clay _{<0.425,PER} (g kg ⁻¹)	Clay _{<0.425,PER} (g kg ⁻¹)
	0.87 (0.001)	0.73 (0.009)	0.39 (0.238)	0.71 (0.015)	-0.09 (0.800)	-0.16 (0.644)	0.64 (0.035)	0.73 (0.009)
		0.29 (0.420)	0.69 (0.027)	0.85 (0.002)	-0.08 (0.830)	-0.13 (0.724)	0.33 (0.352)	0.33 (0.352)
			0.17 (0.647)	0.35 (0.317)	0.25 (0.495)	-0.33 (0.352)	0.72 (0.020)	0.85 (0.002)
				0.78 (0.005)	0.34 (0.300)	-0.49 (0.128)	-0.01 (0.970)	0.29 (0.420)
					-0.09 (0.800)	-0.55 (0.081)	0.03 (0.929)	0.03 (0.929)
						-0.01 (0.977)	0.17 (0.622)	0.17 (0.622)
							0.29 (0.380)	-0.17 (0.622)
								0.91 (0.000)

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498

499 **Table 3: Semi-quantitative mineralogical distribution (%) in the water-dispersed (W) and H₂O₂ pretreated**
 500 **(PER) soil fraction (<0.425mm).**

501

502

ID	Ilt	Sme	Chl	Vrm	Ily-Sme	Ilt-Chl	Ilt-Vrm	Chl-Vrm	Qz	Fsp	EBS (nm)	SSA (m ² g ⁻¹)
W												
1	27	-	5	63	3	-	-	-	1	1	0.122	24.5
4	22	-	5	67	-	-	-	2	1	3	0.145	85.6
6	50	8	28	6	-	-	-	-	2	6	0.020	48.9
7	18	-	4	-	77	-	-	-	1	tr	0.034	48.9
8	31	-	12	27	-	-	27	-	1	2	0.051	48.9
9	20	-	1	6	-	-	71	-	1	1	0.053	12.2
11	19	-	6	23	-	-	49	-	tr	3	0.071	48.9
12	32	-	13	51	-	-	-	-	2	2	0.102	36.7
15	42	-	11	37	-	5	-	-	1	4	0.044	73.4
16	16	4	15	-	61	2	-	-	1	1	0.068	36.7
17	25	tr	12	5	-	57	-	-	1	tr	0.044	85.6
PER												
1	55	2	17	13	4	-	-	3	2	4	0.158	24.5
4	42	1	7	35	-	-	-	5	tr	10	0.274	85.6
6	28	-	13	40	-	-	-	15	2	2	0.278	48.9
7	8	1	1	49	3	-	38	-	tr	tr	0.172	48.9
8	40	-	23	33	-	-	-	-	2	2	0.264	48.9
9	8	-	2	47	-	-	41	-	tr	2	0.182	12.2
11	17	-	11	38	-	-	31	-	tr	3	0.334	48.9
12	41	-	18	17	-	-	17	-	tr	7	0.273	36.7
15	54	-	21	10	-	-	-	10	1	4	0.239	73.4
16	26	7	13	46	2	1	-	-	3	2.1	0.388	36.7
17	87	2	2	-	-	-	7	-	-	2	0.300	48.9

503

504 Ilt (illite), Sme (smectite), Vrm (vermiculite), Chl (chlorite), Qz (quartz), Fsp (feldspars). Abbreviations for
 505 minerals after Withney and Evans (2010).

506 EBS (equivalent basal spacing), SSA (specific surface area). Tr indicates traces.

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