



AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Simulating the effects of wet and dry on aggregate dynamics in argillic fragipan horizon

This is the author's manuscript
Original Citation:
Availability:
This version is available http://hdl.handle.net/2318/1644875 since 2017-07-11T12:39:57Z
Published version:
DOI:10.1016/j.geoderma.2017.06.026
Terms of use:
Open Access
Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)





This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in GEODERMA, 305, 2017, 10.1016/j.geoderma.2017.06.026.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

(1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.

(2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.

(3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en), 10.1016/j.geoderma.2017.06.026

The publisher's version is available at: http://linkinghub.elsevier.com/retrieve/pii/S0016706117301064

When citing, please refer to the published version.

Link to this full text: http://hdl.handle.net/2318/1644875

This full text was downloaded from iris - AperTO: https://iris.unito.it/

1 Title

2 Effects of wet and dry on aggregate dynamics in fragipan: an experimental approach

3

4 Authors

- 5 Gloria Falsone^a, Silvia Stanchi^{b,c}, Eleonora Bonifacio^b
- 6 ^aDIPSA Alma Mater Studiorum University of Bologna, via Fanin 40, 40127 Bologna, Italy
- ⁷ ^bDISAFA, University of Torino, Largo P. Braccini 2, 10095 Grugliasco, TO, Italy
- 8 ^cNATRISK, Research Centre on Natural Risks in Mountain and Hilly Environments, University of Torino, Largo P. Braccini 2, 10095 Grugliasco,
- 9 TO, Italy

10

- 11 Corresponding author
- 12 Gloria Falsone: tel +39 051 209 6229, Email gloria.falsone@unibo.it
- 13

14 Abstract

- 15 Fragipan is a dense and usually brittle subsurface soil horizon, limiting the penetration of roots and the infiltration of water. Genesis of fragipan is
- still unclear; however there is a general agreement on the importance of wet-dry cycles in its evolution. Furthermore, in addition to the effect of

17	water, in argillic Bx horizon, the presence of cations affecting the clay dispersion/flocculation behaviour might be a key factor in fragipan dynamics.
18	In order to gain knowledge on the specific effect of alternating moisture conditions on the evolution of aggregates collected from Btx horizon, we
19	evaluated the variations of physical properties caused by a wet-dry cycle using both deionized and Ca-enriched water on the 1-2 mm aggregate, and
20	on newly formed aggregates (i.e. 2-5 and >5 mm size classes) obtained after a lab experiment. The obtained results were compared with a Bt
21	horizon that did not show fragipan properties. Btx and Bt samples were collected from a Typic Fragiudalf on fluvio-glacial terraces in NW Italy. The
22	two horizons had comparable clay content (around 13%), and their mineralogical composition was dominated by hydroxy-interlayed vermiculite
23	and smectite.
24	The fragipan 1-2 mm aggregates before the treatments had low clay dispersion ratio (11.5%), and typically low volume of macropores (74 mm ³ g ⁻¹),
25	high volume of mesopores (111 mm ⁻³ g ⁻¹), high slaking (30.1%), close packing of coarse particles and open arrangement of fine particles (0.82 and
26	0.31, respectively). The water treatment promoted the enrichment in flocculated-clay in the new-aggregates, and Ca-treatment enhanced clay
27	flocculation both in the newly formed and in the 1-2 mm aggregates. The clay flocculation induced a denser arrangement of clay particles (≥0.44),
28	and a consequent reduction of mesopores (from 56.2 to 66.1 mm ⁻³ g ⁻¹), combined with the opening of the coarser particles packing (≤ 0.78). This
29	new particle arrangement did not correspond to the specific combination of coarse/fine particles arrangement of fragipan. The relative percentage of
30	slaking also decreased. Therefore, upon both deionized water and CaCl ₂ wetting and drying, the aggregates from fragipan changed and the specific
31	physical properties of fragipan, measureable in laboratory, tended to be attenuated.
32	

Highlights 33

- 34 In fragipan, physical properties changes induced by wetting/drying are studied in the lab
- 35 Water and CaCl₂ wetting/drying promoted the enrichment in flocculated-clay
- 36 Flocculation induced a denser arrangement of clay particles and mesopores reduction
- 37 The new arrangement did not correspond to the specific fragipan particle arrangement
- 38 Water and CaCl₂ wetting/drying attenuated the fragipan physical characteristics measurable in laboratory
- 39

40 Keywords

- 41 Argillic horizons, clay dispersion/flocculation, BET, Hg porosimetry, wet aggregate stability
- 42

43 **1. Introduction**

Fragipan is a subsurface soil horizon limiting the penetration of roots and infiltration of water because of its high bulk density, low porosity, and 44 discontinuous void space (Soil Survey Staff, 2014). The occurrence of fragipan (Bx horizons) in a soil profile can strongly reduce soil physical 45 quality and functionality. No specific analytical determinations are however required for fragipan recognition, i.e. the fragic properties are 46 identified in the field (Soil Survey Staff, 2014). Fragipan shows a hard or very hard consistence when dry, but it is brittle when moist, and its air-47 dried clods undergo immediate slaking once immersed in water (e.g., Bockheim and Hartemink, 2013; Lindbo et al., 1994). Falsone and Bonifacio 48 (2009) demonstrated that the low permeability and high bulk density of fragipan result from a specific arrangement of mineral particles that is not 49 found in any other soil horizons, i.e. an open packing of the clay phase is associated to an extremely dense packing of silt and sand. 50 Fragipan horizons occur in all parts of the world and are common in North-American Alfisols (Bockheim and Hartemink, 2013), in Luvisols and 51 Albeluvisols in Ukraine (Nikorych et al. 2014), in Udalfs in Northern Italy (Falsone and Bonifacio, 2006; Ajmone-Marsan et al., 1994). In these 52 environments they typically occur within an argillic (argic) horizon (Btx). Bockheim and Hartemink (2013) reviewed the descriptive models for the 53 genesis of fragipan, and subdivided them based on the approach used. The physical models emphasized either the role that lithologic discontinuities 54 or pore size distribution have on water flow and material accumulation into the fragipan, or the hydrocollapse of soil or parent material that can 55 form hard pans. The chemical models, on the other hand, point to the importance of water translocated weathering products such as clay and Fe, Al, 56 Si phases, as bonding agents and bridges of coarser particles. Wet-dry cycles have been indicated as one of the driving factors for fragipan evolution 57 (e.g., Wilson et al., 2010; Boulet et al., 1998; Bruckert and Bekkary, 1992), but the role of alternating moisture conditions is still not well-58 understood, and contrasting results have been reported. Szymański et al. (2011) and Nikorych et al. (2014) stated that the seasonal soil wetting and 59

60	drying cause fragipan degradation through the formation of vertical cracks. Weisenborn and Schaetzl (2005a) reported that, upon wetting, argillic
61	fragipans can degrade because of clay and Fe leaching due to vertically percolating water, thus developing non-brittle E horizon features. Attou and
62	Bruand (1998) found instead that fragipan originates from successive wetting and drying cycles, because of the effect that alternating water
63	conditions have on clay; wetting favours clay dispersion within the soil matrix and the subsequent dry period allows the reorganization of clay
64	particles into coatings and bridges over and between the skeleton grains. In addition to the effect of water, in argillic Bx horizon, the presence of
65	cations affecting the clay dispersion/flocculation behaviour should be therefore a key factor in fragipan dynamics.
66	This paper aims at understanding the role of wet-dry cycles on aggregates dynamics in Btx horizon, hypothesizing that the wet-dry cycle and the
67	presence of flocculating cation, such as calcium, should differently affect the Bx physical properties. In laboratory conditions, the presence of
68	calcium would favour clay flocculation enhancing the Bx properties both in pre-existing and newly-formed soil aggregates. To obtain a deeper
69	insight into the mechanisms occurring upon wetting and drying in argillic fragipan we performed a laboratory experiment to evaluate the changes in
70	those physical properties that are controlled by clay flocculation/dispersion behaviour and interactions between particles. The specific goals were:
71	(i) to study the evolution of aggregates from a Btx horizon during a laboratory controlled wet-dry cycle, using both deionized water and a solution
72	containing calcium (i.e., CaCl ₂); (ii) to investigate the physical properties of newly-formed aggregates obtained from the Btx horizon upon wet-dry
73	cycle in the laboratory. The results were compared to those of the upper Bt horizon (i.e. non-fragipan argillic).

74.

2. Materials and Methods

77 2.1. The study area

In the catchment of the Stura di Lanzo River (45° 13.366' N, 7° 31.399' E), NW Italy, a fine-loamy mixed Typic Fragiudalf (Soil Survey Staff, 78 2014) was selected for this study. It develops on fluvio-glacial terraces of the Fiano Unit (Middle Pleistocene, i.e. Mindel-Riss interglacial in the 79 Alps) according to Forno et al. (2007). The dominant lithologies of the area eroded by the Pleistocene glacier are prasinites, serpentinites, 80 lherzolites, amphibolites, micaceous and chlorite schists, eclogites, and gneiss. The vegetation is dominated by Robinia pseudoacacia L. and 81 Corylus aveilana L. The morphological description of a representative soil profile of the area is reported in Table 1. At the sampling site, the 82 fragipan horizon was identified at 165-190 cm depth by brittleness and morphology, including vertical seams, coarse prismatic structure, and 83 absence of roots in prisms (Soil Survey Staff, 2014). 84 Samples (~1 kg) of the argillic fragipan (Btcx) and the overlying argillic non-fragipan (Btc2) horizons were collected, air-dried and sieved to pass a 85

2-mm screen. The main properties of the <2 mm fraction of Btc2 and Btxc horizons are reported in Table 2. An aliquot of <2 mm air-dried of Btc2

and Btcx samples was further dry-sieved at 1 mm and the 1-2 mm aggregate class was separated.

88

89 2.2. Sample preparation and treatment conditions

One hundred grams of the <2 mm air-dried samples of each soil horizon were evenly distributed in a container and sprayed with 25 ml of deionized water or 0.25M CaCl₂ (Figure 1). Four tests were thus performed: Btcx horizon plus deionized water, Btcx plus 0.25M CaCl₂, Btc2 horizon plus deionized water, and Btc2 plus 0.25M CaCl₂. The samples were allowed to dry for 2 weeks at room temperature, ensuring the occurrence of both new-aggregates formation and clay flocculation, i.e. the two main processes considered in this study. Both processes are in fact relatively rapid, and

in controlled conditions the formation of aggregates via particle interactions and/or clay flocculation can quickly occur (Fortun et al., 1989; Falsone 94 et al., 2007; Falsone et al. 2016). The experiment was replicated three times, originating therefore 12 samples. At the end of the treatment, the 95 samples were sequentially dry sieved on 5-, 2- and 1-mm sieves. Three fraction of aggregates were thus obtained: 1-2, 2-5 and >5 mm. The weight 96 of each aggregate class was recorded and the result was expressed as percentage. The >2 mm aggregate classes (i.e., 2-5 and >5 mm fractions) were 97 considered as newly formed aggregates (NEW-aggregates). 98 Three samples of 1-2 mm aggregates obtained by dry-sieving of <2 mm of Btc2 and Btcx samples were also put in the same laboratory conditions as 99 described above, but without any treatment. 100 101 The analyses were performed on the 1-2 mm aggregates without any treatment (FRG and NFRG), on the 1-2 mm aggregate fraction after the 102 treatment (FRG-WAT, FRG-CA, NFRG-WAT and NFRG-CA), and on the 2-5 (FRG₂₋₅-WAT, FRG₂₋₅-CA, NFRG₂₋₅-WAT and NFRG₂₋₅-CA) and 103 >5 mm NEW-aggregates (FRG₅-WAT, FRG₅-CA, NFRG₅-WAT and NFRG₅-CA). 104 105 2.3. Chemical and physical analyses 106

The organic carbon was measured by dry combustion (CE Instruments NA2100 elemental analyser, Rodano, Italy). The contents of pedogenic iron oxides (FeDCB) were estimated through extraction with Na-dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) and subsequent determination of Fe by AAS (Perkin Elmer Analyst 400, Waltham, USA). The particle size distribution (PSD) was determined by the pipette method (Gee and Bauder, 1986) after: (i) dispersion with deionized water only; (ii) dispersion with (NaPO₃)₆; (iii) dispersion with (NaPO₃)₆ after H₂O₂ oxidation of

organic matter and Na-dithionite-citrate-bicarbonate removal of Fe-cements. The PSD data were used to calculate the clay dispersion ratio (CDR)
according to Dong et al. (1983) as follows:

113
$$CDR = \frac{Clay \ obtained \ with \ deionized \ water}{Clay \ obtained \ with \ (NaPO_3)_6} \cdot 100$$
 (1)

The wet aggregate stability (WAS) was evaluated after 10 min in rotating 0.2-mm sieves (Kemper and Rosenau, 1986). The material remaining on the sieves was then dried and weighed. Then, the amount of stable aggregates (>0.2 mm) was corrected for the content of coarse sand determined after H_2O_2 oxidation and Na-dithionite-citrate-bicarbonate extraction. The WAS index was calculated as follows:

117
$$WAS = \frac{weight retained-weight of coarse sand}{total sample weight-weight of coarse sand} \cdot 100$$
 (2)

- 118 And the percentage of aggregate loss (Loss) as
- 119 Loss = 100 WAS (3)

To test the wet cohesion independently from slaking, thus regardless of the ruptures due to water saturation, 10 g of aggregates were gently immersed into 95% ethanol solution for 10 min (Le Bissonnais, 1996) before being wet sieved for 10 min. Then, the amount of aggregates that had resisted the sieving (WAS_{et}) and the percentage of aggregate loss (Loss_{et}) was determined according to the equations (2) and (3). The relative percentage of slaking (RPS; Falsone and Bonifacio, 2006) was calculated as:

$$124 \quad RPS = \frac{Loss - Loss_{et}}{Loss} \cdot 100 \tag{4}$$

- 125 The specific surface area was determined by N_2 gas adsorption at 77 K in the relative pressure (p/p°) range of 0.05-0.30 (Gregg and Sing, 1982) with
- a Sorptomatic 1900 surface area analyser (CE instruments, Rodano, Italy) by applying the Brunauner-Emmett-Teller (BET) equation. Enough

sample was used for measurement to ensure a total surface area >10 m² (corresponding to around 1.2 g of sample). All samples were initially degassed for 16 hours at 50°C. The micropore (<2 nm) volume and surface area were evaluated from the adsorption-desorption isotherms, using the t-plot method (V_{MICRO} and S_{MICRO} , respectively; de Boer et al., 1966), while mesopores (2-50 nm; V_{MESO} and S_{MESO}) were derived from the desorption branch according to Pierce's (1953) model.

Porosity characteristics were evaluated by Hg intrusion using a 2000 WS porosimeter equipped with a 120 Macropore unit (CE Instruments, Rodano, Italy). The total volume of intruded Hg (i.e. total pore volume) was expressed on a mass basis (V_{TOT} , mm³ g⁻¹). The cumulative curve of intruded Hg volume as a function of the pore radius was used to calculate the variation of the pore volume following Bruand and Prost (1987):

134
$$slope_{ij} = \frac{V_i - V_j}{\log_{10} R_j - \log_{10} R_i}$$
 (5)

where the volumes Vi and Vj correspond to the radii Ri and Rj at two successive positions i and j. The values of the slope were then plotted against 135 the mean log radius, thus the relative maxima of the slope curve indicated the most represented classes of pores and corresponded to a modal radius 136 (expressed in µm). The volume of each modal class of pores was thus included between two minimum values of the slope, which defined the limits 137 138 of the class. This data treatment returns a bimodal distribution: two modal pore radii attributed to the packing of finer (clay) and coarser (sand and silt) fractions, according to Fiès and Bruand, (1998). The corresponding volumes of pores were labelled as Vf and Vc. The modal pore size 139 corresponding to the coarser particles ranged between 0.152 to 1.565 µm, while the modal pore size corresponding to the finer particles ranged 140 141 between 0.005 and 0.022 µm (data not shown). The modal smaller pores were therefore in the range size of mesopores measured by N₂ adsorption (Echeverría et al., 1999) and in this study we chose to use the N_2 adsorption data for finer pore size measurements. 142

143 The packing density of particles, i.e. the volume occupied by solid particles with respect to the total volume (space occupied by solid plus void 144 space), was calculated according to Falsone and Bonifacio (2009) as:

145
$$packing density = \frac{particle mass}{particle density} \cdot \frac{1}{\frac{particle mass}{particle density} + volume of pores}$$
 (6)

where particle density was taken equal to 2.65×10^{-3} g mm⁻³, the mass was expressed in g (100 g)⁻¹, the volume of pores in mm³ g⁻¹, and the 146 147 resulting packing density was dimensionless. We calculated both the packing density of the sand-silt phase and of clay, using the particle size data obtained after dispersion of sample with $(NaPO_3)_6$ for particle mass, and the modal coarse volume (Vc) and the mesopores volume (V_{MESO}), 148 149 respectively, for sand-silt and clay-clay interactions (Zong et al., 2015; Fiès and Bruand, 1998). All the statistical analyses were carried out using SPSS 20 (SPSS Inc., Chicago, IL). Differences among samples were evaluated using the analysis 150 of variance (ANOVA and Duncan's test). The threshold used for significance in all statistical tests was set at 0.05. 151 152 153 3. Results 154

155 *3.1. 1-2 mm aggregates properties before treatments (without any treatment)*

The 1-2 mm aggregate class of both fragipan (FRG) and non-fragipan (NFRG) horizons had low organic C content (<2 g kg⁻¹; Table 3). The content of pedogenic Fe oxides was high (Fe_{DCB}>60 g kg⁻¹; Table 3). FRG had high coarse sand content (CS: 49.4%; Table 3), while NFRG was rich in fine

- 158 sand (FS: 44.4%; Table 3). The difference in coarse sand content among FRG and NFRG was also observed in the content of primary coarse sand-
- size particles (CS_{ox}: 7.4 and 24.9% for NFRG and FRG). The amount of clay was instead similar in the two horizons (10.7 and 13.0% for NFRG

and NFRG, respectively), as well as the clay dispersion ratio (CDR). The fragmentation behaviour in water of the 1-2 mm aggregate class of FRG 160 showed a relative percentage of slaking of 30.1% (RPS; Table 4), giving a contribution to the wet-aggregate losses, as in general observed in 161 fragipan horizons (Falsone et al., 2006). The N₂ adsorption at 77 K and Hg porosity data clearly evidenced the peculiarity of pores size distribution 162 of FRG-aggregates: FRG had more mesopores than macropores (V_{MESO} and Vc, respectively, Figure 2A; Lamotte et al., 1997; Ajmone-Marsan et 163 al., 1994), in opposition to NFRG. Because of high mesoporosity volume, the corresponding mesopores surface areas (S_{MESO}) were large in FRG 164 (Figure 2B). The packing density of the coarser particles showed that typically FRG had a closer arrangement than NFRG (PDc: 0.82 and 0.73; 165 Table 5). The packing density of the clay fraction showed instead a slightly more open arrangement in FRG than NFRG (PDf values: 0.31 and 0.39 166 for FRG and NFRG samples, Table 5). Before treatments, the 1-2 mm FRG aggregates had thus the highest PDc/PDf ratio (Table 5) as typical of 167 fragipans i.e. an open packing of the clay phase associated to an extremely dense packing of sand and silt (Falsone and Bonifacio, 2009). 168

169

170 *3.2. 1-2 mm aggregates properties after the wet-dry cycle*

171 *3.2.1. Fragipan*

The amount of FRG aggregates maintaining the 1-2 mm size after one wet-dry cycle with deionized water was around 20% of the total mass (Figure 3A), while a lower percentage of 1-2 mm aggregates was obtained after CaCl₂ treatment (10.6%, Figure 3B). The clay fraction was the most affected by the presence of Ca, as expected, and the FRG-CA sample was enriched in flocculated clay with respected to both the untreated and water-treated samples (i.e. the CDR decreased, Table 3; p<0.05). The experiments destabilised all the treated-aggregates, as visible from the increase of the aggregate losses due to wet sieving (Loss and Loss_{et} increased up to 68.8 g (100) g⁻¹ in the case of FRG-CA, p<0.05; Table 4). The

losses due to slaking instead decreased (RPS, p<0.05; Table 4). Finally, also the pore system changed (Figure 2A): the treatments slightly increased the coarser pores volume (Vc) and reduced the mesopores volume (V_{MESO}). The volume of micropores also decreased following the Ca-treatment. As a result of the change in pore distribution, the finer particles in the treated-aggregates became more closely packed, especially in the Ca-treated sample, while the arrangement of coarser particles was slightly looser than those of untreated-FRG (PDf increased and PDc slightly decreased, respectively; Table 5), and the PDc/PDf ratio strongly decreased (p<0.05).

182

183 *3.2.2. Non-fragipan*

The amounts of NFRG aggregates that maintained the 1-2 mm size after wet-dry cycle with both deionized water and $CaCl_2$ were around 20% of the total mass (Figure 3A-B). Differently from FRG samples, the 1-2 mm aggregate class of NFRG samples had lower CS_{ox} content than the samples before the treatment (Table 3; p<0.05). The clay fraction appeared again more affected (Table 3): the NFRG-CA sample had higher clay content and lower clay dispersibility (i.e., lower CDR value; p<0.05) than NFRG before treatment, in contrast to NFRG-WAT that had similar clay content

and higher dispersability (i.e., higher CDR value; p<0.05) than NFRG.

The treatments increased the aggregate losses by wet sieving (Loss and Loss_{et}, p<0.05: Table 4), but, after the Ca-treatment and differently from FRG sample, the losses due to slaking increased (i.e., RPS value increased, p<0.05; Table 4). As regards to the aggregate porosity, the mesopores volume and surface (V_{MESO} and S_{MESO}) increased after treatment (Figure 2A-B), while the volume and the surface of the micro (V_{MICRO} and S_{MICRO}) and the volume of coarser pores (Vc) decreased, especially after CaCl₂-treatment. As a result, the arrangement of finer particles appeared denser, while the packing density of coarser particles did not change with respect to those of NFRG (PDf increased and PDc did not vary, respectively; Table 5). After the treatments, the packing density of the aggregates from NFRG and FRG became more similar than it was before, as visible alsoby the PDc/PDf ratio (Table 5).

- 196
- 197 *3.3. NEW- aggregates properties obtained by wet-dry cycle*
- 198 *3.3.1. Fragipan*

After the treatment with deionized water, the 2-5 and >5 mm newly formed aggregates (FRG₂₋₅-WAT and FRG₅-WAT) composed 23.1 and 45.3% 199 of the total mass of FRG samples (Figure 3A), while after CaCl₂-treatment they represented 16.5 and 66.5%, (FRG₂₋₅-CA and FRG₅-CA; Figure 200 3B). The NEW-aggregate classes of FRG sample had low organic C content and high Fe_{DCB} amount (Table 6), as already observed for 1-2 mm 201 aggregates before and after treatments. The amount of coarse sand decreased in all NEW-aggregates with respect to the aggregates before treatments 202 (p<0.05; CS values in NEW-aggregates ranged from 29.2 to 40.1 g kg⁻¹, CS content was 49.4 g kg⁻¹ in untreated-FRG aggregates; Table 6 and Table 203 3, respectively), as well as the content of primary coarse sand particles (CS_{0x} , p<0.05 Tables 3 and 6). As already observed for 1-2 mm aggregates, 204 after CaCl₂-treatment the clay content increased and this again corresponded to a slightly lower water dispersibility of the clay fraction, as CDR 205 decreased in NEW-aggregates after Ca-treatment (p<0.05; Table 6). In FRG the NEW-aggregates were extremely water fragile, and after wet 206 sieving their losses varied from 64.3 to 76.4% (Loss; Table 7). Similar values were found for Losset. However, the incidence of slaking on FRG 207 losses was extremely low, and for >5 mm NEW-aggregates the RPS values were even <2% (Table 7). The volume corresponding to the larger 208 pores, Vc, did not show any specific trend with the treatment (Figure 4A), as well as the PDc values (Table 8). However, the packing density of 209 coarser particles was lower than that of the FRG aggregates before treatments (p<0.05; for FRG, the PDc values in NEW-aggregates ranged from 210

0.70 to 0.78, while in 1-2 aggregates before treatments it was 0.82; Table 8 and 5, respectively). The FRG NEW-aggregate V_{MESO} ranged from 56.7 and 66.1 mm³ g⁻¹ and S_{MESO} from 30.8 to 34.3 m² g⁻¹ (Figure 4A and B), thus a strong mesoporosity decline has occurred after treatments (p<0.05; V_{MESO} and S_{MESO} of the 1-2 mm aggregates before treatments were 111.0 mm³g⁻¹ and 42.6 m²g⁻¹, Figure 2A-B). The Ca-treatment strongly affected the microporosity, as visible from the very low volume and surface area of micropores in Ca-treated NEW-aggregates (Figure 4A-B). As a consequence of the modification occurring in meso and microporosity, the PDf values increased in NEW-aggregates with respect to the 1-2 mm aggregates before treatments (p<0.05; PDf values always \geq 0.44 in NEW-aggregates vs. 0.31 in aggregates before treatments; Tables 8 and 5, respectively), especially in the Ca-incubated samples.

218 *3.3.2. Non-fragipan*

After treatment of NFRG with deionized water, the 2-5 and >5 mm newly formed aggregates composed 25.0 and 20.1% of the total mass, while 219 after CaCl₂-treatment they represented 21.4 and 43.4%, respectively (Figure 3A-B). The organic C content was similar in all NFRG NEW-220 aggregates (0.6-0.8 g kg⁻¹, Table 6), as well as the amount of pedogenic Fe oxides (50.5-53.0 g kg⁻¹, Table 6), even if the Fe_{DCB} content in NEW-221 aggregates was lower than before treatments (p<0.05; Fe_{DCB} was 62.8 g kg⁻¹ in the untreated-NFRG aggregates; Table 3). Similarly to the NEW-222 aggregates of FRG, the coarse sand content decreased in the NEW-aggregates of NFRG with respect to the aggregates before treatments (p<0.05; 223 CS values in NF-aggregates ranged from 8.2 to 15.0 g kg⁻¹, CS content was 24.8 g kg⁻¹ in untreated-NFRG aggregates; Table 6 and Table 3, 224 respectively), as well as the content of primary coarse sand particles (p<0.05; CS_{ox}: Tables 3 and 6). The clay behaviour was similar to that of FRG 225 samples: the Ca-treated samples were enriched in flocculated clay (higher clay content and lower CDR values than water-treated samples; Table 6). 226 The NEW-aggregates were unstable to water stresses, and high losses of aggregates occurred (Loss and Loss_{et} always >52%; Table 7), even if the 227

incidence of slaking was low (RPS always <13%; Table 7). The NFRG NEW-aggregates were still more stable than FRG ones but the differences were less marked. In the NFRG NEW-aggregates, the Vc values ranged from 97 to 123 mm³ g⁻¹ (Figure 4A) and the corresponding PDc varied from 0.73 to 0.76 (Table 8). Similar Vc and PDc values were thus found in both FRG and NFRG NEW-aggregates. No specific effect of the treatment conditions on the coarser porosity was found. Instead, similarly to FRG samples, the V_{MICRO} and S_{MICRO} strongly decreased after the Ca-treatment (Figure 4A-B). With respect to the sample before treatments, also in the case of NFRG NEW-aggregates, the PDf values increased especially in the Ca-incubated samples (p<0.05; PDf values varied from 0.42 to 0.54 in NEW-aggregates, and in aggregates before treatments PDf was 0.39; Tables 8 and 5, respectively).

- 235
- 236

237 **4. Discussion**

In this work, we wanted to evaluate the variations caused by a wet-dry cycle carried out in laboratory controlled conditions, using both deionized and Ca-enriched water on the 1-2 mm aggregate properties of a Btx horizon, and to investigate the physical properties of newly formed aggregates (i.e. 2-5 and >5 mm size classes) obtained after the experiment. This was performed in order to investigate the specific effect of alternating moisture conditions on the evolution of aggregates collected from Btx horizon. The same soil properties were monitored for the reference Bt horizon that did not show fragipan properties.

243

244 4.1. 1-2 mm aggregates properties of fragipan and non-fragipan before treatments

245	The characterisation of the 1-2 mm aggregates before the treatment experiments confirmed the typical physical properties of fragipans detectable in
246	laboratory and reported in Figure 6: high aggregate fragility against slaking (e.g., Soil Survey Staff, 2014; Falsone and Bonifacio, 2006; Lindbo and
247	Rhoton, 1996), low volume of macropores and high volume of micropores (e.g., Lamotte et al., 1997; Ajmone-Marsan et al., 1994), high density
248	(e.g., Falsone and Bonifacio, 2009; Weisenborn and Schaetzl, 2005b). Conversely, non-fragipan aggregates showed higher resistance to water-
249	breakdown and lower slaking susceptibility, had more macropores than micropores, and showed a more open arrangement of the coarse fraction
250	(Figure 6). The particle size distribution was however similar between the two horizons, and the low CDR values were in agreement with the
251	presence of flocculated clays in argillic horizons formed by lessivage (e.g., Schaetzl and Anderson 2005) and suggested a similar dispersion
252	behaviour of the clay fraction (Dong et al., 1983).

253

4.2. Evolution of fragipan and non-fragipan 1-2 mm aggregates during laboratory controlled wet-dry cycle (deionized water and CaCl₂ effect) 254 The wet-dry cycle affected the properties of the 1-2 mm aggregates from the fragipan, even if they maintained their size after the treatment and thus 255 did not take part in the formation of larger NEW-aggregates. Different effects of deionized and Ca-enriched water on aggregate dynamics were 256 observed. After treatment with deionized water, FRG 1-2 mm aggregates were enriched in easily dispersible clay (CDR values >20%; Table 3), 257 while the CaCl₂-treatment slightly increased the clay flocculation status (CDR values <10%). This means that, as expected, Ca addition enhanced 258 clay flocculation. In the presence of Ca^{2+} ions, the clay outer layer is thinner and electrostatic repulsion among clay particles is lower, allowing for 259 van der Waals' forces to promote the formation of small stacks of clay platelets (i.e., clay domains; Sposito, 1989). This arrangement favours face-260 to-face association between clay particles (van Olphen, 1977), which might have caused the denser packing of the clay fraction indicated by the 261

262	increase of the PDf values. In contrast, water treatment had a lower effect on clay associations because clay arrangement was unaffected, as
263	indicated by the similarity of PDf values between FRG treated and untreated 1-2 mm aggregates. As a result the PDc/PDf ratio, which can be used
264	as a simple index of the combination of the coarser and finer particle density, decreased. Ramos et al. (2015) stated that the face-to-face association
265	of kaolinite platelets favoured fragipan formation, but in our Ca-treated samples it causes the closure of clay packing minimising the differences
266	between coarser and finer particle density. The aggregates after treatment did not thus show anymore the contrasting coarser-finer particles
267	arrangement typical of fragipan (Falsone and Bonifacio, 2009). Moreover, the 1-2 mm aggregates of both treated-FRG were more water fragile after
268	treatment, but they showed a higher relative resistance to slaking. It appeared therefore that the fragipan aggregates that did not take part in the
269	formation of NEW-aggregates markedly lost the typical properties of fragipan investigated in this lab study (Figure 6).
270	
271	4.3. Physical properties of newly-formed aggregates obtained from fragipan and non-fragipan horizons upon the laboratory wet-dry cycles
272	$(deionized water and CaCl_2 effect)$

The formation of new aggregates in fragipan seems to have occurred through the interaction of clay floccules, and other soil coarse particles, likely sand grains and/or already existing aggregates, as indicated by clay quantity and quality in the NEW-aggregates. In fact, after both deionized water and CaCl₂ addition, the clay amount increased in FRG NEW-aggregates and its dispersibility decreased or was steady. The involvement of coarse particles, and thus the formation of aggregates due to clay floccules covering sand particles or already existing aggregates is in agreement with Falsone et al. (2007). They found that in the presence of poorly dispersible clay, the low electrostatic barrier allowed clay sized aggregates to form and subsequently cover sand grains during a wet-dry cycle with deionized water. Although in the present study we did not measure the surface

charge of clay fraction, both the low CDR values of the 1-2 mm aggregates before treatments and the selection of samples from argillic horizons 279 suggested a low surface charge of clay fraction. In these conditions, the addition of Ca^{2+} would further enhance clay flocculation, and the similarity 280 between samples (i.e., water and Ca-treated) in quantitative and qualitative clay data suggest the same pathway of aggregates formation in both 281 deionized water and CaCl₂ treated samples. The NEW-aggregates obtained after the treatments had a lower resistance to water stress than the 282 samples before treatments. This further confirmed the hypothesized aggregation pathway (i.e., clay-clay associations covering coarse particles), as 283 aggregate stability is lower when coarse particles are linked to an already flocculated clay phase (Attou et al., 1998; Falsone et al., 2007). As a 284 consequence of the new particle association, in FRG NEW-aggregates coarser particles had a more open arrangement (i.e., PDc values decreased). 285 The volume of mesopores instead decreased and, again, in the Ca-incubated samples the enhancement of clay flocculation affected the packing 286 density of clay with a closer arrangement after treatment (i.e., PDf values increased). In this study, the aggregates after treatments showed thus a 287 progressive decrease of PDc/PDf ratio. Considering the investigated physical parameters, it appeared therefore that also the FRG NEW-aggregates 288 did not show the typical properties of fragipan after both water and Ca-treatment (Figure 6). 289

290

291 *4.4. The overall experimental effect*

There was a general trend upon treatments that was independent from the type of horizon (FRG and NFRG) and the aggregate size (1-2 mm, 2-5 NF-aggregates, >5 mm NF-aggregates): the wet-dry cycle modified the spatial arrangements of both clay and coarser particles, with a denser packing of the clay phase and an opening of the coarser particles arrangement. This was likely caused by the formation of face-to-face clay associations and by associations between coarse particles and flocculated clays. The new particle arrangement worsened the aggregate water

resistance, and all the aggregates after treatments were indeed less water stable. However, our results suggested that this new particle arrangement contributed to limit the breakdown due to slaking, as the relative percentage of slaking decreased (r^2 always >0.5; Figure 5). This suggests that the opening of the coarse particles arrangement coupled to the closure of the clay particles packing limited aggregate breakdown due to slaking, thus further confirming that FRG samples obtained after treatments moved away from the typical physical behaviour of fragipans measureable in laboratory.

301

302 5. Conclusions

The water treatment promoted the enrichment in flocculated-clay in the NEW-aggregates, and Ca-treatment enhanced clay flocculation both in the NEW- and in the 1-2 mm aggregates that maintained their size. However, the hypothesized enhancement of fragipan properties (such as slaking, particle density and porosity), due to the increase in clay flocculation did not take place in our samples. The clay flocculation in fact induced a denser arrangement of clay particles, and a consequent reduction of mesopores, combined with the opening of the coarser particles packing. This new particle arrangement did not correspond to the specific combination of coarse/fine particles arrangement of fragipans detectable in laboratory conditions. These results point to the importance of the clay fraction, and particularly of the dispersible clay fraction, but more research is needed to understand its role in driving argillic Bx properties.

310

311

312 **6. References**

- Ajmone-Marsan, F., Pagliai, M., Pini, R., 1994. Identification and properties of fragipan soils in the Piemonte Region of Italy. Soil Sci. Soc. Am. J.
 58, 891-900.
- Attou, F., Bruand, A., Le Bissonnais, Y., 1998. Effect of clay content and silt-clay fabric on stability of artificial aggregates. Eur. J. Soil Sci.
 49:569–577.
- Attou, F., Bruand, A., 1998. Experimental study of 'fragipans' formation in soils. Role of both clay dispersion and wetting-drying cycles. C. R.
- 318 Acad. Sci. 326, 545–552. DOI: 10.1016/S1251-8050(98)80205-X
- Bockheim, J.G., Hartemink, A.E., 2013. Soils with fragipans in the USA. Catena 104, 233–242. DOI: 10.1016/j.catena.2012.11.014
- Boulet, R., Fritsch, E., Filizola, H.F., de Araujo Filho, J.C., Leprun, J.C., Barretto, F., Balan, E., Tessier, D., 1998. Iron bands, fragipans and
- duripans in the northeastern plateaus of Brazil properties and genesis. Can. J. Soil Sci. 78, 519-530.
- Bruand, A., Prost, R., 1987. Effect of water content on the fabric of soil material: an experimental approach. J. Soil Sci. 38, 461–472.
- Bruckert, S., Bekkary, M., 1992. Effect of rock permeability on the formation of diagnostic argillic and fragipan horizons. Can. J. Soil Sci. 72, 69-
- 324 88.
- 325 De Boer, J.H., Lippens, B.C., Linsen, B.G., Broekhoff, J.C.P., van den Heuval, A., Osinga T.J., 1966. The t-curve of multimolecular N₂-adsorption.
- 326 J. Colloid. Interf. Sci. 21, 405-414.
- 327 Dong, A., Chesters, A., Simsinan, G.V., 1983. Soil dispersibility. Soil Sci. 136, 208-212.
- 328 Echeverría, J.C., Morera, M.T., Mazkiarán, C., Garrido, J.J., 1999. Characterization of the porous structure of soils: adsorption of nitrogen (77K)
- and carbon dioxide (273K), and mercury porosimetry. Eur. J. Soil Sci. 50, 497-503. DOI: 10.1046/j.1365-2389.1999.00261.x

- Falsone, G., Bonifacio, E., 2006. Destabilization of aggregates in some Typic Fragiudalfs. Soil Sci. 171, 272-281. DOI:
 10.1097/01.ss.0000199703.76278.80
- Falsone, G., Bonifacio, E., 2009. Pore-size distribution and particle arrangement in fragipan and non fragipan horizons. J. Plant Nutr. Soil Sci. 172,
 696-703. DOI: 10.1002/jpln.200800066
- Falsone, G., Celi, L., Bonifacio, E., 2007. Aggregate formation in chloritic and serpentinitic alpine soils. Soil Sci. 12, 1019-1030. DOI:
 10.1097/ss.0b013e31815778a0
- Falsone, G., Celi, L., Stanchi, S., Bonifacio, E., 2016. Relative importance of mineralogy and organic matter characteristics on macroaggregate and
- colloid dynamics in Mg-silicate dominated soils. Land Degrad. Develop. 27, 1700-1708. DOI: 10.1002/ldr.2516
- Fiès, J. C., Bruand, A., 1998. Particle packing and organization of the textural porosity in clay-silt-sand mixtures. Eur. J. Soil Sci. 49, 557–567.
- 339 Forno, G.M., Gregorio, L., Vatteroni, R., 2007. La successione stratigrafica del settore destro del Conoide di Lanzo e il suo significato per l'utilizzo
- del territorio. Mem. Soc. Geogr. It. 87, 237-247.
- Gee, G. W., Bauder, J. W., 1986. Particle-size analysis, in: Klute, A.(Ed.), Methods of soil analysis, Part 1. 2nd edn., Agron. Monogr. No. 9, ASA
- and SSSA, Madison, Wisconsin, USA, pp. 383–411.
- Fortun, A., C. Fortun, and C. Ortega. 1989. Effect of farmyard manure and its humic fractions on the aggregate stability of a sandy-loam soil. J. Soil
 Sci. 40, 293–298.
- Gregg, S.J., Sing, K.S.W., 1982. Adsorption surface area and porosity. 2nd edition. Academic Press. London, UK.

- Kemper, W.D., Rosenau, R.C., 1984. Soil cohesion as affected by time and water content. Soil Sci. Soc. Am. J. 48, 1001-1006.
- Lamotte, M., Bruand, A., Humbel, F. X., Herbillon, A. J., Rieu, M., 1997. A hard sandy-loam soil from semi-arid Northern Cameroon: I. Fabric of
- the groundmass. Eur. J. Soil Sci. 48, 213–225.
- Le Bissonnais, Y., 1996. Aggregate stability and assessment of soil crustability and erodibility: I. Theory and methodology. Eur. J. Soil. Sci. 47,
 425-437.
- Lindbo, D.L., Rhoton, F.E., 1996. Slaking in fragipan and argillic horizons. Soil Sci. Soc. Am. J. 60, 552-554.
- Lindbo, D.L., Rhoton, F.E., Bigham, J.M., Hudnall, W.H., Jones, F.S., Smeck, N.E., Tyler, D.D., 1994. Bulk-density and fragipan identification in
- loess soils of the Lower Mississipi River Valley. Soil Sci. Soc. Am. J. 59, 487-500.
- Mehra, O. P., Jackson, A., 1960. Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate, in:
- Proceedings of 7th National Conference of clay and minerals. Washington, DC. 1958. Pergamon Press, New York city, New York, pp. 317-327.
- Nikorych, V.A., Szymański, W., Polchyna, S.M., Skiba, M., 2014. Genesis and evolution of the fragipan in Albeluvisols in the Precarpathias in
- 357 Ukraine. Catena 119, 154-165. DOI: 10.1016/j.catena.2014.02.011
- Pierce, C., 1953. Computation of pore size from physical adsorption data. J. Phys. Chem. 57, 149-152.
- Ramos, M.R., Melo V.F., Uhlmann, A., Dedecek R.A., Curcio G.R., 2015. Clay mineralogy and genesis of fragipan in soils from Southeast Brazil.
- 360 Catena 135, 22-28. DOI: 10.1016/j.catena.2015.06.016

- 361 Schaetzl, R.J., Anderson, S., 2005. Soils: Genesis and Geomorphology. Cambridge University Press, NY, USA.
- 362 Schoeneberger, P.J., Wysocki, D.A., Benham, E.C., Soil Survey Staff, 2012. Field book for describing and sampling soils. Version 3.0. Natural
- 363 Resources Conservation Service. National Soil Survey Center, Lincoln, NE.
- 364 Soil Survey Staff. 2014. Keys to soil taxonomy, 12th edn. USDA-Natural Resources Conservation Service, Washington, DC.
- 365 Sposito, G., 1989. The chemistry of soils. Oxford University Press, New York City, New York.
- 366 Stanchi, S., Catoni, M., D'Amico, M.E., Falsone, G., Bonifacio, E. 2017. Liquid and plastic limits of clayey, organic C-rich mountain soils: role of
- 367 organic matter and mineralogy. Catena 151, 238-246. DOI: 10.1016/j.catena.2016.12.021
- 368 Szymański, W., Skiba, M., Skiba, S., 2011. Fragipan horizon degradation and bleached tongues formation in Albeluvisols of the Carpathian
- 369 Foothills, Poland. Geoderma 167–168, 340–350. DOI: 10.1016/j.geoderma.2011.07.007
- van Olphen, H., 1977. An introduction to clay colloid chemistry. J. Wiley & Sons, New York City, New York.
- Weisenborn, B.N., Schaetzl, R.J., 2005a. Range of fragipan expression in some Michigan soils: II. A model for fragipan evolution. Soil Sci. Soc.
 Am. J. 69, 178–187.
- Weisenborn, B.N., Schaetzl, R.J., 2005b. Range of fragipan expression in some Michigan soils: I. Morphological, micromorphological, and pedogenic characterization. Soil Sci. Soc. Am. J. 69, 168–177.
- 375 Wilson, M.A., Indorante, S.J., Lee, B.D., Follmer, L., Williams, D.R., Fitch, B.C., McCauley, W.M., Bathgate, J.D., Grimley, D.A., Kleinschmidt,
- 376 K., 2010. Location and expression of fragic soil properties in a loess-covered landscape, southern Illinois, USA. Geoderma 154, 529–543. DOI:
- 377 10.1016/j.geoderma.2009.03.003

378	Zong, Y., Yu, X., Zhu, M., Lu, S., 2015. Characterizing soil pore structure using nitrogen adsorption, mercury intrusion porosimetry, and
379	synchrotron-radiation-based X-ray computed microtomography techniques. J. Soil. Sediment. 15, 302-312. DOI: 10.1007/s11368-014-0995-0
380	
381	
382	Figure Captions
383	
384	Figure 1. Scheme of the experiment.
385	
386	Figure 2. Porosity (A) and surface area (B) of 1-2 mm aggregates of Btcx and Btc2 soil horizon before treatments (horizon code: FRG and NFRG)
387	and after treatments (horizon code: FRG-WAT, FRG-CA, NFRG-WAT, NFRG-CA). The numbers inside the graphs are the absolute values of pore
388	volume $(mm^3 g^{-1})$ and surface area $(m^2 g^{-1})$.
389	
390	Figure 3. Percentage distribution of aggregates classes obtained after wet-dry cycle with A) deionized water and B) 0.25M CaCl ₂ .
391	
392	Figure 4. Porosity (A) and surface area (B) of newly formed 2-5 and >5 mm aggregate of FRG and NFRG (Btcx and Btc2 soil horizon) obtained
393	after treatments (horizon code: FRG-WAT, FRG-CA, NFRG-WAT, NFRG-CA). The numbers inside the graphs are the absolute values of pore
394	volume (mm ³ g ⁻¹) and surface area (m ² g ⁻¹).

395

Figure 5. Relationships between particle density of coarse particle-to-particle density of fine particles (PDc/PDf) ratio and relative percentage of slaking (RPS) in the samples obtained after wet-dry cycles with A) deionized water ($r^2=0.671$; p=0.013) and B) 0.25M CaCl₂ ($r^2=0.514$; p=0.045). Both in the upper and lower figure the 1-2 mm aggregates of Bx and Bt before treatments (FRG_{before treatment} and NFRG_{before treatment}, respectively) are also reported.

400

Figure 6. Qualitative evolution of fragipan properties upon wetting and drying in lab conditions, depicted on an arbitrary scale (from 1 to 5) after A) deionized water cycle and B) CaCl₂-treatment in the different aggregate classes compared to soil fragipan and non-fragipan before treatments. The investigated fragipan properties are slaking (Soil Survey Staff, 2014; Falsone and Bonifacio, 2006; Lindbo and Rhoton, 1996), macroporosity (Lamotte et al., 1997; Ajmone-Marsan et al., 1994), particle density (Falsone and Bonifacio, 2009; Weisenborn and Schaetzl, 2005b) and microporosity (Lamotte et al., 1997; Ajmone-Marsan et al., 1994) measured in this study by high values of RPS values, low amount of Vc, high values of PDc and high amount of V_{MESO} , respectively. The highest is the rank, the best expressed the property. Note that in B) there are overlapping lines for FRG-CA and FRG₂₋₅-CA samples.

408 Tables

Table 1. Main morphological properties of the soil profile. Codes according to Schoeneberger et al. (2012)

Horizons	depth	Boundary	Munsell colour (dry)		Mottles	Structure	Coatings	Concentration	Rock fragments	Roots
	cm	D_T		Q_S_C	colour	G_S_T	Q_K	Q_S_K	volume%	Q_S

Oi	1-0	A_S	-	-	-	-	-	-	-	-
А	0-10	A_S	2.5Y6/4	-	-	2_f_gr		-	1	3_f
Bwc1	10-30	A_W	2.5Y6/6	f_1_d	2.5Y2.5/1	3_m_abk		1_2_FMN	5	3_f
Bwc2	30-60	C_W	2.5Y7/4	c_2_p	2.5Y2.5/1; 7.5YR6/8; 10YR6/8	3_m_abk		2_2_FMN	5	2_f
Btc1	60-120	C_W	10YR7/4	c_2_d	2.5Y5/1; 10YR4/3; 10YR6/8	3_co_abk	1_c	2_2_FMN	5	2_f
Btc2	120-165	A_S	10YR7/6	c_2_d	2.5Y2.5/1; 5YR4/6; 5YR4/3	2_co_abk	2_c	2_2_FMN	5	0
Btcx	165-190	A_S	7.5YR4/6	c_3_d	2.5Y2.5/1; 7.5YR6/8; 10YR7/6	3_co_pr	2_c	2_2_FMN	5	0
BC	190-245	C_W	5YR4/6	c_3_d	5YR2.5/1	3_co_abk	1_c	-	30	0
С	245-300	G_B	10YR4/6	c_3_d	5YR2.5/1; 5YR4/6; 10YR6/2	2_co_abk	-	-	70	0

410 Horizon boundary: (D) Distinctness: A=abrupt, C=clear, G=gradual; (T) Topography: S=smooth, W=wavy, U=unknown

411 Mottles: (Q) Quantity: f=few, c=common; (S) Size class: 1=fine, 2=medium; 3=coarse; (C) Contrast: d=distinct, p=prominent

412 Texture: SCL=sandy clay loam, SL=sandy loam. L=loam, C=clay

413 Structure: (G) Grade: 2=moderate, 3=strong; (S) Size class: f=fine, m=medium, co=coarse; (T) Type: gr=granular, abk= angular blocky, pr=prismatic

414 Coatings: (Q) Quantity: 1=few, 2=common; (K) Kind: c= clay

415 Concentrations: (Q) Quantity: 1=few, 2=common, 3=many; (S) Size class: 3=coarse; (K) Kind: FMN= iron-manganese masses

416 Roots: (Q) Quantity: 0=absent/very few, 1=few, 3=many; (S) Size class: f=fine

417

418 Table 2. Main properties of the <2 mm fraction of the selected Btc2 and Btcx soil horizons

Horizon	pН	Organic C	CS	FS	S	С	Fe _{DCB}	Ca	Total	V _{TOT}	SSA	Clay mineralogy
								saturation	porosity			

		g kg ⁻¹	%	%	$mm^3 g^{-1}$	$m^2 g^{-1}$						
Btc2	6.1	1.2	57.7	29.5	29.5	12.7	56.0	27.6	40	265	34.5	HIV (44%), Sm (28%), IV
												(15%), I (13%)
Btcx	6.1	2.2	59.5	26.2	26.2	14.2	77.3	21.3	38	240	48.4	HIV (37%), Sm (34%), IV
												(15%), I (14%)

CS: coarse sand (2-0.2 mm); FS: fine sand (0.2-0.05 mm); S: silt (0.05-0.002 mm); C: clay ($<2 \mu$ m); Ca saturation: percentage of exchangeable Ca/cation exchange capacity; V_{TOT}: total volume of Hg intruded; SSA: specific surface area; Clay mineralogy was evaluated by X-ray diffraction (Co-Kα radiation) on Mg-saturated, ethylene glycol solvated and 550°C-heated oriented clay fraction-mounts - scans were made from 3 to 35°2θ at a speed of 1.5°2θ min-1 and a semi-quantitative evaluation of mineral abundance was performed as described in Stanchi et al. (2017): HIV, hydroxy-interlayered vermiculite; Sm, smectite; IV, randomly interstratified illite-vermiculite mixed layers; I, illite; numbers inside brackets are the relative abundance

425

427 Table 3. Organic C, pedogenic Fe oxides and particle size distribution of the 1-2 mm aggregate

428 class of FRG and NFRG (Btcx and Btc2 soil horizon) before treatments and after the wet-dry cycle.

sample	treatment	treatment Organic Fe _{DCB} Particle size distribution after dispersion							CDR
code		С			with (N				
				CS	FS	S	С		
		g kg ⁻¹	g kg ⁻¹		9	6		g kg ⁻¹	%
FRG	before treatments	1.9±0.1	86.8±3.2	49.4±2.4	17.4±1.2	20.1±0.8	13.0±0.4	24.9±0.7	11.5±0.2
	(without any treatment)								
FRG-	water treatment	1.7±0.2	88.3±1.1	51.0±0.1	16.2±0.1	23.2±3.0	9.6±3.2	33.0±0.4	20.8±4.3
WAT									
FRG-	CaCl ₂ -treatment	1.4±0.2	94.8±3.9	39.1±0.7	16.6±0.7	25.5±0.2	18.7±0.2	31.5±3.3	9.1±0.8
CA									
NFRG	before treatments	1.3±0.1	62.8±1.8	24.8±5.4	44.4±8.8	20.1±3.3	10.7±0.1	7.4±0.5	12.1±1.8
	(without any treatment)								
NFRG-	water treatment	1.1±0.2	61.5±2.8	20.5±0.3	37.2±7.6	32.0±2.4	10.4±4.9	4.1±0.2	25.0±3.2
WAT									
NFRG-	CaCl ₂ -treatment	0.9±0.3	53.5±0.7	15.6±3.1	30.2±2.9	34.5±0.8	19.6±0.5	4.4±0.5	9.2±1.4
CA									

429 CS: coarse sand (2-0.2 mm); FS: fine sand (0.2-0.05 mm); S: silt (0.05-0.002 mm); C: clay (<2 μm); CS_{ox}:

 $\label{eq:430} \mbox{ coarse sand obtained after H_2O oxidation and Na-dithionite-citrate-bicarbonate extraction followed by}$

431 (NaPO₃)₆ dispersion; CDR: clay dispersion ratio

Table 4. Wet stability of the 1-2 mm aggregate class of Btcx and Btc2 soil horizon before

sample code	treatment	Loss	Loss _{et}	RPS
		%	%	%
FRG	before treatments	30.2±1.1	21.1±0.5	30.1±0.9
	(without any treatment)			
FRG-WAT	water treatment	58.1±0.2	44.5±4.1	23.4±4.2
FRG-CA	CaCl ₂ -treatment	68.8±3.6	58.5±2.9	15.0±8.7
NFRG	before treatments	20.7±2.5	16.2±1.2	21.7±2.4
	(without any treatment)			
NFRG-WAT	water treatment	41.7±1.7	34.8±2.7	16.5±3.0
NFRG-CA	CaCl ₂ -treatment	44.7±1.0	32.6±0.5	27.1±1.8

treatments (horizon codes: FRG and NFRG) and after the wet-dry cycle.

435 Loss: percentage of aggregates lost after 10 min of wet sieving; Loss_{et}: percentage of aggregates

436 lost after pre-wetting in ethanol and 10 min of wet sieving; RPS: relative percentage of slaking

437

- 439 Table 5. Packing density of coarser (sand and silt) and finer (clay) particles (PDc and PDf,
- 440 respectively) of the 1-2 mm aggregate class of Btcx and Btc2 soil horizons before treatments
- 441 (horizon codes: FRG and NFRG) and after the wet-dry cycle.

sample code	treatment	PDc	PDf	PDc/PDf
FRG	before treatments	0.82±0.01	0.31±0.01	2.65±0.06
	(without any treatment)			
FRG-WAT	water treatment	0.79 ± 0.01	0.39±0.08	2.02±0.16
FRG-CA	CaCl ₂ -treatment	0.79±0.01	0.54±0.01	1.47 ± 0.01
NFRG	before treatments	0.73±0.01	0.39±0.01	1.87 ± 0.02
	(without any treatment)			
NFRG-WAT	water treatment	0.73±0.01	0.34±0.10	2.16±0.06
NFRG-CA	CaCl ₂ -treatment	0.74±0.01	0.53±0.01	1.39±0.02

443 Table 6. Organic C, pedogenic Fe oxides and particle size distribution of newly formed 2-5 and >5 mm aggregates of FRG and NFRG (Btcx and

444 Btc2 soil horizons) obtained after the wet-dry cycle.

NF-aggregate	sample code	treatment	Organic C	Fe _{DCB}	Particle size distribution after dispersion with $(NaPO_3)_6$			CS _{ox}	CDR	
class										
					CS	FS	S	С		
			g kg ⁻¹	g kg ⁻¹	g kg ⁻¹		g kg ⁻¹	%		
2-5 mm	FRG ₂₋₅ -WAT	water treatment	1.5±0.1	95.5±0.7	40.1±0.5	24.3±5.1	22.5±4.7	13.0±0.1	24.9±1.3	9.2±2.1
	FRG ₂₋₅ -CA	CaCl ₂ -treatment	1.0±0.1	73.3±0.4	31.7±1.4	21.3±1.0	26.6±2.3	20.4±0.1	22.2±1.2	8.8±1.5
>5 mm	FRG ₅ -WAT	water treatment	1.3±0.1	80.5±0.1	36.2±0.6	29.2±4.9	20.7±2.3	13.9±2.0	17.3±0.1	13.7±2.2
	FRG ₅ -CA	CaCl ₂ -treatment	1.2±0.2	74.3±2.5	29.2±0.7	20.9±5.9	27.3±4.5	22.6±2.1	17.9±1.0	8.4±1.7
2-5 mm	NFRG ₂₋₅ -WAT	water treatment	0.7±0.1	50.8±1.1	14.8±0.2	33.9±0.9	37.8±0.1	13.5±0.8	4.1±0.8	16.3±1.4
	NFRG ₂₋₅ -CA	CaCl ₂ -treatment	0.8±0.2	51.8±0.4	10.8±1.2	35.1±3.1	35.4±1.8	18.8±0.1	3.9±0.3	10.1±0.7
>5 mm	NFRG ₅ -WAT	water treatment	0.6±0.1	53.0±0.1	15.0±0.4	34.8±4.9	36.5±3.2	13.8±1.4	3.2±0.6	17.2±3.2
	NFRG ₅ -CA	CaCl ₂ -treatment	0.6±0.1	50.5±0.2	8.2±1.5	33.3±3.9	38.6±2.2	19.9±0.2	4.0±0.4	11.1±1.8

445 CS: coarse sand (2-0.2 mm); FS: fine sand (0.2-0.05 mm); S: silt (0.05-0.002 mm); C: clay ($<2 \mu$ m); CS_{ox}: coarse sand obtained after H₂O oxidation and

446 Na-dithionite-citrate-bicarbonate extraction followed by (NaPO₃)₆ dispersion; CDR: clay dispersion ratio

Table 7. Wet stability of newly formed 2-5 and >5 mm aggregates of FRG and NFRG (Btcx and
Btc2 soil horizons) obtained after the wet-dry cycle.

NF-aggregate class	sample code	treatment	Loss	Loss _{et}	RPS
			%	%	%
2-5 mm	FRG ₂₋₅ -WAT	water treatment	66.1±0.8	63.2±1.6	4.4±1.1
	FRG ₂₋₅ -CA	CaCl ₂ -treatment	76.4±2.0	67.8±0.7	11.2±1.4
>5 mm	FRG ₅ -WAT	water treatment	64.3±0.1	63.2±3.9	1.8±5.9
	FRG ₅ -CA	CaCl ₂ -treatment	76.1±1.9	75.1±1.4	1.3±0.6
2-5 mm	NFRG ₂₋₅ -WAT	water treatment	57.2±1.0	52.2±0.6	8.7±2.6
	NFRG ₂₋₅ -CA	CaCl ₂ -treatment	60.3±0.6	53.9±1.1	10.7±2.7
>5 mm	NFRG5-WAT	water treatment	58.4±0.5	58.4±0.1	0.1 ± 0.8
	NFRG5-CA	CaCl ₂ -treatment	65.3±0.8	57.2±1.5	12.5±1.3

450 Loss: percentage of aggregate lost after 10 min of wet sieving; Loss_{et}: percentage of aggregate lost

451 after pre-wetting in ethanol and 10 min of wet sieving; RPS: relative percentage of slaking

453 Table 8. Packing density of coarser (sand and silt) and finer (clay) particles (PDc and PDf,

respectively) of newly formed 2-5 and >5 mm aggregates of FRG and NFRG (Btcx and Btc2 soil

455 horizons) obtained after treatments.

NEW-	sample code	treatment	PDc	PDf	PDc/PDf
aggregate class					
2-5 mm	FRG ₂₋₅ -WAT	water treatment	0.75±0.01	0.47±0.01	1.60±0.01
	FRG ₂₋₅ -CA	CaCl ₂ -treatment	0.78 ± 0.01	0.58±0.01	1.34±0.01
>5 mm	FRG ₅ -WAT	water treatment	0.77 ± 0.01	0.44±0.03	1.75±0.14
	FRG ₅ -CA	CaCl ₂ -treatment	0.70±0.01	0.59±0.02	1.19±0.05
2-5 mm	NFRG ₂₋₅ -WAT	water treatment	0.73±0.01	0.43±0.02	1.70±0.06
	NFRG ₂₋₅ -CA	CaCl ₂ -treatment	0.76±0.01	0.48 ± 0.01	1.58±0.01
>5 mm	NFRG5-WAT	water treatment	0.73±0.01	0.42 ± 0.02	1.74 ± 0.10
	NFRG5-CA	CaCl ₂ -treatment	0.75 ± 0.01	0.54±0.01	1.39±0.01















