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Patterns of geochemical variability across weakly developed paleosol profiles and their role as regional stratigraphic markers (Upper Pleistocene, Po Plain)

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Patterns of geochemical variability across weakly developed paleosol profiles and their role as regional stratigraphic markers (Upper Pleistocene, Po Plain)

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Abstract

Weakly developed paleosols from two distinct interfluvial surfaces of Late Pleistocene age provide excellent keys to high-resolution stratigraphic correlation and may serve to trace large-scale genetic packages (systems tract equivalents) across the continental portion of the Po Basin. Twenty-four paleosol profiles from 17 sediment cores were identified and characterized for bulk-geochemical analysis. X-ray fluorescence data were used to trace the degree of weathering. Paleosols, 0.5-1.5 m thick, are pedogenically altered floodplain deposits, developed over time spans of a few thousand of years and mostly partitioned into A-Bk horizons. The most notable paleosol features are dark, organic-matter-rich and carbonate-free mineral surface horizons (A) that overlie bright calcic horizons (Bk) typified by the accumulation of secondary carbonates in the form of pedogenic nodules.

Paleosol profiles exhibit a homogeneous geochemical signature that fingerprints a moderate degree of weathering, with little strike- and dip-oriented variability across the different study localities. Plots of Al-normalized calcification and base loss indices against depth reveal systematic increasing values from intensely altered A horizons to underlying Bk horizons. These trends reflect consistent patterns of Ca translocation from surface horizons deeper into the profile, with significant to almost complete Ca removal from A horizons through leaching and accumulation in Bk horizons. Selected trace element ratios (Ba/Sr, Rb/Sr), redox-sensitive trace elements and Zr contents display opposite, up-profile increasing trends that reflect Sr loss in A horizons, with selective Zr concentration in residual minerals.

Vertical trends in element ratios are laterally extensive and consistent on a regional basis and represent key pedochemical/stratigraphic markers that can be traced over great distances (tens of

36 kms) throughout the inland portion of the basin. Through quantitative assessment of the degree of
37 weathering, geochemical profiling provides high potential for robust subsurface paleosol
38 correlation that might not be captured by visual core descriptions alone.

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40 Keywords: Paleosol stratigraphy; Paleosol maturity; Interfluvial; Sequence stratigraphy; Sequence
41 boundary; Geochemistry

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44 **1. Introduction**

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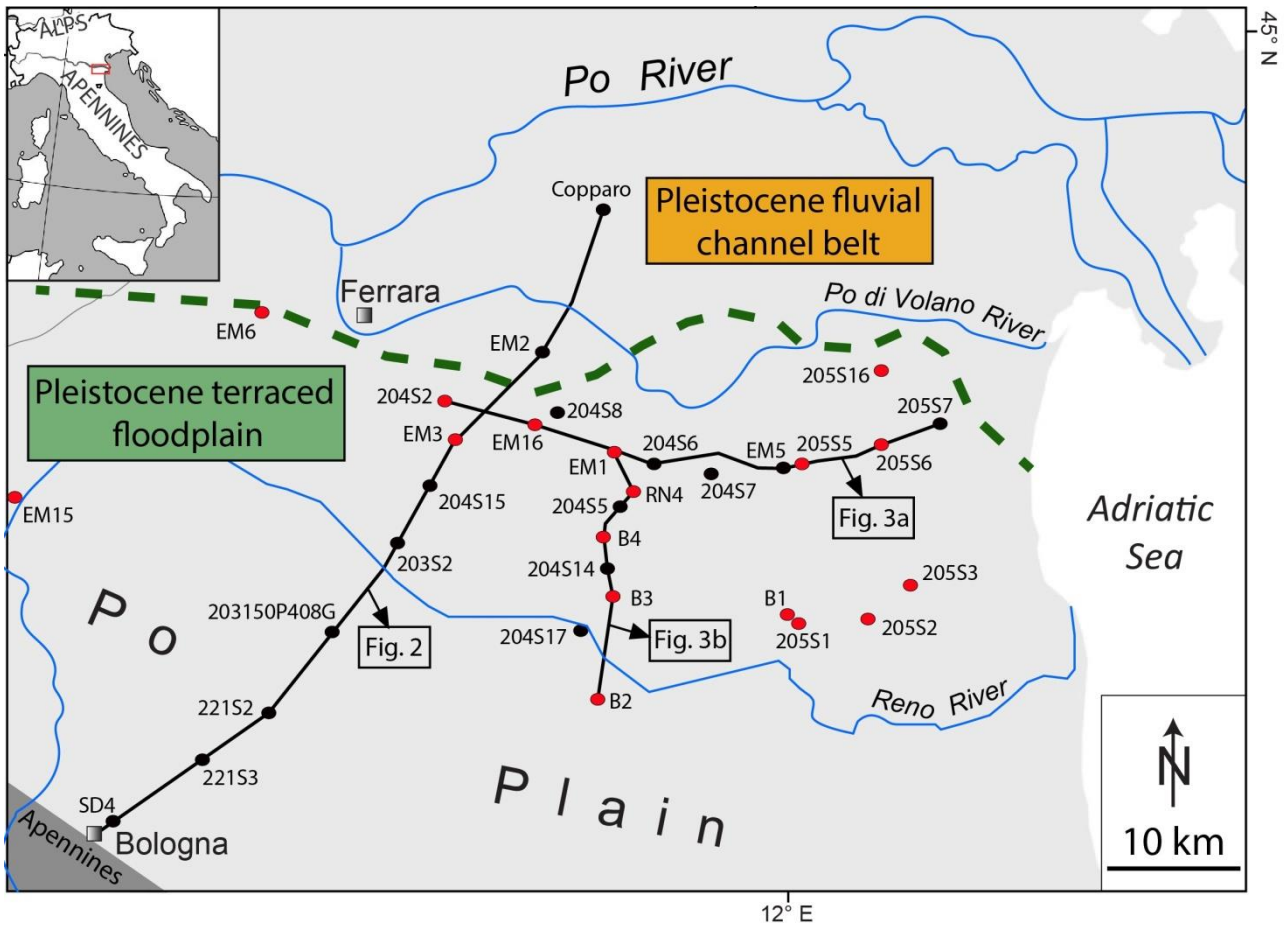
46 Paleosol-bearing alluvial successions contain a hierarchical record of cyclic sediment
47 accumulation produced in response to the combined effect of autogenic and allogenic controlling
48 mechanisms (Cleveland et al., 2007). Paleosols at sequence-bounding unconformities, in
49 particular, may serve as useful regional stratigraphic markers to trace genetic packages across the
50 basin and to determine regional accommodation trends (Demko et al., 2004).

51 According to sequence-stratigraphic models, paleosol units commonly correlate with incision
52 along the major drainage axes (Van Wagoner et al., 1990) and well-developed, mature interfluvial
53 paleosols correlate to valley-floor erosion surfaces (Gibling and Bird, 1994; Aitken and Flint, 1996;
54 Shanley and McCabe, 1994; McCarthy and Plint, 1998; 2003; Plint et al., 2001; Atchley et al., 2004;
55 Blum and Aslan, 2006; Cleveland et al., 2007; Srivastava et al., 2010; Raigemborn and Beilinson,
56 2020).

57 Models of paleovalley architecture and paleosol-valley relations have been evaluated using
58 Quaternary examples, where proxy records are well established for climate and sea level and
59 periods of incision and aggradation can generate discontinuity-bounded sequences on timescales
60 as short as 10^3 to 10^4 years (Gibling et al., 2011). In such examples, valley fills are less distinctive
61 and their bases do not correspond to prominent paleosols. Stacked weakly developed paleosols
62 may form terrestrial condensed sections that record prolonged periods of minimal sedimentation
63 in interfluvial position (Gibling et al., 2011; McCarthy and Plint, 2013).

64 Vertical successions of poorly mature paleosols have been widely described from the Upper
65 Pleistocene subsurface record of the Po Plain, in Italy (Amorosi et al., 2017b; Bruno et al., 2018).
66 Stiff, pedogenized floodplain silts and clays are widely preserved south of the modern Po River and

67 correlate in the north to genetically-related fluvial facies, where thick channel-belt sand bodies
 68 represent the dominant subsurface stratigraphic unit (Fig. 1).
 69



70
 71 *Fig. 1. Location map of studied cores (red dots), with indication of the boundary between the*
 72 *buried Pleistocene (pre-LGM) terraced floodplain and the coeval fluvial channel-belt sand bodies*
 73 *(green dashed line, from Morelli et al., 2017). Section trace of Figure 2, transects in Fig. 3, and*
 74 *location of additional cores used for stratigraphic correlation (black dots) are also shown.*
 75

76 The Upper Pleistocene-Holocene sedimentary succession provides a particularly well-
 77 established temporal framework, founded largely on ¹⁴C data, within which immature paleosols
 78 delineate time-equivalent stratal surfaces and represent key stratigraphic markers that can be
 79 traced on a regional scale. Three paleosols of Late Pleistocene age (P1-P3) and a younger paleosol
 80 marking the Pleistocene-Holocene boundary (PH) were recognized for the first time from core
 81 analysis in the Bologna area (Amorosi et al., 2014a). Subsequent studies examined the basin-scale
 82 distribution of these paleosols (Amorosi et al., 2017b; Bruno et al., 2019) and their likely climatic
 83 significance (Bruno et al., 2020). Morelli et al. (2017) carried out the detailed subsurface mapping
 84 of the youngest two paleosols: paleosol P3, formed at the onset of the Last Glacial Maximum

85 (LGM), and paleosol PH, encompassing the Younger Dryas (YD) cold event, which marked the
86 short-lived return to glacial conditions after the Late Glacial Interstadial. Although upper
87 Quaternary paleosols clearly exhibit a high potential for regional correlations, only reconnaissance
88 geologic investigation has been undertaken and no detailed paleosol characterization has been
89 attempted, so far.

90 In this study, a comprehensive geochemical investigation of paleosols P3 (LGM paleosol) and PH
91 (YD paleosol) was performed for the first time. The aim of this paper is to provide quantitative
92 assessment of paleosol maturity across these two pedogenized key stratigraphic surfaces, which
93 in a sequence-stratigraphic perspective coincide with the sequence boundary (SB) and the
94 landward equivalent of the transgressive surface (TS), respectively (Fig. 2). Specific objective is to
95 document the stratigraphic utility of immature paleosols for regional correlations within a
96 chronologically constrained sequence-stratigraphic framework. Below the Holocene succession,
97 the study area reveals a wide, buried Late Pleistocene interfluvial between the Apennines margin
98 and the coeval fluvial channel-belt bodies in the modern Po River area (Fig. 1). Age-equivalent
99 strata successions are compared from 17 sediment cores, approximately 80 km apart. This study
100 incorporates high-resolution stratigraphic data, paleosol descriptions and geochemistry.

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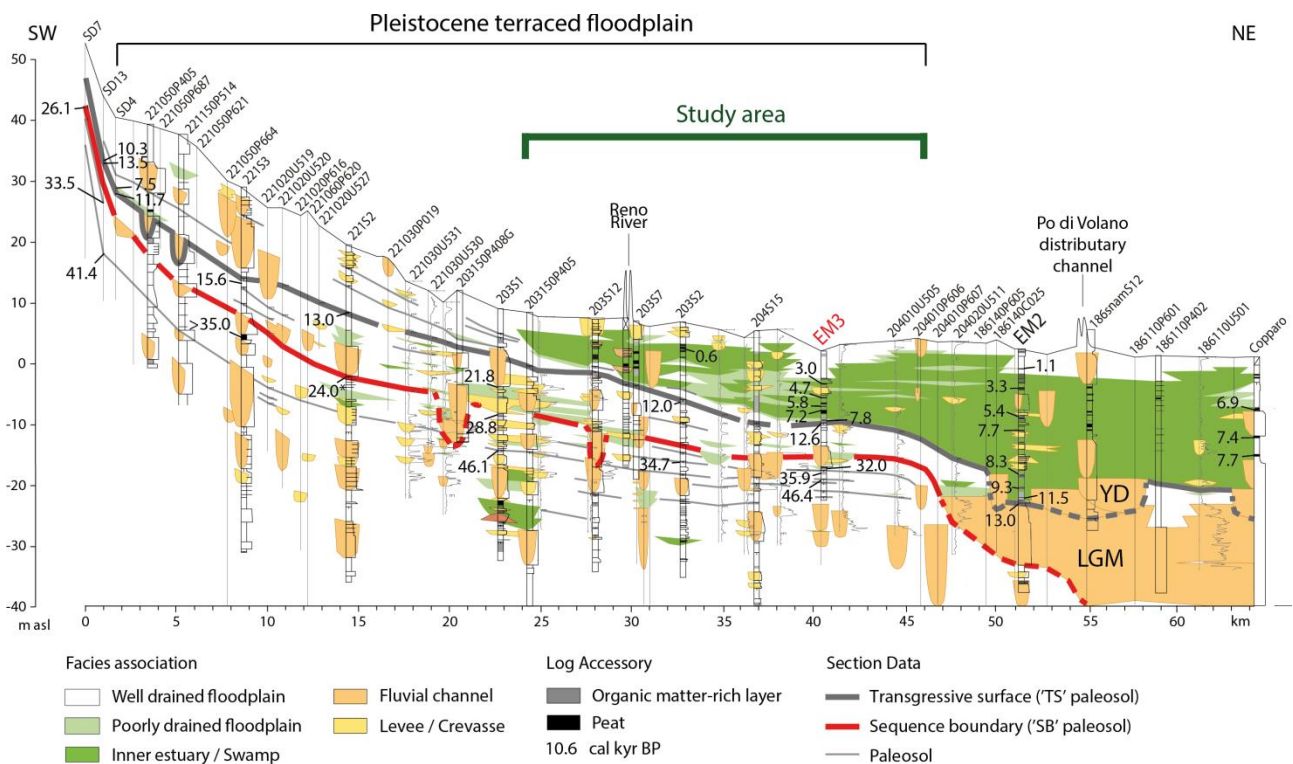
103 **2. Stratigraphic overview**

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105 Previous work provides a solid foundation of the shallow subsurface stratigraphy of late
106 Quaternary continental deposits in the Po Plain (Amorosi et al., 2014a; 2017b; Morelli et al., 2017;
107 Bruno et al., 2018; 2020). In this rapidly subsiding setting with high rates of sedimentation, no
108 persistent incised valley was established during the last interglacial/glacial transition and
109 aggradationally-stacked, shallow-incised fluvial bodies are laterally associated with overbank
110 packages, a few m thick, bounded by poorly mature paleosols (Amorosi et al., 2017b – Fig. 2).
111 These paleosols, which define large-scale, though shallow degradation across the Po Plain
112 interfluvial, associated to short (2-5 kyr) gaps in sedimentation document widespread, but short-
113 lived, subaerial weathering across poorly dissected, interfluvial areas (Amorosi et al., 2017b; Bruno
114 et al., 2020).

115 A hierarchy of Upper Pleistocene paleosols has been identified and framed through high-
116 resolution sequence stratigraphic analysis within a strongly constrained chronological setting,

117 founded on tens of radiocarbon dates (Fig. 2). Two prominent paleosols, in particular, exhibit very
 118 high lateral continuity on a regional scale and are genetically related to fluvial channel-belt sand
 119 bodies identified to the north, beneath the modern Po River (Morelli et al., 2017 – Fig. 2).
 120 Paleosol-bounded overbank intervals have sequence-stratigraphic significance within the LGM
 121 depositional sequence and represent low-accommodation deposits. Based on detailed
 122 stratigraphic correlation with coeval littoral and shallow-marine facies associations, the two
 123 paleosols (paleosols P3 and PH of Amorosi et al., 2014) have been interpreted to represent the
 124 sequence boundary (SB) and the landward equivalent of the transgressive surface (TS),
 125 respectively (Amorosi et al., 2017a – Fig. 2).
 126



128 *Fig. 2. Regional stratigraphic cross-section (section trace in Fig. 1) showing relationship of*
 129 *floodplain paleosols to their contemporaneous fluvial channel-belt sand bodies (modified after*
 130 *Amorosi et al., 2017b). Weakly-developed paleosols are typically arranged in thin, paleosol-*
 131 *bounded overbank sequences and are associated to larger trunk channels amalgamated into*
 132 *multilateral channel belts. The paleosol at the sequence boundary ('SB' paleosol) was generated at*
 133 *the MIS 3/2 transition and correlates to fluvial channel-belt bodies assigned to the Last Glacial*
 134 *Maximum (LGM). The landward equivalent of the transgressive surface ('TS' paleosol) marks the*
 135 *Pleistocene-Holocene boundary and correlates to Younger Dryas (YD) channel belts.*

136
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 138 Sea-level lowering and climate-driven forcing have been invoked to account for shallow incision
 139 and coeval soil development in the Po Plain during the latest Pleistocene (Amorosi et al., 2017b;

140 Bruno et al., 2018; 2020). Pedogenic modification of floodplain silts and clays occurred at the MIS
141 (Marine Isotope Stage) 3/2 transition, between 30 and 24 cal kyr B.P. (SB paleosol), and during the
142 protracted sea-level lowstand, when fluvial entrenchment terraced the formerly active (pre-LGM)
143 alluvial plain, which underwent extensive pedogenic modification. Shallowly-incised tributary
144 valleys (see Kvale and Archer, 2007) form part of a surficial (Cremaschi, 1987; Castiglioni, 2001;
145 Bersezio et al., 2007) and subsurface (Bruno et al., 2017b, 2018; Morelli et al., 2017) mappable
146 drainage network feeding into the much larger Po fluvial system.

147 The SB interfluvial paleosol caps a series of weakly expressed profiles that reflect multiple-step
148 pedogenic history mostly occurring during MIS 3 (Bruno et al., 2020). Individual paleosols are
149 generally stacked and separated by thin layers of overbank material (compound paleosols of
150 Marriott and Wright, 1993). However, they may locally display overlapping profiles with A-B
151 overprinting (composite paleosols) and pedogenic features may extend throughout much of the
152 stratigraphic section. The SB paleosol correlates to the base of highly lenticular, valley-filling sand
153 bodies, typically 20 to 30 m thick and 5 to 20 km wide, that display virtually no pedogenesis (Fig.
154 2).

155 A younger, regionally extensive paleosol (TS paleosol in Fig. 2) correlates with a short-lived
156 episode of shallow fluvial incision developed around the Pleistocene-Holocene boundary (Amorosi
157 et al., 2017b). Radiocarbon dates from this paleosol in the study area cluster around the Younger
158 Dryas cold reversal (Fig. 2). Paleosol TS is simple. In the subsurface of the modern coastal plain it is
159 invariably overlain by a deepening-upward succession of Holocene swamp, lagoonal, coastal and
160 shallow-marine deposits and for this reason it is interpreted as the landward equivalent of the TS.

161 Soil formation at the MIS 3/2 transition has been described from other parts of the world. The
162 primary influence on regional water table lowering at the MIS 3/2 transition was relative sea-level
163 fall (Blum and Price, 1998; Dabrio et al., 2000; Autin and Aslan, 2001; Anderson et al., 2004;
164 Busschers et al., 2007; Kasse et al., 2010; Fan et al., 2018). Similar, coeval paleosols have been
165 reported from the Yangtze River, where compound paleosols (pedocomplexes) resulted from
166 alternating deposition and pedogenesis on the paleointerfluvial (Chen et al., 2008). Fluvial incision
167 and soil development around the Pleistocene/Holocene boundary have been recorded in other
168 European fluvial systems (Mol et al., 1997; van Balen et al., 2010; Janssens et al., 2012).

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173 **3. Methods**

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175 Within detailed measured sections from 17 cores (Fig. 1, Supplementary Table 1), 24 soil
176 profiles were investigated and characterized for geochemical composition. Ten paleosols marking
177 the sequence boundary ('SB' paleosols) and 14 younger paleosols formed at the transgressive
178 surface ('TS' paleosols) were studied. The locations of the cores were chosen to provide as
179 extensive coverage as possible across the two terraced paleosurfaces (Morelli et al., 2017).
180 Geochemical analysis was carried out on all the study cores to extract elemental concentrations. A
181 total of 100 soil samples were analyzed (Supplementary Table 2): 62 from 'TS' paleosols and 38
182 from compound/composite 'SB' paleosols. We also analyzed 11 samples from unaltered floodplain
183 parent material from the same cores. This study is based largely on the stratigraphic distribution of
184 macromorphological features of pedogenesis and on geochemical characterization of paleosols.
185 Micromorphological investigations were not attempted.

186 Cores, 17 to 52 m thick, were split lengthwise and carefully described for their sedimentological
187 characteristics. Facies analysis was carried out on a centimetre scale. Graphic logs of cores include
188 description of lithology, grain size, primary sedimentary structures, lamination styles, bioturbation
189 levels and accessory components.

190 Paleosols at key stratigraphic intervals were recognized by visual inspection of core material.
191 Profile descriptions include horizonation, horizon thickness, color, reaction, redoximorphic
192 features, carbonate accumulations, and other standard soil observations. Moist colors of mottles
193 and matrix were described. Composition, size, and abundance of nodules and other mineral
194 segregations were also characterized. Geotechnical properties were obtained through pocket
195 penetration measurements. Horizon designations are based upon core-observed features in the
196 paleosols after Soil Taxonomy (Soil Survey Staff, 1999).

197 Paleosols were sampled by horizon for bulk chemical analysis. Series of three to six samples
198 were taken per paleosol profile from the top to a maximum depth of 150 cm. Major and trace
199 element geochemistry was determined by X-ray fluorescence spectroscopy (XRF). Cores were
200 analyzed at Bologna laboratories. Samples were oven dried at 50°C, powdered and homogenized
201 in an agate mortar and analyzed using a Philips PW 1480 spectrometer (Philips, Almelo, The
202 Netherlands). The matrix correction methods of Franzini et al. (1972), Leoni and Saitta (1976) and
203 Leoni et al. (1982) were followed.

204 Analytical methods resulted in data for 29 elements: 10 major elements, reported as oxide
205 percent by weight (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , and P_2O_5), 18 trace
206 elements (Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Pb, Rb, S, Sc, Sr, V, Y, Zn, and Zr), and the loss on
207 ignition (LOI). LOI, evaluated after overnight heating at 950°C (LOI_{950}), represents a measure of
208 volatile substances (weight %, wt%), including pore water, inorganic carbon and organic matter.
209 The XRF analytical protocol reports major elements in oxide weight percent and trace elements in
210 parts per million. The estimated precision and accuracy for trace element determinations were
211 better than 5%. For elements with low concentrations (<10 mg/kg), the accuracy was 10%.

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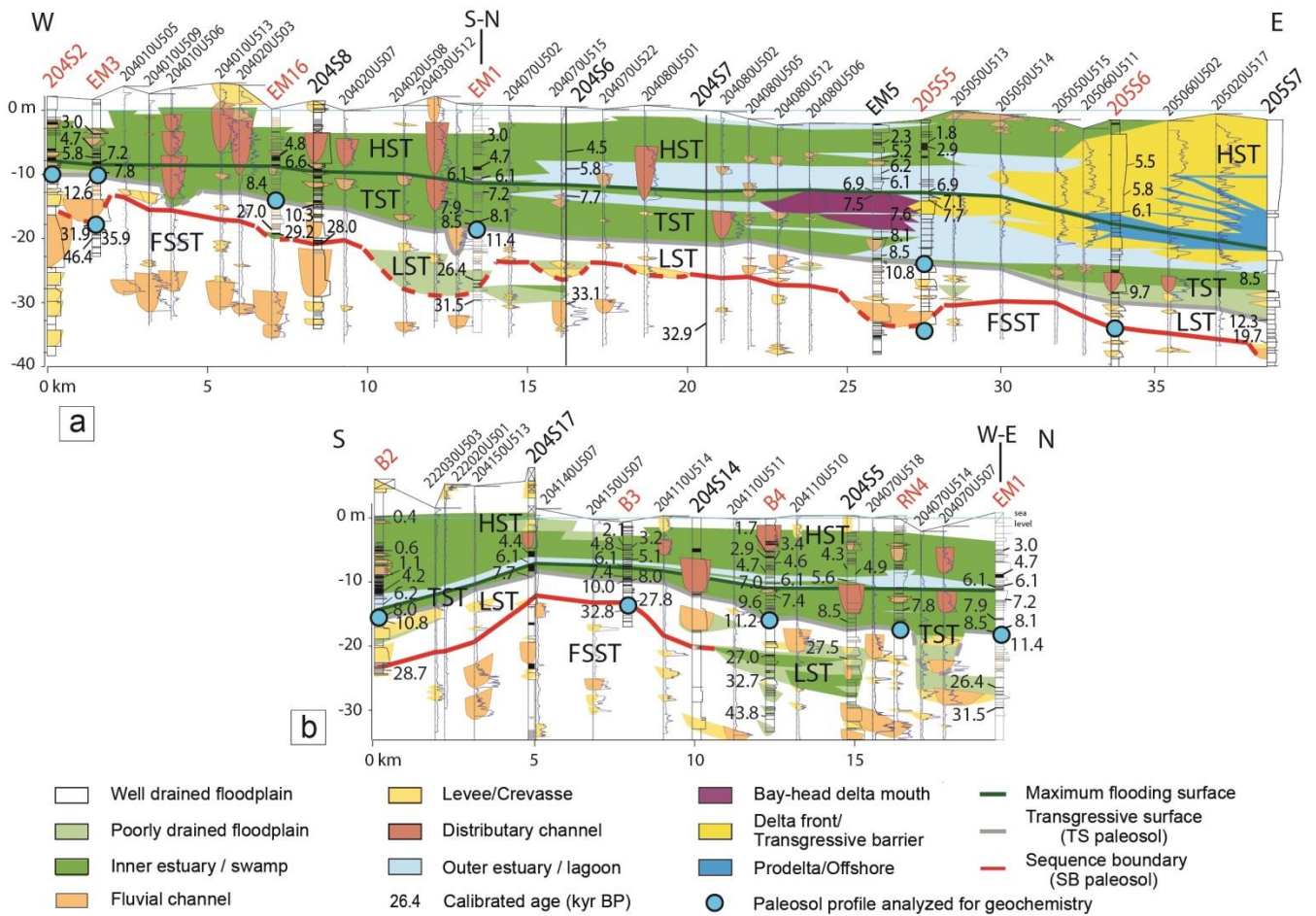
214 **4. Paleosol stratigraphy**

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216 The Upper Pleistocene-Holocene stratigraphy in the study area was depicted along two
217 transects, on the basis of stratigraphic and sedimentological data from 18 continuous cores and 36
218 piezocone (CPTU) penetration tests (Fig. 3). The W-E transect (Fig. 3a) runs roughly in proximal to
219 distal direction across the buried Pleistocene terraced floodplain, 5-15 km from the southern
220 margin of the Po paleovalley system, whereas the S-N transect (Fig. 3b) runs perpendicular to the
221 regional axis of the Northern Apennines (Fig. 1).

222 In this study, we did not focus on facies architecture, which has been the subject of several
223 published papers and that will not be reiterated here. Summary characteristics of major facies
224 associations are summarized in Table 1. For detailed description and interpretation of coastal plain
225 to shallow-marine deposits, the reader is referred to previously published material (Amorosi et al.,
226 2017a; 2020; Bruno et al., 2017b; 2019; Campo et al., 2020). In this paper, we focused, instead, on
227 the identification, characterization and tracing of paleosols at two discrete stratigraphic horizons,
228 corresponding to the SB and TS (Fig. 2). Paleosols identified in cores (Fig. 4) were calibrated against
229 CPTU tests and tracked laterally based on distinctive changes in log character. The key
230 geotechnical features to infer paleosols from CPTU tests include: (i) a subtle, but consistent
231 increase in cone resistance with depth, (ii) a sharp peak in the sleeve friction, recording the sharp
232 contrast between normally consolidated floodplain facies and underlying stiff, pedogenically
233 modified deposits, and (iii) an abrupt decrease in pore pressure (Amorosi and Marchi, 1999; Choi
234 and Kim, 2006; Amorosi et al., 2017b; Bruno et al., 2019).

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237

238 *Fig. 3. Sequence stratigraphy of Upper Pleistocene-Holocene deposits from the subsurface of the Po*
 239 *Plain, with position and correlation of 'SB' (red line) and 'TS' (grey line) paleosols. Cores analyzed in*
 240 *this paper are marked in red. Radiocarbon dates from Amorosi et al. (2017a) (upper transect) and*
 241 *Amorosi et al. (2020) (lower transect). FSST: Falling-stage systems tract, LST: Lowstand systems*
 242 *tract, TST: transgressive systems tract, HST: highstand systems tract.*

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245 In the study area, the SB paleosol bears radiometric dates in the age range of 29.2-27.8 cal kyr
 246 B.P. (Fig. 3). It is underlain by a set of closely-spaced paleosols that exhibit slightly older ages (Fig.
 247 3). Regional stratigraphy above this paleosol includes a thin (4-7 m) lowstand systems tract capped
 248 by the TS paleosol, with age ranges between 12.6 and 11.2 cal kyr B.P. (Fig. 3). The TS paleosol
 249 marks a regional facies change above Pleistocene alluvial deposits and it is overlain by a basinally
 250 mappable transgressive surface (TS in Fig. 3).

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Facies Association	Lithology Sedimentary structures	Fossils
Fluvial channel	coarse to medium sand, FU trend, high-angle cross-lamination, 2-10 m thick	generally barren
Crevasse/levee	alternating sand and silt, parallel lamination, climbing ripples, 0.5-3 m thick	
Floodplain	clay and silty clay, bioturbation, root traces, mottling, paleosols, 1-20 m thick	generally barren, rare freshwater
Poorly drained floodplain	organic-matter-rich clay, roots, plant remains, 1-5 m thick	rare freshwater
Distributary channel	medium to fine sand, FU trend, high-angle cross-lamination, 2-10 m thick	generally barren, rare freshwater to low brackish
Bay-head delta	medium to fine sand, high-angle cross-lamination, plant debris, 2-5 m thick	mixed freshwater/brackish
Inner estuary/swamp	soft clay, plant debris, wood fragments, peat, parallel lamination, 1-20 m thick	freshwater to low brackish
Outer estuary/lagoon	bioturbated clay, clay-sand alternations, 1-5 m thick	brackish
Delta front/beach barrier	fine to coarse sand, high-angle cross-lamination, parallel lamination, 1-10 m thick	littoral
Prodelta/offshore	organic-matter-rich silty clay, bioturbated clay, 1-7 m thick	marine

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Table 1. Summary characteristics of major lithofacies assemblages in the study area.

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The Holocene succession displays a characteristic retrogradational to aggradational/progradational stacking pattern of facies that defines the transgressive systems tract (TST) and highstand systems tract (HST), respectively (Fig. 3). Holocene deposits rest unconformably on the TS paleosol with typical onlap geometries (Fig. 3a) and provide a detailed understanding of the stratigraphic development of the coastal plain under transgressive and normal regressive conditions. They cover a great diversity of facies associations (Campo et al., 2017) that represent coeval depositional environments, ranging from shallow-marine (offshore and prodelta) through coastal, brackish (outer estuary/lagoon) and freshwater (inner estuary/low-lying swamps).

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In the study area, the top surface of the TS paleosol coincides with the landward equivalent of a surface of marine flooding that denotes subsequent transgression (Fig. 3a). Over most of the study area, the overlying Holocene sedimentary succession is dominated by single-story distributary-channel sand bodies encased in organic-rich clays, with a tongue of thin brackish (lagoonal) deposits that demarcate the maximum flooding surface (Fig. 3b). Peat-bearing deposits accumulated in low-lying, permanently waterlogged environments in the inner portion of a transgressive estuary and in the delta plain of a prograding delta system.

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There is no dramatic change in depositional style in the two sections of Fig. 3, except for the notable deformation of Quaternary strata in the 204S17-B3 cores area (Fig. 3b), which has been interpreted to reflect recent tectonic activity of the buried anticline structures (Amorosi et al., 2020). Though discontinuous due to local truncation or poor development onto sandy substrates,

277 paleosols on floodplain deposits can be typically traced laterally for about 40 km and appear to
278 have been developed on a gently inclined slope (Fig. 3).

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281 **5. Paleosol description**

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283 Upper Pleistocene paleosols in the subsurface of the Po Plain are easily differentiated from
284 overlying and underlying (unaltered) units by their stiff texture and color-banded appearance (Fig.
285 4). They all are silt- and clay-rich and are typically formed on muddy (floodplain) deposits.

286 Soil profiles typically consist of a dark, organic-rich and bioturbated silt (A horizon) that
287 gradually overlies a paler horizon (Bk). Paleosol colors are relatively uniform throughout horizons
288 A and B. Dominant colors are grey to brownish grey and dark brown in horizons A and light grey to
289 pale yellow in the deeper horizons (Fig. 4).

290 Organic matter imparts the dark color in A horizons. Macroscopic features include root traces,
291 wood debris, and plant fragments that are scattered throughout the unit. A horizons are barren
292 with fossils and weakly reactive or unreactive to 10% dilute HCl. Pedogenic carbonate appears
293 within 30-80 cm of the soil surface (Bk horizon), persisting to depths of about 100-150 cm (Fig. 4).
294 Calcic horizons (Soil Survey Staff, 1999) can be thick and diffuse or thinner and more concentrated.
295 Within Bk horizons, CaCO_3 concretions are visible to the naked eye, generally as pseudomycelia
296 and few to common hard nodules. Powdery and filamentous carbonate is commonly observed
297 between nodules. Carbonate nodules are well-rounded to sub-rounded and range from diffuse,
298 poorly cemented concentrations to discrete, well-cemented masses. Locally, nodules may be
299 larger than > 1 cm in diameter and may coalesce to form cemented or indurated, thin massive
300 layers (Bkm).

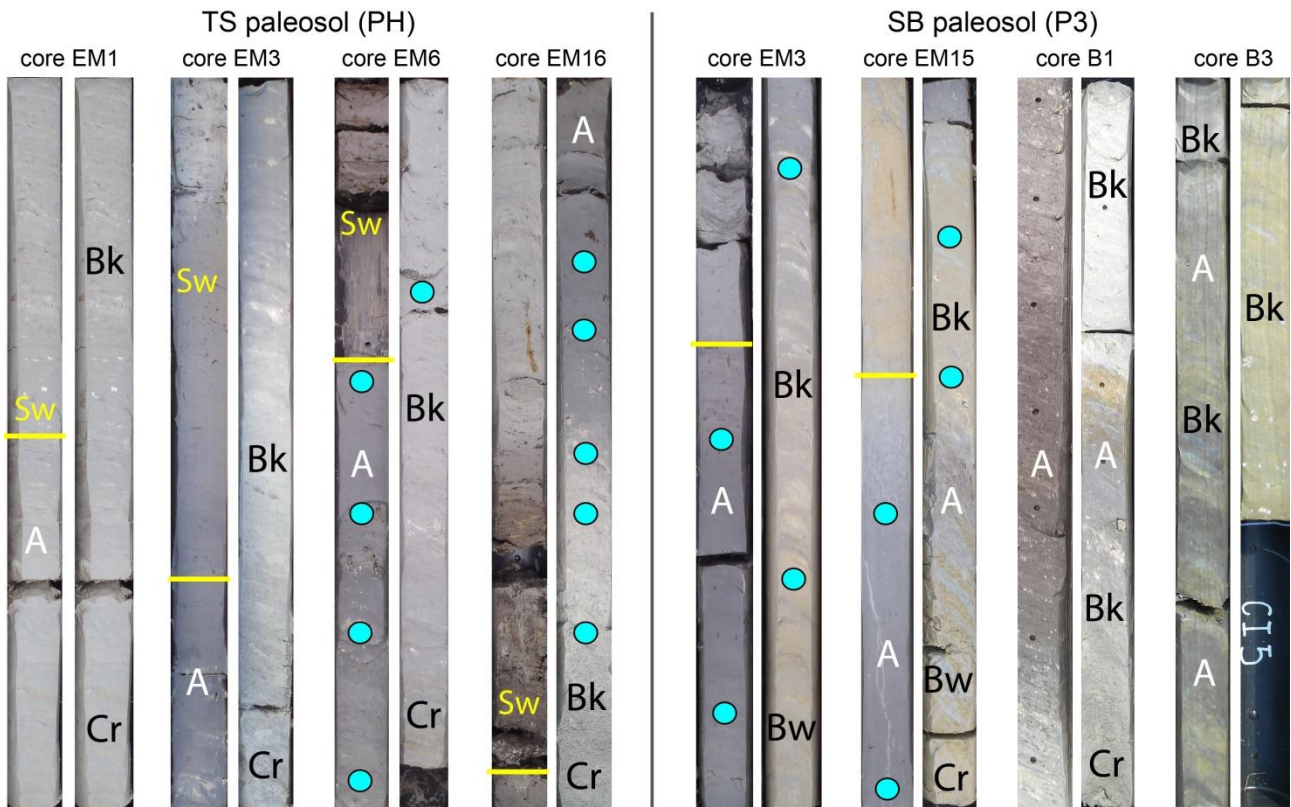
301 A less common subsurface paleosol horizon that may be associated to the Bk horizon is Bw (Fig.
302 4). Pedogenized deposits in this case display root traces, local yellow, brown and orange colors
303 and no carbonates. Black mottles likely derive from different manganese oxide species coating
304 primary particles.

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311 *Fig. 4. Representative profiles of paleosols 'TS' and 'SB' showing A/Bk/Bw/Cr horization (for*
 312 *location, see Fig. 1; paleosol stratigraphy in Fig. 3). TS paleosols are simple A/Bk profiles, invariably*
 313 *overlain by Holocene transgressive deposits (inner estuary/swamp facies association - Sw),*
 314 *suggesting increased waterlogging and flooding in response to a rising water table. Paleosols*
 315 *spanning the sequence boundary (SB) consist of vertically stacked immature paleosols. Light blue*
 316 *dots indicate samples plotted in the geochemical profiles of Fig. 6. Core length is 1 m.*

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318

319 The unweathered (Cr) horizon retains the character of the unconsolidated parent material
 320 (floodplain deposits) and as such does not display pedogenic structure or significant rooting. To
 321 define the original material, we also determined average bulk compositions of unweathered
 322 floodplain sedimentary packages from the same stratigraphic succession.

323 Paleosols identified in cores also exhibit diagnostic engineering properties (Amorosi et al.,
 324 2015), with substantially higher compressive strength coefficients than all other fine-grained,
 325 alluvial (floodplain) facies. Specifically, paleosols are typified by distinctive penetration resistance,
 326 in the range of 3.5-5 kg/cm², with maximum values in Bk horizons (Amorosi et al., 2015). On the
 327 other hand, non-pedogenized floodplain deposits invariably display lower pocket penetration
 328 values (average value: 2.0 kg/cm²).

329

330 6. Paleosol geochemistry

331

332 Major elements are commonly used to define the net effect of ancient chemical weathering
333 from paleosols (Retallack, 2001). Several oxide ratios have been developed to assist with the
334 interpretation of soil-forming processes in paleosols (Birkeland, 1999; Retallack, 2001). In general,
335 alkali (Na and K) and alkaline earth (Ca and Mg) elements are mobile (Sheldon and Tabor, 2009)
336 and are preferentially released from their host minerals during weathering (Mohanty and Nanda,
337 2016), whereas the elements Al, Ti and Zr are considered to be chemically immobile in weathering
338 environments.

339 Several major element indices, such as the Chemical Index of Alteration-CIA,
340 $Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)$ (Nesbitt and Young, 1982), the Chemical Weathering Index-CWI,
341 $Al_2O_3/(Al_2O_3+CaO+Na_2O)$ (Harnois, 1988), or the $\Sigma Bases/Al$ ratio, $(CaO+MgO+Na_2O+K_2O)/Al_2O_3$
342 (Retallack, 1999) provide an indication of leaching of the bases from the soil system in response to
343 weathering intensity, measuring the loss of mobile cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ , given as oxides,
344 with respect to stable alumina (Ruxton, 1968; Retallack, 1999; Sheldon and Tabor, 2009). These
345 indices, based on the ratio of a group of highly mobile oxides to one or more immobile oxides, are
346 the best candidates to characterize weathering-induced changes (Price and Velbel, 2003; Varela et
347 al., 2018).

348 In order to compensate for textural heterogeneity, in general we used elemental ratios over
349 simple single-element measurements (Sheldon and Tabor, 2009). To facilitate interpretation of
350 changes in geochemical composition as a result of soil development, values were also calculated
351 from the unweathered parent material, corresponding to Pleistocene floodplain muds (Table 2).

352 Among the various chemical indices widely used to estimate weathering, we chose key
353 indicators closely related to pedogenic processes (Retallack, 1997a,b,c; Driese et al., 2000; Sheldon
354 and Tabor, 2009): SiO_2 for the framework material, Al_2O_3 for the clay component, CaO and Sr for
355 the carbonate component, labile oxides for the degree of weathering, Zr for residual minerals.
356 Owing to possible biases due to the overwhelming role of Ca relative to Na and K in the study
357 samples (see values of labile oxides in Table 2), we did not use CIA and CWI as primary indicators
358 of the degree of weathering. We also did not select element ratios that include iron in their
359 formulation, because iron concentrations are a reflection of redox conditions, which may be
360 controlled by modern or ancient groundwater levels and may not be consistent throughout the
361 weathering profile (Harnois, 1988).

Horizon	Surface	SiO ₂ (%)	±	TiO ₂ (%)	±	Al ₂ O ₃ (%)	±	Fe ₂ O ₃ (%)	±	MnO (%)	±	MgO (%)	±	CaO (%)	±	Na ₂ O (%)	±	K ₂ O (%)	±	P ₂ O ₅ (%)	±
A	SB	56.50	5.10	0.75	0.08	16.48	1.54	5.72	1.03	0.05	0.02	3.57	0.72	1.78	1.51	1.09	0.22	2.81	0.28	0.11	0.02
	TS	55.11	4.72	0.76	0.08	17.08	1.26	5.98	0.76	0.08	0.04	3.36	0.64	1.54	0.83	0.91	0.30	2.83	0.30	0.10	0.02
Bk	SB	41.25	5.09	0.57	0.08	12.69	1.22	5.68	1.30	0.14	0.04	3.68	0.76	14.10	3.50	0.68	0.18	2.17	0.23	0.10	0.02
	TS	39.77	4.43	0.54	0.08	11.74	1.16	4.81	0.83	0.11	0.03	3.85	0.68	16.49	3.79	0.86	0.73	2.03	0.29	0.10	0.02
Cr		48.71	2.49	0.67	0.05	14.01	1.16	5.92	0.82	0.10	0.04	3.94	0.83	8.59	2.22	0.78	0.13	2.57	0.20	0.11	0.01

Horizon	Surface	LOI (%)	±	Ba (mg/kg)	±	Ce (mg/kg)	±	Co (mg/kg)	±	Cr (mg/kg)	±	Cu (mg/kg)	±	Ga (mg/kg)	±	La (mg/kg)	±	Nb (mg/kg)	±	Ni (mg/kg)	±
A	SB	11.15	6.97	444.54	47.60	80.83	13.19	20.23	5.93	134.04	17.78	38.48	6.53	17.90	4.89	45.38	11.52	15.07	2.91	77.50	12.01
	TS	12.26	3.67	424.72	41.79	85.74	18.31	23.80	8.44	148.49	32.42	41.10	16.96	20.39	5.06	44.48	9.81	17.09	2.43	85.70	14.64
Bk	SB	18.93	3.21	310.56	40.12	58.86	11.15	17.92	6.25	114.11	17.66	35.73	7.73	14.13	4.76	30.20	9.12	11.32	3.06	64.64	6.47
	TS	19.68	2.99	298.73	49.05	55.49	13.50	14.06	5.13	111.34	14.88	31.84	6.70	15.00	3.99	29.93	7.27	12.73	2.48	63.94	6.12
Cr		14.59	1.49	336.55	35.41	59.59	8.67	18.47	4.89	138.11	43.87	39.23	6.89	17.80	1.72	32.68	5.28	14.10	0.92	98.25	41.55

Horizon	Surface	Pb (mg/kg)	±	Rb (mg/kg)	±	S (mg/kg)	±	Sc (mg/kg)	±	Sr (mg/kg)	±	V (mg/kg)	±	Y (mg/kg)	±	Zn (mg/kg)	±	Zr (mg/kg)	±
A	SB	21.03	3.34	136.57	16.29	712.19	1010.04	13.08	4.29	154.32	30.51	121.06	16.62	31.30	3.95	105.66	12.60	194.08	32.00
	TS	21.78	2.89	156.08	18.74	773.26	712.82	15.81	5.81	147.64	22.62	135.84	31.60	33.31	4.61	107.89	15.38	194.16	48.24
Bk	SB	15.19	2.38	89.28	14.24	243.46	164.81	14.63	5.53	342.63	152.41	103.70	15.66	22.23	4.21	83.37	11.77	107.56	22.55
	TS	14.18	3.09	93.54	15.11	520.84	609.23	14.01	6.40	332.30	74.79	93.44	16.58	23.29	3.04	77.58	9.50	121.42	30.09
Cr		17.48	2.34	110.72	17.38	172.73	103.66	13.62	4.18	267.82	53.87	105.51	12.99	25.91	1.85	86.52	8.76	129.54	24.91

Horizon	Surface	(CaO+MgO)/Al ₂ O ₃		(CaO+MgO+K ₂ O+Na ₂ O)/Al ₂ O ₃		Ba/Sr		Rb/Sr		Al ₂ O ₃ /SiO ₂		Al ₂ O ₃ /TiO ₂	
A	SB	0.33	0.12	0.56	0.12	3.00	0.75	0.91	0.17	0.29	0.02	22.17	2.17
	TS	0.29	0.08	0.51	0.09	2.93	0.45	1.08	0.19	0.31	0.04	22.85	2.91
Bk	SB	1.44	0.48	1.67	0.48	1.05	0.45	0.30	0.09	0.31	0.03	22.43	2.21
	TS	1.77	0.48	2.02	0.49	0.96	0.35	0.30	0.09	0.30	0.03	21.85	2.18
Cr		0.91	0.20	1.15	0.21	1.32	0.35	0.44	0.16	0.29	0.02	21.04	1.53

362

363 *Table 2. Summary statistics and major- and trace-element indices for paleosols 'TS' and 'SB' (A and*
364 *Bk horizons) and for unaltered floodplain parent material (Cr horizon). For quantitative primary*
365 *data, see Supplementary Table 2.*

366

367 Key element ratios were calculated (Table 2) along selected paleosol profiles (Fig. 5) and
368 plotted in binary diagrams (Fig. 6). Table 2 permits a comparison of average values for selected
369 geochemical parameters along the study paleosols. Six geochemical indices are reported below as
370 a function of depth.

371

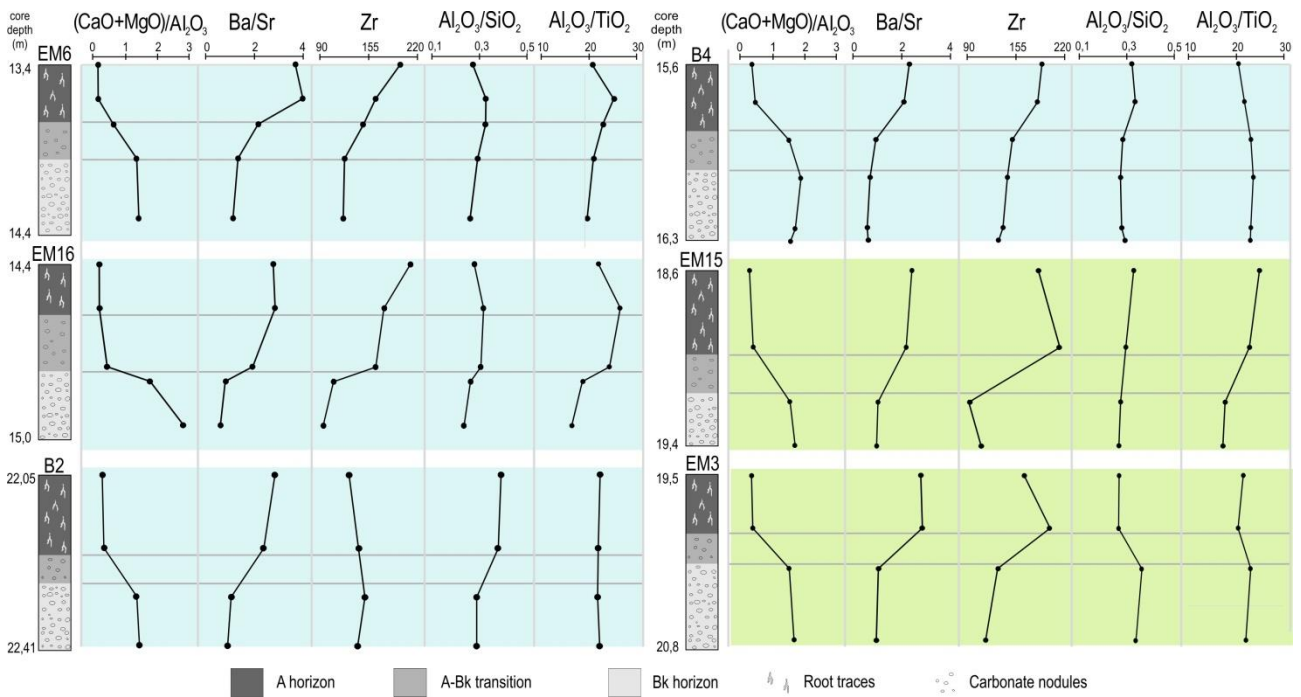
372 6.1. Calcification index

373

374 The (CaO+MgO)/Al₂O₃ ratio (calcification index) is a general proxy for pedogenic carbonate
375 (calcite and dolomite) accumulations (Retallack, 2001a, b; 2007; Mohanty and Nanda, 2016).
376 Generally, calcification is associated with processes that occur in dry climates where evaporation
377 exceeds precipitation (Delgado et al., 2019).

378 In the study samples, the calcification index clearly discriminates between low values in A
379 horizons and moderate values in Bk horizons, with no overlap (Fig. 5, Table 2). CaO is strongly
380 depleted in upper A horizons (average values: 1.78% at the SB, 1.54% at the TS), whereas it is
381 significantly enriched in Bk horizons (average values: 14.10% in SB paleosols, 16.49% in TS
382 paleosols). Unaltered floodplain deposits exhibit intermediate values (8.59%). On the other hand,
383 MgO values are fairly constant across distinct paleosol horizons and very similar to unweathered
384 floodplain silts and clays (Table 2). Calculated (CaO+MgO)/Al₂O₃ ratios for A horizons are all fairly

385 low, average values ranging between 0.29 (TS paleosols) and 0.33 (SB paleosols). On the other
 386 hand, average values for Bk horizons are in the 1.44 (SB paleosols) – 1.77 (TS paleosols) range and
 387 denote marked calcification. The calcification index averages 0.91 in unaltered Cr horizons (Table
 388 2).
 389



390
 391 *Fig. 5. Variations of major- and trace-element indices along selected paleosol profiles (see Figs. 3-*
 392 *4). TS paleosols (cores EM6, EM16, B2 and B4) are in light blue, SB paleosols (cores EM15 and EM3)*
 393 *in light green.*

394
 395 **6.2. Base loss index**
 396

397 The $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$ ratio, $(\text{CaO}+\text{MgO}+\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$, measures the loss of mobile cations Ca^{2+} ,
 398 Mg^{2+} , Na^+ and K^+ , given as oxides, with respect to stable alumina (Ruxton, 1968; Mora and Driese,
 399 1999; Retallack, 1999; Sheldon and Tabor, 2009). This index, which unlike the Chemical Index of
 400 Alteration (Nesbitt and Young, 1982) takes into account the role of Mg-bearing minerals, provides
 401 an indication of leaching of the bases from the soil system in response to weathering intensity
 402 (Retallack, 1999). The $(\text{CaO}+\text{MgO}+\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ index is similar to the Chemical Weathering
 403 Index (Harnois, 1988) and is the reciprocal of the hydrolysis ratio (Sheldon and Tabor, 2009).
 404 Chemical weathering affects plagioclase preferentially, then K-feldspar (Nesbitt et al., 1996).
 405 Calcium, sodium and potassium generally are removed from these minerals by aggressive soil
 406 solutions so that the proportion of alkalis to alumina typically decreases in the weathered product
 407 (Nesbitt and Young, 1982). In case of overwhelming weathering control, mobile elements are

408 expected to be all depleted in surface horizons (He et al., 2020), whereas Bk horizons typically
409 exhibit values higher than 1 (Dal' Bó et al., 2009).

410 In Po Plain paleosols, horizons A and Bk are clearly differentiated through the $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$
411 ratio (Fig. 6a and Table 2), with notably similar results for older (SB) and younger (TS) paleosols.
412 Average values for A horizons range between 0.51 (TS paleosols) and 0.56 (SB paleosols), whereas
413 average values for Bk horizons are in the range of 1.67 (SB paleosols) – 2.02 (TS paleosols). This
414 index has average value of 1.15 in Cr horizons (Table 2).

415

416 *6.3. Leaching index*

417

418 The Ba/Sr ratio quantifies the amount of leaching during the weathering process using the
419 behaviour of alkaline earth metals like Ba and Sr (Retallack, 2001a, b; Sheldon and Tabor, 2009;
420 Scarciglia et al., 2018). Although Ba and Sr have similar atomic radii and the same molecular
421 affinity, Sr is more soluble than Ba (Vinogradov, 1959) and the Ba/Sr ratio increases with
422 increasing weathering (Nesbitt and Young, 1982). Strontium dissolution in soils follows the same
423 pathways as calcium. On the other hand, the chemical behaviour of Ba is less understood than Sr,
424 particularly in soils (Sheldon and Tabor, 2009). The Rb/Sr ratio has been suggested as another
425 indicator of the degree of weathering (Chen et al., 1999; Xu et al., 2010). Because the ionic radius
426 of Rb is close to that of K, Rb generally coexists with K in K-rich minerals, such as K-feldspar and
427 biotite, whereas Sr is preferentially partitioned into Na- and Ca-bearing minerals, such as
428 carbonates, plagioclase and amphibole. Weathering can leach Ca and Sr much easier than Rb and
429 K. As a result, the relict would have higher Rb/Sr ratios compared with the leached fraction. The
430 Rb/Sr has also been used as a paleoclimatic indicator in loess-paleosol complexes (Chen et al.,
431 1999).

432 The behaviour of the Ba/Sr leaching proxy mirrors that of the calcification index, allowing
433 further differentiation between A and Bk horizons (Figs. 5 and 6b). Ba/Sr ratios for A horizons
434 exhibit moderate average values that range between 2.93 (TS paleosols) and 3.00 (SB paleosols),
435 whereas consistent, notably lower average values (0.96 for TS paleosols, 1.05 for SB paleosols)
436 were obtained for Bk horizons. Unaltered floodplain material (Cr horizons) yielded an average
437 value of 1.32 (Table 2). In the study paleosols, the Rb/Sr ratio behaves as the Ba/Sr ratio and
438 decreases steadily downcore (Table 2). An obvious trend of Rb enrichment and Sr depletion is
439 observed in A horizons (Fig. 5). Average values of the Rb/Sr ratio for A horizons range between

440 0.91 (SB paleosols) and 1.08 (TS paleosols), whereas for Bk horizons they are equal to 0.30. In the
441 parent material (Cr horizon), the Rb/Sr ratio has an average value of 0.44 (Table 2).

442

443 6.4. Zr (zirconium)

444

445 Trace element geochemistry of paleosols provides valuable information regarding leaching and
446 the degree of weathering (Retallack, 1999; 2001; Kahman et al., 2008; Mohanty and Nanda, 2016).
447 Certain elements, such as Zr and Ti, are preferentially hosted in the densest minerals (e.g., zircon,
448 ilmenite and monazite – Garzanti and Andò, 2019) and their concentration may vary owing to
449 selective-entrainment effects (Garzanti et al., 2013; He et al., 2020). Zirconium (Zr), in particular, is
450 commonly found in minerals that are resistant to alteration and therefore tends to accumulate as
451 weathering progresses (Maynard, 1992; Mongrain et al., 2013; Driese et al., 2000), especially in
452 the very fine sand-silt fraction (Garcia et al., 2003).

453 In the study paleosols, Zr shows a conspicuous decrease downprofile (Fig. 5 and Table 2), with
454 few exceptions (e.g., core B2). An average value of 194 mg/kg is observed in A horizons,
455 irrespective of paleosol age (SB vs TS), whereas significantly lower average values (108 mg/kg for
456 SB paleosols, 121 mg/kg for TS paleosols) are recorded for Bk horizons. The average Zr
457 concentration for unaltered Cr horizons is 130 mg/kg.

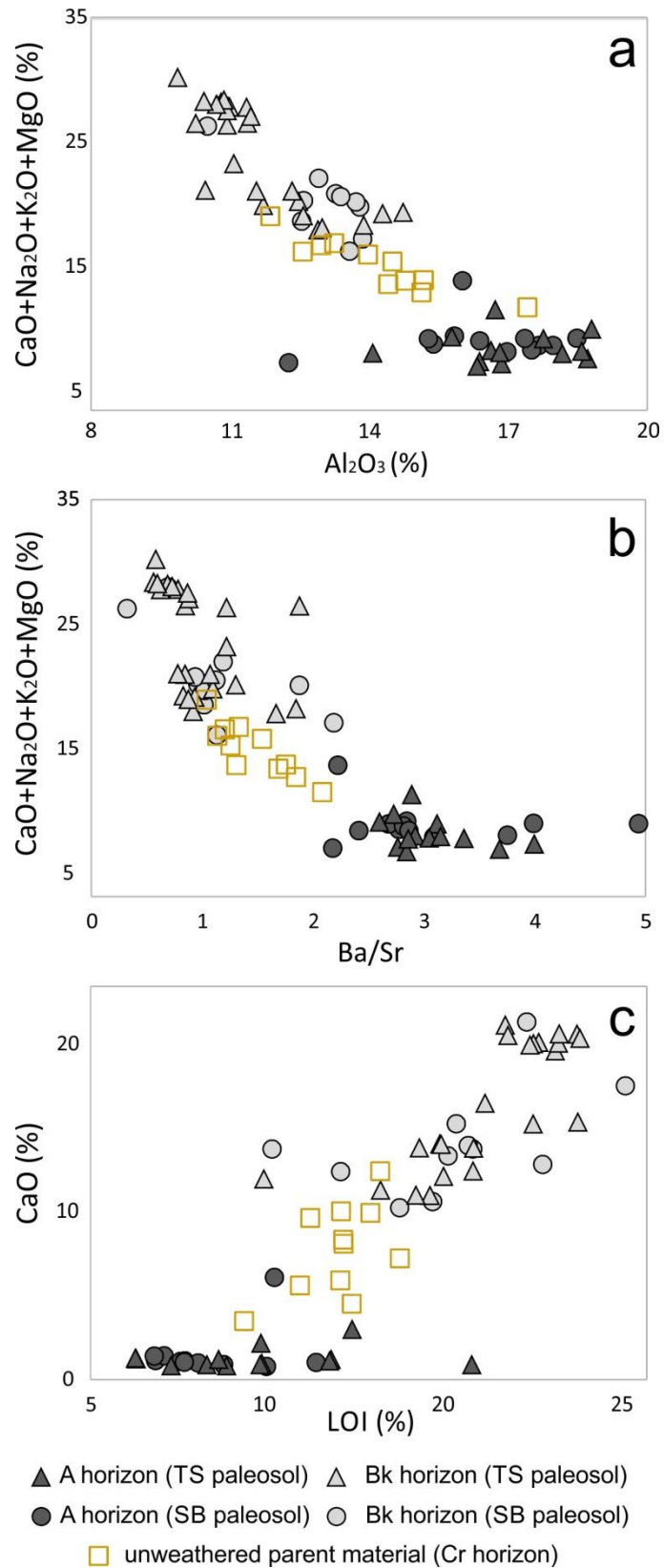
458

459 6.5. Clayeyness index

460

461 The Al_2O_3/SiO_2 ratio is a method for quantifying the amount of clay formation (Ruxton, 1968;
462 Retallack et al., 2000; Prochnow et L., 2006), because Al accumulates in clay minerals relative to a
463 silicate parent material (Sheldon and Tabor, 2009). Higher values are indicative of increasing clay
464 formation with the loss of feldspars and other less resistant minerals (Ruxton, 1968; Sheldon and
465 Tabor, 2009).

466 In the study samples, the clayeyness index contributes little geochemical signal, with minimal
467 variations across the weathering profiles (Fig. 5), irrespective of paleosol horizons (A versus Bk) or
468 ages (SB versus TS paleosols) (Table 2). For A horizons, average values of the Al_2O_3/SiO_2 ratio are
469 narrowly constrained between 0.29 (SB paleosols) and 0.31 (TS paleosols). B horizons yielded very
470 similar average values, ranging between 0.30 (TS) and 0.31 (SB). A similar clayeyness average value
471 (0.29) was also obtained for the unweather floodplain material (Cr horizon in Table 2).



472

473

474 *Fig. 6. Geochemical plots for 24 representative paleosols from 17 sediment cores (Fig. 1), grouped*
 475 *by horizon (A versus Bk) and sequence-stratigraphic position ('SB' versus 'TS' paleosols). Data are*
 476 *plotted against geochemical data from unweathered floodplain silts and clays (Cr horizon) from the*
 477 *same cores. a: Cross-plot of Al_2O_3 vs $(CaO+MgO+Na_2O+K_2O)$; b: Cross-plot of Ba/Sr vs*
 478 *$(CaO+MgO+Na_2O+K_2O)$; c: Cross-plot of LOI vs CaO .*

479

480 6.6. Al_2O_3/TiO_2 ratio

481

482 This ratio is particularly useful as a provenance indicator, because Ti contents may be quite
483 variable among different types of rocks, even as Al contents are relatively constant (Sheldon and
484 Tabor, 2009). As both Al and Ti are relatively immobile elements, their ratio generally remains
485 constant during pedogenesis (Delgado et al., 2019).

486 Average ratios of Al_2O_3/TiO_2 exhibit little variation at different profile localities and are fairly
487 uniform across the various paleosol profiles, with no significant distinction between A horizons
488 (22.17 for SB paleosols, 22.85 for TS paleosols) and Bk horizons (21.85 for TS paleosols, 22.43 for
489 SB paleosols). This implies relatively homogeneous provenance.

490 The major geochemical variations shown along six paleosol profiles (Fig. 5) are consistent with
491 data from 24 paleosols and 17 sediment cores (Fig. 6). In the $\Sigma Bases/Al_2O_3$ cross-plot (Fig. 6a), data
492 points from the A horizons, Bk horizons and the unaltered parent material reveal a strong negative
493 correlation and plot in three distinct clusters, irrespective of the key sequence-stratigraphic
494 surface (SB or TS) at which sampled were collected. Elemental analysis shows that Bk horizons
495 invariably have the highest $CaO+MgO+Na_2O+K_2O$ values. Particularly, $\Sigma Bases$ yielded higher values
496 in Bk horizons than in A horizons by an average factor 3.5 (Table 2). Data from the unaltered
497 parent material invariably fall between these two extremes (Fig. 6a).

498 The roughly linear pattern of the $\Sigma Bases$ versus Al_2O_3 plot is also seen with some trace
499 elements, like Ba/Sr (Fig. 6b), and with LOI (Fig. 6c), that behave as CaO. Figures 6b and 6c reveal
500 that there is a systematic trend in geochemical element distribution, with higher Sr concentrations
501 and LOI values being prevalent in Bk horizons. At the other extreme, A horizons exhibit the lowest
502 values in all paleosols.

503

504

505 7. Paleosol maturity

506

507 As Upper Pleistocene Po Plain paleosols underwent very incipient diagenesis, they still preserve
508 most of their morphological and physico-chemical properties and environmental signatures. In
509 general, paleosols are partitioned into two major pedogenic layers or horizons (Figs. 4-6). Basic
510 identification features of paleosols include differences in color from darker A horizons to

511 underlying lighter Bk horizons that reflect organic matter inputs in A horizons and calcium
512 carbonate accumulation in Bk horizons (Schwertmann, 1993).

513 The relative rates of formation and characteristic stages of morphologies of Bk horizons have
514 been quantified by Gile et al. (1965, 1966), Machette (1985) and Retallack (1988) for modern soils
515 and Quaternary paleosols. According to such classification schemes, the presence of few to
516 common carbonate nodules in calcareous (Bk) horizons allows attribution of Po Plain paleosols to
517 Stage II of carbonate accumulation (Machette, 1985) and to the second stage of paleosol
518 development (weakly developed paleosols of Retallack, 1988), which in fine-grained materials
519 imply a few thousands of years to form (Birkeland, 1999). The rates of carbonate dissolution and
520 reprecipitation in Bk horizons have been modelled by McFadden and Tinsley (1985) and
521 mathematical models are available to estimate carbonate accumulation in soils (Mc Fadden et al.,
522 1991; 1998). These studies are consistent with radiometric dating of Po Plain Inceptisols from the
523 Bologna area, which also concluded that substantial pedogenic carbonate horizons formed during
524 intervals of time of a few thousand years (Amorosi et al., 2014a; Bruno et al., 2020). Dominance of
525 pedogenic carbonates in calcic horizons and weak pedogenic development suggest relatively dry
526 conditions and the presence of a vadose zone and low groundwater table (Demko et al., 2004;
527 Srivastava et al., 2018; Bruno et al., 2020). The presence of calcareous paleosols at the sequence
528 boundary and on lowstand surfaces suggests that pedogenesis took place during times of relative
529 climatic aridity and possibly reduced precipitation (Tandon and Gibling, 1997; Sinha et al., 2007).

530 Examination of geochemistry of Quaternary paleosols yields quantitative estimates of paleosol
531 maturity and shows that paleosols bracketing the SB or developed at the landward equivalent of
532 the TS have nearly uniform chemistry and display broadly similar stages of development
533 throughout both dip-oriented (Fig. 3a) and strike-oriented (Fig. 3b) cross-sections. On
534 homogeneous parent material, such as in the case of Quaternary Po Plain floodplain deposits,
535 weathering indices change systematically with depth (Price and Velbel, 2003). Accordingly,
536 geochemical variations in element ratios are observed at discrete levels within the study paleosols,
537 allowing the clear differentiation between A and Bk horizons.

538 Pedogenesis may increase the relative amount of alumina in sediments. Nearly constant
539 Al_2O_3/SiO_2 values with depth observed in Po Plain paleosols (Fig. 5 and Table 2) suggest that no
540 significant clay illuviation took place in deeper horizons. This is consistent with the lack of well
541 developed argillic (Bt) horizons along the paleosol profiles. Calculated values of the Al_2O_3/SiO_2
542 ratio are consistent with field observations and indicate that there is little textural variation

543 throughout paleosol profiles. They also indicate that pedogenesis occurred on homogeneous silt-
544 and clay-rich floodplain facies (Sprague et al., 2009).

545 Degradation of feldspars and other minerals by the removal of base cations (mostly Ca) by
546 dissolution and concomitant formation of clay minerals is the dominant process during chemical
547 weathering of silicate rocks (Nesbitt and Young, 1982). Mobile elements hosted in A horizons
548 undergo extensive leaching and are progressively subtracted from feldspars. Leaching of mobile
549 components (including CaO and MgO) is associated with enrichment of immobile elements, such
550 as Zr (Fig. 5 and Table 2).

551 All geochemical proxies behave consistently. Selected indices that are commonly inferred to
552 quantify the totality of weathering processes, such as calcification and Ba/Sr (Fig. 5 and Table 2)
553 coherently reflect low degree of weathering under relatively cold climate conditions. It is apparent
554 that several geochemical elements follow distinct patterns of geochemical variability and that
555 downcore geochemical trends from all the study cores are consistent along paleosol profiles and
556 represent pedochemical markers on a basin scale (Delgado et al., 2019). The most notable down-
557 profile variation is increased concentration of labile oxides (CaO and MgO) with respect to Al₂O₃.
558 Such negative Ca translocations from A horizons to underlying Bk horizons largely reflect
559 weathering and removal of this labile cation relative to stable residual constituents. Base cations
560 were leached from upper soil horizons in response to acidification processes and rapidly
561 accumulated within the calcareous subsoil, reflecting the accumulation of pedogenic carbonate.
562 Elevated LOI values in Bk horizons, paralleled by CaO levels (Fig. 6c), are interpreted to reflect the
563 liberation of CO₂ during ignition of samples due to abundant carbonate (Cleveland et al., 2008).
564 LOI data were then not considered further in interpretation.

565 Table 2 outlines the geochemical elements evaluated in this study and provides a comparison
566 of the six element ratios plotted in Figs. 5 and 6. Significant leaching of the parent material to form
567 paleosols is also inferred from the Ba/Sr and Rb/Sr ratios, which increase from Bk to A horizons.
568 The enriched values of these “leaching parameters” in the A horizons are interpreted to reflect Sr
569 removal from A horizons and accumulation of Sr-rich carbonate nodules in Bk horizons in
570 association with Ca. Sequestration of Sr in the pedogenic carbonate phases and substitution of Sr
571 for Ca are likely phenomena in the paleosol profile (Driese et al., 2000).

572 Concentrations of redox-sensitive trace elements, such as Cu, V, Cr, Ni, Co and Zn are notably
573 higher in A horizons (Table 2). For the other trace elements, Zr is typically enriched in A horizons
574 (Fig. 5). The abundance of Zr can be controlled by multiple geological factors other than

575 weathering, including parent-rock material, grain size and hydraulic sorting (He et al., 2020). In the
576 study area, perceptible enrichment in Zr concentration within A horizons is interpreted to reflect
577 weathering: prolonged stability of interfluvial surfaces is suggested by concentration of resistant
578 heavy-minerals, such as zircons, in A horizons (Driese et al., 2000; Mongrain et al., 2013).

579

580

581 **8. Use of immature paleosols for regional correlations**

582

583 Weakly-developed paleosols represent regional surfaces of non-deposition that play a critical
584 role in the high-resolution stratigraphy of the Upper Pleistocene, non-marine succession of the Po
585 Plain. Pedogenic alteration is ubiquitous across the weathered interfluvial surfaces and paleosols in
586 key stratigraphic positions bear unique and consistent physico-chemical characteristics that can be
587 effective in delineating subsurface stratigraphy of low-accommodation (FSST+LST) fluvial deposits
588 on a regional scale (Figs. 2 and 3). Radiocarbon dating of SB and TS paleosols provides values
589 consistent with radiocarbon ages observed from their updip equivalents, in the Bologna region
590 (Amorosi et al., 2014a; Bruno et al., 2020). The remarkably similar stratigraphic architecture of
591 Upper Pleistocene alluvial deposits in the study area (Fig. 3) with respect to regional paleosol
592 stratigraphy (Fig. 2) suggests a similar history of deposition and pedogenesis that was likely
593 produced under relatively cold climate conditions (LGM and YD, respectively) in response to
594 allogenic controlling factors.

595 McCarthy and Plint (2013) have shown that paleosols characteristics at key sequence-
596 stratigraphic surfaces may vary on a basin scale depending upon their paleo-landscape position
597 with respect to valley margins and the marine shoreline, and that they can be partitioned into
598 three distinct spatial zones based on their degree of development and architecture. The study area
599 (Fig. 1) represents a relatively short segment of the wider Po Plain-Adriatic Sea source-to-sink
600 system and displays no remarkable lateral variability in terms of physiographic location (Fig. 2).
601 Within this relatively homogeneous alluvial plain segment, paleosol maturity does not exhibit
602 significant differences in terms of pedogenic features (Fig. 4) and geochemical properties (Figs. 5-
603 6). Poor lateral geochemical variability of paleosol characteristics on a km-scale has also been
604 documented by Driese and Ashley (2016) and by Hyland and Sheldon (2016).

605 Further updip, at a greater distance from the margin of the Po paleovalley system, Late
606 Pleistocene interfluvial surfaces experienced higher intensities of pedogenic processes owing to

607 their more elevated paleo-landscape position. At these locations, the immature paleosols
608 (Inceptisols) described from the subsurface of the Po Plain are replaced by an intensely rubified
609 Alfisol characterized by strong clay illuviation (Cremaschi, 1987; Cremaschi et al., 1990). This soil
610 crops out continuously at the Apennines foothills and documents through a catenary effect a
611 remarkably higher degree of soil development than in the buried distal units (Cremaschi and
612 Nicosia, 2012). For a detailed documentation of alternating phases of sediment aggradation,
613 stabilization and pedogenesis at the Apennines margin during the Late Pleistocene, the reader is
614 referred to Zuffetti et al. (2018).

615 Subsurface control may predict the approximate position of SB and TS paleosols across the Po
616 Basin fill through integration of physical stratigraphy with radiometric data (Figs. 3 and 4). This
617 study has shown that framing precisely paleosol location into three-dimensional analysis can be
618 largely aided by intrinsic geochemical properties (Figs. 5 and 6). Paleosol TS, developed at the
619 Pleistocene/Holocene boundary, is readily recognized by its diagnostic stratigraphic position below
620 Holocene transgressive deposits (Fig. 3). On the other hand, immature paleosols capped by the SB
621 may stack one on another in a welded fashion as accommodation lessens (Figs. 2 and 4). For such
622 paleosols, especially if no radiocarbon dates are available, correlation of soil-forming intervals
623 bracketing the sequence boundary can be more useful than is attempting to correlate individual
624 paleosols (McCarthy and Plint, 2013).

625 Extracting the weathering signal from geochemical data is not straightforward, as: (i) bulk
626 sediment analysis cannot differentiate precisely among the several possible sources of each
627 element (He et al., 2020); (ii) weathering indices might represent the integrated weathering
628 history in the river basin, rather than being reliable proxies of instantaneous chemical weathering
629 (Shao and Yang, 2012); (iii) the geochemistry of sediments can be affected by multiple controls
630 other than climate-induced weathering, including source-rock lithology (Kraus, 2002) and
631 hydraulic sorting (Garzanti and Resentini, 2016).

632 A careful evaluation of these diverse controls on sediment composition is possible in the study
633 area and this can facilitate interpretation of weathering indices as reflecting true weathering
634 indicators. For example, it is apparent that changes in source-rock lithology did not play a major
635 role in controlling geochemical signatures of Upper Pleistocene paleosols. Sediment provenance
636 analysis in the Po Plain based on integrated sand petrography (Tentori et al., 2021) and bulk-
637 sediment geochemistry (Amorosi et al., 2012, 2014b; Amorosi and Sammartino, 2018; Bruno et al.,
638 2017b) has shown that overbank parent material reflects a relatively homogeneous (Apennines)

639 source-rock domain for Pleistocene alluvial deposits, as opposed to a remarkably more complex
640 sediment dispersal pattern developed at the onset of the Holocene (Amorosi and Sammartino,
641 2018). Size sorting during transportation and deposition generally results in some degree of
642 mineralogical differentiation, which may modify weathering indices (Garzanti and Resentini,
643 2016). Restricting paleosol composition to uniform mud grades, as also indicated by remarkably
644 constant $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios (Table 2), makes the influence of grain size on composition minimal
645 (Nesbitt and Young, 1982). Therefore, the composition of muds will primarily reflect the degree of
646 weathering.

647 In summary, weathered horizons of Late Pleistocene age bear distinctive geochemical
648 properties that are laterally traceable for tens of kilometers (Figs. 5 and 6) and that can be used as
649 highly effective stratigraphic markers across the non-marine portion of the Po Basin fill. They also
650 represent the key to unravel the sequence-stratigraphic architecture of the non-marine
651 succession, tracing systems tract boundaries from the downstream segments of the source-to-sink
652 system into the upstream alluvium.

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654

655 **9. Conclusions**

656

657 Two weakly developed paleosols marking the sequence boundary (SB) and the lateral
658 equivalent of the transgressive surface (TS), respectively, in the Last Glacial Maximum depositional
659 sequence are laterally continuous and traceable for tens of kilometers across the non-marine
660 portion of the Po Basin. Such surfaces provide a comprehensive, three-dimensional view of the
661 pedogenic character of Late Pleistocene interfluves. This paper has investigated the modifications
662 induced by chemical weathering on such pedogenically altered floodplain deposits, focusing on
663 the recognition, correlation, and characterization of Inceptisol-like paleosols.

664 A comparison of the paleosols, their distribution, and degree of pedogenic development
665 suggest widespread soil development on short-lived, interfluvial areas. Weakly developed
666 paleosols mark regional unconformities and contain excellent records of the Late Pleistocene
667 depositional history. They are linked to minimal incision and their alternation with overbank
668 deposits into paleosol-bearing cycles reflects conditions of limited accommodation on the
669 floodplain and their formation as a result of alternate aggradation and degradation. The most
670 distinctive feature of SB and TS paleosols is soil partitioning into a well identifiable dark, organic-

671 matter-rich and carbonate-free upper A horizon and a lower Bk horizon, typified by the abundance
672 of calcium carbonate nodules.

673 Weathering patterns, expressed as geochemical trends, of paleosols represent discernible
674 regional features that define a robust correlation scheme, with small lateral variability and suggest
675 that floodplain environments were affected by mild, but laterally extensive weathering conditions.
676 Element ratios used as tracers of the degree of weathering (calcification and base loss indices)
677 represent pedochemical markers that do not show substantial modifications along strike and dip,
678 and that exhibit consistent behaviour with depth across paleosol profiles. Translocation of Ca, with
679 almost complete removal from the upper portions and concentration in lower horizons is a
680 diagnostic feature of Po Plain paleosols. Some trace metal ratios experience significant variations
681 across the weathering zones. Ba/Sr and Rb/Sr typically show a loss in the A horizons and gain in
682 the Bk horizons, which is consistent with the identification of calcic horizons. On the other hand,
683 redox-sensitive trace elements and Zr show increasing values from the parent material to upper
684 paleosol horizons.

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- 991 Supplementary Table 1. Location and elevation of the 17 cores studied for geochemical analysis.
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