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# Pedological formations on old mountain geomorphological surfaces of central Spain

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# ABSTRACT

The chemo-morphological properties of soils on ancient landforms (quarzitic pliocene alluvial fans, pleistocene terraces), namely "rañizos", on middle-high mountains (Eastern-Central System, Iberian Peninsula, Rio Negro, Cogolludo) were investigated. Several properties were analyzed by standard procedures. A detailed soil diagnostics and classification on "rañizos" were done, unlike those widely studied on "rañas" (similar landform), by identifying parallel pedogenetic processes in both formations. The genetic and geographic features of Alfisols, Ultisols and Inceptisols are closely related to the nature of their parent materials, based on quartzite and quartz conglomerates, sometimes with an arkosic matrix, red shale, polygenic gravels and pebbles. Soil features were determined by genuine soil-forming inherent lithological rock properties. Other driving factors were flat topography and enough soil formation time to allow intense pedogenesis. The main soil-forming processes were intense weathering, clay enrichment horizons with illuviation, red color caused by iron oxide dehydration and signs of pseudogleyzation processes. Such pedological formations can be considered endemisms; that is, "rare" soils and, up to a point, "relict". The soil reaction is acid/slightly acid with low base saturation. Despite lying on mountains, soils are characterized by moderate-low organic matter content. Soil conditions and climate provide good vine production requirements despite acidity levels. A common feature of all Rio Negro soils is the presence of gravel (size up to 3-5 cm), which is evenly distributed on arable layers. The results can be used to assess vineyard soil use in a potential Pago (Protected Denomination of Origin) and to extend the database of vineyard soils from poorly studied Mediterranean continental mountain regions.

### 1. Introduction

With today's global climate change, it is important to acquire more detailed data about soils from the insufficiently studied areas used for intensive agriculture, particularly vineyards and as is the case, especially if they are areas with very old complex deposits that have undergone intense pedogenesis processes.

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One of the largest vineyard regions in Spain, and in Europe, is Castilla-La Mancha (CLM) [1]. Some fundamental features of most soil compositions (the basis for viticulture production) are carbonates and moderate basicity. Other soils occupy smaller areas, do not have carbonates and are acidic. Of the last soil type, it is worth mentioning those that develop on old flat, or almost flat, old landforms namely "raña" [2]. A set of landforms exists that can be called "rañizos", which are materials with a similar lithological nature (they are usually associated), but whose geomorphology differs from "rañas" [3].

The genesis, nomenclature and classification of soils on old landforms in the Iberian Peninsula (i.e. "raña" formations) have frequently been addressed to date. This can be explained by these landforms' originality (plioquaternary surfaces and, therefore, one of the surfaces that supports the oldest soils in Europe), and by the consequent abundance data on these soils. However, other morphologically, chemically and physico-chemically similar soils have barely been studied despite their unquestionable agricultural and academic interest. This is the case of the soils that develop from similar materials to those of "raña", which are known as "rañizos".

Conceptually, "rañas" and "rañizos" (local geomorphological terms used throughout the Iberian Peninsula) can be considered old landforms that characterize large surface formations composed of quartzite gravel, encompassed by a fundamentally reddish clayely color matrix generated mainly from the torrential erosion of intense weathered metamorphic materials, fundamentally based on quartzites, schists and shales. More precisely, according to Ref. [4] "Raña" defines any extensive old alluvial planation landform composed of siliciclastic conglomerate sediments of slight stratigraphic thickness (~5 m), which predates the formation of the Quaternary fluvial network. These formations support, among others, well-developed soils that testify to the ancient (almost tropical) climates that dominated central Spain (according to Ref. [2]) during the final Neogene These landforms are specifically attributed to a Plio-Quaternary age that, according to Martín-Serrano [4], would occur before the incision of the current fluvial valleys. In 1988, the last-cited author pointed out that some deposits should not be called "rañas" and insisted we call them "rañizos".

Previous studies have addressed the problem of soils that develop on "rañas", mainly in the geomorphological context, as well as their soil processes and age when they formed [5–13], or by their mineralogy [14]. Other studies point out soil productivity and fertility [7,15,16]. Soil profiles on "rañas" present a characteristic typology that corresponds to the typical A-Bt-C sequence of Alfisols and Ultisols (although Inceptisols sometimes appear) according to Soil Taxonomy [17]; that is, Luvisols and Acrisols (sometimes Cambisols) according to the WRB FAO system [18]. Processes emerging like hydromorphism, which generate Bg horizons, and a series of chemical properties, such as acidity and a low degree of saturation gradis, are also cited. It is, therefore, worth investigating what the main features are of the soils that develop on "rañazo"; do they differ from "raña" landforms or do they present similar features? In any case, soils provide vines with a physical environment and essential nutrients that support their good performance. Hence the need to implement a thorough analysis of the suitability level of different soil types.

Understanding the French term "terroir" and its approval through agro-environmental sciences are gaining more interest every day. Indeed such a way that this term is already very popular and used in many parts of the world, as [19] point out. This has led several authors to redefine the viticultural terroir concept, such as [20,21]. Recently [22]. Spoke of a complex concept whose interest lies in



Fig. 1. Characteristic landscape of the "rañizo" piedmont. The parent material is in the background, with a view of the vineyard in the foreground. Note the typical flat, or almost flat, relief of "rañizos" in vineyards.

expressing the "collective knowledge of interactions", a concept that, according to Ref. [23]., is a very important term in the European Union (EU) to determine suitable viticultural areas. Following the OIV, [24], terroir is understood as a certain area in which an edaphic identity and climatic environment converge to provide certain interactions between the environment and the applied vitivinicultural that confer wine from a certain area distinctive characteristics. However, the role that soil plays in wine's character has barely been appreciated, especially before the 1980s. In line with this [25], introduced a new concept, known as "terron" with which to highlight soil properties (pedon) together with topographic soil-forming factors. In this way, geomorphology and soil science in Mediterranean regions are closely related. This is probably why the terroir concept (i.e., relating soil properties to wine quality) was introduced by geologists.

For a vineyard to grow and properly develop, it is essential for soil to have appropriate intrinsic conditions. Therefore, properties like texture type, structure development and its type, its fertility level, etc., can affect vine root growth because they intervene in the nutrient absorption of mineral elements (i.e. nitrogen, phosphorus, potassium, zinc, etc.). This has been highlighted by Ref. [26], and more recently by Ref. [27] or by [28].

As this type of Plio-quaternary landforms are perhaps the oldest in Europe to support soils, soil are expected to be potential sources of relevant information about the pedological genesis and agronomic conditions after centuries to millennia of use, and can also contribute to ideas about land stewardship and agricultural sustainability. In light of all this, and bearing in mind that the dynamics of the soils that develop on "rañizo landforms" is still barely known, the main purpose of this study was to characterize the macro-morphological, physical and chemical properties of the soils allocated to vineyard production in a key mountain area that develops on "rañizo" landforms: Rio Negro (Cogolludo, central Spain). The second objective of this research is to establish the main aspects of soil genesis in relation to landscape development in this type of Mediterranean mountain climate in the terroir concept context of the terroir concept.

#### 2. Materials and methods

#### 2.1. Description of the study area

The area under study, called Rio Negro, is located in the North Natural Guadalajara Mountain Park sited on the eastern foothills of the Spanish Central System. This area is accessed by the CM-1001 regional road that connects the towns of Cogolludo and Veguillas, both of which are found in the Guadalajara province (Fig. 1). This area covers 600 ha, of which 42 ha are used for vineyard cultivation. It extends and occupies a landscape formed by plioquaternary landforms that are located at altitudes of 800–960 m. a.s.l. A brief analysis of the vegetation table reveals the presence of oaks (*Quercus* ssp.) and pines (*Pinus* ssp.). A rich undergrowth fill is also observed. It, provides the place with aromas of lavender (*Lavandula officinalis* L.), rosemary (*Rosmarinus officinalis* L.), oregano (*Origanum vulgare* L.) and thyme (*Thymus vulgaris* L.). It is estimated that all these plant series can cause polyphenols to appear. It is known that phenols belong to the largest group of secondary metabolites in plants [29], mostly from the family Lamiaceae, as cited,



Fig. 2. Google Earth satellite image of the "rañizo" piedmont in Río Negro (Cogolludo, central Spain).

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and exhibit multidirectional biological activity.

The Rio Negro landforms are probably one of the oldest geological structures to support the soils that develop in Spain and elsewhere in Europe. It is a territorial space that makes up the southern foothills of the north-eastern sector of the Spanish Central System and the Meso-tertiary basin of the Tajo River. In mountains, it is characterized by a smooth relief cut by deep elongated valleys. In hydrological terms, it belongs to the Tajo River basin, and the Henares is the main river course at which its tributaries arrive. The lithological environment is extremely variable due to the nature of both source materials and depositional systems.

Many researchers (i.e. [3,13]) have conducted studies that aimed to identify the origin of these sedimentary deposits known as "raña" and "rañizo" which, while covering basement rocks, are the product of the erosion of the oldest geological reliefs. These piedmont deposits are made up of pebbles, gravels and sands embedded in a clayey matrix, whose colors generally go from reddish hues to ocher ones. According to the "Instituto Tecnológico y Geológico de España" (ITGE) [30], there are specifically Pliocene quartzite fans in which several units can be distinguished. The main unit in the area is made up of quartzite and quartz conglomerates with an arkosic matrix and red shale. The ITGE points out that quartzite dominates in clasts, but granites, glandular gneisses, aplites and pegmatites also appear. Sands are made up of quartz (30–50 %), K-feldspar (5–10 %), metamorphic rock fragments (quartzites, schists, gneisses; 10–15 %), micas and a ferruginous micaceous matrix (14–40 %). All this indicates mixed deposits of epimetamorphic areas (quartzite and Ordovician slate) and sediments are affected by a high degree of metamorphism. Finally, the intercalation of marked levels of red shale is pointed out both distally and laterally, which gives rise to another cartographic unit. Channeled bodies of medium to coarse sands and conglomerates intercalate between shales.

Another unit also appears as a dispersed mosaic made up of polygenic gravels and pebbles, sands, clays and carbonates, which are conceptualized as river terraces and undifferentiated terraces. These terraces are considered to occupy the spaces that constitute the proximal and middle zones of humid alluvial fan-type depositional systems with large reception areas. All these formations and materials appear to be dissected by many intermittent river crossings. Numerous spectacular gullies appear (Fig. 2).

The average temperature of the coldest month in the study area ranges from -1.3 to 5.0 °C. The average temperature of the warmest month lies between 18.0 and 22.3 °C. The annual average temperature is 12 °C. The mean precipitation per year is 561 mm and the dry period lasts about 3–4 months [31]. Therefore, the climate is typical Mediterranean. Following the classification criteria of Köppen-Geiger, the study area is framed within the Csa type [32]. This means a "temperate Mediterranean" climate zone with dry and temperate summers that, represent a "humid Mediterranean". Vineyards are irrigated.

#### 2.2. The rock-forming soils in Rio Negro: "rañizos"

A brief review of the word "raña" indicates that the Real Academia Española (Royal Spanish Academy) [33] accepted the term "rañizo" in 2018 to refer to a similar "terrain" to "raña" to study the vegetation and flowers from the Extremadura Guadiana Basin [34]. One decade later while studying the regional hydrogeology of the Jarama River Basin [35], mentioned the above-mentioned term "rañizo" to refer to similar material to "raña". On the Toledo soil map [36], the units on "destroyed rañas" appear as "rañizo". Other authors refer to alluvial-colluvial-type glacis that are considered to be "rañizo". The authors [37] speak of a rocky spur covered with "rañizo" [38]. When studying lithic industry remains from a geomorphological point of view, these authors mention "rañizo" levels, a term that they also use as remobilized materials from "raña". Likewise, they mention "terraces or glacis terraces" that indistinctly link root levels with terraces and their different levels. Recently [39], mentioned the term "rañizo terraces" in the special issue edited by Ref. [40].

Therefore, the soils in this area that would potentially cover the Protected Denomination of Origin (PDO) developed from "rañizos"type materials, understood as those materials that occupy related or similar geomorphological units to "raña" from which it is sometimes difficult to differentiate because of the certainly similar geomorphological and edaphic characteristics they present. We can,

| Parameters Hor.              |                       | Profile 1         | Profile 1       |                | Profile 2       |                 | Profile 3         |                 | Profile 4       |                  |                  |                 |                   |
|------------------------------|-----------------------|-------------------|-----------------|----------------|-----------------|-----------------|-------------------|-----------------|-----------------|------------------|------------------|-----------------|-------------------|
|                              |                       | Ap                | Bw              | Bwg            | Ap              | Bt              | 2C                | Ap              | Bw              | 2C               | Ap               | Bt              | BtC               |
| Color                        | Moist                 | 7.5<br>YR 4/<br>4 | 5 YR<br>5/6     | 2.5 YR<br>8/4  | 5YR3/<br>4      | 5YR4/<br>6      | 5YR7/<br>6        | 7.5 YR<br>5/4   | 7.5 YR<br>6/6   | 7.5 YR<br>6/6    | 2.5 YR<br>5/6    | 2.5 YR<br>5/8   | 2.5<br>YR 4/<br>8 |
| Structure <sup>a</sup>       | Grade<br>Size<br>Type | MO<br>ME<br>SB    | MO<br>FI<br>SB  | MO<br>ME<br>SB | MO<br>ME<br>AB  | ST<br>ME<br>SB  | VFI<br>ME<br>GR   | MO<br>ME<br>SB  | MO<br>ME<br>PR  | MO<br>FI<br>GR   | MO,<br>ME,<br>SB | ST<br>ME<br>PR  | MO<br>ME<br>SB    |
| Consistency <sup>b</sup>     | Dry<br>Moist<br>Wet   | FR<br>VFI<br>ST   | FR<br>SHA<br>ST | HA<br>PL<br>ST | FR<br>VFI<br>ST | SHA<br>PL<br>ST | SHA<br>NPL<br>NST | FI<br>NST<br>ST | SHA<br>PL<br>ST | HA<br>NPL<br>NST | FI<br>NPL<br>ST  | SHA<br>PL<br>ST | HA<br>PL<br>ST    |
| Cutans<br>Roots <sup>C</sup> | Size and<br>abundance | No<br>F,FR        | No<br>F,FR      | No<br>N        | No<br>F,V       | Yes<br>N        | No<br>N           | No<br>F,FR      | No<br>F,FR      | No<br>N          | No<br>M, C       | Yes<br>F, V     | Yes<br>F, V       |
| Stonines (%)                 |                       | 30                | 5               | 10             | 10              | 5               | 50                | 30              | 5               | 10               | 30               | 20              | 50                |

| Table 1                                  |
|--|
| Main soil morphological characteristics. |

<sup>a</sup> FI: fine/thin, GR: granular, ME: medium, MO: moderate, SB: subangular blocky, PR: Prismatic, and ST: strong.

<sup>b</sup> FI: firm, FR: friable, HA: hard, NPL: nonplastic, NST: nonsticky, ST: sticky, PL: plastic, SHA: slightly hard, VFI: weak.

<sup>c</sup> F: fine, N: none, FR: frequent, A: Abundant, V: very few, and VF: very fine.

therefore, accept the term "rañizos" as those conglomeratic deposits that look like "raña", but have more sand than more worn-looking edges. This topographic landform nature represents the starting point of the formation of unique soils and can be used as a basic information criterion if the intention is to implement effective soil management.

#### 2.3. Soil identification and sampling

Field surveys and sampling were conducted in June 2018. To describe and sample soils, it was necessary to open soil profiles using a backhoe machine. The four soil profiles were described following the criteria established by of the IUSS Working Group WRB [18] and the USDA Soil Taxonomy [17]. The soil profiles are located at different altitudes (947 and 975 m. a.s.l.). Some macromorphological details of the soil profiles appear in Fig. 4 (b and c) and Table 1.

The soil profiles are reddish (2.5 YR) to reddish-brown (5 YR 4/3) or brown (7.5 YR) in color (moist), which could be due to the degree of mineral weathering and the Mediterranean climate (Table 1). The soil structure tends to be dominantly subangular blocky and is only prismatic on argillic horizons (for having a higher clay content). Both surface and subsurface depths are generally sticky and plastic (wet). Although roots do not abound (Table 1), soil physical properties do not limit root growth.

#### 2.4. Analytical procedures

Soil samples were collected in the field and later transported to the Soil Analysis Laboratory at the High Technical School of Agricultural Engineers of Ciudad Real (Universidad de Castilla-La Mancha). In the laboratory, the collected soil samples were air-dried and sieved (2-mm). Another small proportion was sieved (125  $\mu$ m) to analyze soil chemical and physico-chemical properties. The Bouyoucos hydrometer method was followed for the particle size analysis [41]. Bulk density (BD) was determined by the cylinder method [42]. Soil pH was potentiometrically measured at the 1:2.5 soil:water ratio and in 0.1 M KCl solution. Electrical conductivity (EC) was measured by an EC meter in a 1:5 soil:water extract. Organic carbon (C) was determined by the dichromate oxidation according to the Walkley and Black method, as modified by Ref. [43]. Total nitrogen (N) was determined by the modified Kjeldahl digestion procedure [44]. Available phosphorus (P) was estimated by the Olsen method [45]. Exchangeable bases (Ca, Mg, K, Na) were established by the methods described by Thomas [46] using 1 N ammonium acetate extraction, and were further determined by atomic absorption spectrometry. Base saturation (BS) was obtained by dividing the sum of the exchangeable bases by cation exchange capacity (CEC). All the samples were extracted and analyzed in triplicate.

The elemental concentration of soil samples was measured by X-ray fluorescence (XRF), which can be used as a rapid and objective screening tool for total element concentrations in soils [47]. The procedure followed was in a first step, samples were ground in an agate mortar and then pearls with lithium borate formed. Samples were introduced *via* an open-ended sample plastic cell. The collection time was 1000 s. Pearls were analyzed by X-Ray fluorescence using a Philips PW 2404 spectrophotometer at the maximum power of 4 kW (set of crystal analyzers for LiF220, LiF200, Ge, PET and PX1, flow detector, and twinkle detector). Samples were analyzed in triplicate and the quality control was evaluated by certified soil reference materials (NIST 2710 and CRM 039).

The chemical weathering indices were calculated from the geochemical elements according to the obtained results.

# 2.5. Soil index

In order to understand the weathering mineral level, the bibliography offers several parametric indices, whose estimation is necessary to analyze silicon (Si) and aluminum (Al) contents, and base cations calcium (Ca), sodium (Na) and potassium (K). Two of these indices were used in this work (Eq [1]. and Eq [2]).

a. The Chemical Index of Alteration (CIA) proposed by Ref. [48]:

$$CIA = \left[\frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O + K_2O}\right] * 100$$
 Eq. [1]

b. The Chemical Index of Weathering (CIW) proposed by Ref. [49]:

$$CIW = \left[\frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O}\right] * 100$$
 Eq. [2]

In order to evaluate soils on a scale from degraded to good soil conditions, we applied the criteria established by Ref. [50], who propose the so-called soil organic carbon (SOC)/clay index, which relates organic matter protection to the soil structural condition.

# 3. Results and discussion

#### 3.1. Soil morphology and properties

The soil cover patterns of these rañizo-type materials reflect similar macromorphological and edaphogenetic traits to those of the

soils that develop on "rañas". In this way, the soil profiles that derive from "rañizo" present a characteristic typology that corresponds to the typical sequence of A-Bt-C or Ap-Bw-C of Alfisols, Ultisols and Inceptisols [18], or to that of Luvisols, Acrisols and Cambisols (IUSS Working Group WRB) [17]. Hydromorphic processes are also observed, which implies an additional morphological variability character. Besides, physico-chemical properties were added to completely differentiate them from most of the soils employed in vineyards in CLM (Spain), and, of course, elsewhere in Europe.

Another common characteristic to the soils of the typical "rañizo" is the intense alteration of parent material. It is similar to what [13] pointed out and is reflected by the disappearance of much less resistant materials to alterations throughout the profile. Even quartzite appears to be "partially sandblasted" (Fig. 3). Another typical feature of soils is that they tend to present abrupt textural limits on deeper horizons. However, no planosolic features with eluvial horizons were detected, which happens in some soils on "raña", and suggests that they are probably the oldest soils in the region. Sometimes limits are not abruptly textural but show this tendency up to a point: when moving from Ap horizons to Bw horizons, a significant change in clay content occurs. They are as heterogeneous materials as "raña" and the presence of lithological discontinuities is not unusual e.g., Ap-2Bw-3Btg-4C. These are generally deep soils but have rejuvenating effects on profiles. Cambic horizons (and argillic if they appear) are frequently brown or reddish yellow (occasionally red), with 7.5 YR tonality and sometimes with 5 YR tonality [51].

The dominant structure on the different horizons is generally in subangular or prismatic blocks that are strong, which probably favors the appearance of hydromorphy that is, in turn, supported by a flat or quasi-planar topography.

The nature and properties of soils largely influence crop production, particularly vineyards. One peculiar feature observed in the field is lithological and edaphogenetic variability, as evidenced by the particle size distribution data (Table 2). Changes in particle size distribution with depth are detected, which reflects the effect of both weathering processes and translocation within the solum. With profile 1, the slightly higher clay contents in the solum than on the deeper horizon are probably due to depositional variation. In profile 3, the percentage of gravel lies between 12.6 and 73.8 from horizon Bw to horizon 2C. In profile 2, two lithological discontinuities appear.

Table 2 presents other analytical results from a soils study carried out across "rañizo" landforms. On the surface horizons, textural classes vary as follows: loam, clay-loam and clay. Clay contents vary between 9.6 and 46.5 (%) (> than 25 % are not the most frequent in the viticultural soils of the CLM region [52]. Soil pH varies from 5.5 to 7.9 on surface horizons, while this range on subsurface horizons varies between 4.7 and 6.3. These pH values mean that profiles can be classified as "slightly acidic" [53], for which technical farm management has to consider these values to determine possible Fe, Mn, B and Zn deficiencies. The surface addition of calcium amendments for better vineyard development explains this difference between horizons. The suitable pH value for vines goes from 5.5 to 7.0 with tolerance for satisfactory performance, which is ideal for viticulture [54]. In CLM, good wines are obtained mostly from vineyards with carbonated soils that are, therefore, calcium-rich. However as stated by Seguin [55], calcium-rich soil is not a pre-requisite for having good vineyard soil. In fact, some of the world's most renowned wines are not produced in calcium-rich soils (of



**Fig. 3.** (a) During polygenetic evolution, different soil formation phases act and mingle. However, in this case, they are not difficult to separate; soil profile 1, classified as Chromic Acrisol (Clayic, Ochric) according to the IUSS Working Group WRB [18], as Typical Rhodoxeralf according to Soil Survey Staff [17], and as texturally contrasting horizons; (b) Redoximorfic features in soil profile 4.



Fig. 4. a. Temporary hydromorphy and poor permeability; b. Ferruginous pseudo-crusts formed by iron oxides that act as cement; c. Signs of a pseudogleyzation process in root channels.

#### Table 2

Baseline soil properties, including location coordinates, morphology, classification and analytical results.

|  |                  | Profile 1<br>Abruptic Chromic Acrisol<br>(Clayic, Cutanic, Ochric)<br>Typic Rhodoxeralf |                | Profile 2<br>Haplic Chromic Acrisol<br>(Clayic, Raptic, Densic)<br>Inceptic Rhodoxeralf |      | Profile 3<br>Dystric Chromic Cambisol<br>(Ochric, Raptic, Densic)<br>Typic Distroxerept |       |  | Profile 4<br>Skeletic Chromic Acrisol<br>(Clayic, Raptic, Densic)<br>Typic Distroxerept |        |       |       |          |
|--|------------------|---|----------------|---|------|---|-------|--|---|--------|-------|-------|----------|
|  |                  | Ap  | B <sub>t</sub> | B <sub>tg</sub>   | Ap   | Bt  | 2C    | Ap   | $B_{w}$   | 2C     | Ap    | Bt    | $B_{tg}$ |
| Coordinates UTM (30t)<br>Coordinates (WGS84) |                  | 0495113x – 4535800y<br>40°58'24.0″N –03°03'29.1″W                                       |                | 0495104x – 4535444y<br>40°58'12.5″N<br>–03°03'29.4″W                                    |      | 0495825x – 4535139y<br>40°58'02.6″N –03°02'58.6″W                                       |       | 0495753x – 4534748y<br>40°57'49.9″N<br>–03°03'01.7″W |   |        |       |       |          |
| Depth (cm)                                   |                  | 0–28  | 28-60          | 60-102  | 0-33 | 33-60   | 60–92 | 0-32   | 32–74   | >74    | 0-32  | 32-58 | >58      |
| Coarse elements (%)                          | )                | 24.9  | 21.9           | 28.5  | 9.1  | 50.1  | 67.1  | 12.8   | 12.6  | 73.8   | 50.1  | 50.5  | 50.4     |
| Sand (%)                                     |                  | 32.4  | 32.4           | 30.6  | 35.6 | 30.2  | 36.8  | 43.0   | 47.5  | 71.7   | 29.7  | 25.1  | 33.1     |
| Silt (%)                                     |                  | 36.9  | 30.4           | 30.6  | 27.1 | 23.3  | 23.1  | 47.4   | 38.2  | 17.4   | 37.9  | 36.1  | 23.0     |
| Clay (%)                                     |                  | 30.6  | 38.1           | 41.3  | 37.3 | 46.5  | 40.1  | 9.6  | 14.3  | 10.9   | 32.4  | 38.8  | 43.9     |
| Textural class                               |                  | Clay-   | Clay-          | Clay  | Clay | Clay  | Clay  | Loamy  | Loamy   | Loamy- | Clay- | Clay- | Clay     |
|  |                  | loam  | loam           |   |      |   |       |  |   | sand   | loam  | loam  |          |
| Bulk density (g/cc)                          |                  | 1.3   | n.d.           | n.d.  | 1.2  | n.d.  | n.d.  | 1.3  | n.d.  | n.d.   | 1.3   | n.d.  | n.d.     |
| Organic matter (%)                           |                  | 1,9   | 1.3            | n.d.  | 1.4  | 0.9   | n.d.  | 1.9  | 1.8   | n.d.   | 1.4   | 1.1   | n.d.     |
| P Olsen (mg/kg)                              |                  | 12.2  | 10.8           | n.d   | 11.3 | 8.2   | n.d.  | 10.5   | 9.6   | n.d.   | 11.8  | 10.8  | n.d.     |
| Total N (%)                                  |                  | 0.07  | 0.05           | n.d.  | 0.05 | 0.03  | n.d.  | 0.06   | 0.07  | n.d.   | 0.05  | 0.04  | n.d.     |
| C/N ratio                                    |                  | 12.5  | 12.2           | n.d.  | 12.5 | 12.5  | n.d.  | 12.3   | 11.9  | n.d.   | 12.5  | 12.5  | n.d.     |
| pH (water 1:2.5)                             |                  | 7.5   | 5.4            | 5.2   | 6.3  | 5.5   | 6.3   | 7.3  | 6.0   | 6.1    | 7.9   | 4.8   | 4.7      |
| pH (KCl 1:2.5)                               |                  | 6.9   | 4.4            | 4.2   | 5.9  | 4.2   | 5.2   | 6.8  | 4.6   | 4.9    | 7.3   | 3.9   | 3.8      |
| Electrical conductiv                         | ity (dS/         | 0.2   | 0.1            | 0.1   | 0.5  | 0.1   | 0.1   | 0.2  | 0.1   | 0.4    | 0.4   | 0.1   | 0.1      |
| m)   |                  |   |                |   |      |   |       |  |   |        |       |       |          |
| Cation Exchange                              | Ca <sup>2+</sup> | 13.4  | 10.1           | n.d.  | 23.8 | 26.8  | n.d.  | 19.8   | 6.9   | n.d.   | 23.9  | 27.1  | n.d.     |
| (cmol <sup>+</sup> /kg)                      | $Mg^{2+}$        | 1.3   | 1.5            | n.d.  | 0.6  | 0.3   | n.d.  | 0,9  | 1.3   | n.d.   | 1.2   | 0.8   | n.d.     |
| 2.   | ĸŦ               | 0.2   | 0.3            | n.d.  | 0.1  | 0.3   | n.d.  | 0.6  | 0.3   | n.d.   | 1.3   | 0.5   | n.d.     |
|  | Na <sup>+</sup>  | 0.3   | 0.5            | n.d.  | 0.4  | 0.1   | n.d.  | 0.2  | 0.1   | n.d.   | 0.1   | 0.1   | n.d.     |
| C.E.C (cmol <sup>+</sup> /kg)                |                  | 19.1  | 33.9           | n.d.  | 62.2 | 66.5  | n.d.  | 28.3   | 33.0  | n.d.   | 28.5  | 68.8  | n.d.     |
| Base saturation (%)                          |                  | 79.4  | 36.5           | n.d.  | 40.1 | 41.3  | n.d.  | 78.5   | 27.4  | n.d.   | 85    | 41.1  | n.d.     |

n.d.: not determined.

basic nature) but are produced on acidic soils.

The EC values did not indicate salinity problems for all the profiles, which belong to the "nonsaline" class [56]. Surface horizons were characterized by moderate organic carbon content, with a sharp drop in the profile. As the C/N ratio was similar in all the profiles

Table 3a

(around 12), the soil quality organic matter values oscillated from medium to good. Total N was low in all the soil profiles. Some authors, such as [57,58], imply the idea that limited N nitrogen supply to vine can lead to an improved wine quality.

#### 3.2. Pedological processes: weathering indices

The geochemical characteristics of the soils in the study area can be used to assess their weathering process and pedogenesis. After analyzing Na, K, Ca and Al by XRF in the samples from both the surface horizons (horizon 1, horizon Ap-type) and subsurface horizons (horizon 2, horizon Bt or Bw), the results that appear in Table 3a were obtained. Table 3b, also includes the calculated weathering index (Eq. (1) and Eq. (2)). Table 4 shows the criteria set to assess both the CIA and CIW.

After analyzing the results of the studied soils (Tables 3 and 4), the ranges of the different indices were as follows: CIA 72–79 and CIW 84–95. By bearing in mind the criteria of [48], who consider that CIA values can vary between 35 and 55 (values for fresh igneous rocks) and 100 (for kaolinite), the latter case represented the highest degree of weathering. Based on the obtained results (Tables 3 and 4), we concluded a moderate to high degree of parent materials' weathering (C-type horizons), which was much higher for the Bt horizon. The criterion proposed by 59, 61] suggests CIW values of 50 for the unweathered upper continental crust and values of roughly 100 for highly weathered materials. Therefore, by analyzing our results, we detected that these soils had lost a considerable part of alkali and alkaline earth elements during pedogenesis. So, they could be considered to be highly weathered.

According to the geochemical approach, no significant difference appeared in the four profiles and, therefore, moderate to extreme weathering had acted during pedogenesis in the zone according to the aforementioned criteria of [61-63]. The chemical composition of bedrock and intense weathering provide a very high clay mineral content and exchangeable cation capacity.

A significant part of long-term exposed landscapes develops on fine- and medium-textured sedimentary materials. In addition, as a consequence of the flat topography and the high clay content of soils, poor permeability is manifested, which generates temporary hydromorphy (Fig. 4a). Under these conditions, a pseudogleyzation process with iron (Fe) and manganese (Mn) concretion appears (Fig. 4c). Thus, Fe segregations form, which are sometimes accompanied by ferruginous gravels that are formed by, in turn, pinkish edges to produce "ferruginous pseudo-crusts" (Fig. 4b). This formation is associated with pedogenetic processes, including intense weathering processes and consequent clay generation and released Fe. Obviously, acidity is generated, which contributes to Fe mobilization and migration in preferential areas along the profile length.

The soils of the study area exemplify the effect of landform and parent material on soil development. On old stable landforms, like rañizo, weathering on subsurface horizons has led to the formation of cambic Bw. In addition, if clay accumulation (illuviation) has occurred on the soil subsurface, it would lead to the formation of Bt, with a maximum thickness and clay content from up to 46.5 % (Table 2). Thus well-developed soils with a thick well-developed red Bt horizon and strongly acidic pH values were characterized (Rhodoxeralfs).

If the intention is to evaluate pedogenic changes in soil, it is necessary to involve comparing the solum to parent material. The weathering levels of the mineral phase indicate intense weathering processes which, along with the pronounced trends in the profile differentiation of clay minerals, is generally typical of Mediterranean latitudes. From the obtained results, it is feasible to suggest that Mediterranean conditions have long since dominated in the Rio Negro area. The soils with a fersialitic character are widespread. This conclusion is consistent with the presence of the argillic and red-colored horizons in the profile, characteristic of acidic soils in Mediterranean regions, and confirms our statement that argillization and rubefaction affect Rio Negro soils.

When we observed the data of the soil profiles and their location in the territory, we noted that the past pedogenesis which differed from the modern one was scarce. This means that the studied soils are mature and combine the features formed during previous periods and those of current processes, which correspond to environmental stability in this area.

The high clay content obtained in the studied soils can act as a key factor for its effects on SOC protection, as pointed out by Refs. [63,64]. For [65,66], the soil depth and clay contents of soils influence both grapevine development and yield. In our case, the soils on "rañizos" matched this premise. However, the obtained SOC/clay ratio index allowed us to interpret the soils to be assessed on a scale of degraded soil conditions. As in many other soils of Mediterranean regions, the Rio Negro soils show evident low SOC, a circumstance that encourages farmers (who are aware of this) to add organic waste to correct this deficit.

[50] proposed that SOC/clay ratio thresholds of 1/8, 1/10 and 1/13 indicate the boundaries among "very good", "good", "moderate" and "degraded" structural condition levels. The results in Table 5 show a maximum SOC/clay ratio of 0.083, which is a lower value than 1/13. Therefore, it can be concluded that the studied soils have a degraded structural condition.

Soils are crucial because they form the basis for viticultural production. As previously pointed out [55,67], if soils are essential

|                          | Horizon | Profile 1 | Profile 2 | Profile 3 | Profile 4 |
|--------------------------|---------|-----------|-----------|-----------|-----------|
| Na $(g \cdot kg^{-1})$   | А       | 5.1       | 3.7       | 5.7       | 3.1       |
|                          | В       | 4.8       | 2.5       | 3.8       | 2.3       |
| $K (g \cdot kg^{-1})$    | Α       | 27.8      | 35.5      | 32.1      | 28.3      |
|                          | В       | 29.8      | 32.3      | 31.5      | 25.4      |
| Ca (g·kg <sup>-1</sup> ) | А       | 7.9       | 2.7       | 4.1       | 18.2      |
|                          | В       | 2.2       | 2.6       | 2.3       | 1.8       |
| Al (g⋅kg <sup>-1</sup> ) | А       | 71.9      | 103.3     | 77.0      | 88.5      |
|                          | В       | 92.1      | 127.4     | 101.4     | 123.1     |

Na, K, Ca and Al contents (by the XRF technique) in the four soil profiles. Each sample corresponds to three analytical replicates

#### Table 3b

The weathering index obtained from the chemical analysis (see Eq [1]. and Eq [2]).

|     | Horizon | Profile 1 | Profile 2 | Profile 3 | Profile 4 |
|-----|---------|-----------|-----------|-----------|-----------|
| CIA | А       | 72.53     | 79.18     | 73.62     | 72.39     |
|     | В       | 79.28     | 83.97     | 80.53     | 86.52     |
| CIW | А       | 88.33     | 95.7      | 91.55     | 84.93     |
|     | В       | 94.79     | 97.16     | 95.82     | 97.64     |

#### Table 4

Criteria set to assess the degrees of the different indices.

| Chemical Index of Alte | ical Index of Alteration (CIA) Chemical Index of Weathering (CIW) <sup>a</sup> |       | Veathering (CIW) <sup>a</sup> |
|------------------------|--|-------|-------------------------------|
| Value                  | Category   | Value | Category                      |
| 50–60                  | Very slightly weathered  | 50    | Unweathered                   |
| 60–70                  | Slightly weathered   | 100   | Highly weathered              |
| 70–80                  | Moderately weathered   |       |                               |
| 80–90                  | Highly weathered   |       |                               |
| 90–100                 | Extremely weathered  |       |                               |

<sup>a</sup> According to ([59,60].

components of viticultural terroirs and influence vineyard performance and berry and wine composition, then the environment surfaces and the functionality of the Rio Negro soils are singular. Indeed, comparatively speaking, the vineyards on calcareous soils in CLM occupy the largest territorial space (more than 75 %), while the vineyard soils formed from plioquaternary sediments (as herein studied) occupy less than 10 % of the CLM territory. Therefore, the soils developed by "rañizos"-type formations can be considered "endemisms"; that is, "rare" soils. By applying the terminology of [65], these soils are the consequence of unique geological and ecological histories. In this way, profitability is a key factor that influences land being used for a vineyard. Other factors, such as global markets and policies, are not controlled by growers. It is, therefore, necessary to take into account the basic profitability and sustainability concepts of vineyard production being combined and enhanced.

#### 3.3. On the presence of stoniness in vineyards

The recent literature contains numerous research works that have focused on investigating layers of gravel or stone on soils. These are rock fragments of varying sizes that have been investigated in both agricultural and natural settings in several environments [66, 68–71].

According to other authors [72], the main effects of rock fragments are, among others, improved infiltration and water storage, decreased runoff, lower evaporation rates, soil protection from rainsplash compaction and erosion, lower maximum temperatures and greater sunlight reflection due to high rock albedo. Other favorable effects are exerted by the presence of a mantle of rocky fragments: during diurnal heating, rock fragments shield the ground from solar radiation; the soil temperature under them remains cooler than in exposed areas; conversely during nighttime cooling, rock fragments retain and reradiate heat, and the soils below them stay warmer [73].

In the study area, the presence of abundant rock fragments in both surface and depth terms (Fig. 5) and gully erosion are consubstantial with the original soil materials and, in such a way that, during their genesis, a series of geological and geomorphic processes need to occur to supply these large quantities of rocks. In other words, they are not cloaks provided from outside the area, and their size or thickness is not manipulated. Only the new areas are initially cleared for planting. Farmers wish to improve infiltration, and to control evaporation of vineyard soils because heat sinks during the day and then reradiatates at night, while promoting drainage and allowing deep vine root penetration [22,27].

Soil formation on old landscapes comprises a number of not only unstable processes, such as erosion, truncation of soils and subsequent sedimentation, but also stable processes like weathering and undisturbed soil formation. The resulting soils are polygenetic insofar as they have multiple genetic linkages of exogenous and endogenous processes, factors and conditions. This study has its limitations because these soils have evolved over for long periods of time on plioquaternary landforms. In addition, unsustainable management practices and climate change are threatening the natural capital of these soils. Future research should perform more intensive sampling to more fully characterize not only the spatial distribution in this potential PDO, but also the possible toxicity effect of exchangeable acidity and aluminum because it could reduce grape development.

#### 3.4. Cultural landscape and positive economic benefits

The reality of the cultural landscape of the "Rio Negro" viticultural landscape stems from a characteristic natural environment, to which the secular actions of humans have been added to form the vine and wine cultural landscape that we find today. It combines unique features of this natural environment, as well as cultural elements. Despite their soils possibly being considered relatively poor and, therefore, not being particularly suitable for most crops, they offer exceptional conditions for growing vines.

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Estimated SOC/clay ratio.

|                | SOC/clay ratio |                |                |                |  |  |  |  |
|----------------|----------------|----------------|----------------|----------------|--|--|--|--|
| Hor type       | Profile 1      | Profile 2      | Profile 3      | Profile 4      |  |  |  |  |
| Ap<br>Bw or Bt | 0.029<br>0.016 | 0.016<br>0.008 | 0.083<br>0.055 | 0.018<br>0.012 |  |  |  |  |



**Fig. 5.** (a) Mantles of rock fragments (pebbles and gravels of quartzite and some quartz) spreading and covering vineyard soils in Rio Negro. (b) The formation of common large and very deep gullies in the area is facilitated by the deep weathered mantle, which is even more susceptible to erosion. Rills easily turn into gullies when incisions reach saprolites either due to anthropic influence or under natural conditions.

Winemaking activity comprises two aspects: viticulture and winemaking. The viticulture industry in Rio Negro does not involve negative environmental impacts that weaken the ecosystems of the place; that is, they do not pose a risk, among other reasons, because the topography of the landscape has not been modified.

The Rio Negro wine industry provides enormous economic benefits for economies through its earnings from exports, employment and economic growth. Let us remember that the area where Rio Negro is located is a depressed mountain area. In addition, wine tourism is becoming increasingly more relevant, which opens up another door for the area's economy.

To give an idea of the economic and social importance of the vineyard in Castilla La Mancha, it is enough to say that the extension of vineyards in our region, close to 500,000 ha, would place us as the fourth wine-growing country in the world. This surface of vineyard and related industry employs almost 40,000 families. Our exports reached 14,388,673 hls [74], which represents 52.4 % in volume of total Spanish exports of wine products. The value of these exports, according to the same sources, was 867 million euros, which represents almost 10 % of the region's total exports.

# 4. Conclusions

Rio Negro soils are characterized by pronounced morphological, physico-chemical and chemical differentiation, which is due to the activity of mineral phase weathering and soil formation that culminate in a heterogenization of soil profiles. In fact, a complex net of mutual feedback relations between chemical properties of parent materials and the direction of pedogenesis can be observed on the studied Plio-quaternary landforms. The partial destruction/dissolution of unstable minerals in an acid medium was noted in the study area soils. Soil features were determined by the inherent lithological properties of soil-forming rocks and subsequent edaphic processes. The main soil-forming processes were intense weathering, clay enrichment horizons with illuviation, red color caused by iron oxide dehydration and signs of psedogleyzation processes. Such pedological formations can be considered endemisms; that is, "rare" soils and, in a way, "paleosoils". The most outstanding properties of soils were an acid or slightly acid reaction, medium BS and signs of pseudogleyzation. Furthermore, despite being located in a mountain region, another character was moderate to low organic matter contents. The soil conditions in the field offer good vine production requirements despite the acidity levels in soils. These findings can increase our understanding of the reasons for primary productivity and the impact of future environmental changes. However, it is worth noting that the degree and spatial distribution must be evaluated to sporadically identify viticultural importance.

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#### Data availability

The data that support the findings of this study are available upon request from the corresponding author. The data are not publicly

available due to privacy or ethics restrictions.

#### CRediT authorship contribution statement

Raimundo Jiménez-Ballesta: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Conceptualization. Sandra Bravo: Writing – review & editing, Software, Methodology, Investigation, Formal analysis, Data curation. Caridad Pérez-de-los-Reyes: Writing – review & editing, Methodology, Investigation, Formal analysis. Jose A. Amorós: Writing – review & editing, Validation, Investigation. Jaime Villena: Software, Investigation, Data curation. Francisco J. García-Navarro: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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