Clay-carbonate aggregation in alluvial calcareous soils, Central Anatolia, Turkey

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Abstract. An unexpectedly high infiltration capacity was determined for heavy-textured, clayey alluvial calcareous soils (Calcic Haploxerepts) in central Anatolia, Turkey, presumably due to the specific mineralogical contents. In order to unravel the phenomenon, clay mineralogy and morphology, soil microaggregate composition, and carbonate accumulations were studied in these soils via X-ray diffractometry, scanning electron microscopy, and energy-dispersive analyses. Calcite and layered minerals were the principal components of the fine fraction. The percentages of clay, silt, and sand were 45, 54, and 1%, respectively. Illites were dominant in the clay fraction – 43–49%, whereas the content of smectites was rather small – 4–6%. The results indicated that the principal factors of the high hydraulic capacity of the soils were (1) illitization, a process that is typical for arid and semi-arid soils, and (2) microaggregation involving pedogenic calcite, resulted in the formation of clay–calcite ultra-microaggregates maintaining elongated 3–10 μm in diameter micropores.

1. Introduction
Alluvial calcareous soils (Calcic Haploxerepts) have been historically cultivated in central Anatolia, Turkey when irrigation water is available. As a rule, alluvial soils are poorly developed and vulnerable to human impact. The basic processes of their formation are not well understood, and the management strategies in use are usually not sustainable.

In earlier works [1, 2], evaluation of the agrophysical properties of drip-irrigated alluvial calcareous soils in Konya province, central Anatolia revealed a number of important and valuable characteristics of these soils. Despite their heavy texture, low organic matter content, and inadequate aggregate structure (i.e., lack of aggregates of agronomically valuable size), these soils have high porosity, a stable structure of continuous pores, and, high water permeability. The infiltration capacity
of these soils is unusually high – approximately 250–360 cm day$^{-1}$, whereas soils of similar granulometric texture (i.e., light and medium clays) are usually characterized by very low infiltration capacities of approximately 3–7 cm day$^{-1}$. Studies of water absorption capacity in these soils reported a slight decrease in the absorption rate, which indicates high pore stability and stable water permeability. Yet, the causes of these phenomena are not clear. Previous works [3] reported high activity of specific strains of bacteria that produce gaseous metabolites – CO$_2$ and H$_2$ – that can prevent these clayey soils from compaction and maintain their porous and permeable structure.

We hypothesized that an additional factor determined by the specific mineralogical content may be effective in the microaggregation of these soils. To resolve this problem, an investigation of the microstructure of alluvial calcareous soils was undertaken. The objectives were as follows: (1) determine the mineralogical composition of the soils and (2) evaluate the structure and composition of the soil aggregates at the micro level by means of scanning electron microscopy (SEM) supported by energy-dispersive analysis.

2. Materials and methods

The study area was in the Çumra district, Konya province, south-central Anatolia, Turkey between 37° and 38° E and between 33° and 34° N at 1013 m above sea level. The area consists of approximately 172,000 ha of mountainous and hilly landscape with upland landforms and a long arable history.

 According to the Köppen classification, the climate of the area transitions between cold semi-arid (BSk) and Mediterranean continental (Dsb), with sharply contrasting seasons – hot and dry summers as well as cold winters with small amounts of snow cover. The average annual temperature is approximately 11.8 °C, with minimum of -1.5 °C and maximum of 26.1 °C. The average annual precipitation rate is 306 mm, with a maximum that occurs from September to April–May.

A soil profile was set up in the experimental field of the Faculty of Agriculture of the University of Selcuk (Konya) in the winter of 2011. The studied soils were alluvial calcareous (Celic Haploxerepts). The profile has the following horizons:

- **Ap** (0–38 cm) – old-arable, yellowish-brown, heavy loamy (clayey-silty, many loessial silt particles), wet, darkened in the upper 0–10-cm layer; sharp boundary in density and hardness caused by plowing.
- **Bw** (38–62 cm) – brown, compacted, dry, with small 1–2-mm efflorescence of car-bonates at the bottom; sharp boundary in color, size, and the presence of carbonate formations,
- **B$_{ca}$** (62–100 cm) – lighter brown than the upper horizon; accumulations of carbonate forms of up to 10 mm; very dense; containing prismatic pads.

The soil texture was determined with the laser-diffraction technique using an Analysette 22 (Fritsch GmbH, Germany). The samples were preprocessed by ultrasounding in distilled water using a Branson Sonifier (Branson Instruments, Co., USA) at 250 W and 20 kHz. Carbon and N were measured in solid soil samples using a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). The basic physical and chemical properties of the soils can be found elsewhere [4].

The mineralogical composition was determined in the clay fraction (< 2 μm). For analysis, the samples were taken from 0–5 cm of the Ap horizon and from 40–50 cm of the Bw horizon. A Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Japan) was used for the determination of minerals. X-ray exposure was carried out in Bragg–Brentano geometry. The parameters included the following: Cu anode; X-ray tube voltage, 40 kV; current, 30 mA; and power, 1.2 kW. The angle (2θ) was 3° to 90° for the analysis of the entire soil sample and up to 65° for the analysis of the clay fraction. The shooting speed was 1° min$^{-1}$ with a step of 0.02°. Sample preparation for X-ray diffractometry included crushing and grinding (Pulverisette 1 jaw crusher and Pulverisette 6 precise planetesimal microgrinder, Fritsch, Germany). The prepared clay fraction was set without crushing and exposed in an air-dried (20°C) state after saturation with ethylene glycol. The minimal determining mineral percent was 1%, with an accuracy of 5–10%.

The mineralogical analysis was supplemented by electron microscopy (SEM analysis) using a Vega 3 LMN scanning electron microscope (Tescan, Czech Republic). Soil samples were prepared by
spilling and C and Pt spraying, with a magnification of up to 20,000. A backscattered electron detector (BSE-detector) was used in addition to the secondary electron detector to analyze phases with a high atomic number. On the images obtained with the BSE-detector, the phases with a high average atomic number reflected more sharply compared to the phases with a lower atomic number. Energy-dispersive spectrometry (EDX analysis) (Inca Energy 350, Oxford, UK) was used to analyze the elemental composition of the most representative areas. In total, more than 500 images were obtained. The SEM analysis was carried out in the Analytical Centre at the Institute for Tectonics and Geophysics, Far-Eastern Branch of the Russian Academy of Sciences, Khabarovsk.

3. Results and discussion

The mineralogical analysis showed that the upper 50-cm portion of the alluvial calcareous soil contained a high proportion of carbonates – up to one-quarter by weight, represented mostly by calcite together with clay minerals and feldspar. The content of framework minerals – quartz and feldspar – was similar to the content of clay minerals – 36 and 39%, respectively. The high proportion of clay caused the fine texture of the soils. The percentage of clay, silt, and sand fractions were 45, 54, and 1%, respectively.

In general, the infiltration capacity of heavy-textured soils is poor, which is due to the content of swelling smectites rather than to the total clay content. In the clay fraction of the studied soils, the content of illites, which are non-swelling minerals, was predominant (43–49%), whereas the content of smectites was low (4–6%); the content of non-clay minerals such as quartz, feldspar, and calcite did not exceed the method accuracy of approximately 1–2%. The amount of illite-smectite reached approximately 30%. Illitization processes that are typical for soils of arid and semi-arid regions have apparently led to a substantial increase in the illite to smectite ratio and, consequently, to a low soil swelling capacity (figure 1, table 1).

![Figure 1. X-ray diffractograms of the alluvial carbonaceous soil, horizon Ap, 0 – 5 cm: en block (a); silt fraction: before (b) and after (c) saturation with ethylene glycol.](image)

Pedogenic calcite must have an additional effect on the high infiltration capacity of the upper soil profile [5]. The high content of calcite in the entire profile, not only in the lower portion, is displayed by the efflorescence and clusters of carbonates, which indicate the presence of pedogenic microforms of calcite. Usually, pedogenic calcite forms have dimensions of about 0.3–1(2) μm, and these forms can be found in clay plasma, cutans, and separate ultra-microaggregates on the grains of framework
minerals and in the soil microaggregates; calcite forms a stable waterproof microstructure of the soil [6-9]. The primary calcite inherited from rocks is predominantly of coarse silt size.

**Table 1. Mineralogical composition of alluvial calcareous soil studied (%).**

| Horizon, cm | Quartz | Feldspars | Clay minerals | Calcite |
|-------------|--------|-----------|---------------|---------|
|             |        | Al        | An | Or | M | Ch | I | I/S | S | K |          |
| Whole soil  |        |           |    |    |   |    |   |     |   |   |          |
| Ap 0–5      | –      | 3.8       | 3.3 | 3.6 | 1.1 | 5.3 | 20.2 | 6.6 | 1.6 | 4.9 | 25.6     |
| Bw 40–50    | 23.5   |           | 5.3 | 2.9 | 3.2 | 1.3 | 4.8  | 20.9 | 7.2 | 1.9 | 4.7 | 24.3     |
| Clay fraction |        |           |    |    |   |    |   |     |   |   |          |
| Ap 0–5      | –      | –         | –  | –  | –  | –  | 7.2  | 43.2 | 33.2 | 5.9 | 10.5 | 0        |
| Bw 40–50    | –      | –         | –  | –  | –  | –  | 4.9  | 49.5 | 30.8 | 4.1 | 10.7 | 0        |

Al – albite; An – anorthite; Or – orthoclase; M – microcline; Ch – chlorite; I – illite; I-S – illite-smectite; S – smectite; K – kaolinite.

In fact, as the SEM analysis showed in our case, in spite of the absence of aggregates of adequate sizes, the studied soils had a well-developed microstructure: calcite was concentrated within the microaggregates, while separate calcite microcrystals rarely occurred. The microaggregates of 100–200 µm were the most abundant in the Ap horizon (figure 2a); these microaggregates were round in shape and porous, and the pores penetrated through the microaggregates (figure 2b). In the Bw horizon, the number of microaggregates decreased together with the organic matter content (from 1.0 to 0.5%), and their structure changed. The most abundant fraction was finer than that in the Ap horizon – about 25–100 µm (figure 2c). The particles were sharp-angled and loose (figure 2d).

**Figure 2.** Micrographs of alluvial calcareous soil: horizon Ap (a, b), horizon Bw (c, d). Arrows show the clay-carbonate ultra-microaggregates (SEM, BSE-detector, carbon spraying).
The micrographs of samples sprayed with carbon clearly revealed the formation of clay–salt ultra-microaggregates with a high proportion of calcite. The ultra-microaggregates (figure 2b) and the crystalline calcite can be distinguished using the reflection interference contrast technique: the average atomic number of calcite is higher than that of the silicate matrix and the carbon film. The EDX analysis confirmed the calcite-like structure of the clay–salt ultra-microaggregates. The contents of Ca and Si (atom %) in the aggregates were similar, and the alumosilicate base – according to the Si:Al ratio of 2:1 – consisted of minerals of the illite group. The microaggregates also contained Ca but in substantially lower amounts; the Ca:Si ratio was 1:10. Iron-containing clay–salt formations were also detected with the BSE-detector. These formations were brighter due to the higher average atomic number, but they were less common, had a different shape, and had a smaller Si:Al ratio than did the calcite formations, whose ratio was approximately 1.2–1.3.

Calcite microcrystals were occasionally detected in the samples, which consisted of mostly rhombohedral grains approximately 15–20 \( \mu \text{m} \) in diameter with relatively sharp edges and faces (figure 3a). The composition of cutans on the surface of grains corresponded to the composition of the clayey base of the ultra-microaggregates. In the Bw horizon, together with rhombohedral calcite, needle-shaped calcite crystals 5–25 \( \mu \text{m} \) in length and 0.5–1 \( \mu \text{m} \) in width were also observed (figure 3b). These crystals also contained P, S, and Fe, indicating their biogenic, probably microbial origin [7]. In addition, calcite crystals in the form of densely packed plates of approximately 40–60 \( \mu \text{m} \) with a plate thickness of 0.5–2 \( \mu \text{m} \) were observed (figure 3c). These crystals contained a high proportion of illite (Ca:Si = 10:1, Si:Al = 2:1).

Imaging the samples sprayed with Pt did not allow for the determination of calcite and carbonate clay–salt ultra-microaggregates without the EDX analysis (figure 4) due to the non-significant difference between the average atomic numbers of calcite and the silicate matrix compared with that of Pt. The spraying with Pt allowed, however, for the evaluation of the morphology and structure of the
microaggregates, the morphology and packaging of the constituent particles, and the nature and size of the pores in the microaggregates. The pores were 3–10 μm in diameter and highly elongated (figure 4a, b). The predominant arrangement of clay particles in the microaggregates was plane–plane with a shift. Rhombohedral and slightly rounded calcite clay–salt ultra-microaggregates covered the surface of the microaggregates (figure 4c). These microaggregates could also be observed on the quartz grains (figure 4d).

Figure 4. Micrographs of alluvial calcareous soil samples: horizon Ap (a, c, d), horizon Bw (b). Arrows show the calcite-clay-salt ultra-microaggregates (SEM, BS-detector, Pt spraying).

In figure 3d, the contact zone of a quartz grain with clay particles in a microaggregate can be distinguished. The energy-dispersive spectra showed that the contact zone contained mostly calcite (Ca:Si = 1:2) and illite in the clay particles (Si:Al = 2:1). At a distance of approximately 10 μm from the contact zone, the proportion of calcite decreased sharply (Ca:Si = 1:10), and only traces were observed on the quartz grains. This suggested that the illite–calcite formations, together with the calcite clay–salt ultra-microaggregates, were the bonding elements of the microaggregates, and these formations determined the high stability of the porous structure of these soils.

4. Conclusion
The studied soils were rich in pedogenic calcite and clay minerals, which determine their heavy texture; the percentages of clay, silt, and sand were 45, 54, and 1%, respectively. Illites, which are non-swelling minerals, were dominant in the clay fraction – 43–49%, whereas the portion of smectites was small – 4–6%. The unexpectedly high infiltration capacity of these heavy-textured soils is determined by (1) illitization, a process typical for the clay fraction of semi-arid soils, and (2) specific microaggregation, which involves pedogenic calcite, resulting in the formation of clay–calcite ultra-microaggregates maintaining elongated 3–10 μm in diameter micropores. The standard methods of soil physics would be unable to interpret the anomalous hydraulic capacity of these soils.

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