

## THE CALCIUM CARBONATE EVOLUTION INFLUENCING THE PHYSICO-CHEMICAL CHARACTERISTICS OF THE LONG TERM IRRIGATED CHERNOZEMS AND THEIR CLASSIFICATION

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### *Abstract*

*The evolution of the soil architecture after the matrix lost the  $\text{CaCO}_3$  under the water irrigation influence had important consequences on the evolution of the physico-chemical characteristics of the long term irrigated soils. The analytical data results showed that, in the case of the horizons with calcium carbonate pedofeatures, the bulk density reached higher values, comparing to the horizons free of  $\text{CaCO}_3$ . The paper represents also an alarm signal for the soil scientists that classified the long-term irrigated Chernozems from the Romanian Plain (with  $\text{CaCO}_3$  washed deeper than 125 cm), to the Phaeozems, which represents a regrettable mistake. Between Chernozems and Phaeozems there are very important differences concerning: the quality and the quantity of the organic matter; the plasmic material mobility; the leaching process with clay coatings formation;  $\text{CaCO}_3$  morphology, etc. The leaching of the  $\text{CaCO}_3$  to >125 cm depth in the long-term irrigated Chernozems from the Romanian Plain is due to the anthropogenic influence, and it is not pedogenetic, that is why it is not a pertinent condition to classify these Chernozems as Phaeozems.*

**Key words:** Chernozems, long-term irrigation, bulk density, calcium carbonate, Phaeozems.

### INTRODUCTION

The Chernozems are the most fertile and the most friendly soils with the farmers, having a great power of self-restoration of the structure and self-conservation of the fertility.

As showed Huang et al. (2009), the Chernozem had been classified as modern soil by agricultural pedologists, while the geoscientist classified them as paleosols. The high value of Chernozem for biomass production and the environment influenced the decision of the first soil chosen for the “Soil of the Year” (proclaimed for the first time in Germany in 2005, on the occasion of the World Soil Day) was Chernozems (as showed Altermann et al., 2005).

The researches of the Chernozems and Phaeozems extent in Central Germany during the Neolithic period had been achieved by Suchodoletza et al. (2015), using the sedimentologic and micromorphological properties. The decisive factor for the recent and former spatial distribution of Chernozems and Phaeozems (located in the Luvisol region) is the carbonate dynamics under the relatively

dry climate of Central Germany (Suchodoletza et al., 2019).

The former distribution of Chernozems and Phaeozems in regions that are covered by other soil types today, their formation and degradation were studied by many authors during the time (cited by Huang et al., 2009; Lorz & Saile, 2011; Suchodoletza et al., 2019). Apart from a sub-continental climate, the main factor determining the recent and former distribution of Chernozems and Phaeozems in Central Germany was obviously the carbonate content of the parent material (Suchodoletza et al., 2015).

Important generalizations concerning the evolution of Chernozems in space and time have been also performed by different authors (Ivanov & Tabanakova, 2009; Eckmeier et al., 2007).

The climate changes influenced differently the development of the different subtypes of Chernozems in the Late Holocene (Lisietskii et al., 2013).

The researches of Bobrovsky and Leiko (2019) stated that in the dark-humus soils (Haplic Phaeozems) no traditional features of the

Chernozem «steppe» stages of soil formation during the Holocene were found.

Reviewing the hypothesis of a predominantly anthropogenic pedogenesis of Chernozems in Northern Germany during the Early Neolithic, Lorz and Saile (2011) by the aim of an interdisciplinary research (involving geosciences, palaeobotany, and archaeology) rejected the hypothesis, but validated the theory of their natural formation.

The Chernozems area in Eurasian occupies a special place in the history of human society, as well as in the history of soil science (Chendev et al., 2010).

Labaz et al. (2019) showed that diverse chernozemic soils featured by thick mollic horizon, rich in humus, dark-coloured, structural, and saturated with base cations are relatively common in the loess-belt of SW Poland, being defined as soils developed from parent materials predominately rich in carbonates (Eckmeier et al., 2007; Chendev et al., 2010; Suchodoletza et al., 2019), under grassy meadow vegetation supported by high ground-water table. These soils contain larger accumulations of secondary (pedogenic) carbonates in the calcic horizons.

The paper objective was to emphasise evolution of the physico-chemical characteristics of the long term irrigated Chernozems. The paper also focused on the correct classification of these soils, avoiding any regrettable mistake.

## MATERIALS AND METHODS

The investigated territory is located in the Eastern part of the Romanian Plain (Southern Baragan Plain) in Marculesti area, where the climate is temperate continental, with long and warm summers and droughty periods in late summers and early falls. The average annual temperature is 10.6°C and the average annual precipitation is 480 mm. De Martonne aridity index is 23, while the evapotranspiration reaches 700 mm. The water table is at > 10 m depth.

The soil is Vermic Chernozem (according to SRTS-2012 and WRB-SR-2014) formed in carbonate loess like deposits. The studied site is located in the steppe bioclimatic zone (danubian steppe subzone).

Six soil profiles of Chernozems were studied: P1a and P1b - irrigated with carbonates; P2a and P2b - non-irrigated with carbonates; P3a and P3b - irrigated without carbonates.

For a better understanding of the irrigated soils classification, a Phaeozem were also studied, being located in Suceava Tableland characterized by a mean annual temperature of 9.6°C and a mean annual precipitation of 518 mm. According to the Romanian pedoclimatic micro-zonation (Methodology ICPA-1987), the territory belongs to the IIIO-CM - Chernozem-like micro-zone, with cool-humid climate, in the regions with undulated relief.

The soil had been sampled for the physical, chemical and micromorphological analyses and further analyzed and data results interpreted according to the ICPA Methodology-1987.

For the micromorphological investigation, the oriented large (6 x 9 cm) thin (25-30 µm) sections were prepared from the undisturbed soil samples collected from each pedogenetic horizon (in order that the investigation results be statistically covered), after air drayed and impregnated with epoxidic resins. In order to describe and interpret the soil important characteristics and features at the microscopic level, investigation had been proceed by the aim of: microfilm reader Carl Zeiss Jena DL at 5-20X; petrologic microscope Amplival at 50-100X; and Stereomicroscope Nikon SM2800 at 1-6 X; in plain (PPL) and polarized (XPL) light, and using the terminology of Bullock et al. (1985).

## RESULTS AND DISCUSSIONS

The bulk density is a very sensitive property of the soil and also very dynamic, changing proportional with the root grow, biological (macro- and mezofauna) activity, wetting-drying processes etc.

In these conditions, it could give precious information about the soil status at a certain period of time, as well as about the processes that induce changes in the soil evolution.

The four studied Chernozem profiles (P1a and P1b; P3a and P3b) were irrigated and consequently, under the influence of the irrigation water, many transformations of the soil constituents occurred.

The most sensitive is calcium carbonate (as well as other salt accumulated mainly in the deeper horizons). Its dissolution and removal from the soil profiles strongly influenced the physical properties, as showed the data results. The presence of salts, as calcium carbonate, in the deeper horizons, as result of a non-transpercolative water regime, the horizon is more compacted, with higher values of the bulk density (Figure 1).

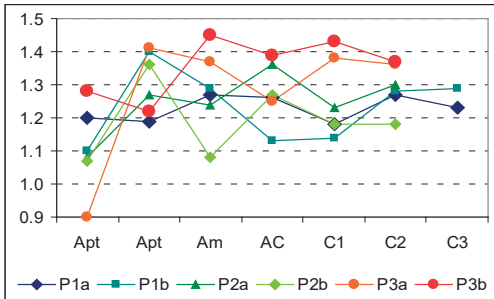


Figure 1. The bulk density ( $\text{g}/\text{cm}^3$ ) of the studied Chernozems

In this respect, the analytical data results showed important differences between the bulk densities (BD) of the studied Chernozems (Figure 1).

Detailing the data results (Figure 2), in the profile P1a (“irrigated with carbonates”), the  $\text{CaCO}_3$  appear from 35 cm depth and its content increased from 9.5% (into the Ck horizon) to 18.5% in the deepest Cca horizon.

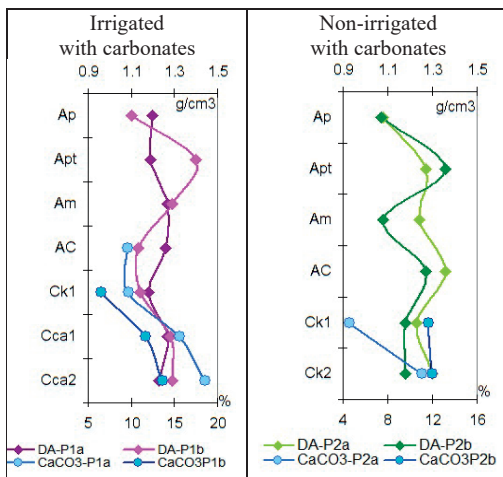


Figure 2. The bulk density ( $\text{g}/\text{cm}^3$ ) values and the calcium carbonate content of the P1 and P2 Chernozems

In the Cca horizons, the BD values increased to  $1.26\text{-}1.27 \text{ g}/\text{cm}^3$ , while in the top horizons the BD is smaller ( $1.19\text{-}1.20 \text{ g}/\text{cm}^3$ ).

In the irrigated P1b profile, the  $\text{CaCO}_3$  appear at 60 cm depth and the content is smaller (comparing to P1a) 6.4% in the Ck horizon, increasing to 13.5% in the deeper calcic horizon (Figure 2).

In this profile, the BD registered the same dynamic as in P1a: smaller values ( $1.1\text{-}1.4 \text{ g}/\text{cm}^3$ ) in the top horizons, and higher values ( $1.28\text{-}1.29 \text{ g}/\text{cm}^3$ ) in the deeper calcic horizons, where both fine silt-sized  $\text{CaCO}_3$  crystals (or crypto-crystals) impregnated the matrix and calcium carbonate pedofeatures (nodules and concretions) had been formed.

It showed be underlined that in Chernozems, the biological activity is very high, improving continuously the poral space and strongly influencing the BD (transforming it in a very dynamic soil parameter).

In P2 soil profiles (“non-irrigated with carbonates”), the  $\text{CaCO}_3$  appear deeper (comparing to P1 profiles): at 70 cm depth in P2a, where the  $\text{CaCO}_3$  content is 11.6%; and at 80 cm in P2b, where the  $\text{CaCO}_3$  content is 4.5 - 11.0%.

In P2a the BD is  $1.08 \text{ g}/\text{cm}^3$  to the top horizon and reached  $1.30 \text{ g}/\text{cm}^3$  in the Ck horizon, while in the P2b the BD is  $1.07 \text{ g}/\text{cm}^3$  in the top horizon and increased to  $1.18 \text{ g}/\text{cm}^3$  in the bottom Ck<sub>2</sub> horizon.

In what concerning the P3 soil profiles (“irrigated without carbonates”), the irrigation for long time (more than fifty years) (Figure 3), removed the  $\text{CaCO}_3$  from the soil profiles, under 125 cm depth.

Consequently, in the deeper horizons (of P3a) free of  $\text{CaCO}_3$ , the BD is lower ( $1.36 \text{ g}/\text{cm}^3$ ), comparing to the higher value ( $1.41 \text{ g}/\text{cm}^3$ ) of the upper horizon of the soil profile (Figure 3).

In the Cn horizon of the P3b, the BD value is  $1.37 \text{ g}/\text{cm}^3$ , comparing to  $1.45 \text{ g}/\text{cm}^3$  reached in the higher horizon.

As pointed out the analytical data, both P3a and P3b soil profiles are more compacted, with higher values of the BD, and specially in the deeper horizons, where the  $\text{CaCO}_3$  had been leached from the soil profile.

The evolution of the soil architecture after the matrix lost the  $\text{CaCO}_3$  under the water irrigation influence had important consequences on the evolution of the physico-chemical characteristics of the long term irrigated soils.

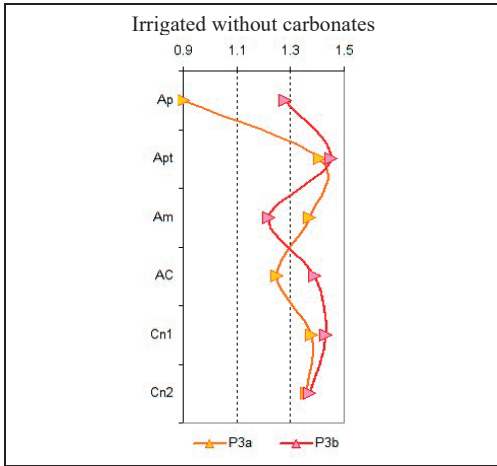


Figure 3. The bulk density ( $\text{g}/\text{cm}^3$ ) of the P3 Chernozems without  $\text{CaCO}_3$

Soil bulk density is a physical parameter that depends on the soil constituents, as granulometry and organic matter as well as on their spatial arrangements.

The results emphasize that in the case of horizons with calcite crystals (and/or crypto-crystals) embedded into the soil matrix, the bulk density is also influenced.

Together with the  $\text{CaCO}_3$ , different salts also accumulated as a result of a non-transpercolative water regime, but in very low quantities.

The analytical data of the cation exchange capacity (Figure 4) showed among the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations, the presence of  $\text{Na}^+$ .

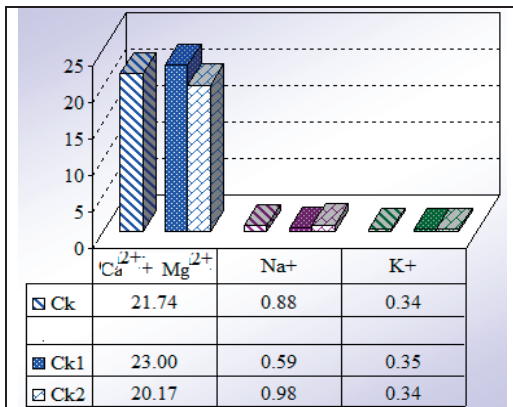


Figure 4. The cations (me/100 g soil) dominating the exchange cation capacity of the P2a (Ck horizon) and P2b (Ck<sub>1</sub> and Ck<sub>2</sub> horizons)

The very low quantities of Na salts also accumulate in the deeper horizons of the Chernozems highlighted by the analytical data that showed (Figure 5) an increased of  $\text{Na}^+$  cations from the lower values (0.16 me/100 g soil) in the top horizons to the higher values (0.90-0.98 me/100 g soil) in the bottom profile. This cation, even in very low quantities, during the high humidity seasons could locally disperse the matrix and change, at the microscopic scale, the soil architecture, and further the bulk density.

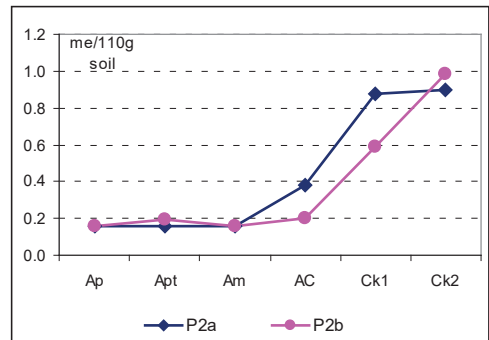


Figure 5. The level of  $\text{Na}^+$  cations along the P2a and P2b soil profiles

Concluding, it could be underlined that the calcium carbonate (secondary and/or inherited from the parent material) in the deeper calcic horizons induced a higher compaction emphasised by the higher values of the BD.

Another important problem concerning the long term irrigation is the leaching of the  $\text{CaCO}_3$  under 125 cm depth, the diagnostic condition for both Chernozems and Phaeozems: for naming a mollisol as Chernozem the condition is the “presence of  $\text{CaCO}_3$  (secondary carbonates) in the first 125 cm”; while for naming a mollisol as Phaeozem, the condition is “without Cca horizon or concentrations of secondary carbonates in the first 125 cm”.

In this respect, the paper represents also an alarm signal for the soil scientists which could classified the long-term irrigated Chernozems (with  $\text{CaCO}_3$  washed deeper than 125 cm) located in the Romanian Plain, to Phaeozems, which would represent a regrettable mistake.

Detailing, it is very important to underline that between Chernozems and Phaeozems there are

many important differences that clearly showed their different pedogenesis and evolution, as for example: the quality and the quantity of the organic matter; the plasmic material mobility; the leaching process with the formation of clay coatings (their quantity and quality respectively); CaCO<sub>3</sub> morphology, etc.

In this respect, the main differences are the quantity and the quality of the organic matter; as well as the difference at the chromatic level: in Chernozems the organic matter is black-very dark brown, while in the Phaeozems, the organic matter is darker, black with metallic chroma (showing higher moisture regime).

Micromorphological investigation showed that plasmic material had a very low mobility in Chernozems. Even if the irrigated Chernozems (with CaCO<sub>3</sub> washed deeper than 125 cm), the plasmic material is still stable, and very thick and rare impure clay coatings formed. In contrast, in Phaeozems, many illuvial coatings varieties formed: from impure clay coatings with abundant organic impurities (micro-particles  $\leq 0.02 \mu\text{m}$ ) to coatings with very rare or no impurities (“argillane”); and also impure clay pore infillings with crescentic fabric. These coatings varieties represent sequences of their evolution in time, as well as the polyphasic evolution of the soil together with its environment.

Plasma of the Chernozems (even irrigated) is more stable which showed that only the CaCO<sub>3</sub> from the calcite pedofeatures and the fine silt-sized CaCO<sub>3</sub> crystals (or crypto-crystals impregnating the matrix) were removed, while the Ca<sup>2+</sup> ions which reinforces the structural edifice of the soil (by binding the clay to the organic matter) have not been removed.

In what concerning the calcium carbonate pedofeatures, in Chernozems pseudo-mycelium formed, which show the fluctuation of the secondary CaCO<sub>3</sub> under the evapotranspiration effect; also the matrix around the CaCO<sub>3</sub> nodules has very strong effervescence (when applying dilute 1 M HCl solution). Contrasting, in Phaeozems only the core of the nodules has effervescence, while the surrounding matrix does not show effervescence (which pointed out the leaching of secondary carbonates under more humid conditions).

In this respect, for naming soils in the classification it is necessary to taking into account all the characteristics of the soils and their pedogenesis, and not only a specific characteristic.

Concluding, the presence of the CaCO<sub>3</sub> to > 125 cm depth is due to the anthropogenic influence, and it is not pedogenetic, that is why it is not a pertinent condition to classify the Chernozems as Phaeozems.

## CONCLUSIONS

The researches results pointed out that calcium carbonate (secondary and/or inherited from the parent material) induced a higher compaction to the calcic horizons, with consequences on the bulk density (BD) which registered higher values into the calcic horizons, comparing to the horizons free of CaCO<sub>3</sub> (with smaller values of BD).

This aspect showed that under the irrigation water influence, the soil matrix lost the CaCO<sub>3</sub> with important consequences on the soil architecture and on the evolution of the physico-chemical characteristics of the long term irrigated soils.

Another important problem concerning the long term irrigation is the leaching of the CaCO<sub>3</sub> under 125 cm depth, the diagnostic condition for Phaeozems.

But, it should taking into account that the presence of the CaCO<sub>3</sub> to > 125 cm depth in the long-term irrigated Chernozems from the Romanian Plain is due to the anthropogenic influence, and it is not pedogenetic, that is why it is not a pertinent condition to classify these Chernozems as Phaeozems, which represents a regrettable mistake.

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