Determination of carbonates in the soils of Ciurea commune

Gabriel – Răzvan Duca[1], Alecsandra Lupu[1], Dan Aștefanei[1]

[1] "Alexandru Ioan Cuza" University of Iași, Department of Geology, 20A Carol I Blv, 700505 Iași, Romania

Abstract

The soil, a complex mixture of organic and inorganic elements, interacts with each other, influenced by weathering, adsorption, and biological processes, making it a dynamic and intricate system. Carbonate content in soils is shaped by various factors including parent rock composition, biological activity, decomposition, and climatic conditions. This study aims to determine carbonate levels in surface soils near Iași using a pressure calcimeter, offering a precise and straightforward method. Surface soils in Ciurea and Picioru-Lupului villages exhibit uneven carbonate distribution, with highest concentrations in northern and southern areas. Carbonate originates from diverse sources such as parent rock, biological processes, organic matter decomposition, atmospheric interactions, and human activities like fossil fuel combustion. The determination method involves measuring pressure following hydrochloric acid reaction, employing a cost-effective calcimeter setup. Swift sample preparation and analysis characterize the process, with drying being the only time-consuming step. This approach provides rapid and reliable results, showcasing its efficacy in soil research and environmental monitoring.

Keywords: soil, calcimeter, carbonate determination, Arduino, Ciurea

1. Introduction

The soil, the superficial layer of the lithosphere with thicknesses ranging from a few centimeters to 2-3 meters, is a complex mixture of organic and inorganic solids, air, water, other substances, micro-organisms, and plant roots that interact with each other, making soil processes dynamic and complex (Daniel et al., 2020). Weathering and adsorption affect the quality of air and water; air and water weather the soil, microorganisms catalyze many reactions, and plant roots absorb and release organic and inorganic substances (Hinrich et al., 2001).

The carbonate content in soils is influenced by several factors. The parent rock from which the soil formed is the initial source of carbonates, either because they were present in the rock's structure or formed due to the weathering of calcium-rich minerals within their structure. Vegetation and microorganisms also contribute to their formation. Plants absorb fluids from the soil through their roots, facilitating the precipitation of salts, and some microorganisms can produce carbonates through their metabolic action. Climate is an essential factor, with carbonate transport and formation being influenced by precipitation levels. Thus, in humid climatic zones, carbonate leaching is prevalent, while in arid and semiarid climatic zones, precipitation is insufficient to remove carbonates from the soil profile (Dorronsoro Fdez et al., 2002).

The purpose of this study is to determine the carbonate content in surface soils from a location near the city Iași, using the pressure calcimeter, a simple and precise determination method.

2. Considerations regarding the studied area

2.1 Geographical considerations

The villages of Ciurea and Picioru-Lupului are administratively part of the Ciurea commune, located approximately 13 km south of the city Iași. Besides the two mentioned villages, the Ciurea commune also includes the villages of Dumbrava, Lunca Cetățuii, Hlincea, Curături, and Slobozia (Obreja, 1979). Geographically, Ciurea is situated in the southern part of the Moldavian Plain, a subunit of the Moldavian Plateau. The predominant soils in the Moldavian Plain are chernozems and leached chernozems. Chernozems, formed on loess deposits of various textures, occur on south-facing slopes and terraces, while leached chernozems, formed on clay with carbonates or fine loess deposits, occur on interfluve surfaces (Florea et al., 1968).

2.2 Geological Considerations

From a geological perspective, the area from which samples were taken for this study is encompassed within the geological structural unit called the Moldavian Platform.

Like any platform unit, the Moldavian Platform consists of two components: the basement or foundation and the cover.

Interception of the basement was only possible with deep drilling: at Todireni (950 m), at Bătrânești (1008 m), or Iași (1121 m), and analysis of the cores revealed that the basement consists mainly of crystalline schists, largely gneiss, with interspersions of granite (Brânzilă, 2003).

The cover is composed of sedimentary deposits that accumulated in three major sedimentary cycles (megacycles), with interruptions occurring locally or across the entire platform. The three cycles are Upper Vendian–Devonian, Cretaceous–Paleocene–Middle Eocene, Upper Badenian–Meotian (Brânzilă, 2003).

Deposits from the Upper Vendian-Devonian megacycle are accumulated in facies of dark limestones and bituminous black clays, with a varied fauna of graptolites, algae, foraminifera, spores, ostra-

cods, and brachiopods (Brânzilă, 2003).

Sedimentation in the second megacycle, Cretaceous–Paleocene–Middle Eocene, began in the Valanginian, followed by a major transgression starting in the Cenomanian. Glauconitic sandstones and cretaceous limestones with specific flints of the Cenomanian deposits appear along the Prut River, while nummulitic-rich limestones and glauconitic sandstones specific to the Paleogene are known from drilling (Brânzilă, 2003).

Sedimentation of the Upper Badenian-Meotian megacycle was not continuous. A marine transgression began in the Upper Badenian and extended across the entire platform. Sedimentary interruptions were recorded between the Badenian and Sarmatian and between the Basarabian and Chersonian. The Badenian deposits consist of gypsums and anhydrites accumulated in lagoon facies. Sarmațian deposits are characterized by a brackish fauna, which can be separated into four sub-stages based on fauna: Buglovian, Volhynian, Basarabian, and Chersonian (Brânzilă, 2003).

In the Badenian, bentonitic clays predominate, with a tuff package in the median area and bioherms from tubicolous worms in the upper part. The fauna is represented by bryozoans, foraminifera, bivalves. Volhynian deposits show facies changes from east to west. Clayey and silty facies predominate in the eastern area, while in the median area, there are sands with interruptions of oolitic limestones and fossil-rich sandstones, and in the western area, there are arenites and rudites of Carpathian nature. The predominant fauna consists of gastropods, bivalves, and foraminifera. Basarabian is also characterized by facies changes from east to west. Thus, clays predominate in the east, sands with intercalations of oolitic limestones and sandstones in the median area, and gravel and sands in the west. The fauna is dominated by foraminifera, vertebrate remains, and mollusks (Mactra podolica). In the southern part of the platform, Basarabian sedimentation is marked by the accumulation of oolitic limestone (of Repedea), with a variable thickness of 3–25m. Chersonian deposits accumulated in distal-clayey and fluvio-deltaic facies, with a fauna dominated by vertebrate remains, small-sized mactrae, and plant remains. The last sedimentary cycle is concluded in the Meotian, where cinerite deposits accumulated. The Quaternary is represented by alluvium accumulated on the terraces of the hydrographic arteries of the platform (Brânzilă, 2003).

3. Soil carbonates

The accumulation of carbonates, especially calcium carbonate, in soils occurs in regions with low precipitation. When evapotranspiration exceeds precipitation, water flow into the soil profile is sufficient to remove only highly soluble weathering products, such as sodium salts. Intermittent rains can wash away soluble salts, even in soils where percolation water is less than 1% of total precipitation. Less soluble components accumulate due to limited water flow. Secondary silicates containing the Ca^{2+} ion in their structure are rare, but Ca^{2+} remains an exchangeable cation and precipitates as $CaCO_3$ (calcite, aragonite, or vaterite),

occasionally precipitating as gypsum ($CaSO_4 \cdot 2H_2O$), a much more soluble mineral. Calcite formed in soils allows very little substitution of Mg^{2+} in its structure, which is why the formation of dolomite ($CaMg(CO_3)_2$) is unusual (Daniel et al., 2020).

Calcite, aragonite, and vaterite can also accumulate in soils when hydrostatic pressure transports groundwater rich in Ca^{2+} and CO_2 to the upper part of the soil profile. The release of CO_2 into the atmosphere and water evapotranspiration lead to the precipitation of $CaCO_3$ (Hinrich et al., 2001).

The solubility of calcium carbonate in soils is more complicated than in surface waters due to limited water content, variation in partial pressure of carbon dioxide (P_{CO_2}), and multiple sources of Ca^{2+}. P_{CO_2} varies depending on the distribution of carbon dioxide in the atmosphere and microbial and plant root respiration. In flooded soils and those rich in roots and microbial activity, P_{CO_2} can be 100 times higher than atmospheric CO_2 partial pressure (Daniel et al., 2020).

Although the environmental conditions that lead to carbonate accumulation in soil are varied, the main factors controlling formation are: the activity of the Ca^{2+} ion in the soil, soil pH, and partial pressure of carbon dioxide (Daniel et al., 2020).

$$CaCO_3(s) + 2H^+ = Ca^{2+} + H_2O + CO_2(g)$$

Acidity favors the dissolution of $CaCO_3$, while an increase in P_{CO_2} promotes the precipitation of $CaCO_3$ if the calcium ion is present. High concentrations of Ca^{2+} and low soil water content favor the calcite precipitation reaction (Daniel et al., 2020).

$$Ca^{2+} + HCO^- = CaCO_3(s) + H^+$$
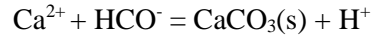
The calcium carbonate content in carbonate-rich soils varies from traces to concentrations of over 80%. Calcite appears in various forms, from nodules of 1 cm or larger to submicron particles. The presence of carbonates is usually associated with neutral to alkaline soils, but solid carbonate nodules are present in some acidic environments (Loeppert and Suarez, 1996).

4. Samples and analytical methods

For this study, a total of 20 samples were collected from the areas of Ciurea and Picioru-Lupului villages (Fig. 1), at a depth of 0-10 cm, without following a distribution network.

The method used to determine soil carbonates was the pressure calcimeter method.

Calcium carbonate is expressed in percentages and represents the total carbonates ($CaCO_3$, $MgCO_3$) in 100g of soil. The determination of $CaCO_3$ (%) is based on measuring the pressure accumulated in a closed system, due to the reaction between the soil carbonates and the hydrochloric acid solution, which releases carbon dioxide (CO_2):

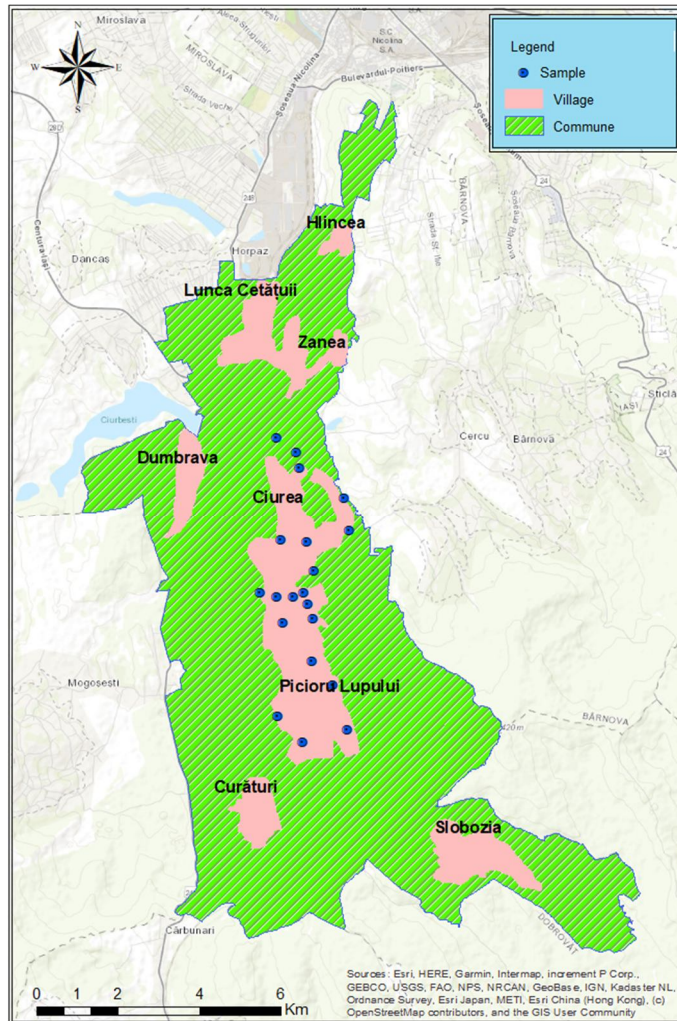$$(CaCO_3, MgCO_3) + 2HCl \rightarrow (CaCl_2, MgCl_2) + H_2O + CO_2 \uparrow$$
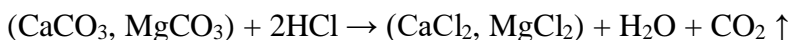
Fig. 1 Samples distribution.

The specific effervescence that occurs when hydrochloric acid is added to the soil sample is evidence of the release of carbon dioxide and thus the presence of carbonates in the sample.

The calcimeter (Fig. 2) consists of: a 250 mL glass container with a lid, a cylindrical plastic tube, a metal reduction with a purge valve, a 2-bar pressure sensor, and an Arduino UNO board. It is connected to a computer via a USB cable, and the analysis results are displayed through the Arduino IDE application.

Calibration

The calibration curve (Fig. 3) is used to convert the signal received by the Arduino board, resulting from the pressure gener-

Fig. 2 Calcimeter composition: (1) glass container with lid, (2) cylindrical plastic tube, (3) metal reduction with purge valve, (4) pressure sensor, (5) Arduino board.

$CaCO_3$ from 0.1g to 1g, with each point representing 100% carbonate for that quantity (Tab. 1). Calibration was conducted at a temperature of 24°C, and the determination of carbonates was performed immediately after calibration.

For the determination of carbonates, the following are required: 1 gram of dried sample, in powdered form, and 20 mL of 10% concentration HCl. The reaction must take place in a closed system; therefore, the acid and the sample are separated in the container using the cylindrical tube. After sealing the lid, the container is agitated until all the acid comes into contact with the sample. The pressure accumulated in the closed system, due to the release of carbon dioxide, is measured by the pressure sensor, which transmits a signal to the Arduino board. This signal is converted and processed to display the resulting carbonate percentage in the application.

5. Results

The values of calcium carbonate content in the analyzed samples range from 0.5% to 11% (Tab. 2), low concentrations typical of chernozem soils.

ated by the reaction of 10% hydrochloric acid and a certain mass of pure $CaCO_3$, into percentages of calcium carbonate. For better accuracy, calibration was performed at multiple points using quantities of

Tab. 1 Arduino values of the calcimeter calibration

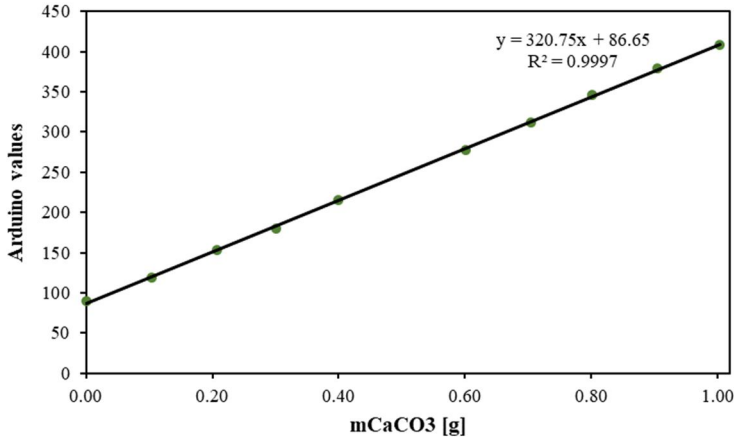| mCaCO$_3$ [g]	Value Arduino (maxim 1024=2^{10} bits)	mCaCO$_3$ [g]	Value Arduino (maxim 1024=2^{10} bits)
0.0000	90.06	0.6008	277.00
0.1034	119.33	0.7040	312.00
0.2075	152.80	0.8017	346.00
0.3003	179.88	0.9053	379.00
0.3996	214.76	1.0041	408.00

Fig. 3 Calibration curve.

Tab. 2 Values of calcium carbonate in samples

Sample	$CaCO_3$ (wt %)	Sample	$CaCO_3$ (wt %)	Sample	$CaCO_3$ (wt %)	Sample	$CaCO_3$ (wt %)
1	5.61	6	2.05	11	10.19	16	0.52
2	7.64	7	1.03	12	10.69	17	3.57
3	2.05	8	3.57	13	1.54	18	1.03
4	10.19	9	1.03	14	7.64	19	6.63
5	2.56	10	3.07	15	2.56	20	1.03

The climate in which these soils formed and evolve is humid, therefore leaching and weathering are more pronounced. With leaching being more pronounced, the washing away of calcium carbonate is more intense, with the carbonate being washed to depths of up to 30–40 cm in the case of chernozem soils and 75–80 cm in the case of cambic chernozem soils (Puiu et al., 1983).

Using the data interpolation function in the ArcGIS Desktop software, we created a map depicting the distribution of carbonate across the surface of the two villages (Fig. 4). The highest concentrations are in the northern and southern extremes of the area. These gradually decrease towards the center, where there is again an increase in content.

6. Conclusions

Surface soils in the studied area, namely the villages of Ciurea and Picioru-Lupului, exhibit an uneven distribution of carbonate, with maximum concentrations present in the north and south of the area. Carbonate can originate
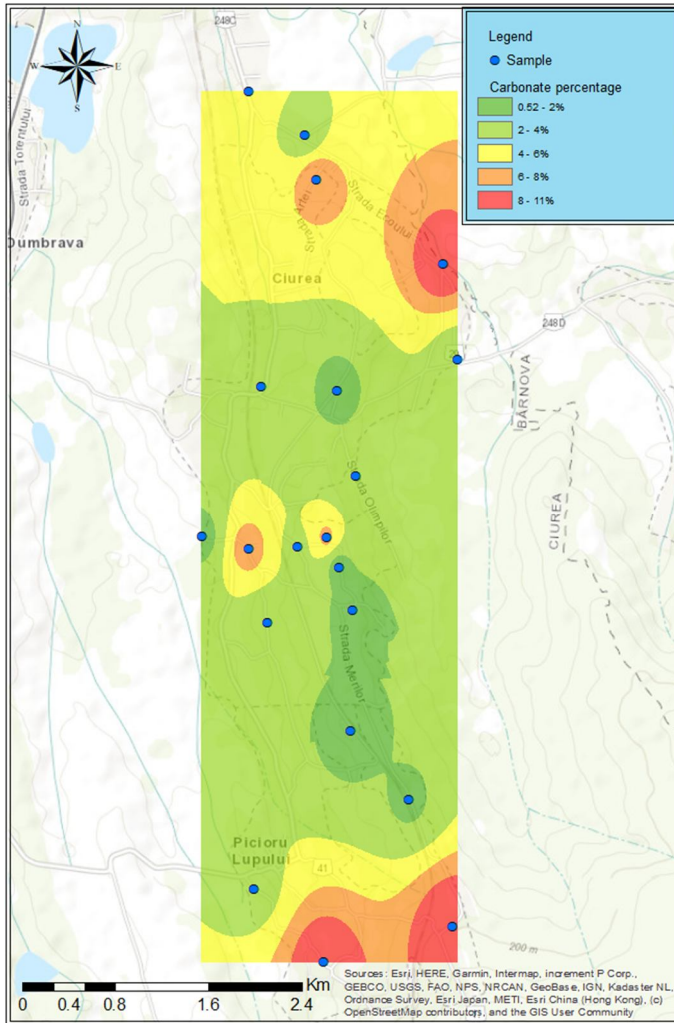
Fig. 4 Distribution of carbonate in the studied zone

from the following sources:
- the rock on which the soil developed;
- biological activity (certain organisms, such as bacteria, produce carbon dioxide during metabolic processes and react with minerals in the soil, forming carbonates);
- decomposition of organic matter;
- atmospheric factors (atmospheric carbon

dioxide dissolves in meteoric water, forming carbonic acid; although weak, this acid reacts with minerals in the soil.);
- anthropogenic sources (combustion of fossil fuels).

The determination method, which involves measuring the pressure released in the closed system following the reaction

between hydrochloric acid and soil carbonates, is simple and accurate. The equipment and reactants used were: calcimeter, oven, analytical balance, mortar and pestle, graduated cylinder, 10% concentration hydrochloric acid. Due to the small number of elements involved in the construction of the calcimeter, the costs are relatively low, with the price being influenced only by the quality of the materials. Its construction is straightforward and involves attaching the reduction and pressure sensor to the lid of the container. The preparation and determination time for a sample is very short, only a few minutes, with the drying of the samples being the only lengthy process.

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