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Geochemical assessment of soil and water in two protected areas from Valcea and Dolj Counties

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Abstract
The purpose of this paper was to assess the quality of environmental factors such as soil and water in some protected areas in Romania. The chosen case studies were the Preajba-Facai lake system from Dolj County and the Vanturarita Buila National Park from Valcea County. Highlighting the evolutionary aspects of the analyzed quality parameters (20 physical-chemical indicators) on a spatial-temporal scale aiming at establishing geochemical thresholds is the final result of a larger project. The results presented in this article were obtained through seasonal monitoring involving water and soil sampling and laboratory analysis. All the results were interpreted in relation to the values in the specific environmental legislation, and following the field visits additional information was brought, which contributed to a good knowledge of these regions. The areas, although protected, are influenced by the anthropogenic factor, which has a negative impact on the environment. In some cases, non-compliances were identified and validated by the analysis performed.

Keywords: *protected areas, metals, national park, soil, water*

INTRODUCTION

Establishing geochemical thresholds for traces of elements present in the soil involves a laborious analysis of varying concentrations and natural background levels, and can be successfully applied over large areas of space, up to the size of a continent [1]. Regional or local geochemical thresholds for the analyzed elements can be determined using geochemical maps.

With these geochemical data maps, it is possible to provide an environmental basis, information for geochemical assessment and advance tracking of management during a large-scale development site [2]. An integrated assessment of the soil and geochemical sediments of river courses can determine the variations of the geochemical threshold for metals. The natural variation of the geochemical background in soil and river sediments should be considered before defining new indicative values. At the regional level, local anomalies are influenced by the predominant lithology rather than any anthropogenic impact [3-6].

Protected areas are the most common and important tool for the conservation of biological diversity and are required under the United Nations Convention on Biological Diversity. As a result, the human population growth, intensified land use, and increasing habitat fragmentation threaten the global ecosystems and protected areas. These are often the only refuge for endangered species. Climate change is an additional threat that can also affect the ecosystems that are currently under protection. It is therefore of major importance to include the potential impact of climate change on the design of future nature conservation strategies and the implementation of protected area management [7]. Wetlands contribute to climate regulation and climate change mitigation, as they are responsible for carbon assimilation, improving water quality, flood control, aquifer loading and unloading, food supply, biodiversity, maintenance and pollution control [8]. Action needed to halt biodiversity loss or mitigate climate change can be achieved by aligning certain targets. These objectives would be: restoring the necessary habitat, reducing greenhouse gas concentrations and promoting / adapting society to climate change. Given the plight of natural ecosystems and humanity's dependence on them for our survival, there is an urgent need to increase the protection of biodiversity targets and provide sufficient space for nature to thrive on and for the world to adapt quickly [9-15].

Knowing the background or threshold concentrations of different soil elements is essential in assessing whether or not a concentration is abnormal. Significant chemical variation of soil samples may be influenced by soil type, climate and topography [16-19].

Globally, 15.5 million km^2 of land is currently identified as protected areas, providing society with many ecosystem services, including climate change. As food demand increases with population and income, the world returns to the use of bioenergy, and current agricultural land is suffering from losses due to changing environments and pressure to convert protected land, either by changes in their legal status or simply as a consequence of the inefficient application of land use conversion [20-22].

Mapping programs for geochemical prospecting have been developed, principles and techniques have been extended to environmental issues, such as land use planning, agricultural development, environmental monitoring and medical geology. The geochemical maps resulting from such surveys show the distribution (background) of the analyzed elements [23, 24]. The relief is considered the abiotic factor that most strongly influences the physical, chemical and biological processes of the soil [25, 26].

The aim of the study consists in a geochemical evaluation of the quality of the soil and water environmental factors, in protected natural areas (Buila Vanturarita Park, Preajba-Facai Lake Complex) in order to establish some reference thresholds for the natural geochemical background. The areas are outside the direct influence of anthropogenic activities.

The anthropogenic impact on natural ecosystems is a problem that can only be managed with proper management, which takes into account the specifics of each area. By implementing control tools and measures, the negative impact on the environment can be controlled to an extent that can be considered acceptable. Therefore, the declaration of areas of Community interest as protected natural areas is the most appropriate instrument by which the European Community manages to control the negative impact of human activities in order to protect the environment.

Buila Vanturarita Park was established in 2004, being the smallest protected natural area in Europe, a member of the "Natura 2000" sites. The park is located on the border with a limestone mining area.

The area affects landscape, geological/paleontological elements, geomorphological elements, karst, habitats flora, fauna, cultural heritage, Arnota Monastery.

Regarding the Preajba-Facai Lake Complex, the non-existence of landfills, sewers and treatment plants near the villages, which largely coincides with an area boundary, lead to negative effects on the biota.

EXPERIMENTAL PART

Topography and geology of the studied areas

The context of the report refers to the investigation and evaluation of soil and surface water quality in two protected areas in Romania, the Preajba-Facai Lake system and the Vanturarita Buila National Park. Figure 1 shows the location of the area and the sampling points for the Preajba-Facai Lake complex.

In the present study, one of the areas studied was the Preajba-Facai Lake Complex, in Dolj County located in the central-eastern part of the County, in the north of Preajba village, near the national road DN55 that connects Craiova with Bechet. The area is a lake complex (lakes, swamps, streams, alluvial forests, sand dunes, arable land, meadows) in the northwest of the Romanatilor Plain. The area is distinguished by a wide variety of flora and fauna specific to wetlands. The area was declared a protected area in 2000 and covers an area of 28 hectares, of which the five component ponds occupy 21 ha. The largest bodies of water are Ciliboaica Pond, Police Pond, Prison Pond and Pond I, each of which has a different shape and surface.

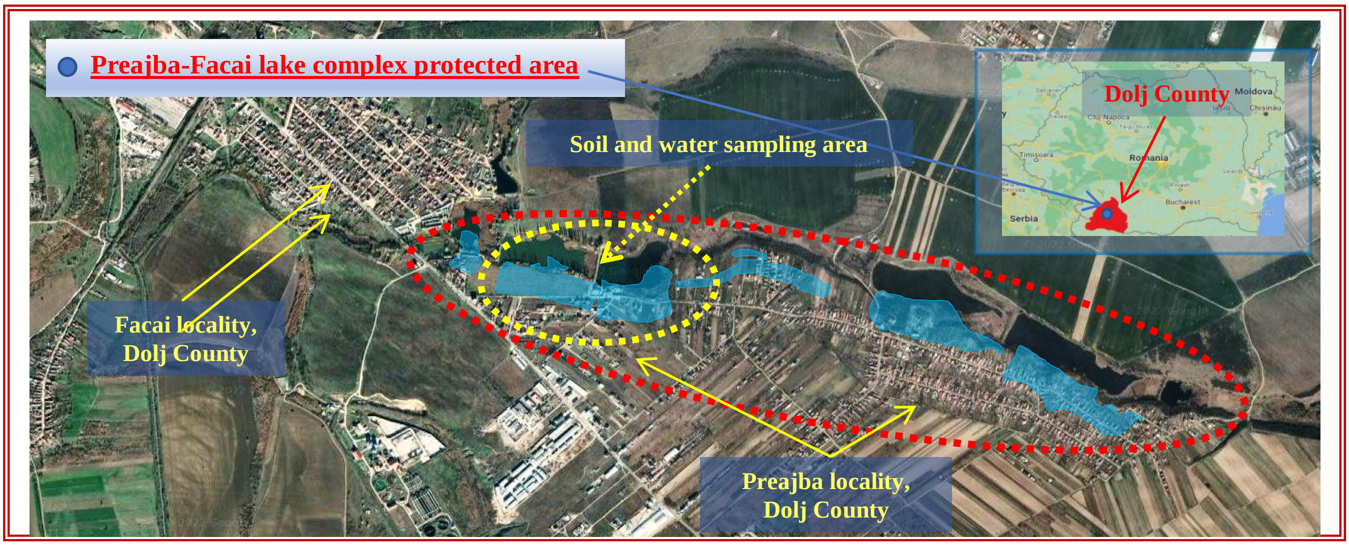

Fig. 1. Location of the protected area and sampling points for the Preajba-Facai Lake Complex
(source of processing map: Google Earth, 2022)

Another evaluated natural area is the Vanturarita-Buila National Park, which is located in the central-northern part of Valcea County and is part of the Capatanii Mountains. It has a well-developed hydrographic network and ensures the drinking water needs of some localities in its vicinity. The soils in Vanturarita-Buila National Park are mostly formed on a calcareous substrate, showing not a great diversification, being different only due to the type of vegetal associations that were formed on them.

Overall, rendzines are predominant (undeveloped soils, cernisols - the parent material is made up of compact limestone, dolomites or calcareous gravels). The entire hydrographic network of the Vanturarita-Buila Massif through its direct or indirect tributaries on its right, with a course direction, flows into the Olt River, broadly speaking, from north to south.

Figure 2 shows the location of the area and the sampling points for the Vanturarita-Buila National Park.

Fig. 2. Location of th sampling points area for Vanturarita-Buila National Park
(source of processing map: Big Maps, 2022)

Surface water and soils sampling

All sampling points were precisely located via a GPS receiver shown in Figures 3 and 4, Garmin supplier, model Montana 610. In addition, a series of sampling points were chosen located in areas

outside the outer perimeter of the protected areas to highlight the anthropogenic pressures on the factors of soil and surface water environment. A soil auger kit from Burkle was used for soil sampling, and a telescopic scoop from the same supplier for surface water.
From Preajba-Facai Lake Complex were collected two surface water samples (A1, A2) and eight soil samples (S1 – S8), Fig. 3, while from Vanturarita-Buila National Park were collected eight surface water samples (A1 – A8) and six soil samples (S1 – S6), Fig. 4.

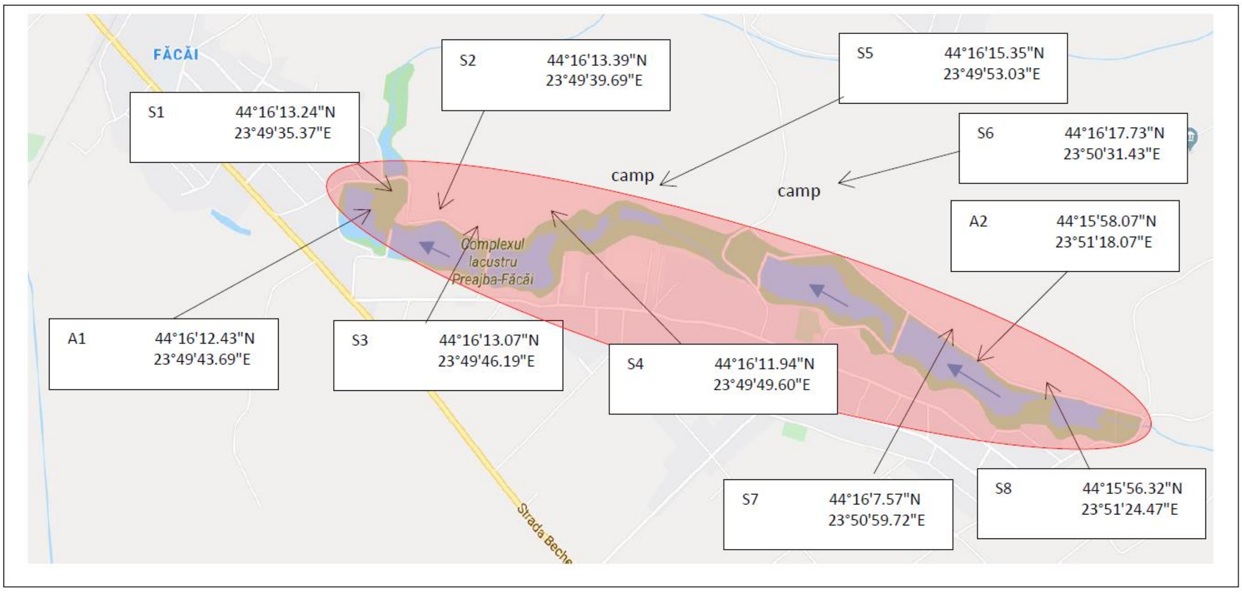

Fig. 3. Location on the map of the sampling points in the area of Preajba-Facai Lake Complex

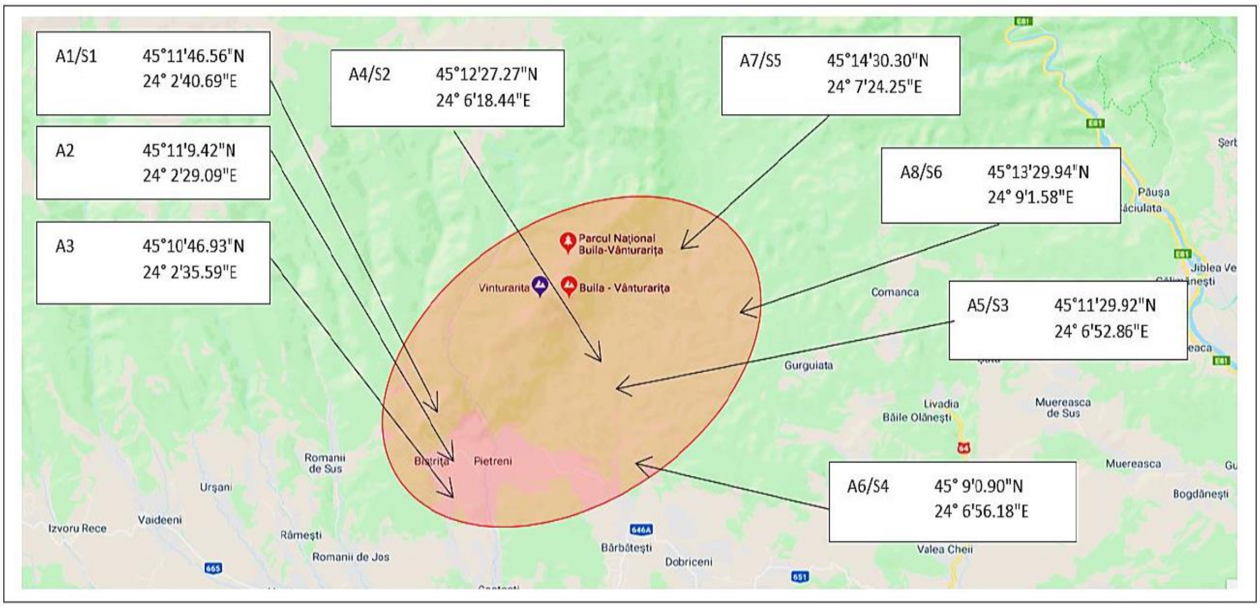

Fig. 4. Location on the map of the sampling points in the area of the Vanturarita-Buila National Park

Sampling techniques and methods of analysis have been performed in accordance with applicable national standards. The samples were uniquely labeled, properly preserved and brought to the laboratory for analysis in the same day.
The equipment used for the experimental studies was calibrated prior to testing, in accordance with applicable laboratory procedures.

Methods applied

The methods used for the analysis of the studied indicators applied techniques such as: electrochemistry (multiparameter Thermo Scientific Orion Star A 215), gravimetry (Precise Balance XB, Memmert Oven), UV-Vis spectrometry (Specord 210 Plus) and inductively coupled plasma optical emission spectrometry (ICP-OES Perkin Elmer Optima 5300DV). Analytical purity reagents were used for both water and soil characterization.

The interpretation of the soil results was performed by comparison with the reference normal values in the specific legislation, respectively with the reference values for the traces chemicals in soil with sensitive land use, practically the most severe quality conditions established for land use [27, 28].

The threshold values and the limits for the ecological status classes of surface water bodies in the national legislation in force were used to interpret the results for the water samples [29].

The quality indicators analyzed for the soil were pH, humus, Kjeldahl nitrogen, iron, arsenic, barium, cadmium, cobalt, total chromium, copper, manganese, molybdenum, nickel, lead, selenium, antimony, vanadium, zinc and potassium.

For the surface water characterization, were analyzed the following indicators: pH, iron, aluminum, ammonium, nitrite, nitrate, cadmium, total chromium, copper, manganese, mercury, nickel, selenium, antimony, lead, zinc, COD, calcium, magnesium and sodium.

RESULTS AND DISCUSSIONS

Quality of surface water and soil from Preajba-Facai Lake Complex

In Figure 5 are presented the graphical representation of nitrates, pH and Calcium in surface water. Regarding the obtained results, we mention that the pH value were situated between 8.3 and 9.15, in basic range; for the nitrogen parameter the value were 7.6 mg/L for the point A1, respectively 0.7 mg/L for the A2 point; calcium concentrations were 25.5 mg/L (A1) and 68.8 mg/L (A2).

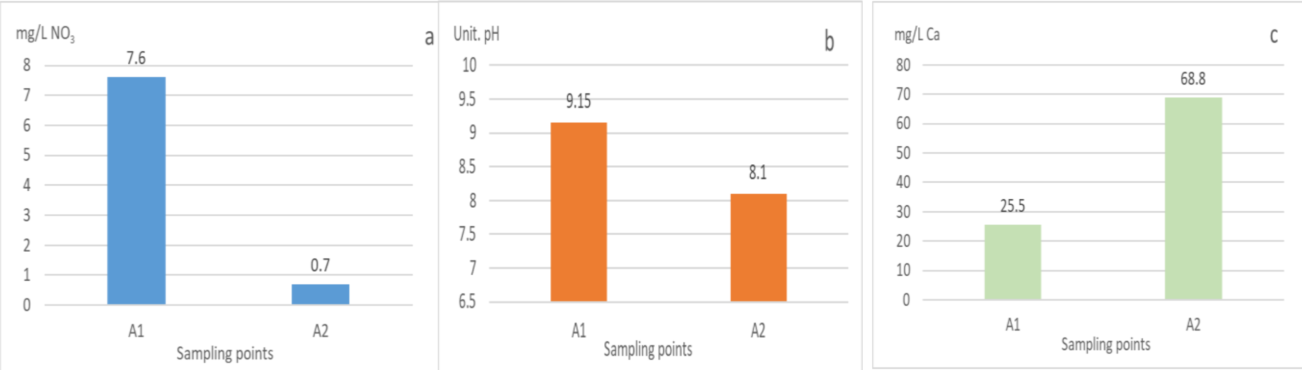

Fig. 5. Variation of water quality indicators depending on the sampling points in the area of the Lacustru Complex Preajba Facai for: a) nitrates, b) pH, c) calcium

In Table 1 are presented the minimum, maximum and average concentrations of other quality indicators in water samples in relation with in force legislation [30].

Table 1. Minimum, maximum and average values of some indicators in the water samples

Quality indicators	Preajba-Facai Lacustru Complex			Vanturarita-Buila National Park			Order no. 161/2006 [30]
	Min.	Max.	Average	Min.	Max.	Average	
COD-Mn	0.13	0.38	0.24	0.26	1.28	0.83	Class I
Magnesium	48.5	52	50.8	2.10	10.9	8.2	Class III / Class I
Sodium	42.8	45.1	44.5	1.35	17.2	6.3	Class II / Class I
Total Chromium	<1.3*	<1.3	<1.3	<1.3	15.4	3.5	Class I
Copper	<1.0*	<1.0	<1.0	<1.0	3.6	1.9	Class I
Zinc	15.0	30.8	28.6	<2.0*	112.8	15	Class I / Class II

*Quantification limit

The graphical representation of the soil quality indicators is presented in the Fig. 6. The pH values were recorded in the range 5.99 to 8.86, from slightly acidic to basic domain. The humus indicator was situated between 0.26 % and 0.42 %, while lead concentrations varied between 7.45 mg/kg dry matter (d.m.) and 14.2 mg/kg d.m.

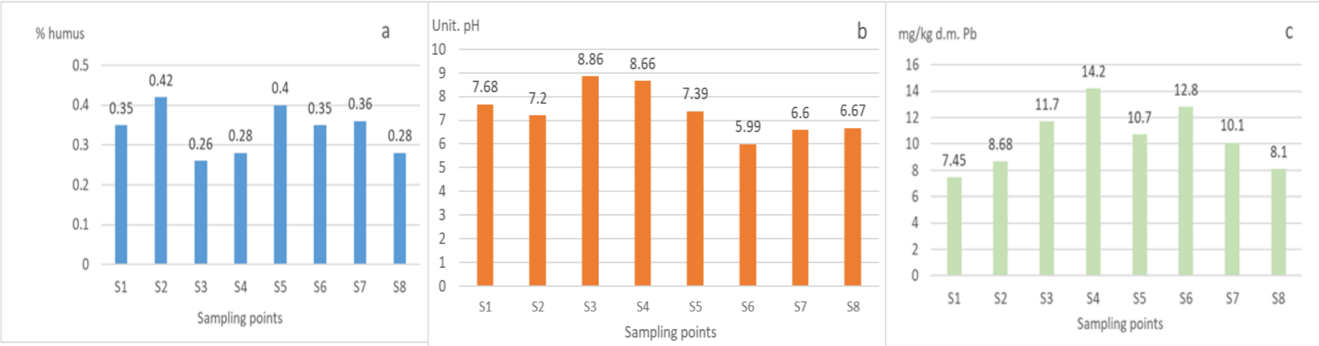

Fig. 6. Variation of soil quality indicators depending on sampling points in Lacustru Complex Preajba Facai area for: a) humus, b) pH, c) lead

Quality of surface water and soil from Vanturarita-Buila National Park

Figure 7 shows the graphical representation of the quality indicators of the sampled water. Regarding the results obtained, we mention the following: the pH value were ranged between 7.67 and 8.23, from neutral to slightly basic domain. The nitrogen content was situated from less than 0.05 mg/L to 5.48 mg/L, while calcium concentrations varied between 11.6 mg/L and 74.2 mg/L. the calcium content of the waters in this analyzed area corresponds to the mineralization specific to the karst areas indicated by the specialized literature.

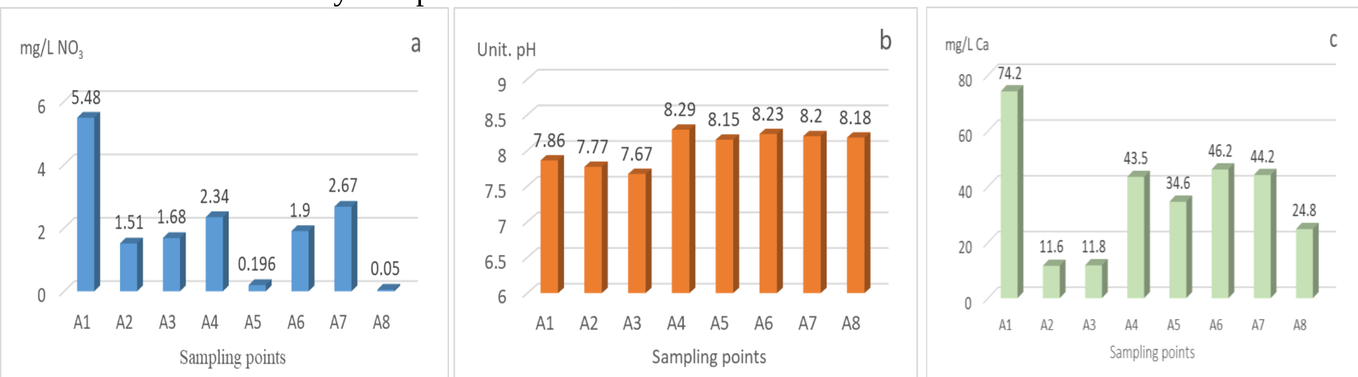

Fig. 7. Variation of water quality indicators depending on sampling points in the Vanturarita-Buila National Park area for: a) nitrates, b) pH, c) calcium

The graphical representation of the soil quality indicators is presented in Fig. 8. The results obtained indicate the following conclusions: pH value were situated between 5.38 and 8.42, from slightly acidic range to basic domain. The humus content was reported in the range 0.41 % to 1.25 %, lead concentrations varied between 5.49 mg/kg d.m. and 20 mg/kg d.m.

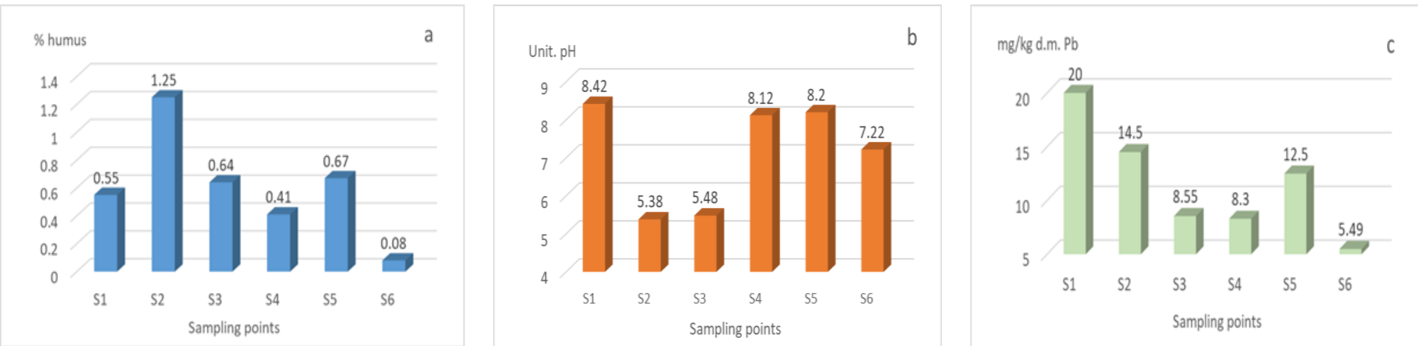

Fig. 8. Variation of soil quality indicators depending on sampling points in the Vanturarita-Buila National Park area for: a) humus, b) pH, c) lead

In Table 2 are presented the minimum, maximum and average values of some metals determined from soil samples compared to the reference values from Romanian Order 756/1997 [31] for the approval of the regulation on environmental pollution assessment.

Table 2. The minimum and maximum concentrations of some metals from the soil samples of the two locations, mg/kg d.m.

Metal	Preajba-Facai Lacustru Complex			Vanturarita-Buila National Park			Normal Reference values from Order 756/1997 [31]
	Min.	Max.	Average	Min.	Max.	Average	
Cadmium	0.11	0.28	0.18	<0.1*	<0.1	<0.1	1
Cobalt	4.35	8.88	6.18	4.53	11.2	7.64	15
Total Chromium	10.5	17.2	13.1	10.3	26.3	19.7	30
Copper	6.67	12.9	9.61	3.06	19.6	8.89	20
Manganese	184	500	310	71.5	700	293	900
Nickel	7.90	18.2	13.1	9.50	18.6	16.2	20
Lead	7.45	14.2	10.5	5.49	20.0	11.3	20
Zinc	18.4	47.3	29.3	20.7	69.4	39.5	100

*Quantification limit

The results indicated that all maximum values both from Natural Park Vaturarita Buila and Preajba Facai samples were situated below the normal values for soil quality [31]. Values from the soils collected from Vanturarita-Buila National Park were recorded higher values for Cu, Ni and Pb.

CONCLUSIONS

In this paper, two areas Preajba-Facai Lake Complex and Vanturarita-Buila National Park, were studied.

The results obtained for the collected soil samples were compared with the reference values for soil quality and all parameters falls within the normal range. The values registered for Vanturarita Buila Natural Park were slightly higher than the values recorded in Preajba-Facai Lake Complex, which could be evidence of the anthropic economic activities carried out in the zone of this protected area.

Regarding the surface water quality, the obtained results were compared with in force legislation for ecological status of water bodies, and it was observed that, surface water from Preajba-Facai Lacustru Complex was situated in class III (moderate) quality, while surface water collected from Vanturarita-Buila National Park was within limits of class II quality (good).

The evaluation of the water and soil environmental factors from the studied protected areas is important in order to highlight and quantify the evolutionary aspects regarding their quality.

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