

## ENVIRONMENTAL ASSESSMENT OF THE AREA WITH NATURAL CO<sub>2</sub> EMISSIONS IN BĂILE LĂZĂREȘTI

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### Abstract

*Băile Lăzărești, located 16 km north-east from Băile Tușnad, is a representative area for post-volcanic regions where gases emitted at the surface contain over 85% carbon dioxide. Nineteen stations were set up for collecting soil samples for analysis of heavy metals, TOC, carbonates, and lithology and four water stations for nutrient analysis in July and August 2022. The impact of increased CO<sub>2</sub> emissions on the soil is evident through the exceeding normal concentrations of heavy metals such as Cr, Cu, Hg, and Ni in areas with high CO<sub>2</sub> emissions and their reduction in areas with lower volcanic gas emissions. Water sample analysis, all with high CO<sub>2</sub> concentrations, showed elevated levels of nitrites, inorganic phosphorus, and sulphates, classifying the water quality into categories II and III, according to national classification. The impact of high CO<sub>2</sub> concentrations is clearly visible in the vegetation, which is absent at CO<sub>2</sub> concentrations above 20%, predominantly consists of grasses, and shows distinct colorations at concentrations below 20%. These observed and analysed elements could serve as surface indicators for potential CO<sub>2</sub> leaks from anthropogenic storage sites.*

**Key words:** Băile Lăzărești, Băile Tușnad, carbon dioxide emissions, CO<sub>2</sub> impact, soil sampling, water sampling.

### INTRODUCTION

Since the 1950s, studies on mineral springs, chemical composition of waters, and emitted gases from post-volcanic gas vents have been conducted in the vicinity of Lăzărești. Various analyses from these studies are mentioned in Artemiu Pricăjan's books "Mineral and Thermal Waters in Romania" (1972) and "Therapeutic Mineral Substances of Romania" (1985). Additionally, Zoltán Rákósy's chapter in the 1974 publication of the People's Council of Harghita County mentions the inventory of 44 mineral water springs in Lăzărești (Karátson et al., 2022). Furthermore, detailed cartography and chemical analyses of carbonated mineral waters and post-volcanic gas vents in the Ciomadul area were carried out between the 1970's and 2000's by geologists and chemists from the Harghita Geological Research and Exploration Company. These findings were later published in various works such as "The Mineral Waters of the Kelemen-Görgényi-Harghita Mountain Range" (2000) by Berner, Z., Csaba Jánosi, C., and Péter, E. Szadeczky, Gy. (1929),

Torok, Z. (1956), Bányai, J. (1929, 1934), Atanasiu, I. (1939), Ianovici, V., Giușcă, D. (1981) and Ghițulescu, P.T. (1975) significantly contributed to deepening the knowledge of the volcanic activity within the Eastern Carpathians. Essential insights into the geological structure of the entire volcanic chain were provided by D. Rădulescu and collaborators. Hydrogeological research in the region was conducted by Pricăjan, A. (1972, 1974, 1985), Pascu, R. (1929), Slăvoacă, D. (Slăvoacă, 1971; Slăvoacă et al, 1978), Lungu, P., Geamănu, N. (1971), Bandrabur, T. (1961) and Vasilescu, Gh. (1964), with a primary focus on mineral waters. The most prominent and active post-volcanic manifestation within the Eastern Carpathians is found in the Gurghiu and Harghita mountain massifs, characterized by predominantly calc-alkaline volcanic activity, resulting in the formation of stratovolcanoes and a complex volcanic chain surrounded by volcanoclastic deposits and monogenetic or polygenetic dome complexes (Airinei & Pricăjan, 1972). Adjacent to the Lăzărești site are parasitic cones or lava domes formed along faults and linked to the

Ciomadu Mare volcanic complex (Seghedi et al., 2019). These domes, with steep or abrupt slopes, rise about 100-250 meters above the general terrain level and develop in various directions, such as from northeast to northwest and from southwest to northeast, including those at Dealul Cetății (1079 m), Haromul Mare (1140 m), and Lăzărești or Haromul Mic (880 m). The Lăzărești site is situated on a succession of deposits ranging from Cretaceous flysch (Sânmartin-Bodoc, Barremian-Albian layers) at the base to terrace deposits. Lăzărești site, with its dry and wet gas vents, can be also considered as a natural laboratory for the study of the environmental impact of a CO<sub>2</sub> leakage from an anthropic reservoir and for testing and designing monitoring strategies. One of the key points of monitoring CO<sub>2</sub> geological storage sites would be to find early indicators of a potential leakage through soil and water sampling and vegetation surveys. Considering Lăzărești to be a suitable site to find these indicators, several field campaigns were conducted in 2022 including measurements of CO<sub>2</sub> concentration, soil and water sampling and vegetation observation. The aim was to correlate abnormal variations of some soil and water parameters and constituents with different CO<sub>2</sub> concentrations and emissions.

## MATERIALS AND METHODS

### Study area

The study area encompasses the region around Băile Lăzărești, situated approximately 16 km north-east of Băile Tușnad, renowned for its significant post-volcanic activity and characterized by surface emissions with high concentrations of carbon dioxide, exceeding 85%. The site was divided for study purposes in two perimeters, one northern perimeter with high CO<sub>2</sub> emissions and many wet and dry gas vents, including some baths used for therapeutic purposes and one southern perimeter with much lower emissions including only dry gas vents.

### Methodology for water and soil analysis

During the field campaigns (conducted in July and August 2022), soil samples were collected from 19 points aligned along two profiles, one with 10 points in the northern perimeter of the

site and one with 9 points in the southern perimeter, for the analysis of heavy metals, total organic carbon (TOC), carbonates, and lithology (Figure 1). The samples were collected in plastic containers, closed with lids, and securely sealed, after measuring CO<sub>2</sub> concentration at the surface. The amount of material collected was approximately 50-100 g, depending on its physical state (solid or with high water content). Measurement of CO<sub>2</sub> concentration at the surface of the sampling points was conducted using a portable gas analyser from West Systems. The soil analysis methods involve determining calcium carbonate (CaCO<sub>3</sub>) concentrations through volumetric analysis with 0.5N HCl and 0.5N NaOH, as well as total organic carbon (TOC) using a titrimetric method with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and concentrated sulfuric acid (Dean, 1974; Van der Veer, 2006), while elements such as Ti, V, Cr, and others are analysed via energy dispersive X-ray fluorescence spectroscopy for simultaneous qualitative and quantitative determination (Emelyanov & Shimkus, 1986). The sediment samples were analysed for their main lithological components, including water content (WC %), dry matter (DM %), total organic matter (TOM %), total carbonates (CAR %), and siliciclastic fraction (SIL %). The lithological analysis relied on standard techniques and procedures used in sedimentology, specifically employing the Loss of Drying (LOD) method for water content and dry matter estimation, and the Loss on Ignition (LOI) method for determining total organic matter, total carbonates, and the siliciclastic fraction through calcination (Ricken, 1993; ASTM-D2216, 2010). Additionally, 4 surface water samples were collected from the spring (Nagyborvív) and the wet gas vents - baths (Nyírfüzdő) present at the site for nutrient analysis (Figure 1). Nutrient and chlorophyll concentrations were determined by analysing water samples for PO<sub>4</sub><sup>3-</sup>, SiO<sub>4</sub><sup>4-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>, which were preserved through freezing (-24°C) using standard methods for water analysis. Analytical methods for nutrient concentrations involved spectroscopic techniques in accordance with HACH water analysis methods.

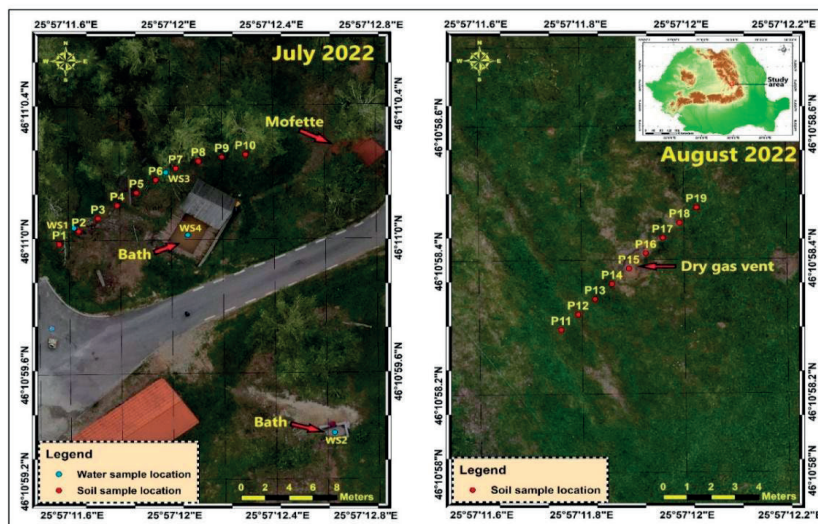


Figure 1. Sampling stations on the Băile Lăzărești area

## RESULTS AND DISCUSSIONS

### Water analysis

Nitrogen, a crucial nutrient in aquatic ecosystems, enters water through various pathways and exists in multiple forms, including molecular nitrogen, nitrogen oxides, ammonia, ammonium, nitrites, and nitrates (Table 1) (Popa et al., 2022; Sandu et al., 2023).

*Nitrate concentrations* exhibit high spatial variability in the study area, ranging between 0.02 mg/L and 0.30 mg/L. All nitrate concentration values correspond to Class I water quality in the study area (<1 mg/L). The maximum value of 0.30 mg/L was observed in sample WS3, while the minimum concentration was measured in sample WS2 (0.02 mg/L). Slightly higher values (0.08 - 0.21 mg/L) were recorded in the other two samples from the analysed stations.

*Nitrite concentrations*, the intermediate form of inorganic nitrogen, varied widely between 0.006 mg/L (WS2) and 0.033 mg/L (WS1). Generally, nitrite values were low, confirming that inorganic nitrogen is the limiting nutrient in primary production. All samples exceeded the threshold value of 0.01 mg/L for nitrites, suggesting classification of the study areas between Class I and Class II water quality, considering the oxidized form of inorganic nitrogen.

Concentrations of *inorganic phosphorus* in the studied sectors exhibited high values, ranging

between 0.08 mg/L and 2.20 mg/L. The highest value exceeding 0.4 mg/L, the limit between Class II and Class III water quality, was determined in sample WS3. However, three out of four values of the samples studied regarding phosphate concentrations fell within the range of 0.1 mg/L to 0.4 mg/L, suggesting, overall, the classification of waters in the study area into Classes I, II, and III in terms of inorganic phosphorus.

*Sulphate concentration* values exceeded the limit threshold of 60 mg/L according to Order 161/2006. Regarding *silicon*, all samples studied recorded concentrations below the maximum allowable limit according to Order 161/2006. The lowest concentration values of this parameter were recorded in sample WS2 (0.073 mg/L), while the highest value was obtained in sample WS1 (0.140 mg/L). These values indicate the water quality at the studied stations and their classification into Class I according to Order 161/2006.

### Soil analysis

The measured CO<sub>2</sub> concentrations at the surface of the sampling points for soil analysis are presented in Tables 2 and 3. As can be seen, on the profile from the northern perimeter, analysed in July 2022, there is a large variation in CO<sub>2</sub> concentrations found, ranging from 485 ppm to 46221 ppm.

Table 1. Nutrient results from water samples

Station	N-NO <sub>3</sub> <sup>-</sup> , mg/L	N-NO <sub>2</sub> <sup>-</sup> , mg/L	PO <sub>4</sub> <sup>3-</sup> , mg/L	SO <sub>4</sub> <sup>2-</sup> , mg/L	SiO <sub>2</sub> , mg/L	Hg, µg/L
WS1	0.08	0.033	0.08	125	8.34	0.140
WS2	0.02	0.006	0.32	165	8.00	0.091
WS3	0.30	0.012	2.20	210	7.75	0.092
WS4	0.21	0.018	0.21	72.5	10.88	0.073

The smallest CO<sub>2</sub> concentration was found for P10 (485 ppm), while the highest CO<sub>2</sub> concentration belongs to P7 (46221 ppm), near a bath used for therapeutic purposes, followed by P1 (42654 ppm), near the spring. On the profile from the southern perimeter, analysed in August 2022, the variation in CO<sub>2</sub> concentrations is lower than the northern one, ranging from 786 ppm to 3448 ppm. The smallest CO<sub>2</sub> concentration was found for P19 (786 ppm), at the northern end of the profile. As expected, the highest CO<sub>2</sub> concentration was found at the sampling point corresponding to the dry gas vent observed in the field, P15 (3448 ppm). To assess the degree of *soil pollution/contamination*, the values obtained from the analysed samples in July and August were compared with normal reference values, alert thresholds, and intervention thresholds for soils of sensitive use provided by Order 756/1997 of the Ministry of Waters, Forests, and Environmental Protection. The results are presented in Tables 2 and 3. Statistical analysis of the data (Tables 2, 3) revealed slightly variability in all chemical components (CV>20%), with coefficients of variation of concentrations ranging from 18.32% for V to 93.35% for MnO (July 2022) and from 30.97% for V to 53.08% for MnO (August 2022). The higher values of the coefficient of variation for MnO concentrations are due to its high redox sensitivity. As for the other minor component, TiO<sub>2</sub>, its relatively high variability (though lower than MnO) (14.38 ppm in July 2022 and 15.67 ppm in August 2022) is likely due to environmental conditions in the analysed area, which may lead to dispersion or concentration of titanium as rutile. Higher TiO<sub>2</sub> values are observed in sample P1 with 4114 ppm (July 2022) and in P16 with 4899 ppm (August 2022). The normal content of chromium in soils (Ord 756/1997) is 30 mg/kg, with an alert threshold of 100 mg/kg and an intervention threshold of

300 mg/kg. Analysing the data obtained for chromium in both campaigns (July and August), exceedances of the normal values of 30 mg/kg are observed in both July and August. Sample P15 (101 ppm - August) even exceeds the alert threshold according to Order 756/1997, while in July the highest chromium values were 78.50 ppm - P5.

Similarly, copper has a normal content in soils of 20 mg/kg, an alert threshold for sensitive uses of 100 mg/kg, and an intervention threshold of 200 mg/kg. The concentrations of copper in the soil at a depth of 0-25 cm for both campaigns are presented in Tables 2 and 3. In the July campaign, exceedances of the normal value were recorded in 70% of the analysed samples. The highest copper concentration was recorded in sample P5 (32.71 ppm), while the lowest copper concentration was recorded in P3 (17.89 ppm), below the normal value of 20 mg/kg. In the August 2022 campaign, the frequency of exceedances compared to the normal value was only 11.11%, compared to July, with only one exceedance of the normal values in sample P15 (96.6 ppm). Thus, for this sample, copper was 4.83 times higher than the normal value.

*The lithological analyses* conducted in July 2022, on the sediment samples collected revealed significant variations in the main lithological components: total organic matter (TOM%), carbonate content (CAR%), and siliciclastic fraction (SIL%). The analysis results are presented in Table 4. The determined lithological parameters (Table 4) show that the main component of the investigated sediments is represented by organic matter, which has a high proportion, accounting for over 30% of the total weight of the dry sediment in several samples. The range of values is relatively wide, ranging from 3.91 to 76.12 (TOM%), with an average value of 30.76 (TOM%). The carbonate content varies, with values ranging within a narrow interval, namely between 1.55 and 3.18

(CAR%), with an average value of 2.59 (CAR%). The remaining sedimentary material analysed corresponds to the siliciclastic fraction; the values are in the range of 22.33 to 93.63 (SIL%) with an average value of 66.65 (SIL%). Based on the mass percentage content of organic matter ( $\geq 15-30\%$ ), total carbonate content ( $\text{CaCO}_3 \leq 10\%$ ), and siliciclastic fraction ( $\leq 15-30\%$ ) from the total weight of the dry sediment, the tested sediments (P3, P4, P5, P6, and P7) can be classified as organic sediments, subordinated to organo-mineral sediments, without a carbonate component (Figure 2 and Figure 3). Similarly, based on the mass percentage content

of the siliciclastic fraction ( $\geq 15-30\%$ ), total carbonate content ( $\text{CaCO}_3 \leq 10\%$ ), and organic matter ( $\leq 15-30\%$ ) from the total weight of the dry sediment, the tested sediments (P1, P2, P8, P9, and P10) can be classified as mineral sediments, subordinated to mineralo-organic sediments, without a carbonate component.

*The lithological analyses* conducted in August 2022 on the sediment samples collected revealed significant variations in the main lithological components: total organic matter (TOM%), carbonate content (CAR%), and siliciclastic fraction (SIL%).

Table 2. CO<sub>2</sub> concentrations and heavy metal content results from July 2022

	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
CO <sub>2</sub> , ppm	42654	13162	3199	602	5397	2531	46221	993	631	485
TOC, %	0.03	3.6	6.9	7.14	7.06	7.28	4.99	4.5	3.47	1.63
CaCO <sub>3</sub> , %	0.57	2.22	2.1	0.51	0.53	0.9	0.1	1.41	1.18	1.05
Na <sub>2</sub> O, %	0.45	0.47	0.28	0.32	0.33	0.48	1.08	0.41	0.56	0.61
MgO, %	0.41	0.54	0.28	0.36	0.31	0.27	0.33	0.61	0.66	0.65
SiO <sub>2</sub> , %	22.3	18.08	12.79	17.24	16.75	17.01	19.02	17.92	20.38	20.67
P <sub>2</sub> O <sub>5</sub> , %	0.02	0.04	0.07	0.16	0.25	0.03	0.03	0.04	0.08	0.04
K <sub>2</sub> O, %	1.68	1.65	1.11	1.49	1.35	1.44	1.86	1.61	1.78	1.85
CaO, %	0.42	0.51	0.2	0.29	0.21	0.51	0.79	0.91	0.89	0.63
Ti, ppm	4114	3538	2514	3298	3732	3298	2653	3264	3692	3508
V, ppm	59.1	67.7	57.7	77	94.9	68	49.53	74.7	79	74.3
Cr, ppm	53	59	39.33	59.1	78.5	60.4	38.3	60.7	68.3	64.7
MnO, %	0.008	0.012	0.005	0.007	0.005	0.007	0.012	0.043	0.045	0.042
Fe <sub>2</sub> O <sub>3</sub> , %	0.85	1.47	3.53	1.03	0.71	0.52	0.79	2.36	3.22	2.76
Ni, ppm	14.03	20.15	11.48	44.19	24.82	10.94	9.52	22.39	25.64	27.85
Cu, ppm	18.4	19.84	17.89	25.21	32.71	26.69	22.8	23.39	24.72	22.31
Zn, ppm	31.33	49.37	28.26	105	73.5	16.95	20.64	49.79	71	64.8
As, ppm	5.31	7.67	10.04	8.99	9.89	6.18	3.66	7.12	8.23	8.23
Sr, ppm	197	214	180	226	160	213	612	254	245	281
Zr, ppm	314	215	170	165	185	179	179	169	206	199
Sn, ppm	6.82	5	4.36	4.98	6.2	6.24	3.51	4.89	4.58	4.13
Hg, ppm	0.059	0.06	0.056	0.064	0.119	0.078	0.042	0.078	0.093	0.054
Pb, ppm	22.82	26.2	17.64	30.15	30.69	23.89	26.42	26.11	29.07	25.97

Table 3. CO<sub>2</sub> concentrations and heavy metal content results from August 2022

	P11	P12	P13	P14	P15	P16	P17	P18	P19
CO <sub>2</sub> , ppm	1505	930	977	1609	3448	1457	1174	1520	786
TOC, %	0.98	4.2	2.01	3.49	5.53	0.73	4.91	4.74	4.47
CaCO <sub>3</sub> , %	0.2	0.83	0.45	0.09	1.04	0.08	0.03	0.63	0.6
Na <sub>2</sub> O, %	0.73	0.57	0.76	0.74	0.17	0.81	0.55	0.54	0.59
MgO, %	0.9	0.73	0.71	0.76	0.27	0.48	0.55	0.67	0.71
SiO <sub>2</sub> , %	22.16	17.05	20.46	21.25	13.74	26.12	17.64	18.52	18.61
P <sub>2</sub> O <sub>5</sub> , %	0.02	0.03	0.02	0.04	0.02	0.08	0.06	0.04	0.04
K <sub>2</sub> O, %	1.94	1.58	1.77	1.86	1.91	2.01	1.53	1.65	1.62
CaO, %	0.7	0.8	0.71	0.6	0.03	0.29	0.33	0.69	0.76
Ti, ppm	3725	3291	3756	3712	4550	4899	3281	3294	3330
V, ppm	83.9	66.3	72.7	74.9	143	78.5	62.6	67.3	67.7
Cr, ppm	68.2	61	68.4	62.4	101	75.3	53.9	57.2	58.9
MnO, %	0.027	0.036	0.03	0.03	0.002	0.008	0.014	0.026	0.03
Fe <sub>2</sub> O <sub>3</sub> , %	4.34	2.54	2.67	3.07	0.44	1.99	3.11	2.98	3.31
Ni, ppm	33.39	25.72	28.81	28.87	7.86	11.17	19.07	25.13	27.22
Cu, ppm	19.25	17.52	18.55	19.91	96.6	14.09	15.87	18.23	19.88
Zn, ppm	78.1	65.7	62.5	70.8	13.67	22.34	47.49	65.6	71.4
As, ppm	9.67	7.48	7.99	8.56	14.58	18.04	7.64	8.24	9.23
Sr, ppm	315	263	305	304	70.6	227	236	263	254
Zr, ppm	287	220	263	228	117	343	226	243	232
Sn, ppm	5.16	4.5	4.17	4.97	7.66	4.3	4.05	3.86	4.23
Hg, ppm	0.056	0.051	0.043	0.05	0.148	0.037	0.051	0.054	0.055
Pb, ppm	26.6	27.11	27.58	31.22	21.06	43.49	29.83	26.34	29.44

Table 4. The variation of the main lithological parameters analysed in the sediment samples in July 2022 (water content (WC %), dry matter (DM %), total organic matter (TOM %), total carbonates (CAR %), and siliciclastic fraction (SIL %))

Station	WC %	DM %	TOM %	CAR %	SIL %	
P1	19.64	80.36	3.91	2.46	93.63	
P2	28.11	71.89	18.75	3.18	78.07	
P3	39.98	60.02	76.12	1.55	22.33	
P4	34.92	65.08	48.89	2.43	48.68	
P5	28.62	71.38	36.99	2.64	60.36	
P6	29.1	70.9	38.55	3	58.45	
P7	21.89	78.11	41.69	1.85	56.46	
P8	17.88	82.12	11.47	3.17	85.37	
P9	22.64	77.36	17.66	2.65	79.69	
P10	17.34	82.66	13.54	2.97	83.49	
(n=10)	<i>Min.</i>	17.34	60.02	3.91	1.55	22.33
	<i>Max.</i>	39.98	82.66	76.12	3.18	93.63
	<i>Media</i>	26.01	73.99	30.76	2.59	66.65

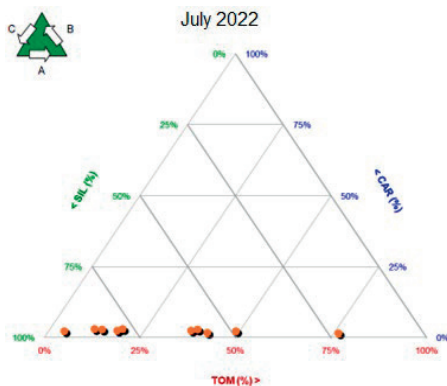


Figure 2. Ternary diagram representing the distribution of total organic matter (TOM %), carbonates (CAR %) and siliciclastic fraction (SIL %), July 2022

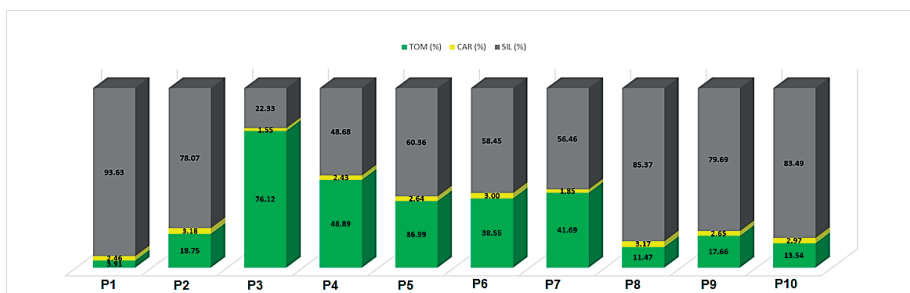


Figure 3. Binary diagram representing the distribution of total organic matter (TOM %), carbonates (CAR %) and siliciclastic fraction (SIL %), July 2022

The analysis results are presented in Table 5. The determined lithological parameters (Table 5) show that the main component of the investigated sediments is represented by the siliciclastic fraction, which accounts for over 30% of the total weight of the dry sediment in most samples. The range of values is wide, ranging between 0.32 and 91.74 (TOM %), with an average value of 72.91 (TOM %).

The carbonate content varies, with values within a relatively narrow interval, namely between 1.59 and 16.20 (CAR %), with an average value of 3.65 (CAR %).

The remaining sedimentary material analysed corresponds to organic matter, with values ranging from 6.34 to 83.48 (SIL %) and an average value of 23.44 (SIL %). Based on the mass percentage content of the siliciclastic fraction ( $\geq 15-30\%$ ), total carbonate content ( $\text{CaCO}_3 \leq 10\%$ ), and organic matter ( $\leq 15-30\%$ ) from the total weight of the dry sediment, the analysed sediments (P11, P12, P13, P14, P16, P17, P18, P19) can be included in the domain of

mineral sediments and subordinated to mineralo-organic sediments, without a carbonate component (Figure 4 and Figure 5). However, based on the mass percentage content of organic matter ( $\geq 15-30\%$ ), total carbonate content ( $10\% < \text{CaCO}_3 \leq 30\%$ ), and the siliciclastic fraction ( $\leq 15-30\%$ ) from the total weight of the dry sediment, the tested sediment from a single sample (P15) can be included in the domain of organic sediments and subordinated to organo-mineral sediments, with a slight carbonate component.

*The impact of increased CO<sub>2</sub> emissions on vegetation* was assessed through field observations, combined with measurements of CO<sub>2</sub> concentration at the surface. Complete vegetation absence was observed at points with emissions exceeding 20% CO<sub>2</sub> (Figure 6a). In areas with elevated emissions, with concentrations up to 10% CO<sub>2</sub>, the prevalence of simple grasses with increased CO<sub>2</sub> tolerance was observed (Figure 6c).

Table 5. The variation of the main lithological parameters analysed in the sediment samples in August 2022 - water content (WC %), dry matter (DM %), total organic matter (TOM %), total carbonates (CAR %), and siliciclastic fraction (SIL %)

Station	WC %	DM %	TOM %	CAR %	SIL %	
P11	13.65	86.35	6.34	1.92	91.74	
P12	16.81	83.19	14.42	2.21	83.38	
P13	15.59	84.41	14.25	1.78	83.96	
P14	11.05	88.95	16.62	1.72	81.66	
P15	28.22	71.78	83.48	16.20	0.32	
P16	13.42	86.58	8.16	1.64	90.20	
P17	25.09	74.91	19.45	2.12	78.43	
P18	14.49	85.51	20.47	1.59	77.94	
P19	15.05	84.95	27.80	3.64	68.56	
(n=9)	<i>Min.</i>	<i>11.05</i>	<i>71.78</i>	<i>6.34</i>	<i>1.59</i>	<i>0.32</i>
	<i>Max.</i>	<i>28.22</i>	<i>88.95</i>	<i>83.48</i>	<i>16.20</i>	<i>91.74</i>
	<i>Media</i>	<i>17.04</i>	<i>82.96</i>	<i>23.44</i>	<i>3.65</i>	<i>72.91</i>

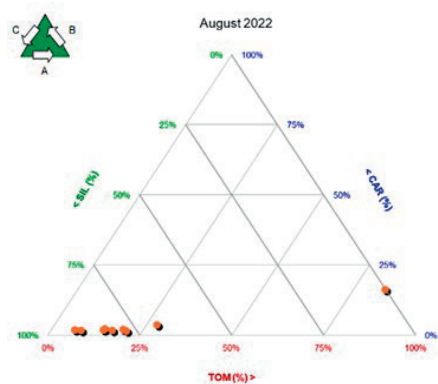


Figure 4. Ternary diagram representing the distribution of total organic matter (TOM %), carbonates (CAR %) and siliciclastic fraction (SIL %), August 2022

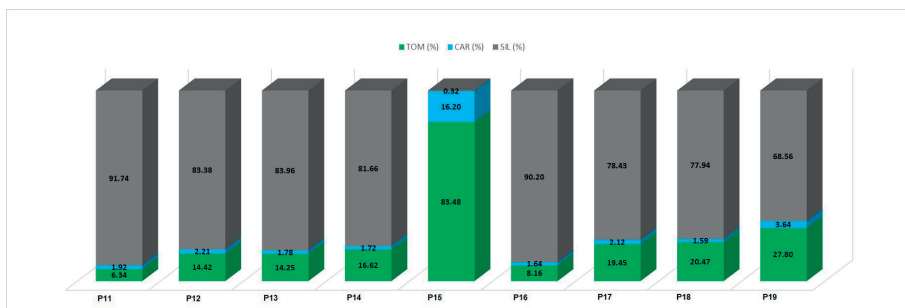


Figure 5. Binary diagram representing the distribution of total organic matter (TOM %), carbonates (CAR %) and siliciclastic fraction (SIL %), August 2022

This phenomenon has been observed in similar sites worldwide and is documented in scientific literature. Additionally, distinct coloration was noted in certain plant species (Figure 6b) at

points with high emissions of CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S. All these observations can serve as surface indicators of potential CO<sub>2</sub> leaks from anthropogenic storage sites.



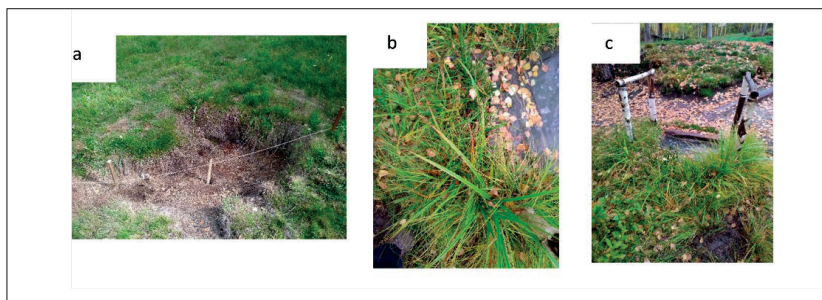


Figure 6. The impact of increased CO<sub>2</sub> concentration on vegetation: a. area without vegetation, b. vegetation with distinct coloration; c - predominance of grasses

## CONCLUSIONS

Based on the conducted analyses, it can be concluded that the impact of increased CO<sub>2</sub> emissions on soil manifests in the exceeding of normal concentrations of heavy metals such as chromium, copper, mercury, and nickel at points with high CO<sub>2</sub> emissions, while their levels are reduced at points with lower or normal emissions of post-volcanic gases. Regarding the analysis of water samples, those with high CO<sub>2</sub> concentrations exhibited exceeded levels of nitrites, inorganic phosphorus, and sulphates, suggesting a classification of these waters in quality classes II and III. The influence of high CO<sub>2</sub> concentrations is evident in vegetation, with absence observed at CO<sub>2</sub> concentrations exceeding 20%, predominance of grasses at concentrations below 20%, and distinct coloration noted. These observed and analysed elements could serve as surface indicators of potential CO<sub>2</sub> leaks from anthropogenic storage sites. Consequently, surface monitoring of CO<sub>2</sub> should include periodic sampling of soil and water to monitor exceedances of the aforementioned compounds. Additionally, vegetation monitoring is highly relevant for detecting CO<sub>2</sub> leaks.

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