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SOIL FLUX AND SOIL GAS MONITORING OF A NATURAL LABORATORY FOR THE STUDY OF CO_2 LEAKAGE

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Abstract

Carbon capture and storage (CCS) is a technology designed to reduce greenhouse gas emissions by capturing CO_2 from industrial processes or power generation and securely storing it in geological formations. Băile Lăzărești serves as a promising natural laboratory for studying the environmental effects of potential CO_2 leakage from an anthropogenic CO_2 storage site and for testing monitoring solutions. One effective method for environmental monitoring of CO_2 geological storage involves soil flux and soil gas surveys, which can identify potential CO_2 leakage points by determining the natural variability of CO_2 flux. Since 2019, several soil flux surveys have been conducted at Băile Lăzărești across different seasons, combined with soil-gas measurements. By analyzing seasonal CO_2 variation along with geological knowledge, we have determined the natural variability of post-volcanic emissions and important for monitoring CO_2 geological storage sites, aiding in the identification and understanding of potential leakage in the near-surface environment.

Key words: *CO_2 geological storage, monitoring, natural laboratory, soil flux surveys, soil gas-surveys, leakage detection.*

INTRODUCTION

Carbon capture and storage is an important tool for reducing CO_2 emissions (IPCC, 2022; IPCC, 2023) and it is expected to be deployed large-scale to achieve the climate targets. From all the components of the CCS chain, the storage seems to be the most debated since there are some public concerns related to the risks of storing CO_2 underground, although the storage occurs in the deep environment at more than 800 m depth. Environmental monitoring in this respect is very important since it can easily demonstrate the absence of leakage and its undesirable effects in the environment (West et al., 2005; Beaubien et al., 2008; Ziogou et al., 2013). One important monitoring method which has been successfully applied at all the current and past storage projects is soil flux monitoring (Beaubien et al., 2008). Its application was also demonstrated on natural laboratories (Beaubien et al., 2008; Ziogou et al., 2013), sites where CO_2 is leaking naturally, mostly related with volcanic or post-volcanic activity. The study of these sites can provide valuable insights on the natural variability of soil fluxes and on the migration pathways of CO_2 in the near-surface (Beaubien et al., 2008).

In Romania, a promising natural laboratory can be considered Băile Lăzărești site (Harghita County). The site is located at approximately 16 km north-east from Băile Tușnad and it is renowned for its post-volcanic activity (Pricăjan, 1974; 1985; Karátson et al., 2022).
The site was selected for further research as a natural analogue for CO_2 leakage in 2019 (Dudu et al., 2021; Dudu et al., 2024) in the context of a national research project. Several soil flux and soil gas surveys have been conducted in the following years in order to determine the natural variability of CO_2 soil fluxes and concentrations and to highlight migration pathways, contributing to the understanding of CO_2 leakage mechanisms in the environment and therefore to the design of monitoring for future CO_2 storage sites. During the last 6 years, the site underwent significant landscaping projects, which also complicated its assessment.

MATERIALS AND METHODS

Study area

The Gurghiu-Harghita post-eruptive chain represents the most intense post-volcanic manifestation in the Eastern Carpathians, with a significant release of gases. The ascent of volcanic gases to the surface is favoured by deep tectonics, through a complex crustal, regional, and local fracture system, of which regional and local fractures have different degrees of current mobility (Airinei & Pricăjan, 1972). The post-volcanic emissions in the Lăzărești area propagate along a system of deep fractures, which are then taken over by surface faults. These emissions are redistributed with varying intensity throughout the entire sedimentary volume of the Cretaceous flysch (Airinei & Pricăjan, 1972).

From a lithostratigraphic perspective, the post-volcanic emissions in the Lăzărești area traverse a series of deposits, starting with the Cretaceous flysch (Sânmartin-Bodoc strata, Barremian-Albian) at the base, continuing with terrace deposits (Mutihac, 1990). The Cretaceous flysch (Barremian-Albian) is characterized by accentuated flysch features (pronounced rhythmic alternations of rusty grey sandstones, often bituminous, and shales), while lacking marl-limestones. The flysch, with its low permeability due to the alternating layers of shale and sandstone, can act as a barrier, limiting the free migration of gases. However, tectonic activity and the presence of fractures within the flysch can create pathways for volcanic emissions to reach the surface. These fractures and fault systems essentially create a "stratigraphic screen," which can either trap or channel gases depending on their alignment and mobility. Quaternary deposits are terrace deposits, composed of coarse sediments, locally or at the base of the slopes covered with finer alluvium, such as fine sands and sandy shales, marls, and grey shales. The formation of carbonated mineral water deposits in the region results from the interaction of moffetic carbon dioxide with the aquifer layers within the mentioned geological formations. Additionally, the specific hydrodynamic characteristics of the known springs (sulfonated, ferruginous, etc.) are directly influenced by the chemical composition of the volcanic, flysch, Neogene and Quaternary formations through which the groundwater flows.

In 2019 several gas measurements were made near important elements such as the dry and wet mofettes, mineral spring and therapeutic bath. The level of CO_2 emissions was determined to reach more than 85% inside the dry mofette cabin (Dudu et al., 2021). From the measurements made across several location across the site, it was decided to divide it into two perimeters, completely different considering the level of emissions and the presence and number of the gas vents (Figure 1).

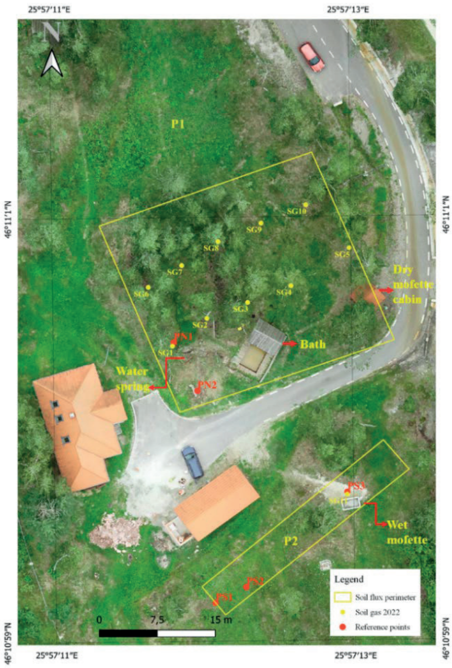

Figure 1. Location of study perimeters, reference points, soil gas sample points and touristic features

The northern perimeter (P1) presents high CO_2 emissions and many wet and dry gas vents, including most of the touristic features such as the baths used for therapeutic purposes and the dry mofette. The southern perimeter (P2) presents much lower emissions and includes a wet mofette and some dry gas vents reduced in intensity and area. This perimeter also was mostly affected by an extensive landscaping process over the years (see example in Figure 2 and Figure 3).

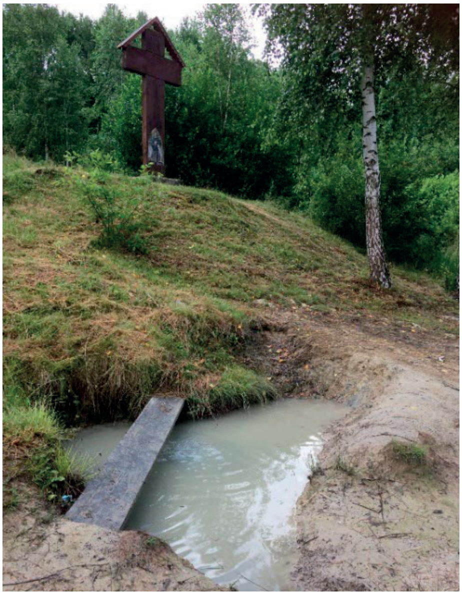

Figure 2. Wet mofette from P2 (PS3) in 2020

Figure 3. Wet mofette in P2 (PS3) in 2024

Soil flux surveys

Starting with 2020, several field campaigns of soil flux measurements have been conducted in the dry (summer) and wet (autumn and spring) seasons of 2020, 2022 and partially in 2024 (after the site underwent an extensive landscaping project).

The most extensive surveys were made in 2022 (Figure 1). Several key points (reference points in Figure 1) were monitored during all this time to see the flux variation in time and its dependence on hydrological regime. The soil flux measurements were made using the closed chamber accumulation method and were conducted with a West Systems portable fluxmeter equipped with CO_2, H_2S and CH_4 sensors (Figure 4).

Figure 4. Soil flux survey conducted with West Systems portable fluxmeter in October 2022

The raw data was processed with FluxRevision software and the calculated flux values were interpolated using ArcGIS software to obtain the maps showing the flux variation.

Soil gas surveys

Soil gas surveys were also implemented on selected sample locations in 2020 and 2022.

In 2020, the soil gas measurements were done during July and focused mainly around the identified wet and dry mofettes of the site.

In 2022, the soil gas measurements were done mostly on 2 selected profiles from P1 (including a reference point) and on a reference point from P2 located around the wet mofette. The measurements were done using the Gas Data GFM 436 portable gas analyser coupled with a hardened steel probe from Durridge (Figure 7). This ensemble allows measuring CO_2 concentrations at different depths, in this case 25, 50 and 75 cm.

RESULTS AND DISCUSSIONS

Soil flux surveys

The extensive soil flux surveys from 2022, conducted in the summer (dry) and autumn (wet) season, shown a significant difference in the level of CO_2 fluxes, most probably due to the difference in the hydrological regime.

In the summer (July for P1 and August for P2), the CO_2 flux varied on P1 between 0.43 and 185 mol/m^2/day and on P2 between 0.20 and 178 mol/m^2/day (Figure 5). The highest CO_2 fluxes on P1 were measured next north of the therapeutic bath (where several smaller baths exist), near the water spring and on the alignment of the dry mofette cabin. On P2 the maximum CO_2 fluxes were measured near the wet mofette and on the alignment of the water spring.

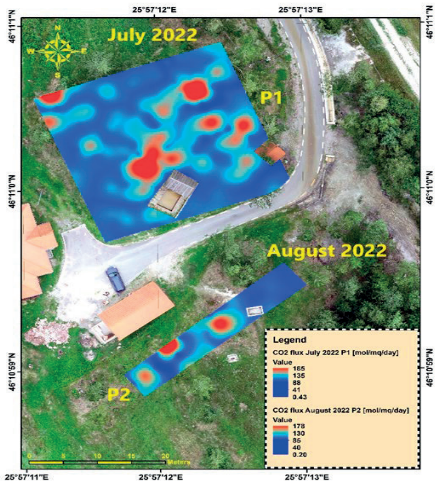

Figure 5. CO_2 soil flux variation in July and August 2022

In October 2022 (Figure 6), CO_2 flux shows much larger values, between 0.17 and 893 mol/m^2/day on P1 and between 0.27 and 625 mol/m^2/day on P2. The maximum values are located, as in the summer, around the water spring, wet and dry mofettes on P1 and on the alignment of water spring and bath and near the wet mofette on P2.

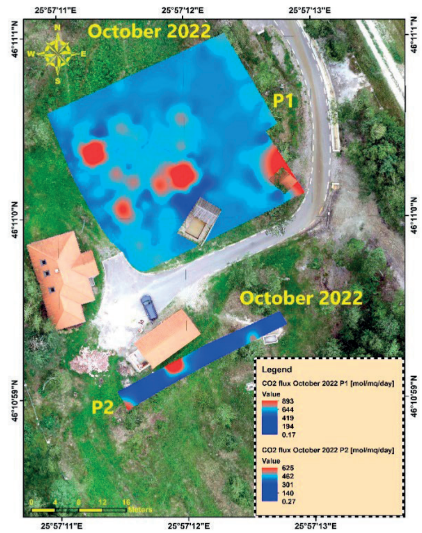

Figure 6. CO_2 soil flux variation in October 2022

The variation of fluxes recorded for the reference points in 2020, 2022 and 2024, show a clear difference between summer and autumn seasons (Table 1).

Table 1. CO_2 flux values in the reference points measured in the surveys from 2020, 2022 and 2024

Ref. point	CO_2 flux October 2020 (mol/m^2/day)	CO_2 flux July/August 2022 (mol/m^2/day)	CO_2 flux October 2022 (mol/m^2/day)	CO_2 flux September 2024 (mol/m^2/day)
PN1	130.2	1.994	262.1	323.3
PN2	32.25	1.898	51.71	60.64
PS1	2.092	3.017	3.17	9.985
PS2	6.688	2.309	12.29	13.78
PS3	1.532	0.939	4.103	2.877

Soil gas surveys

As mentioned before, soil gas surveys from July 2020 have focused around the wet and dry gas vents identified at the site. Two of the sample stations measured then are corresponding with the reference points PN2 (near the water spring) and PS3 (near the wet mofette). For PN2, the measured CO_2 concentrations were 30.6% at 25 cm depth, 16.8% at 50 cm depth and 13.4% at 75 cm depth. For PS3, the measured CO_2 concentrations were 33.3% at 25 cm depth, 31.5% at 50 cm depth and 4.7% at 75 cm depth.

The drop in CO_2 concentration with depth, opposite to what have been expected, can be explained with the water ascension in the steel probe. At 25 cm depth, the measurement time was stopped at 2 minutes, but for larger depths, the measurement was stopped at 1 minute due to water intake.

The same situation was encountered also in October 2022 (Table 2), especially near the water spring (SG 1), the smaller wet mofettes (SG2 and SG3) from P1 and near the wet mofette from P2 (SG11).

Table 2. CO_2 soil concentrations in October 2022

Point	CO_2 conc. (%) 25 cm depth	CO_2 conc. (%) 50 cm depth	CO_2 conc. (%) 75 cm depth
SG1	95.6	97.1	n.d.
SG2	9.5	2.2	95.9
SG3	97.2	22	4.6
SG4	1	16.8	2.4
SG5	11.9	2.7	3.6
SG6	0.7	0.3	80
SG7	8.7	96.3	96.7
SG8	13.3	96	27
SG9	35.8	38.8	11.8
SG10	2.3	7.2	12.3
SG11	71.2	0.3	0.1

For SG1, due to water intake, the CO_2 concentration could not be measured at 75 cm depth, considering the specifics of the used equipment. For SG6 and SG7, located north of the water spring and very close to PN 1 (where large CO_2 fluxes have been measured), the increase of CO_2 concentration with depth is clear, having a normal variation in the absence of water at depth.
For SG8 and SG9, the increase of CO_2 concentration was measured at 50 cm depth, but decreased rapidly at 75 cm depth together with the water ascension. SG10, located north of the dry mofette cabin, shows an increase of CO_2 concentration with depth in the absence of water. The most drastic drop of CO_2 concentration with depth can be seen for SG11 (Figure 7), where water intake was higher than in any other point.

Figure 7. Soil gas survey using Gas Systems portable gas analyser and Durridge hardened steel probe next to a wet mofette (SG 11) in October 2022

CONCLUSIONS

During the 2022 campaign, measurements highlighted significant fluctuations in CO_2 flux, both in terms of intensity (concentration) and diffusion area. During the dry season (July-August), CO_2 emissions were relatively low. In contrast, during the wet season (October), CO_2 fluxes increased significantly.
These measurements suggest a correlation between CO_2 emissions and the water regime, with higher emission tendencies in the wet season and lower ones in the dry season. The diffusion of carbon dioxide occurs both at the level of Cretaceous aquifer complexes (a succession of sandstones, marls, and clays) and Quaternary formations, as well as in non-aquifer levels that generate dry mofettes.
Soil moisture plays an important role in how CO_2 diffuses through the soil. In wetter soils, water aids in CO_2 transfer, as moisture appears to facilitate CO_2 mobility, allowing it to migrate more easily to the surface. In wet soils (such as the marshy areas in the northern perimeter - P1), porosity is higher, enabling better CO_2 circulation. As a result, CO_2 concentrations in the soil can increase since it can migrate more easily to the surface. Conversely, in dry soils (during the dry season), porosity may be lower, restricting CO_2 mobility, which leads to the accumulation of CO_2 at deeper levels.
The arrangement of the maximum fluxes mapped, could be possibly associated with migration pathways of CO_2 in the near environment. Possible paths are distinctly highlighted on a north to south direction on the alignment of the water spring, of the therapeutic baths and on the alignment of the dry mofette cabin.
The soil gas surveys revealed a rather strange correlation of CO_2 concentration with depth. In the dry sample locations, the CO_2 concentration increased with depth. In wet locations, the water intake at 50 to 75 cm depth in soil decreased due to water intake.
The studies conducted so far showed the importance of determining the seasonal variability of CO_2 fluxes and concentrations for establishing future monitoring solutions. Apart from this seasonal variability, the hydrological regime and landscaping can play very important roles.

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