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CLUJ-NAPOCA

Faculty of Environmental Science and Engineering

GEOGENIC GREENHOUSE GAS EMISSIONS IN THE SOUTHERN PART OF EASTERN CARPATHIANS

- SUMMARY -

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Table of contents

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Introduction

Quantification of gaseous emissions in geological systems is an important branch of research in environmental science, which is a major source of greenhouse gas to the atmospheric budget. Of geological environments, there are two different categories: the first category includes emissions are the predominant carbon dioxide (CO_2), while the second category includes emissions of predominantly methane (CH_4). The first category includes active volcanoes, extinct volcanoes and geothermal systems, while in the second part generally demonstrations occurring hydrocarbon-bearing basins namely mud volcanoes and everlasting fires.

Geochemical studies based on the isotopic composition of carbon and hydrogen, along with helium isotopic ratios has become a good indicator of the origin of the gas. The isotopic ratio $^{13}C/^{12}C$ of CO_2 expressed in $\delta^{13}C$ (‰), provides important information about the amount of CO_2 released from the Earth's crust or mantle. For methane, the same report in relation to the hydrogen isotopic ratios of methane can deduce the origin of methane: thermogenic, biogenic or mixed, while the helium isotopic ratios provide information about crustal or mantle origin of the gas.

Research on gaseous emissions proved to be a useful indicator for many research areas such as predicting occurrence of earthquakes, geochemical exploration of active faults, or prediction of volcanic eruptions (Badalamenti et al., 1988; Rogie et al. 2001). Changes occurring in the amount of gas emitted in volcanic areas can provide information about the level of volcanic activity as well (Allard et al., 1991; Baubron et al., 1990; Chiodini et al., 1998).

The manifestations in which methane is the predominant gas, can provide important information on geology and oil exploitation, structural and tectonic studies, and environmental issues such as geological hazards and greenhouse gas budget. The occurrence of these events is an indicator of tectonic discontinuities, providing information about the location of hydrocarbon reservoirs. Mud volcanoes have been studied mainly due to their sensitivity to seismic activity (Mellors et al., 2007). Among natural sources, geological emissions of methane represents the second most important source after wetlands (Etiope et al., 2008). Globally, geological methane emissions were estimated at 40-60 Tg year-1 (Etiope and Klusman, 2002), of which more than 10% are attributed to methane derived from geothermal and volcanic systems (Lacroix, 1993; Etiope and Klusman, 2002). For Europe the emission was estimated at 3 Tg year^{-1} derived from geological emissions, which represents 8% of anthropogenic emissions in Europe (Etiope, 2009).

The southern part of the Eastern Carpathians represents an area quite varied in terms of the types of gas manifestations. In the eastern part there are manifestations where the predominant gas is CO_2 represented by numerous inactive from Harghita Mountains. Post-volcanic phenomena such as mofettes, diffuse CO_2 emissions and mineral springs with bubbling gas are abundant in this area. In the eastern and south-eastern part of the Eastern Carpathians there are many manifestations where the predominant gas is CH4, represented by mud volcanoes and everlasting fires.

This paper aims to locate different areas with geogenic gas emissions in terms of gas composition, gas origin and to estimate total CO_2 and CH_4 flux. Among the manifestation with CO_2 as the predominant gas, particular attention was paid to the Ciomadul volcano, which represents the volcano with the most recent activity of the whole Carpathians Mountains. Ciomadul volcano has been studied from the point of view of the origin of the gas and the gas emissions in the context of studying the phase in which the volcano is. In addition, several large areas have been investigated with diffuse CO_2 emission, in order to locate some areas with geogenic CO_2 emissions.

Among the areas with the predominant CH_4 emission, special attention was carried out to the eternal fires from the southeastern part of Eastern Carpathians and the mud volcanoes from Beciu, Buzău County. They were studied in terms of the origin of the gas, and estimating the total emissions of greenhouse gases from these areas.

Finally, the contribution of geogenic sources from the studied area, resulted in a first brief outline of CO_2 and CH_4 emission in the southern part of the Eastern Carpathians. Interpretations in terms of gas geochemical samples investigated locations provided additional information about the processes occurring during gas migration to the surface and the origin of the gas.

Chapter VI Geological approach

The case studies presented in this thesis correspond to some geological units from the southern part of Eastern Carpathians. The Carpathians Mountains are part of the Carpathian Orogen beeing the result of collision of several tectonic plates with East Europe plate micro, (Royden, 1988; Csontos 1995). They were formed and evolved in the structural assembly of Carpathian Orogen having common features with the entire orogenic system butin some cases it has developed some particular structural characters. The Carpathians are characterized by an individuality which is given by the development of the Neogene volcanoes and the great development of flysch formations.

The oldest unit of the Eastern Carpathians, belonging to the median Dacidelor is composed of metamorphic rocks, which has a Triassic-Jurassic-Cretaceous sedimentary bottom, and is known under the name of Mesozoic crystalline area.

In the Cretaceous period begins the generation and compression of the first tectonic structures. Thus, in the middle Cretaceous appear the early dacides. Towards the end of the Cretaceous, during subhercynian phase, begins the forming a second generation of structures, and begins the formation of the late dacides. The compression phenomenon continues also in Tertiary, when the accumulation area starts to move, limited at a marginal depression, which serves as Foredeep. The orogenic movements that occur in the middle of Miocene, leads to the formation of the early moldavides. The area covered with Moldavides area is characterized by the presence of several blades which are arranged in folded structures and jump (Săndulescu 1984 Badescu, 1998), This area is composed of Cretaceous marine sediments and flysch and molasse deposits of Paleogene to Neogene in age. These rocks consist of clay and sandstone and marls, limestones, tuffs and conglomerates. The outer blades contain evaporitics Neogene formations represented by salt and gypsum (Săndulescu, 1988; Matenco and Bertotti, 2000).

In the Lower Sarmatian, an important stage took place in the tectonic arrangement of the Eastern Carpathians, when the movement of the moldavide phase leads to formation of the late Moldavides. After uplifting of the Eastern Carpathians, the sinking of a small area occur, leading to the formation post-tectonics intermountain depressions. At the contact zone between the Eastern Carpathians and the Transylvanian Basin starts to evolve the Neogene volcanites.

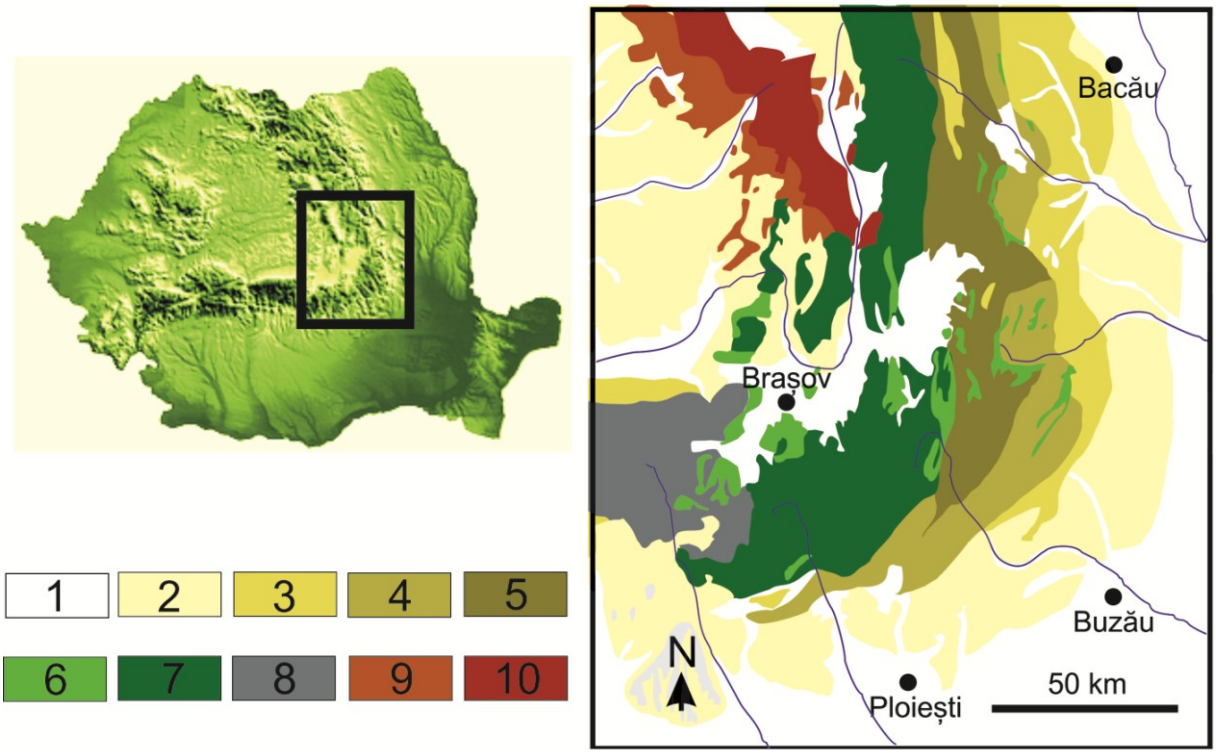

Figure 6.1 The geological of the southern part of Eastern Capathians 1 - Guaterrnary, 2 – Pannonian-Sarmatian, 3 - Palaeozoic, 4 - Palaeogene-Miocene , 5 - Oligocene, 6 - Neocomian,7 - Titonian-Neocomian , 8 – Midle palaeogene, 9 – Neogene vulcanogene deposits, 10 - Neogene volcanoes(after Szakács and Seghedi, 1986; 1990)

Chapter VII Methodology

7.1 Portable diffuse CO_2 and CH_4 flux meter

The CO_2 and CH_4 flux measurements were performed by using the closed chamber technique (Figure 7.1). The chamber is placed on the ground, completely sealed from the atmospheric air. The air is circulated in a closed loop between the chamber and the CO_2 detector. The flux is calculated based on the increase of CO_2 concentration during time. If the rate of increase of CO_2 concentration in the chamber is constant, linear regression can be used to calculate the flux by the equation (Livingston and Hutchinson, 1995):

$$F = (Vc / Ac) \times [(c_2 - c_1) / (t_2 - t_1)] \quad [\text{g m}^{-2} \text{ day}^{-1}]$$

where Vc (m^3) is the volume of the chamber, Ac (m^2) is the footprint area of the chamber, c_1 and c_2 (mg m^{-3}) are gas concentrations at time

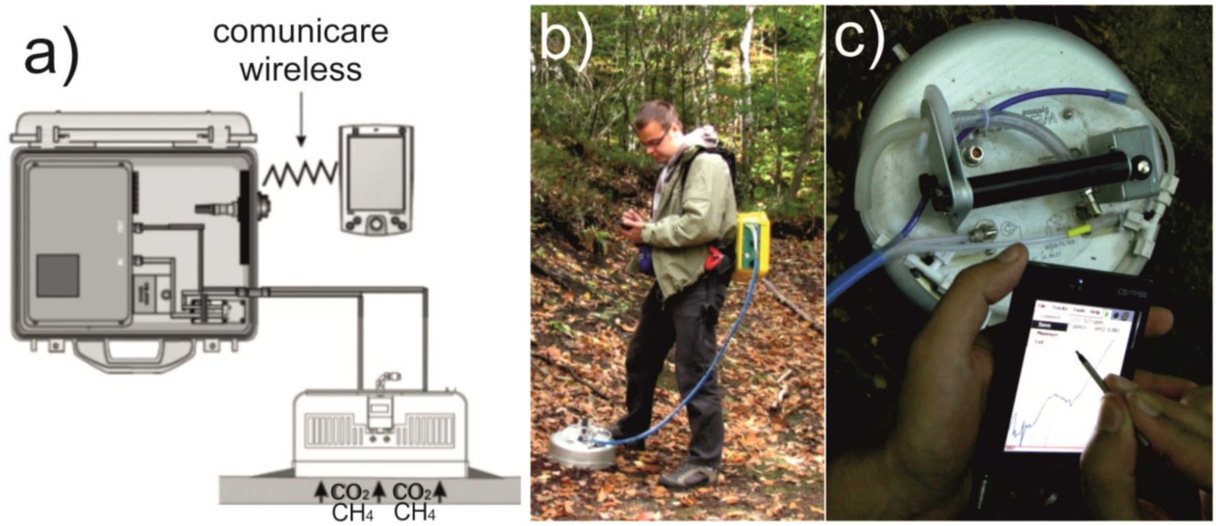

Figure 7.1 a) Schematic representation of the portable diffuse CO_2 and CH_4 flux meter; b) a flux measurement in a field campaign; c) The storage of a measurement

The components of the portable diffuse CO_2 and CH_4 flux meter are: the acumulation chamber, the methane and carbon doxide detectors, the pump, the batery, cables and a palmtop.

Data evaluation

For estimation of the flux corresponding for an area, there are many softwares to interpolate the measurements. Every measurement has a goegrafical coordinate, and these measurements are used to construct the distribution map of the gas emission.

To estimate the total emission of methane and carbon dioxide the ”Kriging” and ”Natural Neighbour” interpolation are used.

7.2 The measurement of stable isotopes

The various isotopes of an element have slightly different chemical and physical properties because of their mass differences. For elements of low atomic numbers, these mass differences are large enough for many physical, chemical, and biological processes or reactions to "fractionate" or change the relative proportions of various isotopes.

Figure 7.4 Thermo Finnigan Delta plus XP type stable isotope mass spectrometer (http://www.atomki.hu)

Changes of isotope ratios can provide important information about the underlying processes. Natural isotope fractionation processes change the ratios only to a very small amount therefore very precise, high sensitivity measurements are needed. For the geological and hydrological applications a Thermo Finnigan Delta plus XP type stable isotope mass spectrometer is operated in the lab to study the five most important elements in geochemistry (S, C, H, O, N). Accuracy of the device:

$\delta^{2}H$: ±3‰

$\delta^{18}O$: ±0,2‰,

$\delta^{13}C$: ±0,1‰,

$\delta^{15}N$ and $\delta^{34}S$: ±0,3‰

Chapter VIII Results

8.1 Case study: Ciomadul volcano (Harghita Mountains)

The aim of this work is to provide a background evaluation of the diffuse CO_2 emission of Ciomadul volcano, in order to evaluate the geogenic CO_2 exhaled inside the craters. We report a new set of results for $\delta^{13}C$ along with $^3He/^4He$ ratios. Gas samples were analysed for isotopic composition of Ne ($^{20}Ne/^{22}Ne$) and Ar ($^{40}Ar/^{36}Ar$), in order to find additional evidence for the contribution of mantle and crustal origin.

Methodology

The CO_2 flux measurements were performed by using the closed chamber technique. The chamber is placed on the ground, completely sealed from the atmospheric air. The air is circulated in a closed loop between the chamber and the CO_2 detector. The flux is calculated based on the increase of CO_2 concentration during time. If the rate of increase of CO_2 concentration in the chamber is constant, linear regression can be used to calculate the flux by the equation (Livingston and Hutchinson, 1995):

$$F = \frac{Vc}{Ac}\frac{c2-c1}{t2-t1} \, [\mathrm{g\ m^{-2}\ day^{-1}}]$$

where Vc (m^3) is the volume of the chamber, Ac (m^2) is the footprint area of the chamber, c_1 and c_2 ($mg\ m^{-3}$) are gas concentrations at time t_1 and t_2 respectively (days).

The CO_2 detector is a double beam infrared sensor (LI-COR) with a range of 0 to 20,000 ppmv. The device is equipped also with methane sensor which includes semiconductor (range 0-2,000 ppmv, detection limit 1 ppmv, resolution 1 ppmv), catalytic (range 2,000 ppmv – 3% v/v) and thermal conductivity (range 3-100% v/v) detectors.

The diffuse CO_2 emission was measured inside of both craters in August 2012. A number of 91 were performed inside the Sfânta Ana crater, homogenously distributed around the lake-filled crater in order to obtain a spatial distribution pattern. Soil CO_2 flux measurements were selected to cover a distance up to 150 m from the lake shore. The measurements were distributed in groups of measurements up to 6 measurements at about 20 m distance, starting from the shore lake toward the edge of the crater. The spacing between these groups was about 100 m (Figure 8.1.4). At Mohoș crater, the flux measurements were distributed inside the crater. A 700 m long transect was set-up, and the flux measurements were performed every 50 m starting from the edge of Mohoș crater, towards the flank.

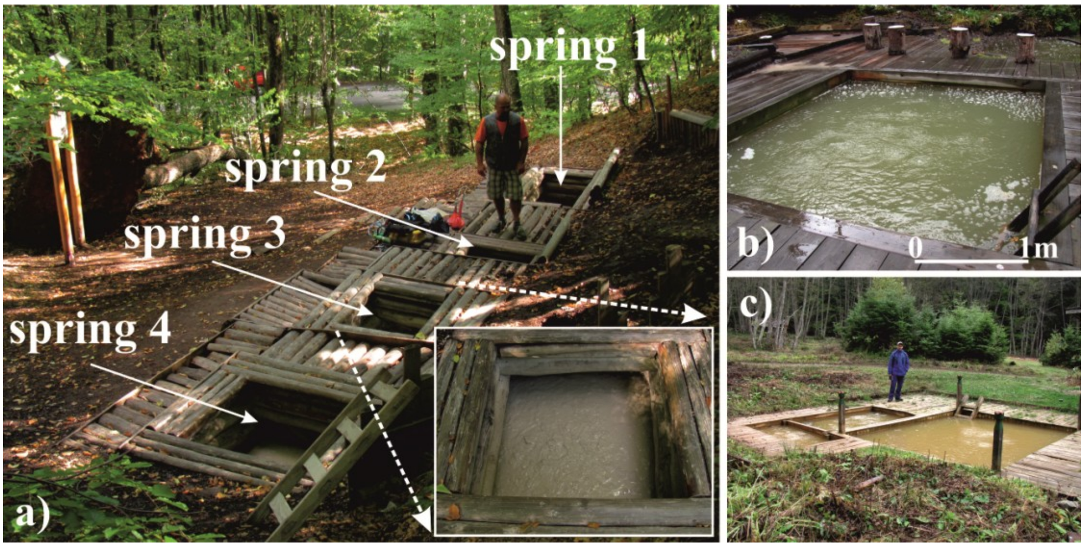

Figure 8.1.2 a) The springs from Izvoarele Tămăduitoare, b) bubbling water pool from Hammas, c) Vallato

The main focused degassing areas were identified by visible observation of the gas bubbles of the springs, most of them developed by human intervention as wooden water baths which are now used for medical purposes (Figure 8.1.2). Most of them are located in the south eastern part of the main edifice (Băile Transilvania, Baia Rece, Izvoarele Tămăduitoare, Băile Apor, Grota Sulfuroasă, Băile Hammas, Băile Mikes (Vallato). The others are located to the east (Răbufnitoarea peat bog), and north north-west of the main edifice (Tușnad spring and Băile Nadaș and Lăzărești). Due to the difficult accessibility of the chamber on the gas emitting surface, it is worth to be mentioned that when we calculated the flux we considered only the areas with visible emanations. The total CO_2 emission at the water surface was estimated by summing up all the measured fluxes in each vent. In some cases, where the flux was relatively constant for a larger area, more measurements were performed and the average value of the measured fluxes was multiplied with the surface area of the bubbling zone.

Results

The values of the 91 carbon dioxide flux measurements inside the Sfânta Ana crater ranged from 6 g m^{-2} day^{-1} which is typically of biogenic source, to anomalous high emissions up to 255 g m^{-2} day^{-1}. In the case of the Mohoș crater, the results of the 29 measurements showed quite low values which ranged from 3.6 g m^{-2} day^{-1} to 57.9 g m^{-2} day^{-1}. A 700 m long transect was set-up at Mohoș crater, and the flux measurements were performed every 50 m starting from the edge of the crater, towards the flank. An interesting decrease tendency of the CO_2 flux was observed, with the highest values recorded at the edge of the crater and progressively lower values for the measurements from the flank (Figure 8.1.8). The same decrease tendency was observed also in October 2011, when another set of measurements were performed on the south flank by respect to Sfânta Ana crater (Frunzeti and Baciu, 2012).

This may suggest an extra amount of endogenic CO_2 that is exhaled around the areas surrounding the two craters.

Table 8.1.1 presents the statistical results of the diffuse CO_2 in the Mohoș and Sfânta Ana crater. For the October 2011 campaign, the flux values were significantly lower than the results from August 2012, although also in autumn campaign the highest values overcome the flux of biogenic origin. This may indicate that the upward migration of the gas depends on the meteorological parameters; because the air temperature recorded negative values with a minimum value of -4 ºC for the night prior of the field measurements and the shallower layers of the soil could be frost. By comparison, the minimum temperature recorded on the previous night for the August 2012 campaign was 13.1 ºC (Klein Tank et al., 2002).

To estimate the total diffuse CO_2 emission around Sfânta Ana Lake, we considered the positive volume of the soil CO_2 flux corresponding for the measured area of ~0.12 km^2 (11.6 hectares). The result gives a total emission of ~6.5 t of CO_2 day^{-1}.

Table 8.1.1. Statistics of diffuse carbon dioxide flux measurement inside the craters of Ciomadul volcano

Place of the measurements	Number of meas.	Min. (g m^{-2} day^{-1})	Max. (g m^{-2} day^{-1})	Mean (g m^{-2} day^{-1})	Standard deviation	Standard error	Reference
Sfanta Ana October 2011	34	6.3	87.9	29.3	13.7	0.14	Frunzeti & Baciu, (2012)
Sfanta Ana August 2012	91	6.4	255.8	69.7	49.7	0.48	This work
Mohoș	29	3.6	57.9	14.9	10	1.86	This work

The measured fluxes for the areas were the gas bubbles were up to 25,000 g m^{-2} day^{-1}, located in some isolated spots of the water pools, in general corresponding for areas less than 1 m^2. The closed chamber technique could not be applied to measure the flux of Grota Sulfuroasă, which is a 14 m long cave; therefore, the flux will make the subject of another work.

The most active degassing area is located in the south eastern part of the main edifice were large abundance of CO_2 rich springs and bubbling water pools occur. Among this locations (excluding Grota Sulfuroasă) Băile Hammas represent the location with the highest CO_2 emission of ~60 t $year^{-1}$.

By summing up all the investigated locations, a total amount of ~230 t $year^{-1}$ of CO_2 is estimated (Table 8.1.2). The total emission may be even higher if we take into account also the non visible emission around these places or the surface area that could not be measured due to its human intervention.

Table 8.1.2. Molecular composition of gas and CO_2 output for the investigated areas

Location	type	Elevation	Flux (t y^{-1})	CO_2 (%)	CH_4 (%)	N_2 (%)	Ar ppb	Xe ppb	Ne ppm	He ppm	$\delta^{13}C/CO_2$	$^{18}O/^{16}O$
1. Băile Transilvania	springs	786	6.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2. Băile Reci	springs	890	47.8	99.99	0.008	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3. Izvoarele tamaduitoare	springs	904	15.2	97.2	1.34	1.42	153	2.5	0.046	35.24	-3.3	-7.4
4. Baia Apor	speings	930	18.2	96.8	1.31	1.93	115	2.23	0.013	34.93	-3.7	-4.9
5. Grota Sulfuroasă	moffete	1055	n.d.	96.7	1.19	2.11	111	1.38	0.046	27.09	-3.1	-7.5
6. Hammas	swamp	886	60.1	97.2	1.32	1.51	258	3.79	0.05	32.91	-3.2	-9.9
7. Vallato	springs	852	7.32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8. Răbufnitoarea	swamp	940	55.4	96.9	1.59	1.52	286	7.2	0.02	36.74	-2.8	-9.3
9. Tușnad	springs	739	0.12	95.7	0.003	4.42	212	2.74	0.073	0.53	-4.7	-8.2
10. Nadas	springs	725	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
11. Lăzărești	springs	744	17.1	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The CO_2 flux measurements emission of the four springs from Izvoarele Tămăduitoare (Figure 8.1.3) was performed in three campaigns and the total output is presented in the same figure. As it may be observed the results show a high variability of the CO_2 emission of the springs. The highest differences were between the results of August 2011 and 2012. In the case of the spring 1 and 2, the CO_2 output varied with -58% and -26.5% respectively. For the spring 3 and 4 the variation was positive: 37.9% and 46.7% respectively. It is worth to be mentioned that the overall emission of the springs remained relatively constant during time, with an increase of only 5.8%. This may indicate that even if the variation at small scale is high, the emission remains in the same order of magnitude on a larger scale. A high variability of the flux may be interpreted as a deep perturbation within the magma chamber, but in the case of Izvoarele Tămăduitoare the results show that the emission remains constant over time.

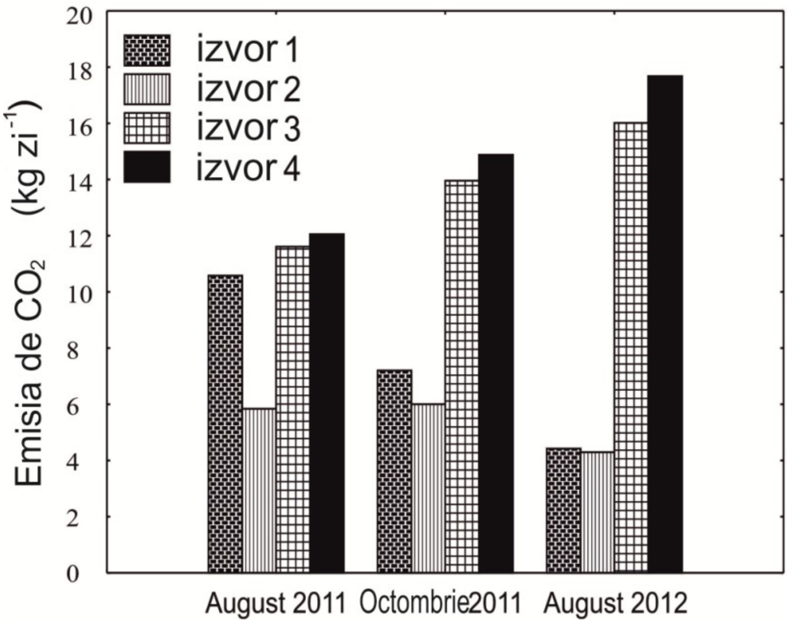

Figure 8.1.3 CO_2 emission at Izvoarele Tămăduitoare

The isotopic composition of six gas samples collected from different areas of the Ciomadul volcano is reported in table 8.1.3. The values of $\delta^{13}C$ in CO_2 ranged from -4.7 to -2.7‰.

Table 8.1.3. Isotopic composition of Ne and Ar

Location	R/Ra (Helium)	$^{20}Ne/^{22}Ne$	$^{40}Ar/^{36}Ar$
Grota Sulfuroasă	2.199	10.444	339.74
Hammas	2.242	10.361	263.37
Răbufnitoarea	2.291	10.626	357.21
Izvoarele Tămăduitoare	2.302	9.920	1386.60
Baia Apor	2.438	11.470	
Tușnad	0.724	9.790	282.96

The Helium isotopic composition displays some elevated values of R/Ra, most of the samples being above 2‰ with a maximum of 2.44‰. A lower value of 0.72 was measured at Tușnad termal spring, north-west of the main edifice.

Measured $^{40}Ar/^{36}Ar$ ratios range from 263.4 to 1386.6, the maximum value being significantly above the atmospheric value of 295.5 (Steiger and Jäger, 1977). Two samples however are characterised by lower than atmosphere $^{40}Ar/^{36}Ar$ ratio.

The $^{20}Ne/^{22}Ne$ displays a large range from 9.8 measured at Tușnad thermal spring up to 11.47.

8.2 Case study Băile Homorod (Harghita County)

Băile Homorod is located on the western slope of the Harghita Mts., at the boundary with the Transylvanian Basin, under the volcanoclastic deposits, where Miocene deposits belonging to the sedimentary basin occur. The Badenian consists of marls alternating with sands, volcanic tuffs, and salt deposits. The Sarmatian is formed by silty clays, lenticular conglomerate deposits and sandstones. The Pannonian consists of gravel, clays, silty clays and sand (Ticleanu et al., 1980). The area is fragmented by faults which have an important contribution to the circulation of post-volcanic gases and mineral waters (Peltz et al., 1983, Szabó et al, 1957).

Figure 8.2.1 The measurements performed close to the bubbling water pool

Results

The molecular and isotopic composition of gas is presented in table 8.2.1 and 8.2.2. The main component is CO_2 (98.1%), followed by N_2 (1.7%) and CH_4 (0.19%). The measured values of $\delta^{13}C$ in CO_2 was -4.7‰ and the $^3He/^4He$ ratio (as R/R_A) = 0.45.

Table 8.2.1 Molecular composition of Homorod gas sample

CO_2 (%)	N_2 (%)	CH_4 (%)	He (ppm)	Ne (ppm)	Ar (ppb)	Kr (ppb)	Xe (ppb)	Reference

98.1	1.7	0.19	10.41	0.0302	91.8	24.24	3.71	This work
98.24	1.16	0.36	0.48	-	-	-	-	Vaselli et al., 2002

Table 8.2.2 Isotopic composition of Homorod gas sample

$^{13}\delta C\text{-}CO_2$	$^{18}\delta O\text{-}CO_2$	$^{3}He/^{4}He$ (R/R_A)	$^{20}Ne/^{22}Ne$	$^{40}Ar/^{36}Ar$	Reference
-4.7	-8.3	0.45	9.59	319.53	This work
-2.03	-	0.62	-	-	Vaselli et al., 2002

The values of the diffuse CO_2 emission performed around the bubbling water pool ranged from 2.2 g m^{-2} day^{-1} to 40.7 g m^{-2} day^{-1}. By comparison, the measured fluxes for the springs and bubbling water pool where the gas bubbles were observed, was up to 20,000 g m^{-2} day^{-1}. The gas bubbles were located in some isolated spots of the water surface, in general corresponding for areas less than 1 m^2. The results of the CO_2 emission released into the atmosphere are presented in table 8.2.3. By summing up all the average values of the springs, a total emission of about 4.25 kg day^{-1} of CO_2 was estimated. Assuming that the emission is more or less constant over the year, the emission of CO_2 may be around 1.6 t y^{-1}.

Table 8.2.3 Carbon dioxide output of the springs and for the bubbling water pool

	Field Campaign	**Spring no.2 (Kálmán spring)**	**Spring no.3 (Fenyős spring)**	**Spring no. 8 Unnamed spring (within pension area)**	**Water pool**
CO_2 output ($kg\ day^{-1}$)	October 2011	0.5	n.m	0.68	2.51
	August 2012	0.54	n.m	0.89	n.m
	September 2012	0.55	0.1	1.72	n.m
	Average value	**0.53**	**0.1**	**1.09**	**2.51**

***n.m – not measured**

8.3 Case study Geogenic emission of methane and carbon dioxide at Beciu mud volcano, (Berca-Arbănași hydrocarbon-bearing structure, Eastern Carpațhians)

The mud volcanoes from Berca area were described for the first time by H. Coquand in 1867 in relation with the early petroleum exploration works performed in the area (Peahă, 1965). The zone around these mud volcanoes represents one of the oldest area of petroleum extraction in Romania. Starting with 1900, the extraction system had rapidly developed and hundreds of oil wells were drilled. During the First World War, the petroleum drilling rigs and refinery were partly destroyed. In the interwar period new wells were drilled and Berca Arbănași - Sărata Monteoru became the most important petroleum area in Romania. Along with the decrease of oil commercial reserves in the area, the extraction activity diminished.

Currently there are a few active wells, but the area is important for the occurrence of the biggest mud volcanoes in Romania and for the history of petroleum extraction. In the framework of studies on gas emissions to the atmosphere from geological sources in Romania, the mud volcanoes of the Berca-Arbănaşi hydrocarbon-bearing structure (Eastern Carpathians) represent a main gas seepage system with considerable emissions of methane, as evidenced by flux measurements performed at Pâclele Mari, Pâclele Mici and Fierbători mud volcanoes (Etiope et al., 2004a). The present work completes these gas emission studies by reporting the flux of methane and carbon dioxide at Beciu mud volcano, not measured previously.

Results

4.1. Gas flux from vents (macro-seepage)

The measured gas output from single vents ranged from 0.014 to 32 t CH_4 year-1 and 0.003 to 2.9 t CO_2 year^{-1}. The highest output of 32 t CH_4 year^{-1} corresponds to the cone-shaped vent which has a surface area of 0.785 m^2 (Fig. 8.3.2.b). The area of the vents (bubbling pools) ranged from 0.07 m^2 (corresponding to the accumulation chamber size) to 7 m2 (an irregular shape pool with three connected vents; Fig. 8.3.2.c). The total surface area of all vents amounts to approximately 30 m^2, which represents only 0.65% of the total area covered with recent mud.

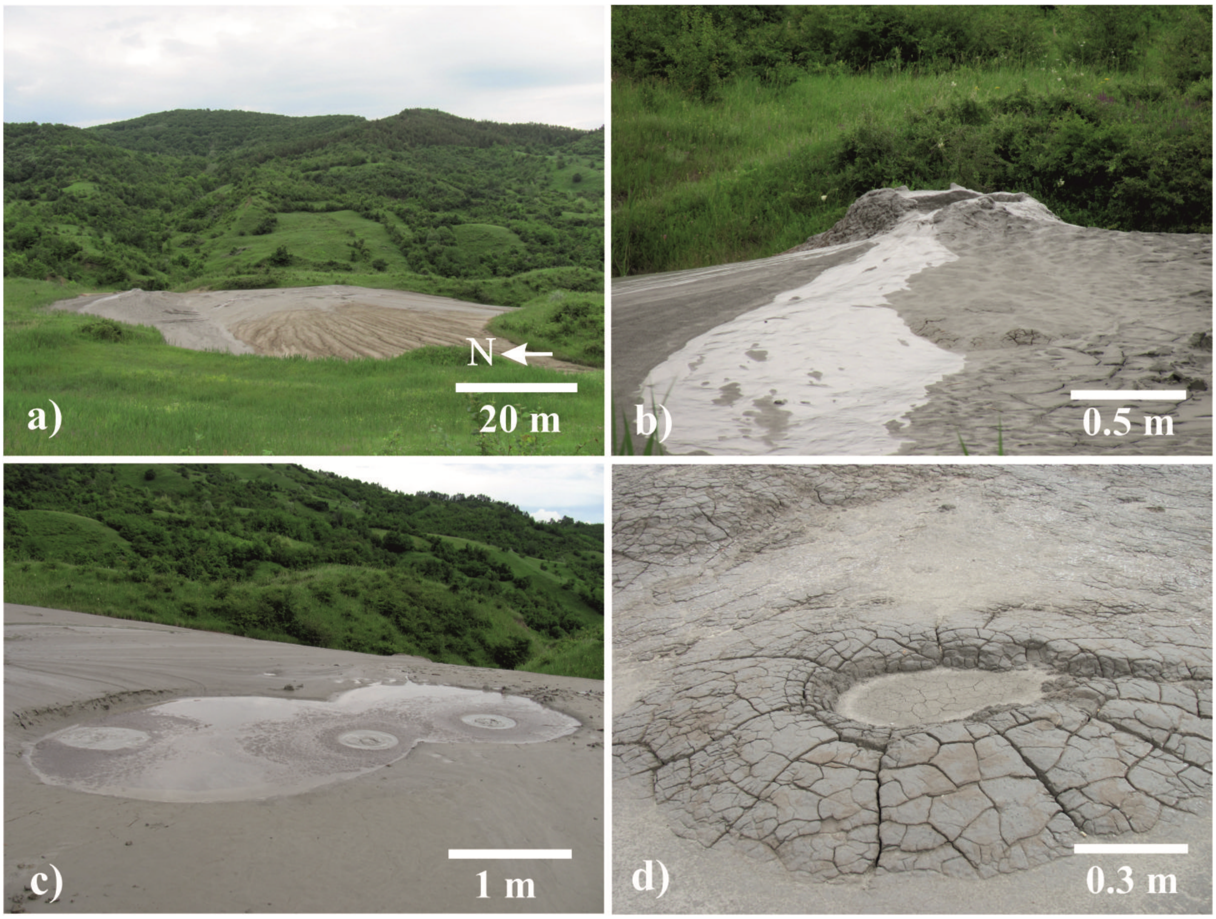

Figure 8.3.2. a – Overview of Beciu mud volcano; b – the main vent with mud flow (cone-shaped); c – circular pool vent (pie-shaped); d – inactive vent

Using the theoretical model for calculating the gas flux for those vents not accessible for direct measurements (Etiope et al., 2004a), a total of 8 t year^{-1} of methane and 0.8 t year^{-1} of carbon dioxide were estimated. For some vents the theoretical flux was compared with the measured values. The total output from the vents is about 182 t year-1 of methane and 21 t year^{-1} of carbon dioxide.

4.2. Diffuse miniseepage fluxes

Diffuse soil emissions were found ranging from 10^2 to 10^5 mg CH_4 m^{-2} day^{-1}, and 10^2-10^4 mg CO_2 m^{-2} day^{-1}. The maximum soil degassing flux measured was 2.1×10^5 mg m^{-2} day^{-1} of methane and 5×10^4 mg m^{-2} day^{-1} of carbon dioxide. These measurements were performed at 1 m distance from the main vent. A sudden decrease in soil gas fluxes was observed at a distance of 2 m from the main vent (9.6×10^2 mg m^{-2} day^{-1} of CO_2 and in the order of 10 mg m^{-2} day^{-1} of CH_4; Fig. 8.3.3b).

The CH_4 flux was relatively low up to 8 meters from the main vent, and then slightly increased up to 6×10^3 mg m^{-2} day^{-1}. The lowest CH_4 flux zone might be due to methanotrophic bacteria which may occur very close to the vent. On the other hand, the carbon dioxide flux recorded a more constant value along the transect than methane flux.

More measurements were performed randomly to cover the total surface of the mud volcano (Fig. 8.3.4.b and c). The mean flux was 4.4×10^3 mg CH^4 m^{-2} day^{-1} and 8.9×10^3 mg CO_2 m^{-2} day^{-1}. Basically, we observed that gas seepage occurs pervasively throughout the muddy cover, even if it appears to be saturated with water. The four measurements performed beyond the active area, where vegetation is abundant, show a quite constant but low flux of methane and carbon dioxide. The mean value on this surface was 3.7×10^2 mg m^{-2} day^{-1} of methane and 1.9×10^3 mg m^{-2} day^{-1} for carbon dioxide. From the surface area covered with mud, a total output of methane of 7.5 t $year^{-1}$ and at least 14.7 t $year^{-1}$ of carbon dioxide was calculated by using the Natural Neighbour interpolation. The spatial distribution of CH_4 and CO_2 fluxes of Beciu mud volcano from macro and mini-seepage (without the other two small group of vents) obtained by using the Surfer software is represented in figures 4.b and 4.c.

One may observe that CH4 and CO2 fluxes have the same spatialpattern, indicating that both are components released by the mud volcano seepage system.

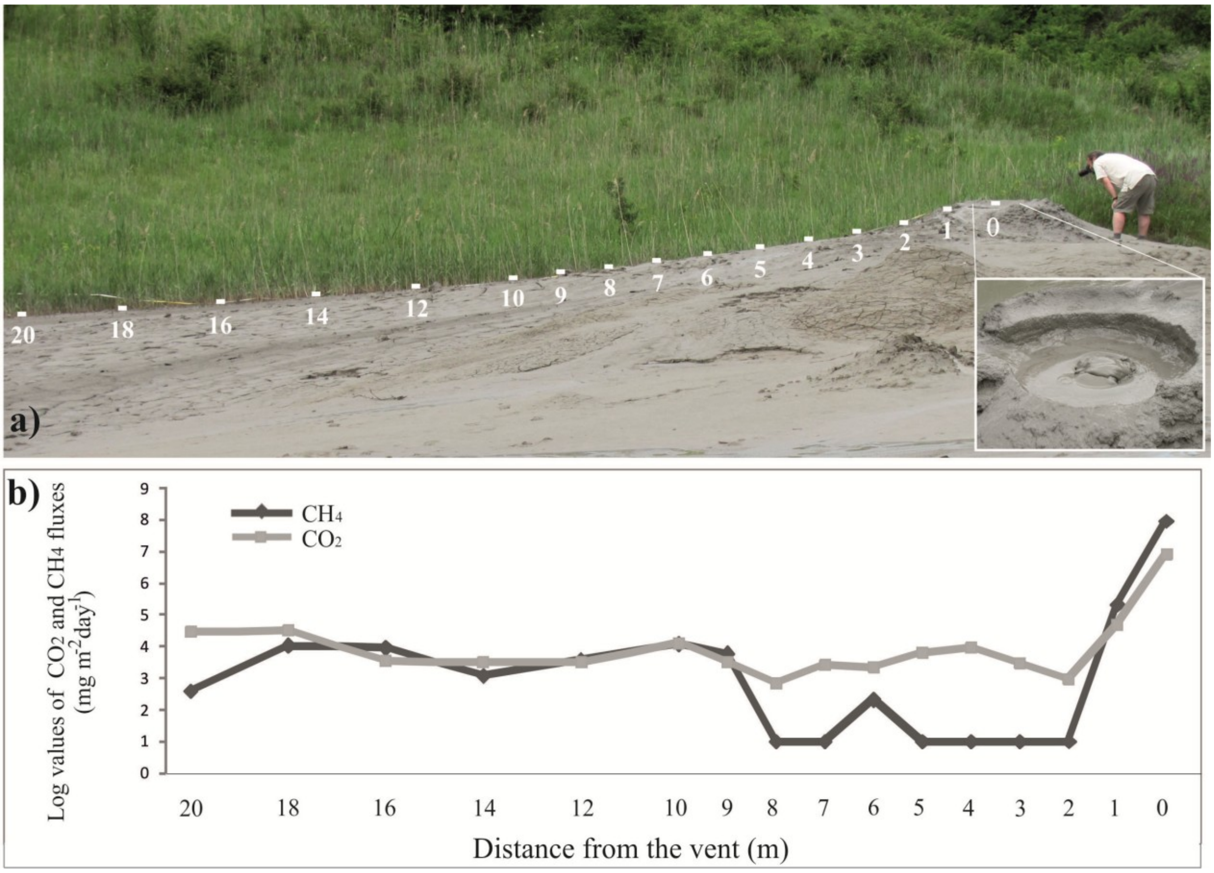

Figure 8.3.3The transect setup for gas flux measurements; b. CO2 and CH4 fluxes on the transect. Zero marks the position of the active ejecting vent and position 20 is already within vegetation

The only exception was observed at the edge of the mud volcano, where the CO_2 flux was relatively higher than the methane flux, probably due to additional biogenic CO_2 from soil (e.g. roots respirations and decomposition of organic matter).

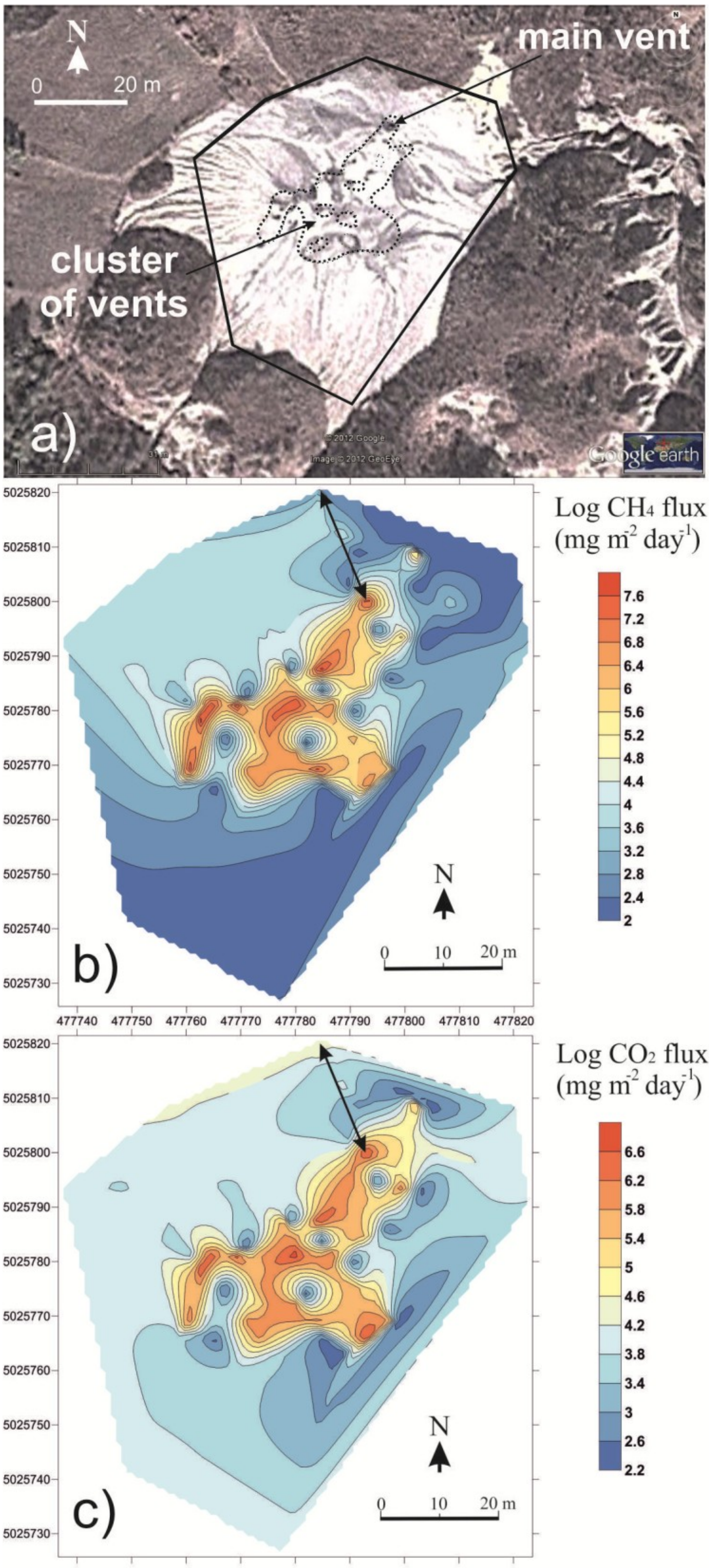

Figure 8.3.4 a) Aerial view of Beciu mud volcano (Google Earth); b) The flux distribution of the logarithmic values of CH_4; c) The logarithmic values of CO_2; Arrows of the Fig. b and c indicate the position of the transect of figure 8.3.3.

8.4 Case study: Everlasting fires from south-eastern part of Eastern Carpathians

In this case study, we studied the gas origin of four everlasting fires (namely Andreiaşu, Lepşa, Răiuţi and deer) and a small mud volcano located in the vicinity of Andreiașu everlasting fire. Moreover, we report also the estimates for CH_4 and CO_2 emissions of these gas manifestations.

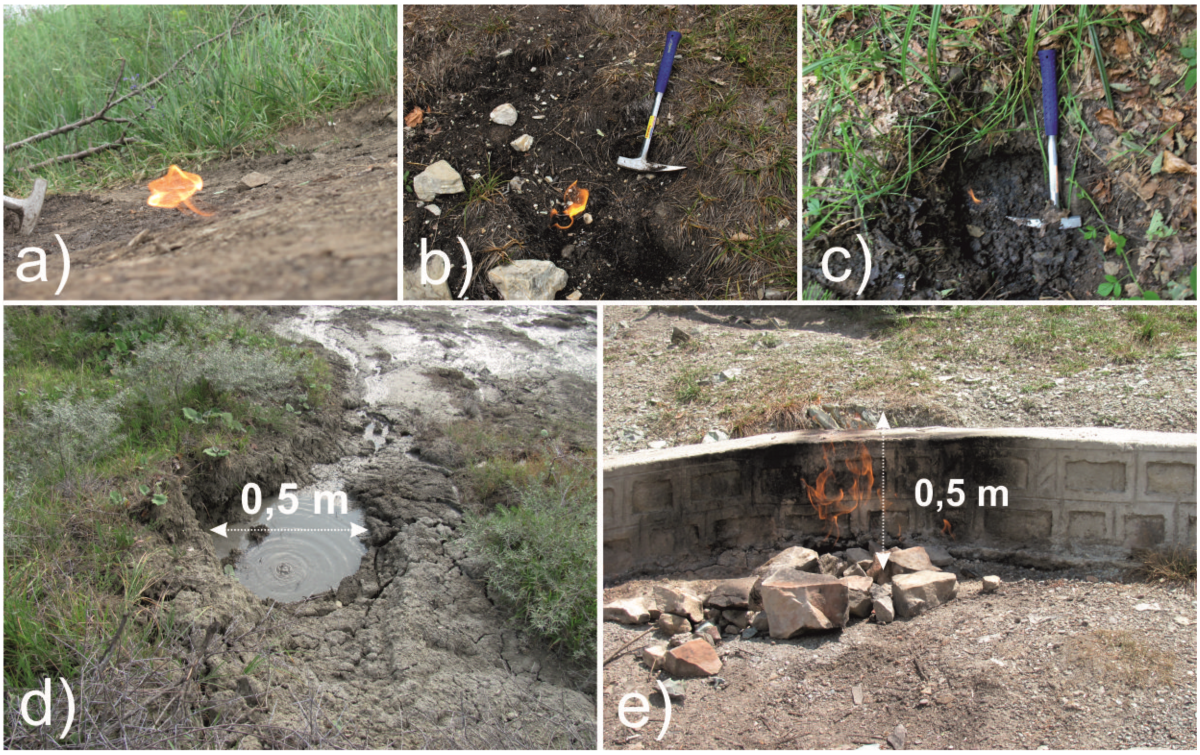

Figure 8.4.1 Everlating fire from: a) Lopătari; b) Răiuți; c) Lepșa; e) Andreiașu and the small mud volcano from Andreiașu area

8.4.3 Results

Methane composition ranges from 78.6% at Andreiaşu mud volcano to 95.3% at Răiuţi everlating fire. The amount of carbon dioxide was pretty elevated at Andreiaşu mud volcano (20.85%) as well as for Lepşa everlasting fire (7.82%) compared with the other investigated locations where CO_2 value was quite low , at around 1% (Table 8.4.1).

Table 8.4.1 Molecular composition of the samples

Location	He %	H_2 %	Ar %	O_2 %	CO_2 %	N_2 %	C_1 %	C_2 %	C_3 %	iC_4 %	nC_4 %	iC_5 %	nC_5 %	C_6+ %
Lepșa	**0.0016**	**-**	**0.0270**	**0.38**	**7.82**	**3.18**	**87.73**	**0.757**	**0.0777**	**0.0178**	**0.0006**	**0.0080**	**-**	**0.0027**
Andreiașu (v.n.)	**0.0013**	**-**	**0.0070**	**0.090**	**20.85**	**0.35**	**78.60**	**0.0454**	**0.0358**	**0.0185**	**0.0002**	**0.0009**	**-**	**0.0016**
Andreiașu (foc viu)	**nd**	**-**	**0.0053**	**0.10**	**1.96**	**0.41**	**94.60**	**1.93**	**0.568**	**0.121**	**0.143**	**0.0598**	**0.0367**	**0.0707**
Răiuți	**0.0126**	**0.0032**	**0.0124**	**0.056**	**1.07**	**1.62**	**95.30**	**1.23**	**0.367**	**0.0678**	**0.104**	**0.0432**	**0.0345**	**0.0840**

Lopătari	**0.0040**	**-**	**0.1500**	**0.501**	**0.40**	**0.79**	**94.90**	**1.80**	**0.74**	**0.1500**	**0.28**	**0.1020**	**0.084**	**0.1000**

The isotopic composition of carbon from methane ($\delta^{13}C_1$ ‰) ranged from -48.46 ‰ at Lepşa everlasting fire to -32.23 ‰ at Lopătari everlasting fire. There was a greater variation in the hydrogen isotopes composition of methane (δDC_1 ‰), with a minimum at Lepşa and -227.8 ‰ and a maximum of -144.5 ‰ at Lopătari (Table 8.4.2).

Table 8.4.2 Isotopic composition of gas samples

Locations	$\delta^{13}C_1$‰	δDC_1‰	$\delta^{13}C_2$‰	$\delta^{13}C_3$‰
Lepşa	**-48.46**	**-227.8**	**-30.43**	**-**
Andreiaşu (v.n.)	**-41.68**	**-171.6**	**-**	**-**
Andreiaşu (f.v.)	**-35.73**	**-151.0**	**-25.54**	**-24.50**
Răiuți	**-32.23**	**-148.9**	**-27.51**	**-26.08**
Lopătari	**-32.29**	**-144.5**	**-26.78**	**-26.51**

In Table 8.4.3 are presented the statistical data for CH_4 and CO_2 fluxes from the investigated sites. The minimum values for CO_2 flux were comparable to typical values biogenic origin, however the maximum values indicates clearly an addition of CO_2 from geogenic sources. In addition, average values were above the mean values derived from biogenic sources, indicating that most of the CO_2 is of geogenic origin, particularly for the Andreiaşu mud volcano. Regarding the results of the measurements methane flux, minimum values were below the detection limit, indicating measurements where the geogenic methane was not intercepted. However, the values measured where fires were burning reached values of up to ~ 16,000 g m^{-2} day^{-1}.

Table 8.4.3 Statistical data of flux measurements of CO_2 and CH_4

			CO_2			CH_4		
Location	surface(m^2)	No. of measurem.	Min.	Max.	Med.	Min.	Max.	Med.
Andreiaşu (ev. fire)	337	31	19,7	970,6	173,7	0,07	7150	583,5
Andreiaşu (m. volcano)	<1	8	3,3	38273,1	8255,7	0	15996,2	3892,2
Lopătari	38	14	24,7	494,3	144,5	0	15794	1265,3
Lepşa	<1	6				1,4	4240,8	835,9
Răiuți	5	6	81,1	1297,2	350,5	0	30227,9	5410,6

The emission of methane and carbon dioxide from the investigated locations are reported in table 8.4.4.

Table 8.4.4 The emission of methane and carbon dioxide from the investigated locations

Location	The flux of CH_4 (t y^{-1})	The flux of CO_2 (t y^{-1})
Lepșa	**1,5**	**0,64**
Andreiașu (m.v)	**3**	**3,5**
Andreiașu (e.f.)	**38**	**4,2**
Răiuți	**8**	**0,5**
Lopătari	**21,9**	**0,5**

Total emission of methane from the investigated locations is estimated at approximately 70 t $year^{-1}$. For carbon dioxide the emission was estimated at approximately 10 t $year^{-1}$.

Final conclusions

The effects of carbon dioxide and methane on climate change are well known, because they represent one of the most important greenhouse gases after water vapor.

This paper aims to locate and to estimate the carbon dioxide and methane emissions in the southern part of Eastern Carpathians. For the case studies were choose different gas manifestations where the predominant gas is methane (mud volcanoes, everlasting fires) and manifestations where the predominant gas is carbon dioxide (mineral springs with bubbling gas, mofettes, and diffuse emissions through soil). Many of these gas manifestations are modified by human intervention (water pools with bubbling water).

The methodology used for measuring gas fluxes with "portable diffuse CO_2 and CH_4 flux meter (WEST Systems)" is an innovative, which allows a fast measurement and direct calculation of CO_2 and CH_4 flux in the field.

The case studies presented in this paper are from different geological environments including inactive volcanoes from Harghita Mountains and petroleum hydrocarbon-rich areas from southeastern part of Eastern Carpathians.

Harghita Mountains is known for its abundance of post-volcanic phenomena such as mineral springs and mofettes that people use them for medical purposes. Two case studies were chose from this area: Ciomadul volcano and Băile Homorod (Harghita County).

Ciomadul volcano was chosen for the case study because it represents the youngest volcano in the whole Carpathian chain, and many post-volcanic phenomena occur. Gas samples were taken from different areas of the volcano and were analyzed in terms of molecular and isotopic composition. Geochemical interpretations suggest that the majority of samples have a significant amount of carbon dioxide of mantle origin. A single source was identified that appears to have a crustal origin. Inside the Sfânta Ana a surface of about 0.12 km^2 with diffuse geogenic CO2 emission was identified. The total emission of carbon dioxide for the investigated area is estimated at about 2300 t year^{-1}. Many other CO_2 degassing areas were investigated in terms of flux, but due to the fact that the method cannot be applied everywhere, the measurements were carried out only on the water surface. The results show an emission of about 230 t year^{-1}. Ciomadul volcano represents an important area and a representative location for investigating the whole Călimani-Gurghiu Harghita volcanic chain. Future studies will be able to evaluate different locations in order to assess the evolution of the geothermal system or even the reactivation of volcanic system. Presently, there are no geochemical signals indicating the reactivation of volcanism.

The mineral springs from Băile Homorod are located along a straight line and this may indicate the presence of a fault. The flux measurements of carbon dioxide performed on soil surface show higher values in the direction of the presumed fault. This result may indicate that higher values contain an addition of geogenic carbon dioxide, which migrate to the surface in the direction of the fault lines. At Băile Homorod, the contribution of mantle gas is very low, the gas being derived from the crust. A total emission of the four springs and the bubbling water pool is estimated at about 1.5 t year^{-1}.

In Berca-Arbănași area, the gas uprising from the hydrocarbon reservoir through deep faults leads to the formation of four important mud volcanoes (Fierbători, Pâclele Mari, Pâclele Mici and Beciu). This work represents the first detailed investigation of Beciu mud volcano, the northernmost mud volcano from this hydrocarbonbearing structure. Beciu mud volcano is relatively small compared to Pâclele Mari or Pâclele Mici, with mostly calm effusive activity. Despite its relatively small size, Beciu mud volcano has a high degassing activity. Beciu is the northernmost mud volcano along the Berca Arbănași fault and probably it corresponds to the more active (younger) and permeable sector of this structure; this sector is also characterized by the presence of minor transversal faults (trending NW-SE) which cross the main N-S Berca-Arbănași lineament. The total emission of CH_4 and CO_2 from Beciu mud volcano is conservatively estimated to be at least 190 t year^{-1} and 35 t year^{-1}, respectively. The results confirm the previous estimation by reporting a total emission in the same order of magnitude. But the total emission of Beciu mud volcano might be slightly larger since the area investigated in this work was not extended too much further from the area covered with mud. The Beciu output leads the total CH_4 emission from the four Berca mud volcanoes to at least 1350 t year-1, a value comparable with that reported for a similar number of giant mud volcanoes in Azerbaijan. A total output of at least 120 t year-1 of carbon dioxide was estimated. This work completes the gas flux survey in the Berca mud volcanoes, updating the geogenic gas flux data-set of Romania and contributing to extend the global data-set of methane and carbon dioxide emissions from mud volcanoes.

The fourth case study includes several locations in south-eastern part of Eastern Carpathians: four everlasting fires (Lepşa, Andreiaşu, Răiuţi and Lopătari) and a small volcano in Andreiaşu area. The gas composition is dominated by methane, and ranges from 88.7% at Lepșa and 95.3% Răiuţi. At Andreiaşu mud volcano, the composition of methane was 78.6%, compared with 94.6% at Andreiaşu everlasting fire, the distance between these two locations being approximately 500 m. The contribution of methane to the atmospheric budget is approximately 70 t $year^{-1}$, while the contribution of carbon dioxide is about 10 t $year^{-1}$.

In conclusion, the southern part of Eastern Carpathians, represent a diverse area in terms of the gas manifestations. A conservative estimation of the methane emission for the investigated areas (Beciu and Andreiaşu mud volcanoes and the following everlastin fires; Andreiaşu, Lepşa, Lopătari and Răiuţi) is about 260 t $year^{-1}$. Regarding the emission of carbon dioxide from geothermal areas (Ciomadul volcano and Băile Homorod), and for the manifestation with methane as predominant gas the estimated value is about 3,000 t CO_2 $year^{-1}$.

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