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GEOGENIC EMISSION OF METHANE AND CARBON DIOXIDE AT BECIU MUD VOLCANO, (BERCA-ARBĂNAŞI HYDROCARBON-BEARING STRUCTURE, EASTERN CARPATHIANS, ROMANIA)

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Abstract: As shown by previously performed flux measurements, the mud volcanoes of Berca-Arbănaşi hydrocarbon-bearing structure in Eastern Carpathians Foredeep, including Pâclele Mari, Pâclele Mici, and Fierbători, represent a main gas seepage system in Romania, with considerable emissions of methane. The present work completes these gas emission studies by reporting the flux of methane and carbon dioxide at Beciu mud volcano, belonging to the same structure, not measured previously. In total, 78 measurements were carried out in June 2011 (40 on the vents, 34 on the area covered by mud and 4 in the external area, covered by vegetation). Diffuse fluxes from mud 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 emission from individual vents was in the range of 0.014 to 32 t CH_4 $year^{-1}$ and 0.003 to 2.9 t CO_2 $year^{-1}$. These values are comparable with those typically documented for mud volcanoes worldwide. Gas seepage occurs pervasively throughout the muddy cover, even if it appears to be saturated with water. 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 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. This work contributed to update the geogenic gas flux data-set of Romania and to extend the global data-set of methane and carbon dioxide emissions from mud volcanoes.

Keywords: mud volcanoes, greenhouse gas emissions, methane, carbon dioxide, gas flux, soil degassing

1. INTRODUCTION

Mud volcanoes occur in various tectonic settings, especially in compressional tectonic areas. They can be a potential indicator of regional tectonic stress and faults (Kopf, 2002; Bonini & Mazzarini, 2010). Due to the relevant amounts of gas released, they are important sources of methane for the atmosphere (Etiope & Milkov, 2004; Etiope et al., 2004a; 2004b). Genesis, geology and geochemistry of worldwide mud volcanoes are described in detail by a wide literature (e.g. Dimitrov, 2003; Etiope et al., 2009 and references therein), and estimates of the total amount of methane released to the atmosphere were reported by Etiope & Milkov, (2004) and Etiope et al., (2011b).

Methane and carbon dioxide are greenhouse gases with relevant role in global climate change.

Though knowing their natural sources is critical for understanding and managing the atmospheric carbon budget, the geologic contribution has been object of studies only in the last decade (Morner & Etiope, 2002; Etiope et al., 2008). The main geo-CO_2 emission sources are related to volcanic and geothermal systems, while geo-CH_4 is predominantly released by natural gas seepage systems in sedimentary and petroleum-bearing basins. These sedimentary seepage systems however also release apparently minor CO_2 amounts and the global output of such a sedimentary CO_2 has not been quantified. Presently, it is well known that geo-CH_4 emissions are an important component of the atmospheric methane budget as they represent, globally, the second most important natural source of methane, after wetlands (Etiope et al., 2008). For Europe, a total emission of 3 Tg CH_4 $year^{-1}$ from geological sources was estimated, representing 8% of European anthropogenic emission (Etiope, 2009). Regarding the mud volcanoes in particular, global emission estimates are around 6-9 Tg CH_4 year^{-1} (Etiope & Milkov, 2004), but they may exceed 10 Tg year^{-1} (Etiope et al., 2011b).

Romania hosts tens of mud volcanoes, with variable size and activity. The biggest and most renowned mud volcanoes are located on the south-eastern boundary of the Carpathian chain, on the Berca Arbănaşi hydrocarbon-bearing structure. Many smaller mud volcanoes and methane seeps have been reported in the Transylvanian Depression and on the Moldavian Platform (Spulber et al., 2010; Baciu & Etiope, 2005; Baciu et al., 2007, 2008). All these mud volcanoes release predominantly methane, except one small mud volcano in Transylvania, Homorod, whose gas is dominated by N_2 (up to 92% vol.). Homorod is an interesting case, because it also shows the highest content of helium (He) ever found in surface seeps (up to 1.4%) and the highest value of δD in CH_4 (deuterium isotopic composition) ever found in nature, +124 ‰ (Etiope et al., 2011a).

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 inter-war period new wells were drilled and Berca-Arbăna□i - 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.

Methane and carbon dioxide flux data acquired from both focused gas emission spots (macro-seepage: bubbling pools, vents) and diffuse, invisible seepage from the muddy ground (mini-seepage, as defined in Etiope et al., 2011b) are presented here. The results allow to enlarge the global data-set of gas flux from mud volcanoes and may contribute to refine the "emission factor" of mud volcanoes, which is the key parameter for bottom-up scaling and global emission estimates (a wide discussion on "emission factor" and its significance in natural methane sources is reported in Etiope et al., (2007 and 2011b).

2. GEOLOGIC SETTING AND SITE DESCRIPTION

Beciu mud volcano is located within the Berca-Arbăna□i hydrocarbon-bearing structure, a strongly tectonized anticline fold, N-S orientated and about 20 km long, geomorphologically corresponding to Berca Depression (Fig. 1). The most active mud volcanoes from Romania occur here. Four large mud volcanoes dominate the area from south to north: Fierbători, Pâclele Mari, Pâclele Mici and Beciu (Fig. 1). The wells drilled for oil exploration and extraction, and the surface mapping have revealed the geological structure of the area. The pile of sedimentary deposits hosting the hydrocarbon reservoirs is Neogene in age, including the Sarmatian, Meotian, Pontian and Dacian regional stages. In Beciu area the Meotian marls occur at the surface. According to Filipescu & Humă (1979), the gas accumulations are Sarmatian in age and they are localized just in certain tectonic blocks. The numerous faults reaching the hydrocarbon reservoirs provide preferential pathways for gas and mud upwelling, leading to mud volcano formation. The data recorded by the Berca borehole suggests that the main gas reservoir is more than 3 km deep (Sencu, 1985).

Beciu mud volcano, extended of an area of 4560 m^2 is located at an elevation of 280 m above sea level, on an important dislocation line approximately perpendicular to the anticline axis, 3 km N from Pâclele Mici mud volcano, on Arbănaş Valley (Fig. 1).

The activity of the mud volcano is generally calm, with low amounts of fluid mud flowing on the flanks of the cones, although some eruptive episodes were recorded (Sencu, 1985). The area occupied by Beciu mud volcano has a polygonal shape, hosting 46 active and a few inactive vents.

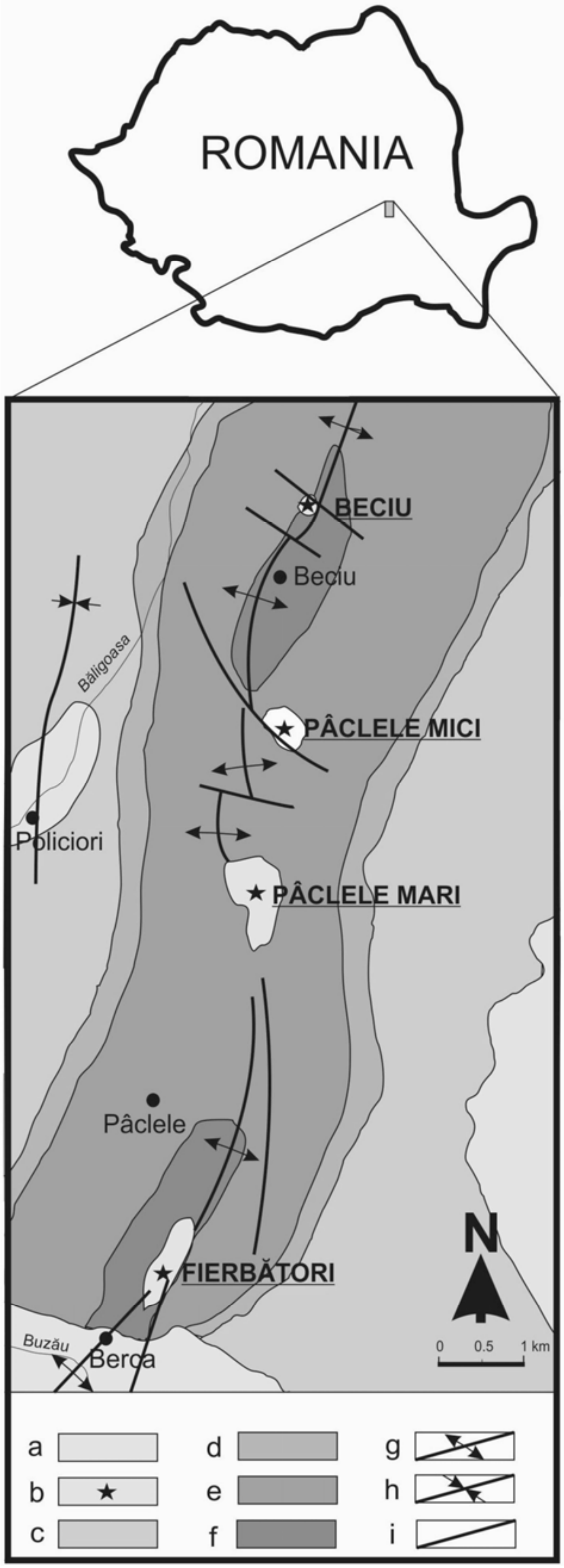

Figure 1. Geological sketch map of Berca Depression (after Ciocârdel, 1949, from Sencu, 1985):
a - Terrace and floodplain deposits; b - Mud volcanoes and their products; c - Levantin marls; d - Dacian marls; e Pontian marls; f - Meotian marls; g - Anticline; h - Syncline; i – Fault

The active vents include a main cone and ”circular pools” of muddy water (Fig. 2). The released gas is mainly thermogenic CH_4, with a content of 93.15 % (Etiope et al., 2009).

The mud brought to the surface consists of pelitic material of brown-yellow or gray colour, and when dried it is breaking into small polygonal plates. The water is salty and after evaporation a white crust is left, on which vegetation doesn't grow. The mud released by the main cone is more viscous than the mud from other vents, generating a cone-shaped feature with a diameter of about 35 m and a slope of 1:10. (Fig. 3.a.). From time to time the mud changes the flow direction covering all areas around the vent. The mud flow from the other vents is more fluid and the upwelling gas produces a relatively intense bubbling. There is no vegetation on recently erupted mud, although at the outer margins of the older ejecta sparse plant growth is found.

Two other small groups of vents releasing muddy water occur in distinct areas close to the main mud volcano. The first is situated 10 m E and the other is located ca. 100 m S of the recent ejected products of Beciu mud volcano. The first is located in a small valley; the other covers a restricted area on the slope of a hill, separated by a small valley from the main mud volcano.

3. METHODOLGY

Methane and carbon dioxide fluxes were measured in June 2011 by using the closed chamber method, the same technique that was used in many other mud volcanoes in Italy, Azerbaijan, Japan and Taiwan (e.g. Etiope et al., 2011b; Hong et al., 2012). A portable diffuse flux meter (West System srl, Italy) equipped with CH_4 and CO_2 sensors, and wireless data communication to a palm-top computer was used. If the rate of increase of gas concentration in the chamber is constant, linear regression can be used to calculate the gas flux (F) by the equation (Livingston & Hutchinson, 1995):

$$F = \frac{V_c}{A_c} \times \frac{c_2 - c_1}{t_2 - t_1} \text{ [mg m}^{-2}\text{ day}^{-1}\text{]} \qquad (1)$$

where V_c (m^3) is the volume of the chamber, A_c (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 methane sensor 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. Based on a 10 min long chamber exposition, the system allows measuring a flux down to 30 mg m^{-2} day^{-1}. The CO_2 detector is a double beam infrared sensor (LI-COR) with a range of 0 to 20,000 ppmv.

Total emission from macro-seepage (vents and bubbling pools) was estimated by summing all fluxes measured in each vent (bubbling plume). Total emission from the diffuse miniseepage was estimated by the Natural Neighbour interpolation method.

The gas fluxes were measured on 40 vents out of 46. The other 6 were not accessible for direct field measurements, and the released amount was estimated by using a theoretical plot of bubble flux vs. bubble size vs. bubble frequency, developed by Etiope et al., (2004a). Thirty-four flux measurements on mud (miniseepage) were also performed.

A 20-meters long transect, starting from the main vent was set and the flux was measured every meter for the first 10 meters and every two meters for the next 10 meters (Fig. 3.a).

The other mud flux measurements were randomly distributed in order to cover the whole area of the recent mud products (vegetation free). Additionally, a number of four measurements were performed beyond the active area where the soil is covered with vegetation.

A total CH_4 macro-seepage emission of about 260 t $year^{-1}$ was previously roughly estimated on the basis of visual observations using the bubble flux vs. size vs. frequency theoretical plot (Etiope et al., 2004a).

4. 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. 4.b).

The area of the vents (bubbling pools) ranged from 0.07 m^2 (corresponding to the accumulation chamber size) to 7 m^2 (an irregular shape pool with three connected vents; Fig. 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.

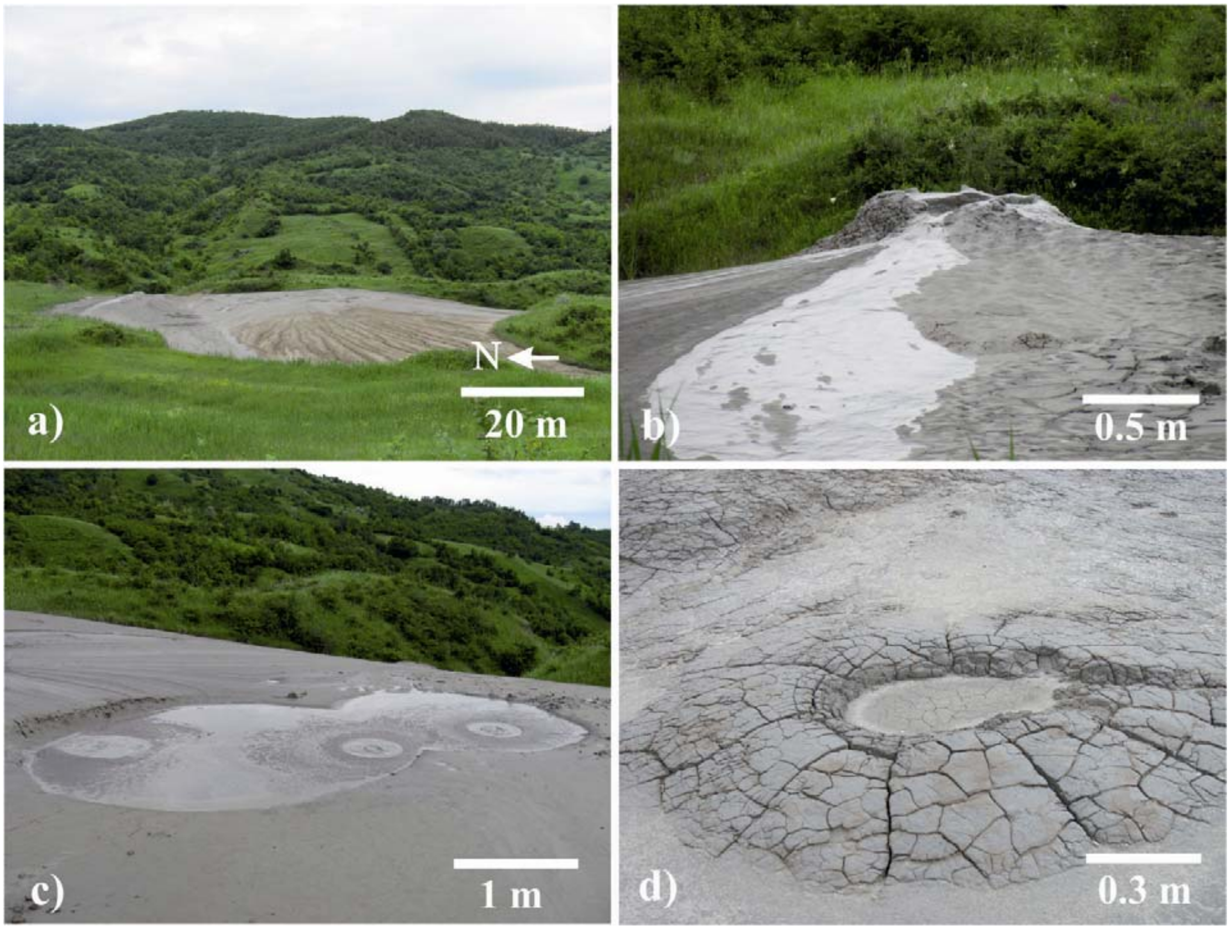

Figure 2. a – Overview of Beciu mud volcano; b – the main vent with mud flow (cone-shaped); c – circular pool vent (pie-shaped); d – inactive vent

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. 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. 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 CH_4 and CO_2 fluxes have the same spatial pattern, indicating that both are components released by the mud volcano seepage system.

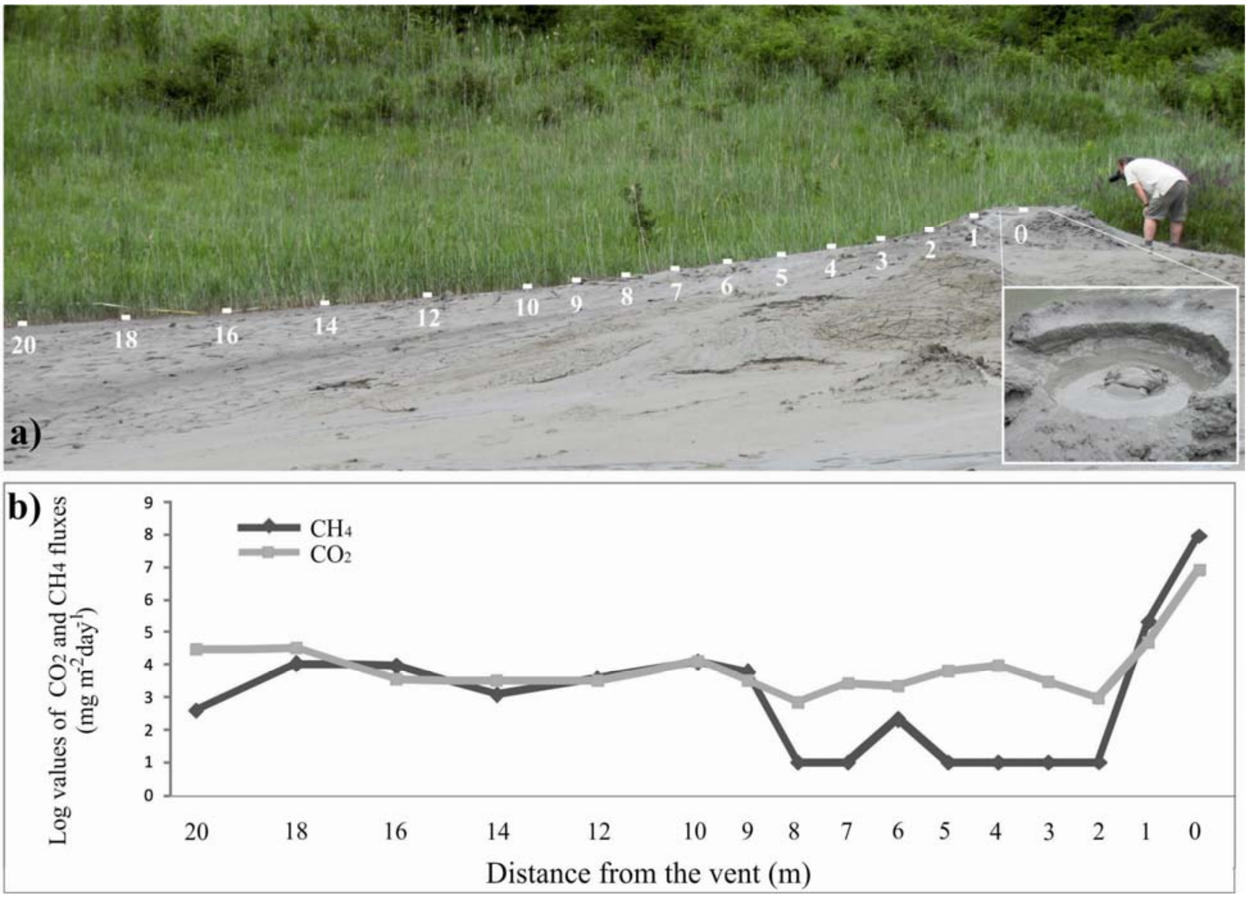

Figure 3. a. The transect setup for gas flux measurements; b. CO_2 and CH_4 fluxes on the transect. Zero marks the position of the active ejecting vent and position 20 is already within vegetation

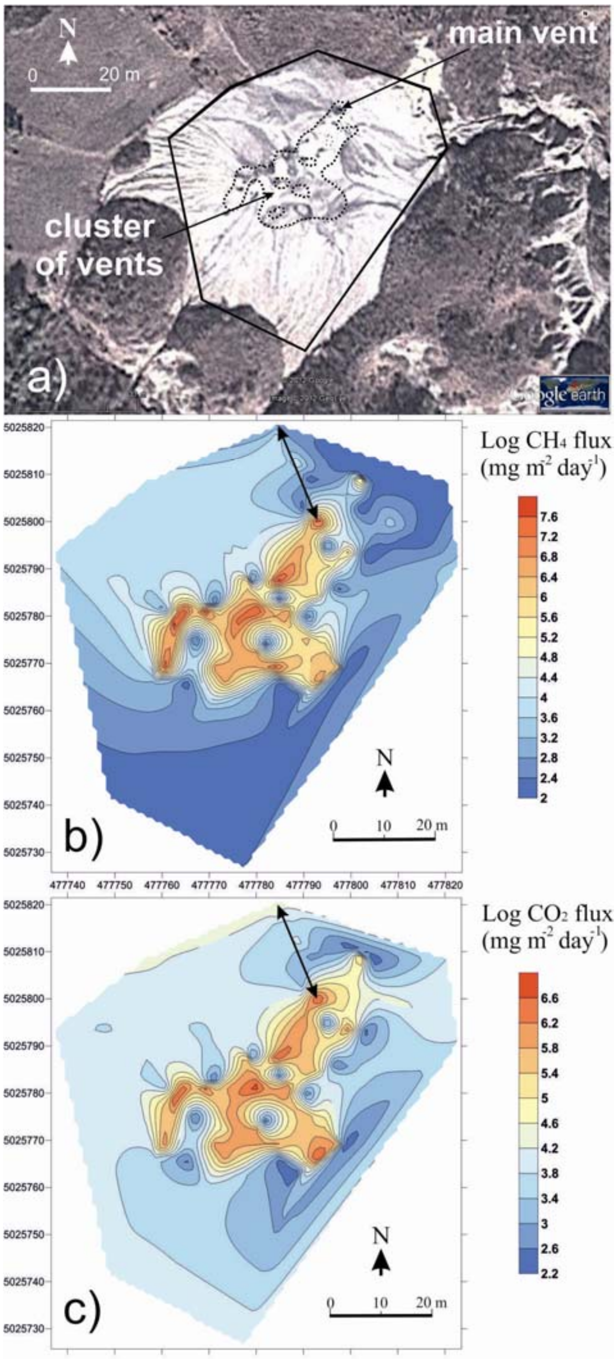

Figure 4. a) Aerial view of Beciu mud volcano (Google Earth); b) The flux distribution of the logarithmic values of CH_4; c) The logarithmic values of CO_2; Arrows of the Fig. b and c indicate the position of the transect of figure 3.

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).

5. DISCUSSION

The total emission from a mud volcano divided by its area gives the ”emission factor”, typically expressed in t km^{-2} $year^{-1}$ (see Etiope et al., 2007 and 2011b for detailed description). The emission factor must take into consideration not only the visible manifestations (craters, bubbling pools, gryphons), but also the diffuse degassing through mud or soil (Etiope & Kluman, 2010). Etiope & Milkov (2004) estimated an average emission factor of methane for mud volcanoes in the range of 10^2 – 10^3 t km^{-2} $year^{-1}$. Some gas emitting features in Romania may show much higher emission factors, (up to 10^5 t km^{-2} $year^{-1}$; Spulber et al., 2010).

The investigated surface area of Beciu mud volcano includes mostly the area of recent mud. The emission factor calculated for this area is about 4.3×10^4 t km^{-2} $year^{-1}$, which represents the highest value of emission factor from recent mud, of all mud volcanoes from Berca area (1.6×10^3 for Pâclele Mari and 1.7×10^3 for Pâclele Mici; Etiope et al., 2004a). Such a difference is due to the higher areal density of vents (46 vents on only 4560 m^2) in comparison with in the other mud volcanoes.

The total methane and carbon dioxide emission from the measured area in Beciu mud volcano, including vents and diffuse miniseepage is about 190 t $year^{-1}$ and about 35 t $year^{-1}$ respectively. Table 1 summarise the values of methane emission of all mud volcanoes from Berca area and also the results of $\delta^{13}C_1$, δD_1, CH_4, and $C_1/(C_2+C_3)$. The $\delta^{13}C_1$ and δD_1 value determine the origins of CH_4 (Schoell, 1988). All mud volcanoes from Berca area release thermogenic methane. It may be noticed that CH_4:CO_2 emission ratio (t $year^{-1}$) was found to be 9:1 on vents and 1:2 on the surface covered with mud.

Table 1. Methane output, isotopic relations and gas composition of the four Berca mud volcanoes

Mud volcano	**Beciu***	Pâclele Mici**	Pâclele Mari**	Fierbători**
Area (km^2)	**0.005**	0.62	1.62	0.025
Number of vents	**46**	65	62	18
Vent output (t yr^{-1})	**181.6**	255	300	17
Soil degassing (t yr^{-1})	**7.5**	128	430	20
$\delta^{13}C_1$ (‰)***	-37.28	-44.46	-37.88	-47.96
δD_1 (‰)***	-170.2	-184.6	-164.9	-172.5
CH_4 (%)***	93.15	94.55	94.8	95.53
$C_1/(C_2+C_3)$***	33	1501	49	31

(* **This work**, ** Etiope et al. 2004a, *** Etiope et al. 2009)

It is noteworthy that the CO_2 emission (t year^{-1}) was directly proportional to CH_4 emission but only at vents, where methane flux was approximately nine times higher than CO_2. In the case of diffuse miniseepage from mud, the CO_2:CH_4 emission ratio became inconstant, with an average of one to two, probably due to CH_4 consumption by methanotrophic bacteria and additional CO_2 from the biologic processes (independent from mud volcanism), as reported by Etiope et al., (2011b).

Etiope et al., (2004a) estimated a total CH_4 output of at least 1150 t year^{-1} of three mud volcanoes on Berca-Arbănaşi structure (Fierbători, Pâclele Mari and Pâclele Mici). With the results from Beciu mud volcano, a total CH_4 output of at least 1350 t year^{-1} is estimated for all four mud volcanoes from Berca area. Similar gas emission rates were reported for mud volcanoes from Azerbaijan which have a wider area (>0.7 km^2 Etiope et al., 2004b).

Etiope et al., (2004a) estimated a total CO_2 output in the range of 70-75 t year^{-1} for those three mud volcanoes. The CO_2 flux measured on Beciu mud volcano suggest that the CO_2 output from all the mud volcanoes on Berca-Arbăna□i structure is probably higher than previously estimated.

6. CONCLUSIONS

In Berca-Arbăna□i 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 hydrocarbon-bearing 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 Arbăna□i 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-Arbăna□i 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.

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