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METHANE SEEPAGE FROM GEOLOGIC SOURCES ON THE MOLDAVIAN PLATFORM (EASTERN ROMANIA)

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Abstract: The paper describes the gas emitting features from the Moldavian Platform, including the first direct measurements of the methane flux from geologic sources in this region. The gas is released from relatively small mud volcanoes and seepage areas, most of them currently exhibiting a weak activity. The mud volcanoes are often covered by a crust of dry mud. The closed chamber method with in-situ measuring of the methane flux has been used for assessing the gas output from the seeps. The methane fluxes measured on 20 seeps distributed in the eastern part of the Moldavian Platform are in the range of $10^2 – 10^6$ mg m^{-2} d^{-1}. The calculated output of the individual gas seeps varies in the range $10^{-3} – 10^1$ t y^{-1} CH_4. The observed activity of the gas seeps seems to be lower than several decades ago, as described in the literature. No commercial oil and/or gas reservoirs are known in the investigated area, although some exploration wells have been drilled, and low amounts of gas have been found. The obtained data allows a better understanding of the natural degassing process on the Moldavian Platform. The gas-emitting features are relatively densely distributed, especially along rivers, suggesting the importance of erosion in creating pathways for the degassing of sediments. This first set of data is of particular interest as a baseline for any future hydrocarbon exploration works, especially taking into account the inferred shale gas potential of the Moldavian Platform. The present work also contributes to the enlargement of the Romanian and global databases of methane flux to the atmosphere.

Keywords: greenhouse gases, methane emission, mud volcanoes, gas seepage, Moldavian Platform.

1. INTRODUCTION

Methane seepage is a relatively common process in hydrocarbon-prone areas throughout the world. Seeps may appear at the ground surface as mud volcanos, dry gas emitting areas, or gas-rich springs. The methane apparition at the surface may indicate the existence of hydrocarbon accumulations, not necessarily with an economic potential. Earth degassing generates an important contribution to the atmospheric budget of greenhouse gases, especially methane and carbon dioxide. The total output of methane released by the geological seepage in Europe was estimated at about 3 Tg yr^{-1} (Etiope, 2009). On a global scale, the total output of methane from geologic sources is approximated at 60 Mt y^{-1}, most than half of it being released by mud volcanoes and gas seepage from sedimentary basins (Etiope, 2012) This important amount of geogenic methane is worth to be taken into account in the atmospheric budget of greenhouse gases, as recognized by IPCC (2013).

Numerous gas seeps have been identified and described in the scientific literature in Romania. The biggest Romanian mud volcanoes are located in the East Carpathian Foredeep (Paclele Mari and Paclele Mici mud volcanoes), with a continuous and vigorous activity and prominent positive relief forms (Etiope et al., 2004). Strong dry emissions of methane, generating everlasting fires, are also present in the Carpathian Foredeep and flysch areas. The Transylvanian Basin, a Neogene back-arc unit with important gas reservoirs, hosts tens of gas seeps, appearing as small mud volcanoes or dry emissions (Spulber et al., 2010). On the Moldavian Platform, gas emissions have been described for the first time more than 100 years ago (Simionescu, 1903). Later on, more detailed studies were published by Enculescu (1911) and Sevastos (1914). Some localities with gas emissions were mentioned by Tufescu (1937). Further data about the existence and location of mud volcanoes on the Moldavian Platform were published by Peahă (1965). All these works are based only on visual observations; no instrumental measurements of the gas flux have been performed so far.

The current work gives a thorough description of the gas manifestations (mud volcanoes and seepage areas), and presents the results of the first methane flux measurements performed on the Moldavian Platform. Based on the existing literature data, a field campaign was designed and carried out in 2013 for identifying the gas manifestations and measuring the methane flux. A number of 47 sites mentioned in the literature have been surveyed in order to verify the occurrence of the methane emissions.

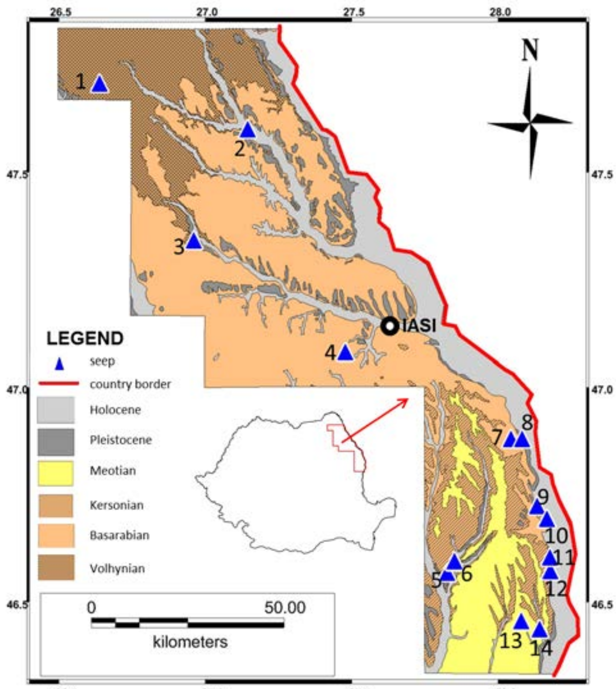


Figure 1. Geological map of the Moldavian Platform and location of the investigated sites: 1 – Curtesti, 2 – Hlipiceni, 3 – Cotnari, 4 – Vocotesti, 5 – Manjesti Deal, 6 – Manjesti Coada Iazului, 7 – Cozmesti, 8 – Gorban, 9 – Chersacosu, 10 – Poganesti, 11 – Stanilesti, 12 – Otetoaia, 13 – Musata, 14 – Berezeni.

2. GEOLOGIC SETTING AND STUDY SITES

The Moldavian Platform is considered to be the oldest platform unit in Romania and corresponds to the south-western extremity of the large East European Platform (Ionesi 1994). It is a crustal block with Proterozoic basement, covered by a pile of sediments with thicknesses of 6 to 12 km towards the western margin, which becomes gradually thinner to the East. The Moldavian Platform is in contact along Bistrita Fault with the Scythian Platform, a relatively narrow continental block, with a younger Palaeozoic basement. The Scythian Platform is extending to the north-west, and its characteristics have been recognized between Solca and Câmpulung-Bicaz faults. Towards north and east, the Moldavian Platform is conventionally delimited by the state border.

The basement of the Moldavian Platform consists of crystalline schists intensely metamorphosed (plagioclase paragneisses, quartz-feldspar gneisses) crossed by granitic intrusions and with some dispersed basalt veins. The metamorphites support a sedimentary cover including three sedimentation cycles separated by major unconformities (Mutihac, 1990). The first cycle (Upper Vendian – Carboniferous) is mainly detrital, with layers of carbonate rocks and argillites. The Upper Jurassic – Cretaceous cycle predominantly includes carbonate rocks. The sedimentary succession continues in some marginal areas of the Platform with Paleocene and Eocene detrital rocks. The formations of the third cycle (Badenian – Lower Pliocene) have the biggest extension in surface (Fig. 1). They consist of alternating strata of sands, limestones, marls and clays.

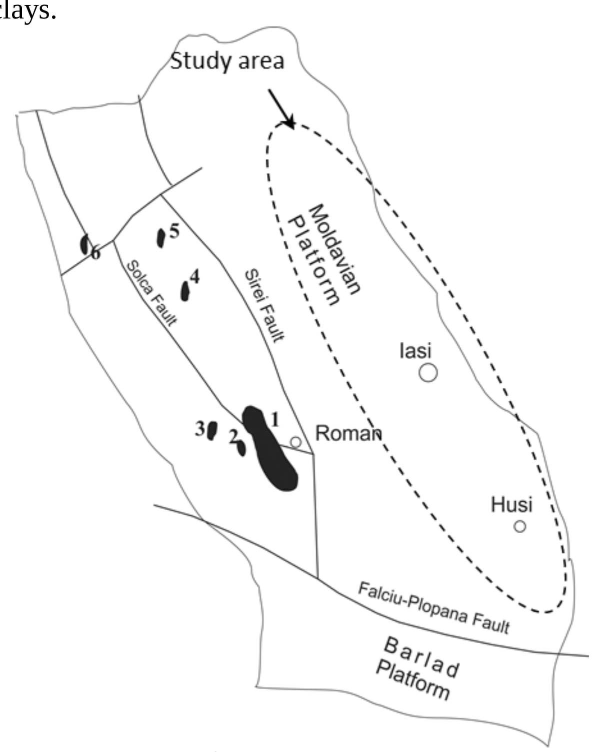


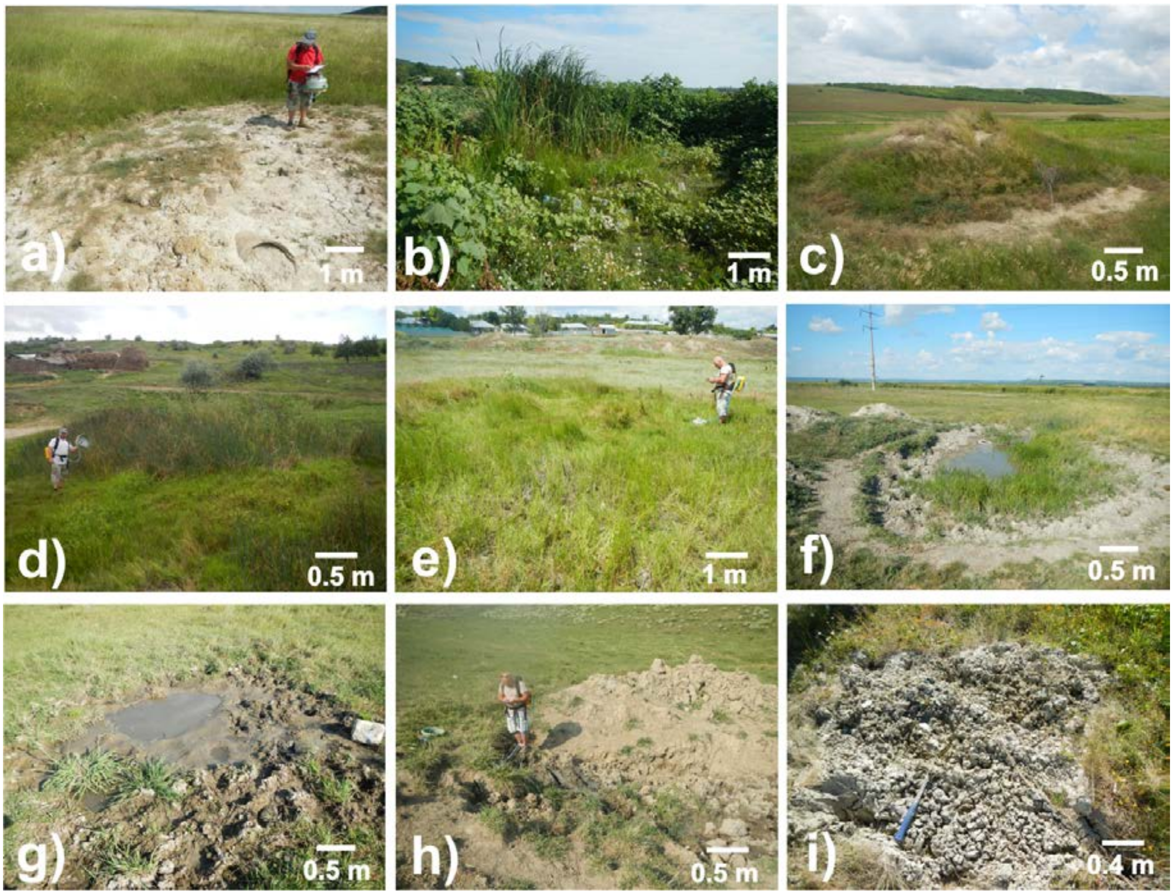
Figure 2. Position of the investigated area relative to the known commercial hydrocarbon reservoirs. Gas-bearing structures: 1-Roman-Secuieni; 2-Margineni; 3-Cuejdiu; 4-Malini; 5-Valea Seaca; 6-Frasini (Beca & Prodan, 1983).

The general appearance of the Miocene deposits on the Moldavian Platform suggests a vast monocline, sinking westward to the Carpathian Foredeep, and southward, to the Bârlad Depression. Pelitic rocks rich in organic matter that could play the role of source rocks occur in the Proterozoic – Lower Palaeozoic strata, as well as in the Middle Miocene. Potential reservoir rocks have been identified within the Vendian - Palaeozoic formations (detrital intercalations), the carbonate deposits and sandstones of Mesozoic cycle, and the Badenian - Sarmatian sands and sandstones (Paraschiv, 1979). Relatively few hydrocarbon deposits are known on the Moldavian Platform until now. All of them are confined to Badenian and Sarmatian formations, on the western side of the platform. Paraschiv (1979) inventories mainly gas and condensate deposits, at Frasin-Gura Humorului, Mălini, Cuejd, Valea Seacă, Roman-Secuieni, and Bacău (Fig. 2). Excepting the Roman-Secuieni gas field, all others are small. Insignificant occurrences of gas have been also found in other areas of the Moldavian Platform, at Iași, Hârlău, Pașcani, etc., proving the hydrocarbon generating potential of the Miocene sediments, although the reservoirs able to store the gas are lacking.

The investigated sites are located on the eastern side of the Platform, between Siret and Prut rivers, in Vaslui, Iași, and Botoșani counties (Fig. 1). In most of the cases, the gas is emitted by small features, appearing as dome-shaped bodies, up to 10 m in diameter and not exceeding 1.5 meters in height. In some cases, the water is present and a weak gas bubbling activity was observed. No mud flow has been observed during the field work. Similar to other locations, the mud volcanoes probably are more active during the rainy seasons. Beside mud volcanoes, gas seepage areas without the typical morphology of mud volcanoes occur. Such areas have a diameter between 2 and 15 meters, they are generally flat, and more humid than the surrounding zone. Some of them are partially covered by vegetation. Due to the low degree of compaction of sediments and the presence of fluids, the ground of the mud volcanoes and seepage areas trembles when a person steps on.

3. MATERIALS AND METHODS

Methane fluxes have been measured by using the closed chamber technique. 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 (e.g. Spulber et al., 2010; Etiope et al., 2011).



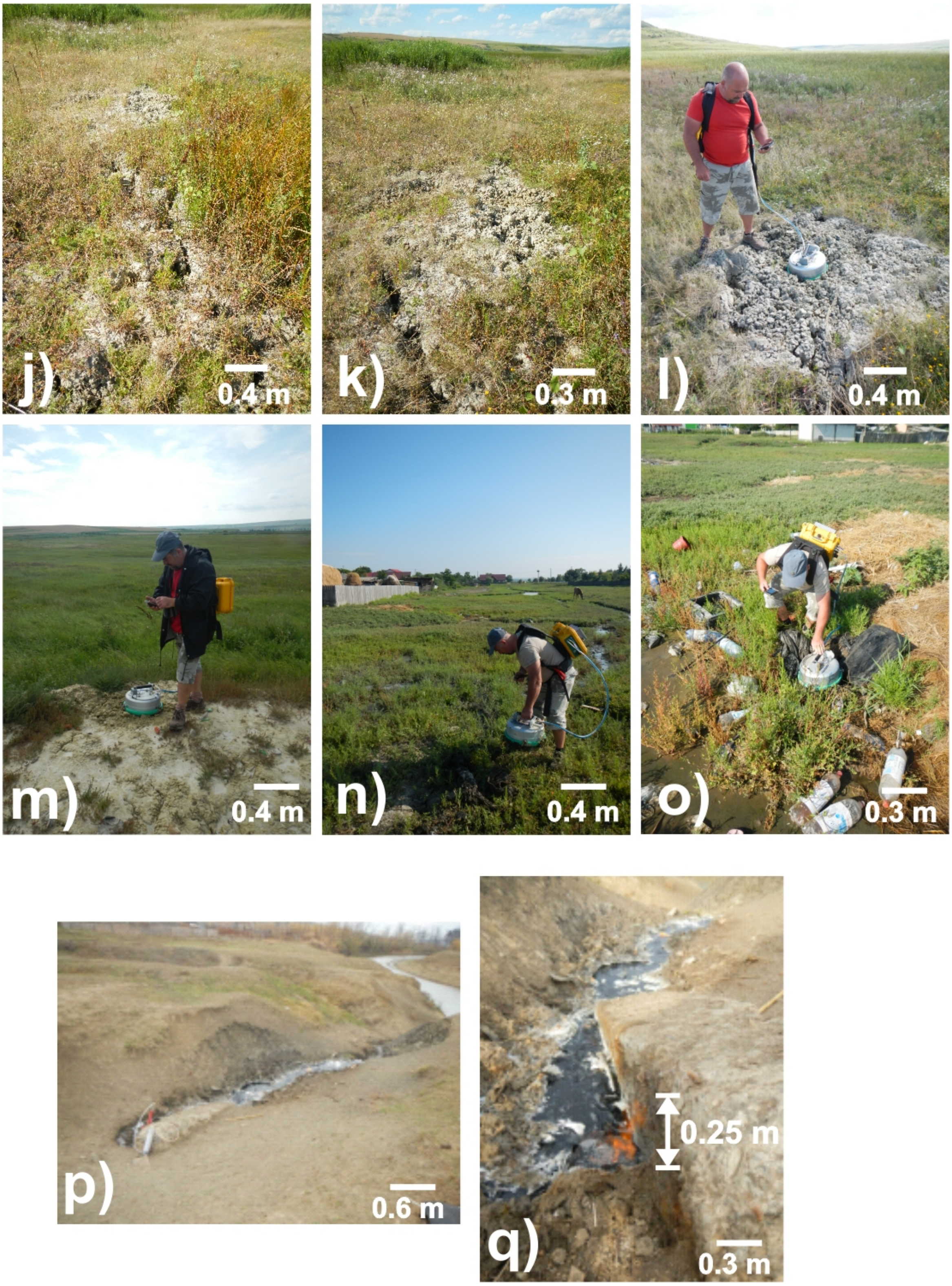


Figure 3. Gas seeps from the Moldavian Platform: a – Vocotesti; b – Gorban; c – Cozmesti; d – Chersacosu; e – Stanilesti; f,g – Oțetoaia; h – Curtesti; i,j,k,l – Manjesti; m – Cotnari; n, o – Poganesti; p,q – Hlipiceni abandoned well.

If the rate of increase of gas concentration in the chamber is constant, the linear regression method can be used to calculate the gas flux (F) with the following equation (Livingston & Hutchinson, 1995):

$$F = \frac{V_C}{A_C} \cdot \frac{c_1 - c_2}{t_1 - t_2} \quad [\mathrm{mg \cdot m^{-2} \cdot day^{-1}}] \qquad (1)$$

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 three detectors: a semiconductor one (range 0-2,000 ppmv, detection limit 1 ppmv, resolution 1 ppmv), a catalytic one (range 2,000 ppmv – 3% v/v) and a thermal conductivity one (range 3-100% v/v).

The measuring points were distributed following regular sampling grids, with variable spacing from 0.5 to 2 m, depending on the features of the investigated area. The type of gas manifestation, dimensions, surface appearance, GPS coordinates were noted, and digital photographs have been taken at each location.

The natural neighbour interpolation method was used for calculating the methane output for the sites where a sufficient number of measurements was available.

4. RESULTS AND DISCUSSION

A field campaign has been completed in 2013 in the eastern part of the Moldavian Platform, consisting of identification of the sites with gas emissions, description of the seeps, and gas flux measurements. A short description of the investigated sites is presented in the following paragraphs. The fluxes of methane are summarized in table 1.

Cotnari (Fig. 3m) mud volcano is a 0.5 m high cone with an elongated elliptical shape (a length of approximately 11 m and a width of 1.5 m) covered by a dry crust without visible mud flow. The highest recorded flux is around 9 g m^{-2} day^{-1} CH_4. A total output of 0.01 t year^{-1} CH_4 was estimated from 10 measuring points. Nearby there are several small (1 to 2 m^2) mounds, without visible mud flow or activity.

Gorban (Fig. 3b) – a 1-m high cone with circular shape (3 m in diameter) covered by rich vegetation, without visible mud flow has been identified. The maximum measured flux is around 270 g m^{-2} day^{-1} CH_4.

Berezeni feature consists of 3 cones, 0.3- to 0.4-m high, with elongated shapes (length between 2 and 8 m and width between 1.5 and 3 m), and covered by dense vegetation. They are located on a same line, at distances of 10 m and 7 m apart. No gas bubbling has been noticed. The highest recorded flux is around 300 g m^{-2} day^{-1} CH_4, a total output of 0.73 t year^{-1} CH_4 was estimated from 10 measuring points.

Manjesti (Fig. 3i) mud volcano appears as a 1.5-m high cone with irregular shape (length of approximately 6.6 m and width of 4.4 m) partially covered by vegetation. Old mud flows are visible and a very weak water flow was observed in the middle part of the cone and on the edge. The measured flux is around 8000 mg m^{-2} day^{-1} CH_4.

Manjesti Coada Iazului (Fig. 3j, k, l) – four small mud pools were identified (1 to 3 m in diameter), covered by a dry crust and partially by poor vegetation. Three of them are close to each other, and the fourth is located some 200 m apart. No mud flow has been observed. Gas emissions are quite low. Flux measurements have been performed in 6 points. The highest recorded flux is around 30g m^{-2} day^{-1} CH_4.

Table1. Methane emissions from geologic sources on the Moldavian Platform

No. site	Site	No. measurements	Area (m^2)	Range flux CH_4 (mg m^{-2} day^{-1})	Output CH_4 (t y^{-1})
1	Cotnari	10	27	200 - 9,000	0.01
2	Gorban (Izlaz)	3	7	45,000-270,000	N/A
3	Berezeni (Ferma Sarata 1+2+3)	10	30	2,500-300,000	0,73
4	Manjesti	3	29	7,600-7,800	N/A
5	Manjesti (Coada Iazului 1)	2	9	18,000-31,000	N/A
6	Manjesti (Coada Iazului 2+3+4)	4	13.5	1,200-8,400	N/A
7	Cozmesti	3	54	200-8,000	N/A
8	Musata (Cumpăna)	7	113	200-8,000	0.05
9	Vocotesti	2	28	Nil	Nil
10	Chersacosu (Budai)	21	108	200-350,000	3.45
11	Poganesti 1	4	7	8,000 -120,000	N/A
12	Poganesti 2	2	13	18,000-2,000,000	N/A
13	Stanilesti (Pichet)	10	28	4,000-3,300,000	2.65
14	Otetoaia 1	3	7	7,000-8,000	0.02
15	Otetoaia 2	5	5	50,000-1,200,000	0.78
16	Curtesti (Fantana lui Tiganu)	3	5	200-1,600	N/A
17	Leosti	5	5	0-8,000	0,001
18	Hlipiceni	3	N/A	N/A	11

Vocotesti (Fig. 3a) is a small mound about 7x4 m wide, with irregular shape. No mud flow or breccia sediments were observed, therefore it is not possible to confirm whether it is really a mud volcano. Anyway, we did not detect any methane exhalation.

Cozmesti (Fig. 3c) is a 1.5 m high cone with a length of 9.4 m and a width of 5.7 m covered by a dry crust and partially by vegetation, without visible mud flow. Methane fluxes measured in 3 points are relatively low. The highest measured flux is around 8 g m^{-2} day^{-1} CH_4.

Musata is a small flattened cone 2 m in diameter, covered by a dry crust and partially by vegetation, without visible mud flow. The gas emissions are very low, with the highest recorded flux around 8 g m^{-2} day^{-1} CH_4.

Chersacosu (Fig. 3d) is a 300 m^2 flat and swampy area located at the base of a hillslope. The whole area is covered by dense vegetation. Within the low lying area, there is a sulphurous spring, that was developed some years ago by the local community. According to the local people, there used to be a mud volcano on the same place, but the mud release stopped once the development works have been done. The methane flux was measured in 21 points. The highest recorded flux is around 367 g m^{-2} day^{-1} CH_4 and a total output of 3.45 t CH_4 $year^{-1}$ was estimated.

Poganesti includes two seepage areas, about 2 m in diameter (Fig. 3n, o), covered by plant debris. The distance between the seeps is about 15 m. The maximum measured flux is around 2000 g m^{-2} day^{-1} CH_4.

Stanilesti (Fig. 3e) is a 220 m^2 flat and swampy seepage area covered by vegetation. The highest recorded flux is around 3300 g m^{-2} day^{-1} CH_4. A total output of 2.65 t $year^{-1}$ CH_4 was estimated from 10 measuring points distributed on 28 m^2.

Oţetoaia – two gas emission areas have been identified. The first one appears as a water pool 1.5 m in diameter, surrounded by a vegetated wet area, 3 m in diameter (Fig. 3f). The second one is a wet area, about 2 m in diameter (Fig. 3g), surrounding a bubbling water pool, 0.5 m in diameter. A curious periodical slow raise of the water level, followed by decline, can be observed at intervals of tens of minutes. When the water fills the crater, gas bubbling can be observed. The diameter of the pool varies between 0.5 and 2 m depending on the water level. The highest recorded flux is around 1200 g m^{-2} day^{-1} CH_4 and a total output of 0.80 t $year^{-1}$ CH_4 was estimated from 8 measuring points.

Curtesti (Fig. 3h) is a 3 m^2 irregular seepage area with mud and water. Gas emissions are very low, and no bubbling has been observed. The highest recorded flux is 1.6 g m^{-2} day^{-1} CH_4.

Leosti includes five degassing areas, each of them smaller than 2 m^2, widespread on about 1 ha. The highest measured flux does not exceed 8 g m^{-2} day^{-1} CH_4.

Hlipiceni (Fig. 3p, q) is an abandoned drilled well, located on the right bank of Jijia River. The drilling was carried out to a depth of 200 meters. Currently, only a small portion of the tubing is visible, from which bubbling water flows out. Due to the very high flux, the released gas can be ignited, and the flames may reach 20-25 cm in height. Three consecutive measurements were performed, and the total output was estimated as an average, based on the three measurements, at 11 t $year^{-1}$ CH_4.

The measured flux in the investigated sites is in the range of 10^2 to 10^6 mg m^{-2} day^{-1} CH_4, and the areas with indications of current or previous activity rarely exceed several tens of square meters. Compared to other regions with methane emissions in the world, these manifestations can be considered as small. However, the seeps are relatively densely distributed on a large area of the Moldavian Platform, thus indicating the extension of the gas releasing formations. The output of the individual gas emitting areas that have been investigated on the Moldavian Platform is in the order of 10^{-3} to 10^1 t $year^{-1}$ CH_4, most of them are releasing less than 1 t $year^{-1}$ CH_4. The gas emissions are mainly distributed along river valleys. Taking into account the geological context of the Moldavian Platform, with tabular and almost horizontal Neogene strata, this observation may suggest a slow degassing of the Neogene sediments that is facilitated by the incision of the valleys. There is a hydrocarbon generating potential of the sediments, however no important accumulations have been formed, presumably due to the lack of appropriate structural/lithologic conditions for creating effective traps. Popescu (1995) has defined a Central Moldavian Petroleum System that includes Silurian shale source rocks and Miocene clastic reservoirs. Some wells have been drilled at Hârlău, Iași and Pașcani, but all of them have been abandoned due to the low economic potential, although gas has been found. The Central Moldavian Petroleum System, as delimited by Popescu, partly overlaps our study area. However, no commercial hydrocarbon reservoirs are known from the area.

We were not able to retrieve in the field all the gas emitting features described in the old literature. Only 20 gas manifestations have been found, compared to 47 that have been described in the literature. It is very likely that many of them have disappeared due to natural causes, or to the land use change induced by humans. As an example, Enculescu (1911) has observed much more gas emitting features, some of them with a vigorous activity. Comparing our observations with the descriptions from the literature, the seeps that still can be found in the field seem to be less active than they were one century ago, at the time of the first description. Most of the mud volcanoes are covered by a crust of dry mud. According to local people, the emissions are stronger, and more visible mud flow occurs during the rainy season. This phenomenon has also been observed in other areas with gas emissions.

According to US EIA (2013) the Carpathian Foreland is a prospective shale gas area in Eastern Europe. The area investigated in the present work partly overlaps an inferred shale gas play corresponding to Silurian shales. Exploration works have recently been initiated. Our survey is important as a first assessment of the gas seepage naturally occurring in the area. Controversies related to the origin of such gas emissions have arisen in gas shale development areas worldwide.

5. CONCLUSIONS

Small mud volcanoes and gas seepage areas occur on the Moldavian Platform. In many of the cases, the mud volcanoes do not exhibit a visible activity. The present paper, for the first time gives a quantitative estimation of the gas emission from seeps on the Moldavian Platform. The methane output for the individual gas seeps varies in the range $10^{-3} – 10^{1}$ t y^{-1} CH_4. Although these values are low, the distribution of the methane emissions provides information on the mechanism of the degassing process that occurs on the Moldavian Platform. This geological unit is also a shale gas prospective area, currently explored by wells, and it is important to outline the existence of a natural degassing process. The completed survey contributes to the definition of a baseline concerning the methane emission in the area. This first survey on the gas emissions from the Moldavian Platform adds new data to the Romanian and the global database of methane release to the atmosphere from geologic sources. The performed measurements can be resumed in the future with more detailed and precise determinations, in order to better evaluate the microseepage, and consequently, the total output of methane to the atmosphere.

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