BABEŞ-BOLYAI UNIVERSITY

FACULTY OF ENVIRONMENTAL SCIENCE

PhD THESIS
(Summary)

GEOGENIC EMISSIONS OF METHANE IN TRANSYLVANIA AND THEIR ENVIRONMENTAL IMPLICATIONS

Scientific coordinator:

Prof. Univ. Dr. **Şerban-Nicolae Vlad**

PhD student:

Liana Spulber

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Note: Tables and figure numbers in this paper are the original ones used in the thesis

INTRODUCTION

Methane is the most abundant hydrocarbon from the atmosphere and one of the main greenhouse gases. Methane emissions from soils situated above hydrocarbon accumulations are found in multiple petroleum-gas systems.

The Transylvanian Basin, one of the largest hydrocarbon basins from the continental Europe, is characterized by the presence of multiple zones with high methane degasifications. Macroseeps (mud volcanoes, everlasting fires, and gas-water seeps) or diffuse emissions from soils in the area of gas deposits are geological methane sources and the study of these represents the main purpose of this paper.

Estimation of methane flux from geogenic sources proved to be in the past years a significant element in better delineating the methane budget on a global scale.

The main purpose of this thesis is the identification of as many areas with a geogenic source potential as possible, while performing measurements with the purpose of estimating methane emissions for every investigated area.

Chapter I – General Geological Setting

The Transylvanian Basin is recognized by most authors as being a sedimentary basin, situated inside the Carpathian Romanian arch, hosting important hydrocarbon deposits. It extends on an area of approximately 20000 km^2 (POPESCU, 1995; CIULAVU ET AL., 2000) and has a sedimentary fill with a thickness that surpasses 5 km, even 8 km in some areas (CIUPAGEA ET AL., 1970; CIULAVU ET AL., 2000). The forming and evolution of this basin spurred different opinions from one author to another.

History of the Transylvanian Basin is tied to the evolution of the central Paratethys domain and changes that interfered marking it tectonically or ecologically influenced the basin too.

Recognized at the European level as an important hydrocarbon basin, the presence of methane gas is mentioned for the first time in literature in 1863 by HAUER and STACHE. WANEK (2005) clarifies the history of discovering gas in the Transylvanian Basin, differentiating three stages. Thus, the first mentioned gas discovery is attributed to some shepherds in year 1671, in the vicinity of Bazna, where gas instantaneously ignited; the second discovery (1807-1808) was due to the study of gas emissions led by Ferenc Nyulas, András Gergelyffi and György Mészáros; the third mention and until recently the most well known report, places the discovery of the first methane gas deposit in Romanian in 1909, when the Sărmăşel well exploded.

The Transylvanian Basin is situated on the 56th place in the world based on its size and accounts for 0.2% of the world's gas and petroleum resources, as presented in the USGS World Energy 2000 (PAWLEWICZ, 2005) report.

Two petroleum systems are now recognized in the Transylvanian Basin, while a third is considered speculative. The first and most important, the *Transylvanian System* (12,000 km^2; Middle to Late Miocene), hosts the largest gas reserves in Romania but did not generate oil (POPESCU 1995). The system includes the main seepage systems (PAWLEWICZ 2005) and therefore will be examined in greater detail below. The second system, *Deleni* (Jurassic and Cretaceous), generated oil in the carbonate series (POPESCU 1995, KOVÁCS ET AL. 2007) with no commercial accumulations. Dry gas was likely generated by thermal maturation that was reached in the carbonate rocks (KRÉZSEK ET AL. 2010). A third speculative system is named *NW Transylvanian (Jibou)* (Late Cretaceous to Early Miocene) and is located in the post-tectonic sedimentary-fills Gilău-Maramureş and Someş. It extends south-east under the Transylvanian Basin (POPESCU, 1995).

Chapter II –Earth's energy budget and Greenhouse Gases

Chapter II discusses Earth's radiative exchange balance, the greenhouse effect, as well as the main gases responsible for producing it under the aspect of major characteristics (sources, atmospheric lifetimes, sinks and emissions budget).

Main gases responsible for producing the greenhouse gas effect in the atmosphere are: water vapors (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and ozone (O_3). Furthermore, there are a number of greenhouse gases produced entirely by human activities, such as halocarbons and other substances that contain chlorides or bromides, mentioned in the Montreal Protocol. Aside CO_2, N_2O and CH_4, the Kyoto Protocol added in the category of greenhouse gases sulphur hexafluoride (SF_6), hydrofluorocarbons (HFC) and perfluorocarbons (PFC).

Chapter III - Methane

In chapter III the main element of this paper, methane, is detailed. Methane was treated as a chemical compound, but the origin and modality of forming in geological environments was also insisted on, accentuating on pointing out its greenhouse character.

Methane is formed in a natural way, but can be the result of several human activities too. In nature, this gas is formed as a result of many processes from the biosphere, atmosphere and geosphere.

Table 3.1

Origin of methane sources (modified after JUDD, 2000*)*

Source type	**Category**	**Escape pathways**	**Time from source to escape**	**^{13}C‰**	**Depths**
Microbial degradation of organic matter in sediments – *current activity*	biogenic	- diffusion - bioturbation - seepage	days → years	-60 to -70‰	few meters ↓
Microbial degradation of organic matter in sediments – *past activity*	biogenic*	- seepage - diffusion - mud volcanoes	years → tens of millions of years	-60 to -70‰	tens of meters
Thermal degradation of organic matter in sediments / sedimentary rocks	thermogenic*	- seepage - diffusion - mud volcanoes	millions → hundreds of millions of years	-20 to -52‰	1-4 km (dependent on upon geothermal gradients)
Abiogenic sources	abiogenic*	Volcanic geothermal hydrothermal activity etc.	→ billions of years	-5 to -45‰	grater depths in crust or underlying mantle

*fossil methane

The origin of methane in geological environments is synthesized by JUDD (2000) in **Table 3.1** after MACDONALD, 1993; SCHOELL, 1988; KADKO ET AL., 1995 and WHITICAR (2000). Sources can be structured in three categories: biogenic, thermogenic and abiogenic, as a result of four source types, discussed all through this chapter.

Methane (CH_4) is the third most important greenhouse gas responsible for the intensification of the Greenhouse Effect, after water vapors and carbon dioxide (CO_2), thus being among gases responsible for Planet's climatic changes. Methane has a global warming potential 25 times larger than carbon dioxide's (GWP for a given time horizon of 100 years). Its concentration is almost 200 times smaller than carbon dioxide's. Lifetime of CH_4 in the atmosphere varies between 7-12 years, a mean lifetime being around 8.4 years.

Methane emissions from different sources contribute to a global total with approximately 600 Tg/y, out of which 60% are due to human activities such as agriculture, the use of fossil fuels and waste deposits.

The total methane sources (the ratio between burden and lifetime) are 598 Tg/y, the sink being 576 Tg/y, and the atmospheric increase resulting from the difference between the two values being 22 Tg/y.

Estimations made by the Intergovernmental Panel on Climate Change in 2001 highlight the existence of a methane surplus which isn't attributed to any source. Therefore, this disequilibrium must be due to an important methane source, such as emissions from geogenic sources, not taken into consideration until recently (ETIOPE, 2004).

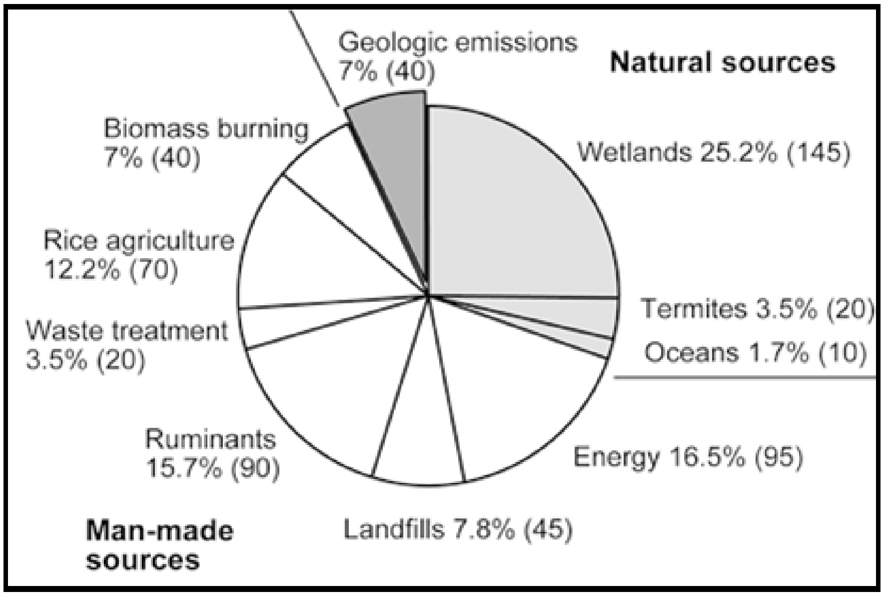

Fig. 3.5 Atmospheric methane sources after IPCC 2001 and emissions from geologic sources (Tg) y^{-1} *(modified after* ETIOPE, 2004*)*

According to Etiope (2004), the total of medium values of all the sources offered by IPCC, 2001 is 548 Tg y^{-1}, resulting a surplus of 50 Tg y^{-1} due to the difference between sources and consumption. This surplus can be covered by geogenic methane sources, which can contribute with a value of methane emissions of 40-60 Tg y^{-1} and a mean value of 50 Tg y^{-1} (**Fig. 3.5**). Results show clearly that the geogenic sources aren't insignificant and actually have an important role in the budget of greenhouse gases in our atmosphere.

Estimations related to geological methane sources having an impact on the budget of this greenhouse gas, have been made by researchers as ETIOPE & KLUSMAN, 2002; JUDD ET AL. 2002; ETIOPE, 2004; KVENVOLDEN & ROGERS, 2005.

In 2007, the Intergovernmental Panel on Climate Change accepted the contribution of geogenic methane emissions among the sources which increase the methane global budget.

The majority of studies suggest that significant amounts of CH_4, produced within the Earth's crust (mainly by microbial and thermogenic processes), are released into the atmosphere through faults and fractured rocks, mud volcanoes on land and the seafloor, submarine gas seepage, microseepage over dry lands and geothermal seeps. Emissions from these sources are estimated to be as large as 40 to 60 Tg (CH_4)/y.

Chapter IV – Characterization of main types of geogenic manifestations

Methane emissions recorded from sedimentary hydrocarbon basins derive from different types of geogenic manifestations, such as mud volcanoes, everlasting fires, gas-water seeps or in soils above gas deposits.

This chapter details genetic aspects, morphological types and evolutionary stages of mud volcanoes. In time, several genesis were indicated as being responsible for the formation of mud volcanoes (SENCU, 1985; KHOLODOV 2002), however the genesis *accepted today by most of the researchers, in order to explain the formation of mud volcanoes, is exclusively attributed to sedimentary basins with hydrocarbons.*

The morphologic classifications and terminology used for mud volcanism nationally and internationally, as well as an up-to-date inventory regarding the distribution of mud volcanoes in Transylvania are well described in this chapter.

The classification proposed by ALIYEV ET AL. (2009), includes terrestrial and aquatic mud volcanoes. Terrestrial volcanoes can be active or extinct (inactive for over 100 years) but also fossil/buried (their activity stopped in past geological times; destroyed cones and the volcano structure itself buried in sediments). Underwater volcanoes are either localized at the bottom of the sea, or appear as islands.

Classification above is applicable for intensely monitored regions, where volcanic structures were studied for a long time. *For mud volcanoes from the Transylvanian Basin, due to precarious bibliographic data as well as lack of interest for these phenomena in time, a simplified classification was proposed that reduces to separating the mud volcanoes by their activity state in: active volcanoes, inactive (with recent flow traces) and fossil (difficult to establish, due to topographic changes that interfered).*

Mud volcanoes from Transylvania have attracted the attention of researches once the first field works were done after 1910, when these phenomena were associated with salt and gas reservoirs. A first classification of the “Gloduri” was done by VANCEA in 1929A, followed by BÁNYAI (1932).

Present distribution, with contributions from the author, of mud volcanoes and other gas seeps from the Transylvanian Basin is summarized in **table 4.2** and **figure 4.12.**

In the category of macroemissions, other than mud volcanoes, three other case studies were included in this paper. Thus, dried gas emissions from the Sărmăşel everlasting fires (BACIU AND ETIOPE, 2002; SPULBER & BACIU, 2007; SPULBER ET AL., 2009; 2010), are detailed in the first case study. An emission mentioned for the first time in literature, that doesn’t have to be omitted from the suite of lithosphere degasifications, is the one from Praid (HR) (SPULBER & BACIU, 2007; SPULBER ET AL., 2009; 2010). The last one is represented by the manifestation of gas and salt water seeps from Deleni (MS).

Everlasting fires represent emissions of dry gas that reach the surface and burn naturally for a longer period of time.

There are situations when the flames are put away by unfavorable meteorological conditions, but a characteristic for the everlasting fires is the fact that when the weather gets better, they spontaneously reignite. Areas around the flames are powerful gas sources, sometimes by “stoking” the ashes you can easily obtain a flame. The gas flow is influenced by the level of precipitations and aquifers.

Another particularity of the everlasting fires is the instability of the chimney. Tectonic conditions or layer permeability can cause the displacement of the fire on certain distances, usually not very large (the case of Sărmăşel everlasting fires, for which the chimney where the fire burns is often moving).

The literature doesn’t point very well, maybe because of the vulnerability of these phenomena in time, the age after which a natural fire is considered an everlasting one.

In Romania are known the everlasting fires from the area of Subcarpaţilor de Curbură, in the region of Vrancea (Andreiaşu de Jos, Tulnici) and Buzău (Terca and Ploştina, both villages being part of Lopătari) counties. An everlasting fire is mentioned in the Vrancea Mountains, on the right side of the Văii Strâmbă, the lower flow, affluent of the Lepşa creek, being the only one mentioned as found in mountains. The everlasting fires from Terca and Andreiaşu de Jos are protected areas. In Transylvania we find the Sărmăşel everlasting fire, Mureş county. VANCEA (1929B) mentions other locations with everlasting fires at Şaroş (MS), Bazna (SB), Copşa Mică (SB).

Miniemissions (SPULBER ET AL., 2010) and methane macroemissions from the Transylvanian Basin, as in any other hydrocarbon prone basin, are possible throughout the entire basin.

Measurements of miniemissions were performed mainly in areas close to structures that generated macroemissions (for instance the flanks of mud volcanoes, area around the everlasting fires chimneys) but also regions situated as much as possible on top of gas deposits, where no visible manifestations were found. Microemissions were measured at distances larger than the source of macroemissions, sometimes independent from these.

The difference between the two consists in the order of magnitude, miniemissions being fluxes of methane in the order of 10^2-10^3 mg m^{-2} day^{-1}, while microemissions defined in the previous chapter are situated in between 10^1-10^2 mg m^{-2} day^{-1}.

Such measurements were performed in a random manner, in soils from the perimeter of known gas domes (from the literature), in several places in the Transylvanian Basin (e.g. Bazna (SB), Buneşti (BV), Cucerdea (MS), Târnăveni (MS), Zau de Câmpie (MS) etc.), as well as in soils that have nothing to do with geogenic methane sources.

Table 4.2 Distribution of mud volcanoes and gas seeps/degasifications in the Transylvanian Basin

		ANDRAE - 1853	VANCEA - 1929a	VANCEA - 1929b	BÁNYAI - 1932	VANCEA - 1942	BARTKO - 1943	PEAHĂ - 1965	PAUCĂ – 1969	CIUPAGEA et al. - 1970	FLOREA - 1985	SENCU - 1985	GÁL - 2005	BACIU&ETIOPE - 2002	SPULBER&BACIU - 2007	SPULBER et al. - 2009/2010
1.	Aiud (AB)					x			x	x		x				
2.	Aiud-Băgău (AB)									x						
3.	Apold (MS)									x		x				
4.	Archita (MS)				x											
5.	Avrig (SB)								x	x		x				
6.	Bazna (SB)			o												
7.	**Băile Homorod (BV)**								**x**		**x**			**x**	**x**	**x**
8.	Bercheşiu (CJ)		x													
9.	Beţa (AB)					x		x	x	x		x				
10.	**Boz (AB)**							**x**								**x**
11.	Călăraşi (CJ)					x		x	x							
12.	Ceanu Mare (CJ)		x													
13.	Cenade (AB)					x		x	x	x		x				
14.	**Cobăteşti (HR)**				**x**		**x**						**x**			**x**
15.	Copşa Mică (SB)			o												
16.	Corund (HR)				x					x		x	x			
17.	Crăciunel (HR)				x											
18.	Cristuru Secuiesc (HR)				x								x			
19.	Dârjiu (HR)				x											
20.	**Deleni (MS)**			**o**											**o**	**o**
21.	Dumbrava (AB)					x		x	x	x		x				
22.	Făgăraş (BV)									x		x				
23.	**Filiaş (HR)**				**x**								**x**		**x**	**x**
24.	Frata (CJ)		x													
25.	Ghijaşa de Sus (SB)					x			x	x		x				
26.	Goagiu (HR)				x											
27.	Guşteriţa (SB)								x	x		x				
28.	**Haşag (SB)**					**x**		**x**		**x**	**x**	**x**			**x**	**x**
29.	Homorod (BV)									x		x				

30.	Iclod (AB)							x								
31.	Jimbor (BV)				x											
32.	Loamneş (SB)									x		x				
33.	Ludoş (SB)								x							
34.	Lupu (AB)					x		x	x	x		x				
35.	Măhăceni (AB)					x		x	x	x		x				
36.	Mănărade (AB)								x							
37.	Mărculeni (MS)								x							
38.	Mărtiniş (HR)				x		x									
39.	Merghindeal (SB)								x							
40.	Mihăileni (HR)				x		x									
41.	Miheşu de Câmpie (MS)		x													
42.	**Monor (BN)**															**x**
43.	Morăreni (HR)						x									
44.	Ocnişoara (AB)							x								
45.	Odorhei (HR)				x								x			
46.	Pănade (AB)							x								
47.	Pogăceaua (MS)									x		x				
48.	**Porumbenii Mici (HR)**				**x**		**x**						**x**			**x**
49.	**Praid (HR)**														**o**	**o**
50.	Reghin (MS)									x		x				
51.	Rugăneşti (HR)				x											
52.	Ruşi (SB)	x						x								
53.	Sânbenedic (AB)								x							
54.	Sângeorgiu de Pădure (MS)				x								x			
55.	Sânger (MS)		x							x		x				
56.	Sânpaul (HR)				x											
57.	Saschiz (MS)									x		x				
58.	Săcădate (SB)								x							
59.	**Sărmăşel (MS)**			**o**						**x**		**x**		**o**	**o**	**o**
60.	Soroştin (SB)					x		x	x	x		x				
61.	Spătac (AB)							x	x							
62.	Stejeriş (CJ)					x		x	x							
63.	Şaeş (MS)									x		x				
64.	Şeica Mare (SB)								x							
65.	Şincai (MS)									x		x				
66.	Şoimuşu Mic (HR)				x								x			
67.	Şomartin (SB)								x							
68.	Tăureni (MS)		x													
69.	Ţeline (SB)									x		x				
70.	Valea Sasului (AB)								x							
71.	**Vălişoara/Gloduri (MS)**															**x**
72.	Veseud (SB)								x							
73.	Vişinelu (MS)		x													

x – mud volcanoes
o – gas seeps

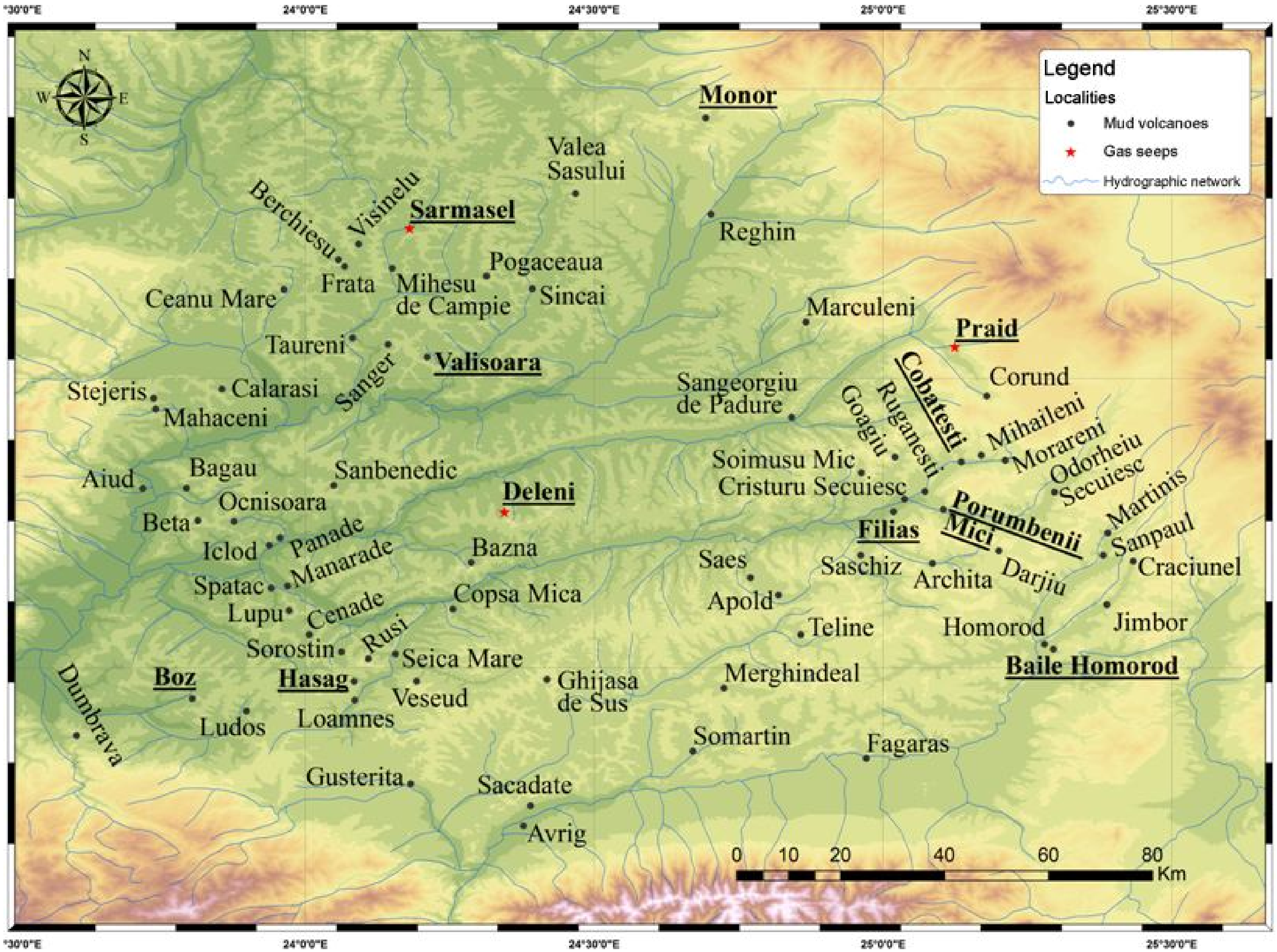

Fig. 4.12 Distribution of some mud volcanoes and gas seeps in the Transylvanian Basin, according to table 4.2

Chapter V – Investigation methods

Over the time, different systems based on the closed chamber technique (e.g. LIVINGSTON & HUTCHINSON, 1995; ETIOPE ET AL., 2004) were used to measure the methane flux in the Transylvanian Basin

One of the newest systems based on the closed chamber technique, the **Portable diffuse flux meter for carbon dioxide and methane** (**Fig. 5.3**), was used for the measurements of methane in several locations in the Transylvanian Basin, the results being included in this paper.

Fig. 5.3 Portable diffuse flux meter for carbon dioxide and methane **(**WEST Systems**)**

This new portable closed-chamber system for CH_4 flux measurement has been developed by WEST Systems (Italian based company) and National Institute for Geophysics and Volcanology (INGV, Rome). The system is based on a sensitive semiconductor CH_4 sensor (lower detection limit: 1 ppm; resolution 1 ppm) with wireless data communication to a Palmtop PC, for data storage and immediate flux calculation (based on linear regression). The system is able to detect quite low values of CH_4 exhalations (orders of a few tens of mg CH_4 m^{-2} d^{-1} in 10-15 minutes).

The system has been tested in the Transylvanian Basin, especially on the vicinity of gas reservoirs and over mud volcanoes apparently extinct.

In order to start measuring the flux, the accumulation chamber has to be placed on soil in the measuring site, ensuring that it is well isolated from the atmospheric air. To obtain an optimal flux curve recording, a period of time between two and four minutes is recommended (if very low methane fluxes need to be measured, the interval has to be 5-6 minutes).

Between the measurement intervals, the methane is captured in the accumulation chamber, and through the pump is distributed to the methane detectors that transmit the recorded data to the portable computer.

FluxManager (release 6, 2007) is the software installed on the palmtop, which allows recording in real-time the methane flux curves and performs the flux calculations. This information is also stored on the memory card that can be used after that on a desktop computer for further analysis.

To calculate the emission, for each investigated point a measured flux value is associated (mg or g) and its spatial coordinates (GPS Garmin). With the help of GIS software, the values of the flux are transposed on a map to obtain a distribution of emissions (area of distribution), analyzed later in statistical software.

Estimating the total methane quantity from the measured area was done using interpolation methods such as „linear kriging” and „natural neighbor”. The „linear kriging” method is generally used for values with a reduced variation, homogenously distributed; „natural neighbor” is recommended for points with irregular spacing, showing high flux values, avoiding in the same time the allotment of large fluxes to sectors where no actual measurements took place. Due to the increased variation of gas flux values from an emission area, it was necessary to differentiate and interpolate the data in separate groups for fluxes having a difference of at least three orders of magnitude.

Generally, in an area with macroemissions it is possible to differentiate one or several degassing areas (or around the evacuation exits, with values > 10^4 - 10^6 mg m^{-2} day^{-1}), and areas with a low miniseepage flux (values between 10^1 - 10^3 mg m^{-2} day^{-1}). The procedure is coherent with the upscaling methods “emission factor” and “homogenous area” as recommended by EMEP/EEA (ETIOPE ET AL. 2007).

Chapter VI – Results

The experimental part of this doctoral thesis had as goal the investigation of macro-, mini- and micro- methane emissions from several representative areas in the Transylvanian Basin. These are: Sărmăşel (MS) Everlasting fires area; gas and salt water seeps from Deleni (MS); mud volcanoes from Monor (BN); mud volcanoes from Băile Homorod (BV); mud volcanoes from Vălişoara (BN); mud volcanoes from Cobăteşti (HR); mud volcanoes from Filiaş (HR); mud volcanoes from Porumbenii Mici (HR); mud volcanoes from Boz (AB); mud volcanoes from Haşag (SB) and seepages from the Corund creek in Praid (HR).

Beside the investigations mentioned above, for a better understanding of the methane emissions from hydrocarbon basins, additional measurements were done in different zones of the Transylvanian Basin, tied mainly to the existence of gas deposits. Thus, several measurements were performed in the immediate vicinity of exploitation wells (Buneşti (SB); Miheşu de Câmpie (MS); Viforoasa (MS); S67/European road E60, section Tg. Mureş - Cluj Napoca; Haşag (SB)) or randomly in areas with well known seepage structures, such as those from Sărmaşu (MS), Zău de Câmpie (MS), Cucerdea (MS), Târnăveni (MS), Bazna (SB).

Some measurements were performed in locations from Cluj that had no gas structures, such as Rădaia, Mihăieşti, Cluj-Napoca (Babeş and Raluca Ripan parks) as a way to establish a comparison criterion and for setting the base flux.

Due to the large volume of information, only two case studies (Sărmăşel – everlasting fires and Monor – mud volcanoes) will be fully presented in this summary. Final results for all the measurements done for this thesis are presented briefly for each case study or area of investigation, as Conclusions (presented entirely) and in this summary.

Mini- and microemission measurements were performed in several locations of interest from the Transylvanian Basin and on its north-west ledge (**Fig 6.1.1**). As mentioned before, this study is focused on main areas linked with well known gas structures (Sărmăşel, Deleni, Cucerdea, Bazna, Zău, Buneşti, Beia, Grebeniş etc.), like those from the hydrocarbon digging wells region or visible manifestations similar to mud volcanoes, everlasting fires etc.

Several measurements, exclusively for the study of micro- and miniemissions, were performed in the area of gas exploiting wells, named in this paper using the closest locations in their vicinity: Buneşti (SB); Miheşu de Câmpie (MS); Viforoasa (MS); Haşag (SB) and well 67 situated in the close vicinity of European road E60, section between Târgu Mureş - Cluj Napoca.

To evaluate the methane flux in Transylvania, a number of 357 measurements were taken from 25 points of interest, structured in **table 6.1.1**.

All measurements were taken using DPMFD (West Systems), with the exception of Sărmăşel 2007.

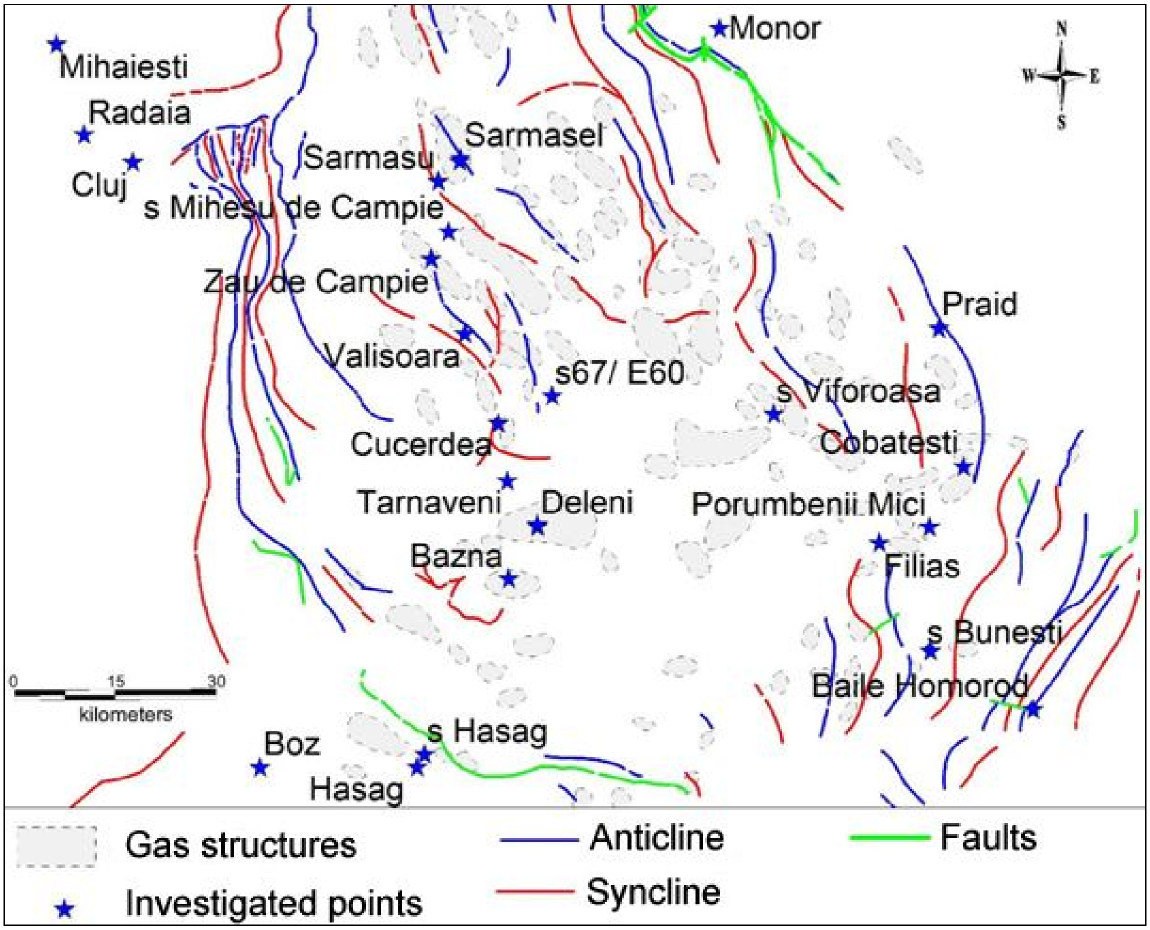

Fig. 6.1.1 Distribution of points of interest investigated for the micro-, mini- and macroemissions from the Transylvanian Basin and that of the closest gas structures

Table 6.1.1

Emissions investigated in the Transylvanian Basin

Nr. Crt.	Location	No. of measurements	Distance to the closest deposit (km)	Type of measured emission	The characteristic of investigated methods	Lowest recording CH_4 (ppm)	Highest measured flux CH_4 (mg m^{-2} day^{-1})
1.	Băile Homorod 2008	5	12 NV Beia	mi + m	Mud volcanoes	< 10 ppm	464
	Băile Homorod 2009	16		M + mi + m	Mud volcanoes	< 10 ppm	126 279
2.	Buneşti	8	2.5 SV Buneşti	M + mi + m	well; tillage soils	< 10 ppm	5120
3.	Cobăteşti 2008	10	- 0.9 N Cadaciu - 0.4 S Simoneşti	M + mi + m	Mud volcanoes	< 10 ppm	184 000
	Cobăteşti 2009	18		M + mi + m	Mud volcanoes	< 10 ppm	342 451
4.	Sărmăşel 2007	15	on Sărmăşel	M + mi	Everlasting fires; Tillage soils	-	2 500 000
	Sărmăşel 2008	44		M + mi	Everlasting fires; Tillage soils	< 10 ppm	12 368 000
5.	Sărmaşu	1	1.9 E-NE Sărmăşel	M	Tillage soils	-	2928
6.	Miheşu de Câmpie	1	2 E-SE Grebeniş	mi	well	-	656
7.	Zau de Câmpie	2	on Zau-Şaulia	m	Tillage soils	< 10 ppm	-
8.	Cucerdea	1	0.5 E Cucerdea	mi	Tillage soils	-	416
9.	Târnăveni	1	4.5 N Cucerdea	m	Tillage soils	< 10 ppm	-
10.	Bazna	3	on Bazna	m	Tillage soils	< 10 ppm	-
11.	Deleni 1 2008	14	on Deleni	M + mi + m	Gas and water seeps	< 10 ppm	4 672 000
	Deleni 1 2009	25		M + mi + m	Gas and water seeps	< 10 ppm	367 761
	Deleni 2 2008	16		M + mi + m	Gas and water seeps	< 10 ppm	1 664 000
	Deleni 2 2009	4		M + mi + m	Gas and water seeps	< 10 ppm	7 100 446
12.	Mihăieşti	3	43 E Puini	m	Tillage soils	< 10 ppm	-

13.	Rădaia	1	41 NE Puini	m	Tillage soils	< 10 ppm	-
14.	Cluj – I. Haţieganu	7	-	m	soil	< 10 ppm	-
15.	Cluj – R. Ripan	20	-	m	soil	< 10 ppm*	-
16.	Viforoasa	4	on Gălăţeni	M + mi + m	well	< 10 ppm	14263
17.	S67/E60	3	2.9 V Sanpaul	M + mi + m	well	< 10 ppm	1346
18.	Haşag	4	1.7 E Loamneş	M + mi + m	well	< 10 ppm	7009
19.	Haşag	3	3 NV Sadinca	M + mi	Mud volcanoes	< 10 ppm	893
20.	Monor	66	13 SV Lunca Tecii	M + mi + m	Mud volcanoes	< 10 ppm	1 794 744
21.	Vălişoara	15	on Sânger	M + mi + m	Mud volcanoes	< 10 ppm	65644
22.	Filiaş	11	1.2 E Cristur Sud	M + mi + m	Mud volcanoes	< 10 ppm	117267
23.	Porumbenii Mici	14	0.3 S-SV Porumbenii	M + mi + m	Mud volcanoes	< 10 ppm	374982
24.	Boz	15	12.2 E Alămor	M + mi + m	Mud volcanoes	< 10 ppm	70925
25.	Praid	7	- on Praid** - 4 S Cuşmed	M	Water emissions	-	592872

M = macroemissions; mi=miniemissions; m = microemissions
* ~10-12 ppm (close to the streets)
** FILIPESCU & HUMĂ (1979)

Case study: Sărmăşel (Ms) – Everlasting fires

Local geologic setting

The Sărmăşel everlasting fires (**Fig. 6.2.1**) are situated above the Sărmăşel gas reservoirs, located in the Nordic group where gas-bearing structures have as main characteristic the reduction of productive levels due to their surface appearance.

The structure has a form similar to an elongated dome on the N-S direction, with inclinations of the flanks below 6º. The 15 gas-bearing productive levels of Sărmăşel are hosted in Sarmatian (11) and Badenian (4) (PARASCHIV, 1975; FILIPESCU & HUMĂ, 1979).

The Sărmăşel structure is crossed by an anticline with pericline endings on the NV-SE direction. Its lithology is characterized by the presence of Sarmatian rocks with marly clays, sands and tuffs as well as recent deposits from creeks containing gravels and sands belonging to the superior Holocene.

The stratigraphic sequence from Sărmăşel is started by Sarmatian deposits, followed by Badenian ones, where we find the salt sequence, which contains salt deposits that can have widths of almost 900 m. The Dej tuff was discovered at the base of this sequence.

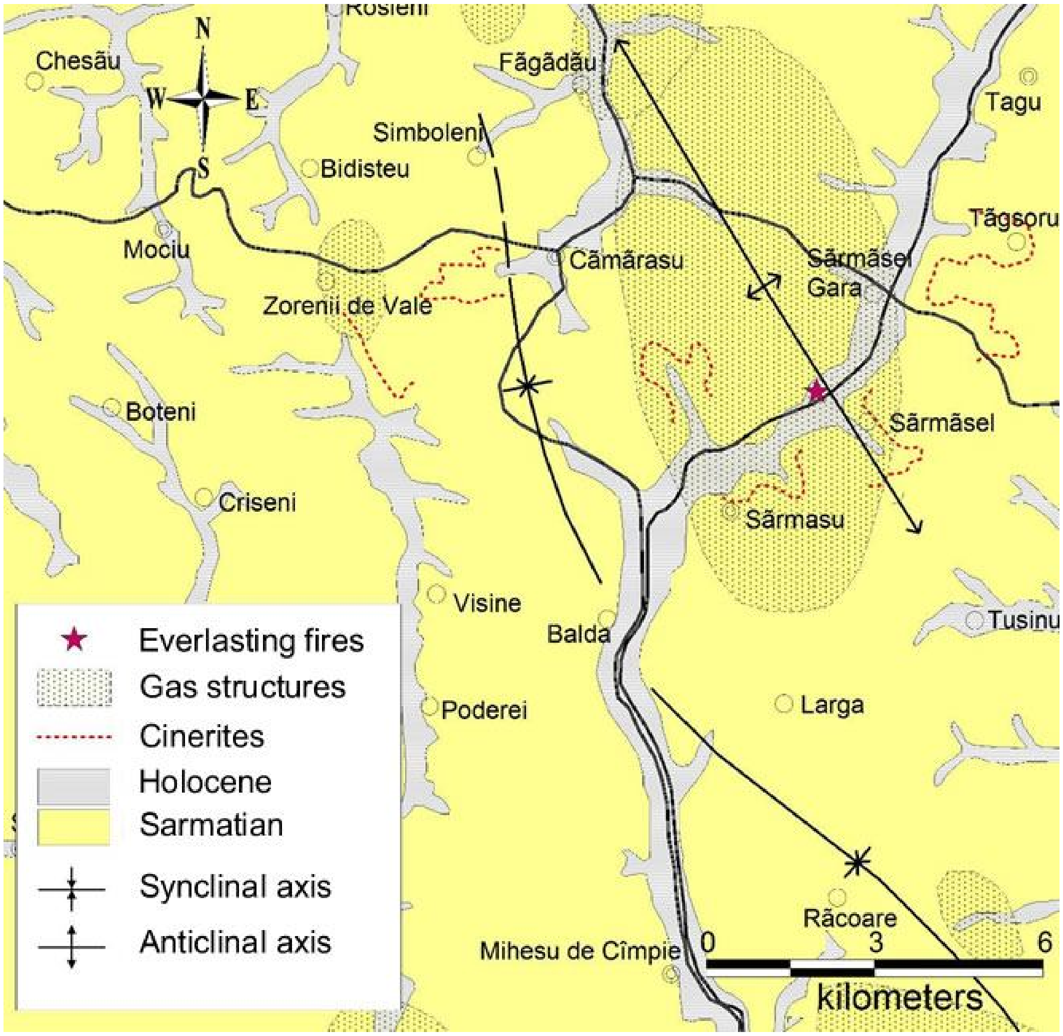

Fig. 6.2.1 Geologic situation of the Sărmăşel area (modified after Harta geologică 1:200000, Foaia Bistriţa, RĂILEANU ET. AL., 1967)

Site characterization

According to a local habitant, Rusu Vasile, a powerful explosion took place in the chimneys area in 1912, which blew up a house. The explosion was so powerful that its intensity reached the nearby villages, resulting flames remaining active for two years, until it was put down by covering it with mud.

Nowadays, the terrain is not cultivated, the active chimneys (**Fig. 6.2.2**) being easily recognizable because of the lack of vegetation and the deposits of waste brought by locals to be burned. The fire is intentionally lit by locals in order to destroy wastes, even if in several places the methane emissions are so high that they can be considered “grisou” and powerful enough to increase the risk of another explosion

Emissions from the "Everlasting Fires" site in Sărmăşel were studied several times using different types of instruments (BACIU & ETIOPE, 2002; ETIOPE ET AL., 2003; BACIU ET. AL., 2007).

The investigation methods for measuring the flux directly from the studied perimeter were done using the methane detection device, METREX 2, Huberg, for studies performed in May 2007 and DPMFD (West Systems) for the measurements done in May 2008.

Fig. 6.2.2 The chimneys of Sărmăşel everlasting fires, characterized by the lack of vegetation

Interpretation of measurements and results

In May 2007, in normal atmospheric conditions on dry land, emissions (Sărmăşel First Survey) from two chimneys with active fires were measured and from another one where there was no fire but whose activity could be deducted from the lack of vegetation in the area (**Fig. 6.2.3**).

Fig. 6.2.3 Measurements of the methane flux in one of the chimneys of the Sărmăşel everlasting fires, using METREX 2, Huberg, to record the methane values in air, close to the fires.

Aside these, other measurements were performed in the perimeter close to the chimneys. The investigated area was approximately 3610 m^2. Geogenic methane emissions were measured for 15 different locations, the values being recorded in **Table 6.2.1.**

Table 6.2.1

Measured methane flux, Sărmăşel I – May 2007

Nr. Crt.	Measurement point name	Latitude	Longitude	CH_4 Flux ($mg\ m^{-2}\ day^{-1}$)
1	S1	46 46 08.3	024 11 21.7	320
2	S2	46 46 08.6	024 11 23.1	209000
3	S3	46 46 07.8	024 11 24.1	61000
4	S4	46 46 07.5	024 11 23.8	27000
5	S5	46 46 06.7	024 11 24.2	70
6	S6	46 46 07.4	024 11 24.9	3400
7	S7	46 46 07.4	024 11 25.2	2300
8	S8	46 46 08.0	024 11 24.4	3200
9	S9	46 46 08.6	024 11 23.9	15000
10	S10	46 46 09.2	024 11 23.5	3400
11	S11	46 46 10.0	024 11 23.0	65000
12	S12	46 46 10.5	024 11 22.4	12000
13	S13	46 46 09.7	024 11 23.2	52000
14	S14	46 46 08.2	024 11 23.6	2000000
15	***S15***	***46 46 08.1***	***024 11 24.4***	***2500000***

The second round of measurements to delineate emissions from Sărmăşel was performed in May 2008, when an area seven times larger than the first one was investigated, approximately 25450 m^2. Emissions from the chimneys area were targeted this time too, but it was considered necessarily to expand the perimeter studied previously.

Methane flux was measured in 45 locations, the results being presented in **Table 6.2.2.**

Table 6.2.2

Measured methane flux, Sărmăşel II – May 2008

Nr. Crt	Measurement points name	Latitude	Longitude	CH_4 Flux (mg m^{-2} day^{-1})
1	S1	46 46 10.1	024 11 22.8	3040
2	S2	46 46 09.9	024 11 22.7	8080
3	S3	46 46 09.7	024 11 23.4	252800
4	S4	46 46 10.2	024 11 22.5	1696
5	S5	46 46 10.4	024 11 21.9	2624
6	S6	46 46 09.7	024 11 21.3	2928
7	S7	46 46 09.4	024 11 21.2	1872
8	S8	46 46 08.5	024 11 20.2	1616
9	S9	46 46 07.3	024 11 18.7	1280
10	S10	46 46 06.6	024 11 19.4	1792
11	S11	46 46 05.8	024 11 20.9	1712
12	S12	46 46 05.0	024 11 19.7	384
13	S13	46 46 04.4	024 11 18.5	880
14	S14	46 46 04.2	024 11 17.5	1008
15	S15	46 46 04.7	024 11 16.9	720
16	S16	46 46 05.8	024 11 17.1	656
17	S17	46 46 06.2	024 11 22.2	688
18	S18	46 46 07.1	024 11 21.6	1408
19	S19	46 46 07.1	024 11 23.1	1328
20	S20	46 46 07.6	024 11 23.4	600000
21	S21	46 46 07.8	024 11 23.9	43824
22	M22	46 46 08.1	024 11 24.2	1120000
23	M23	46 46 08.0	024 11 24.3	992000
24	M24	46 46 08.3	024 11 24.7	976000
25	M25	46 46 08.0	024 11 24.7	1792000
26	S26	46 46 08.6	024 11 24.1	161600
27	M27	46 46 08.3	024 11 23.5	251200
28	M28	46 46 08.3	024 11 23.6	6592000
29	S29	46 46 08.1	024 11 23.9	528000
30	***M30***	***46 46 07.9***	***024 11 24.0***	***11104000***
31	S31	46 46 07.5	024 11 24.7	8960
32	S32	46 46 07.8	024 11 26.2	1696
33	S33	46 46 08.4	024 11 28.6	2080
34	S34	46 46 08.9	024 11 20.5	1872
35	S35	46 46 09.1	024 11 26.5	1008
36	S36	46 46 08.6	024 11 25.3	1360
37	S37	46 46 08.4	024 11 24.9	432
38	S38	46 46 08.2	024 11 24.6	2112
39	S39	46 46 08.2	024 11 24.6	1168
40	***M 28 bis***	***46 46 08.3***	***024 11 23.6***	***12368000***
41	S40	46 46 09.1	024 11 23.3	156800
42	S41	46 46 09.2	024 11 23.2	180800
43	M42	46 46 09.3	024 11 23.0	966400

44	S43	46 46 08.8	024 11 22.2	3824
45	S44	46 46 09.5	024 11 21.1	2560

Sărmăşel I - 2007

The Natural Neighbor (NN) interpolation method was chosen to interpret the values from Sărmăşel 2007, due to the non-homogenous fluxes encountered (extremely high in the chimneys area). So, for the 15 values of the methane flux from Sărmăşel, resulted a total emission of 251 t CH_4/y distributed on an area of 1408.05 m^2 (**Fig 6.2.4**). Points s1 and s5 were not taken into account.

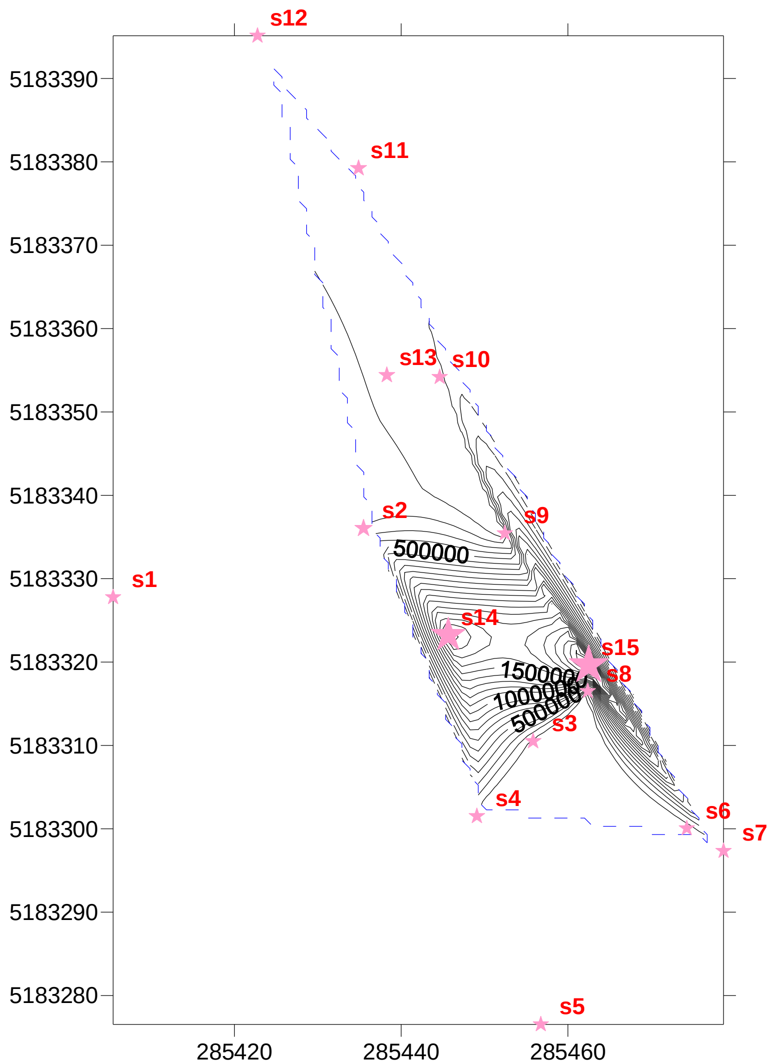

Fig. 6.2.4 The distribution of methane fluxes for Sărmăşel I, as a result of NN interpolation

A map with a possible vectorial model of the methane flux from points with high fluxes to those with low values indicates the radial directions from the area of the two chimneys (s14, s15) (**Fig 6.2.5**).

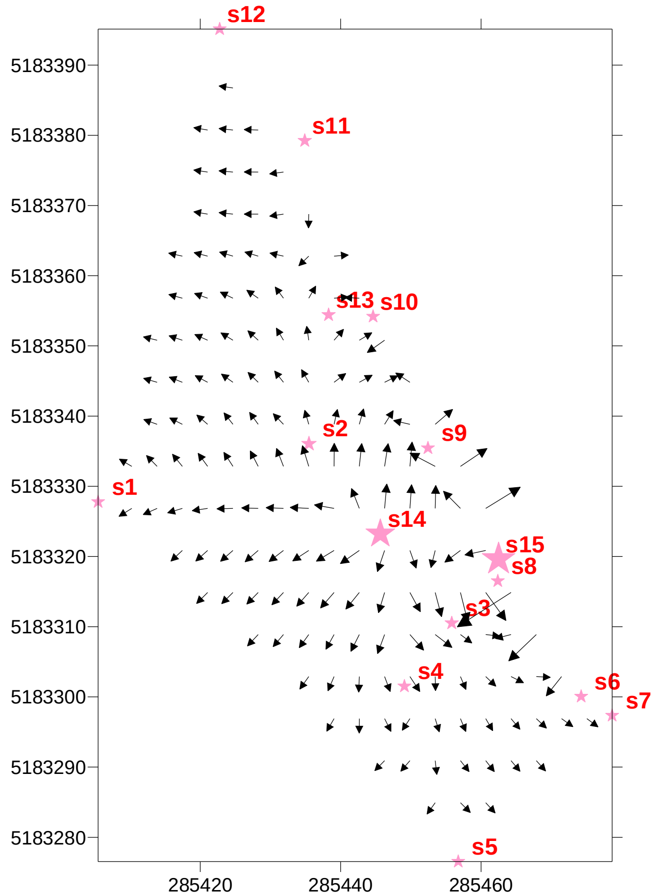

Fig. 6.2.5 Vectorial distribution of methane fluxes for Sărmăşel I

A 3D interpretation of the methane flux from the chimney areas, s14 and s15, shows the obvious contrast between fluxes from the chimneys area and those of neighboring areas (**Fig 6.2.6**).

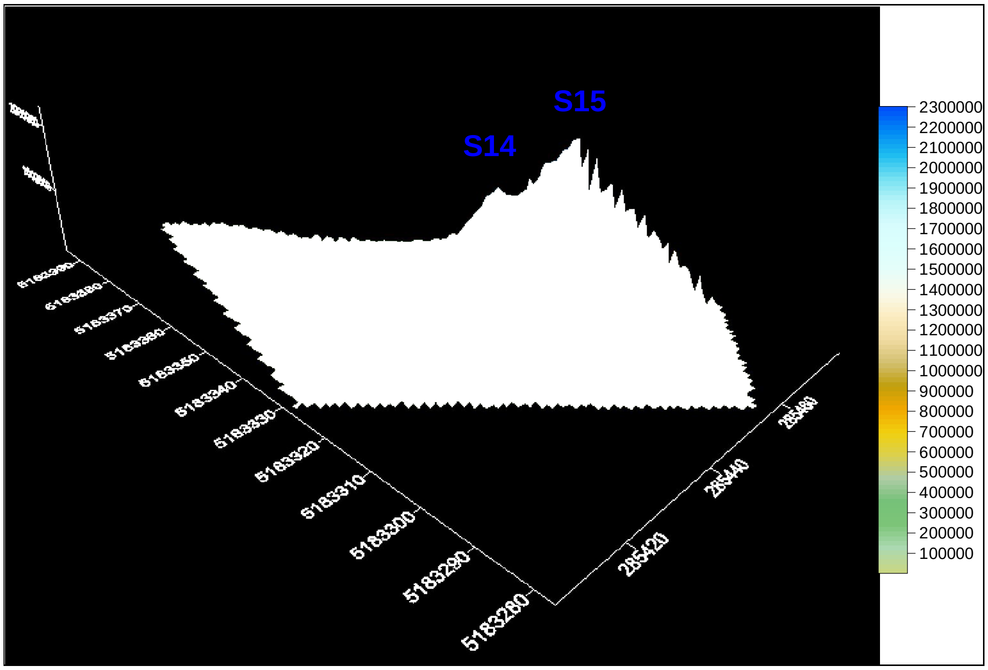

Fig. 6.2.6 3D representation for methane fluxes from the chimneys area (Sărmăşel I)

Sărmăşel II - 2008

Following the Sărmăşel II campaign, 45 points were investigated from the area of everlasting fires.

The methane flux from the chimneys area is the highest measured with DPMFD (West Systems) in Transylvania (**Fig 6.2.7** and **Fig 6.2.8)**. Most of the measurements started recording methane in the air, long before placing the accumulation chamber on soil. A methane measurement starting from zero was impossible to record in the chimneys zone and the area close to these. *Thousands of ppms are in intervals of under 10 seconds in the area of everlasting fires.*

As in the first campaign, the flux values were interpolated and representation of the distribution of points taken into account are noticeable in **Fig 6.2.9 a;b;c** and **d.**

The Kriging interpolation method was chosen for the distribution of flux in areas with micro- and miniemissions, where points with values over 100 g CH_4/m^2/day were not taken into account. This method had as result an emission of 165 t CH_4/y on ~25000 m^2 **Fig 6.2.9 a**

The area with macroemissions (chimney's area where the fire was burning) was estimated through the Natural Neighbor interpolation to be 483 m^2 resulting an emission of 429 t CH_4/y **Fig 6.2.9 b**.

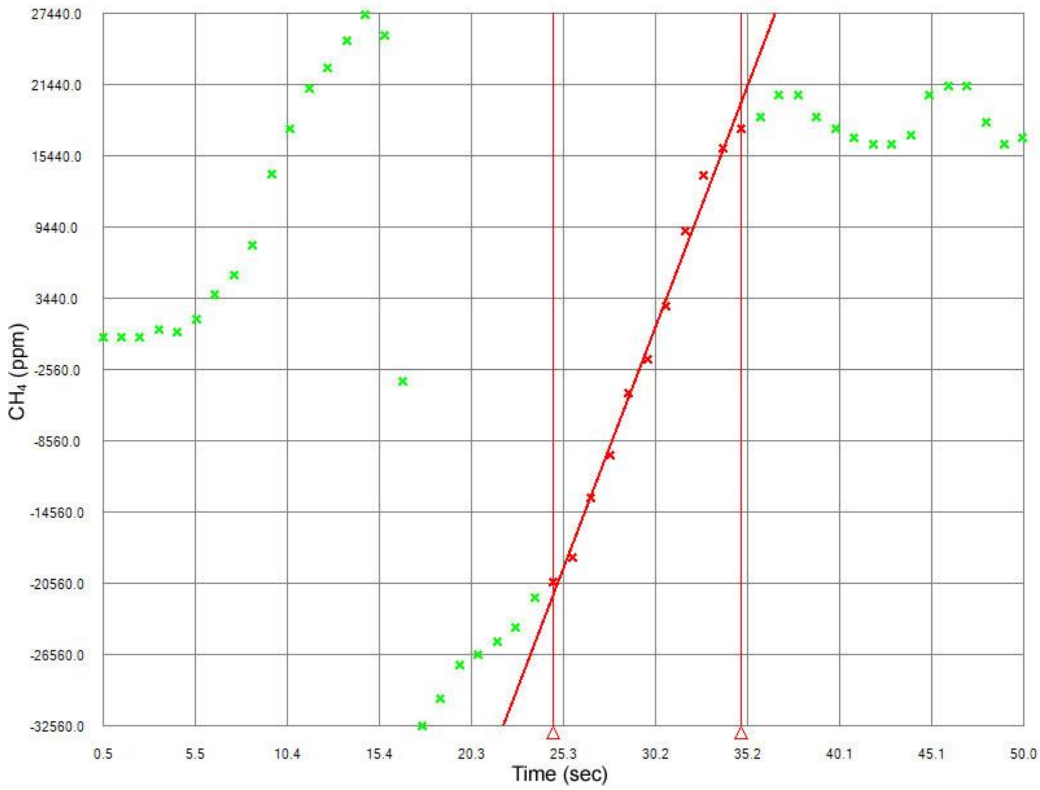

Fig. 6.2.7 Highest value of the flux recorded in Sărmăşel II, M28bis

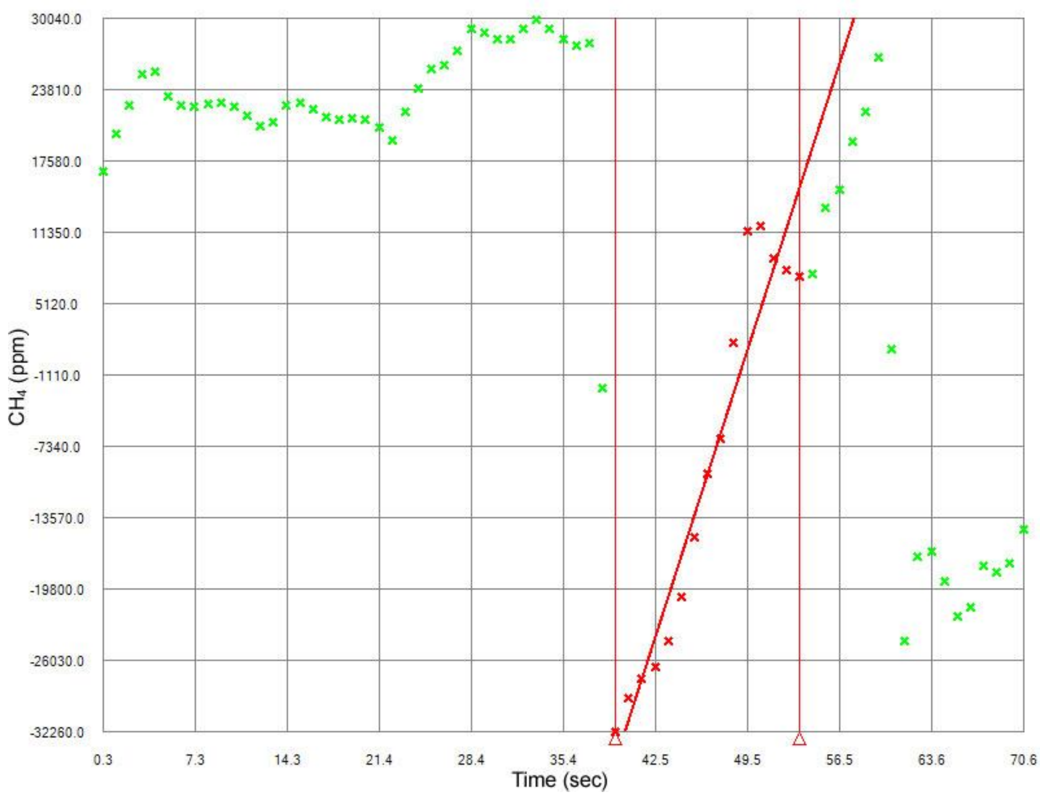

Fig. 6.2.8 One of the highest recorded flux values for Sărmăşel II, M30

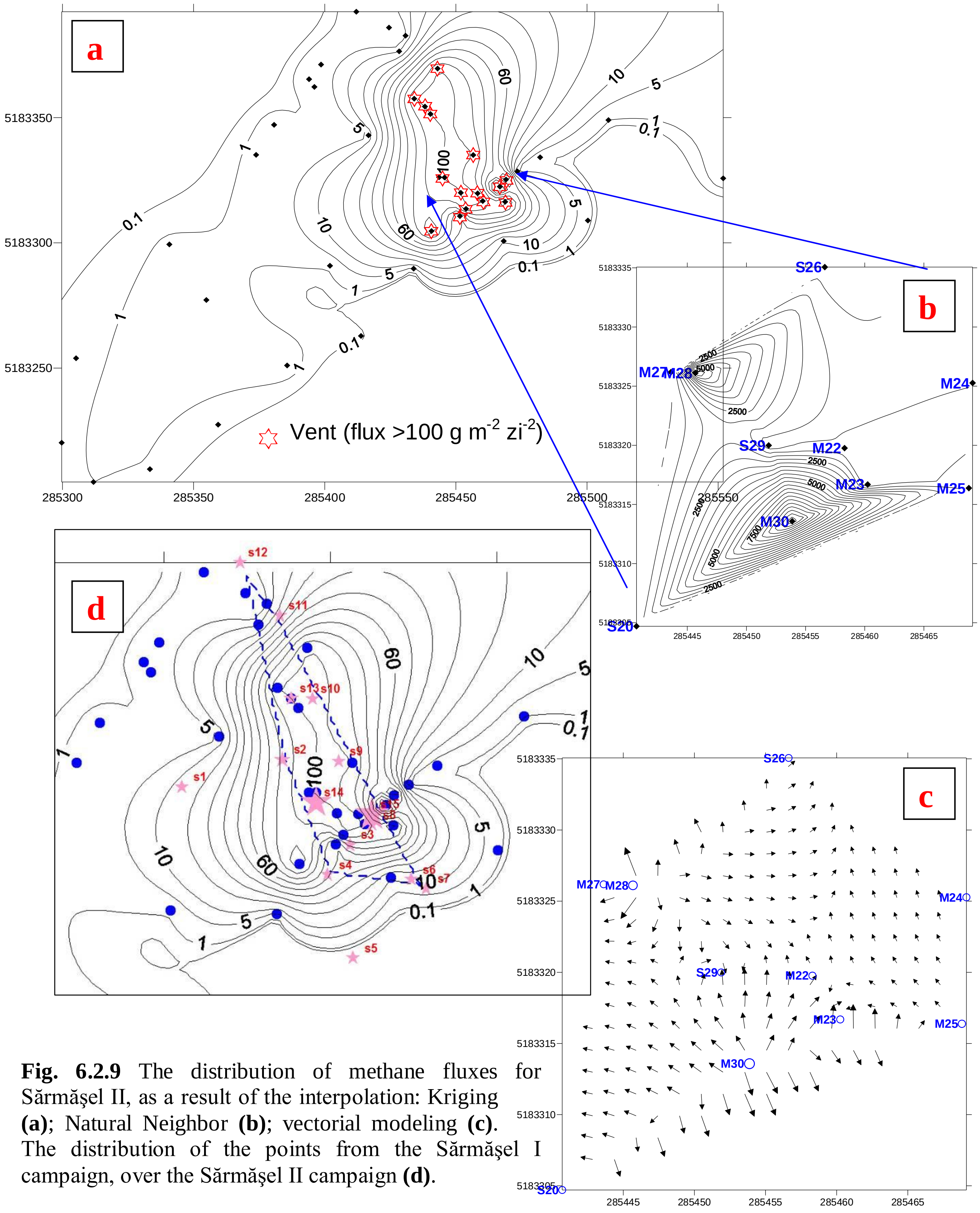

Fig. 6.2.9 The distribution of methane fluxes for Sărmăşel II, as a result of the interpolation: Kriging **(a)**; Natural Neighbor **(b)**; vectorial modeling **(c)**. The distribution of the points from the Sărmăşel I campaign, over the Sărmăşel II campaign **(d)**.

For the highest recorded values, 3 points (M28, M28bis, M30), were calculated separately. An emission of 0.5 t CH_4/y on 3 m^2 was estimated from these points. The possible distribution of methane in soil is reproduced vectorial in **Fig 6.2.9 c**, where the vectors are distributed radial from the areas with high emission to those with low emissions.

The Sărmăşel II campaign of measurements enriched the data from the first campaign, marking out the areas with high micro-emissions situated at a large distance from the investigated area of the first campaign **Fig 6.2.9 d.**

The investigation campaigns of the everlasting fires from Sărmăşel totaled 60 measurements. The statistical analysis of all the gathered data is synthesized in **table 6.2.3**.

Table 6.2.3

The main statistical elements extrapolated from the methane emission interpretation in Sărmăşel

	Sărmăşel I Portable sensor, Metrex 2, Huberg	**Sărmăşel II** Portable device (WEST Systems), with incorporated Metrex 2, Huberg
Number of measurements	15	45
Median (mg m^{-2} day^{-1})	15000	2560
Minimum value (mg m^{-2} day^{-1})	70	384
Maximum value (mg m^{-2} day^{-1})	2 500 000	12 368 000
Investigated area (m^2)	3610	25453
Distribution area of emissions - Surfer (m^2)	1408	25000
Flux estimations for the total area (t CH_4/y)	251	595

The estimations of macro-emissions from the everlasting fires in the chimneys' area and recorded micro-emissions from the neighboring area, place Sărmăşel along with sources having record levels of emissions, worthy to be taken into account.

So, if we assume that the emissions conditions are the same as the ones recorded by us, we can propose an emission of 251 t CH_4/y corresponding to an area of 1408 m^2 for Sărmăşel I and a total emission of 595 t CH_4/y on a surface of 25000 m^2 for Sărmăşel II.

Case study: Monor (Bn) – Mud volcanoes

Local geologic setting

The geologic reservation hosting the mud volcanoes from Monor extends on large areas totaling up to 2 hectares. The volcanic structures found here, considering their aspect and density, are the top structures of their kind in the Transylvanian Basin.

Monor mud volcanoes, **Fig. 6.4.1**, are situated on quaternary terrace deposits with sands and gravels. The sediments expulsed are marly clays, sands, sandstones, tuffs and sometimes salt.

The closest gas reservoir to the Monor mud volcanism is the one from Lunca, part of the group of Eastern structures. Gases from the productive horizon of the brachy-anticline Lunca, contain 98.9-99.02% methane (PARASCHIV, 1975).

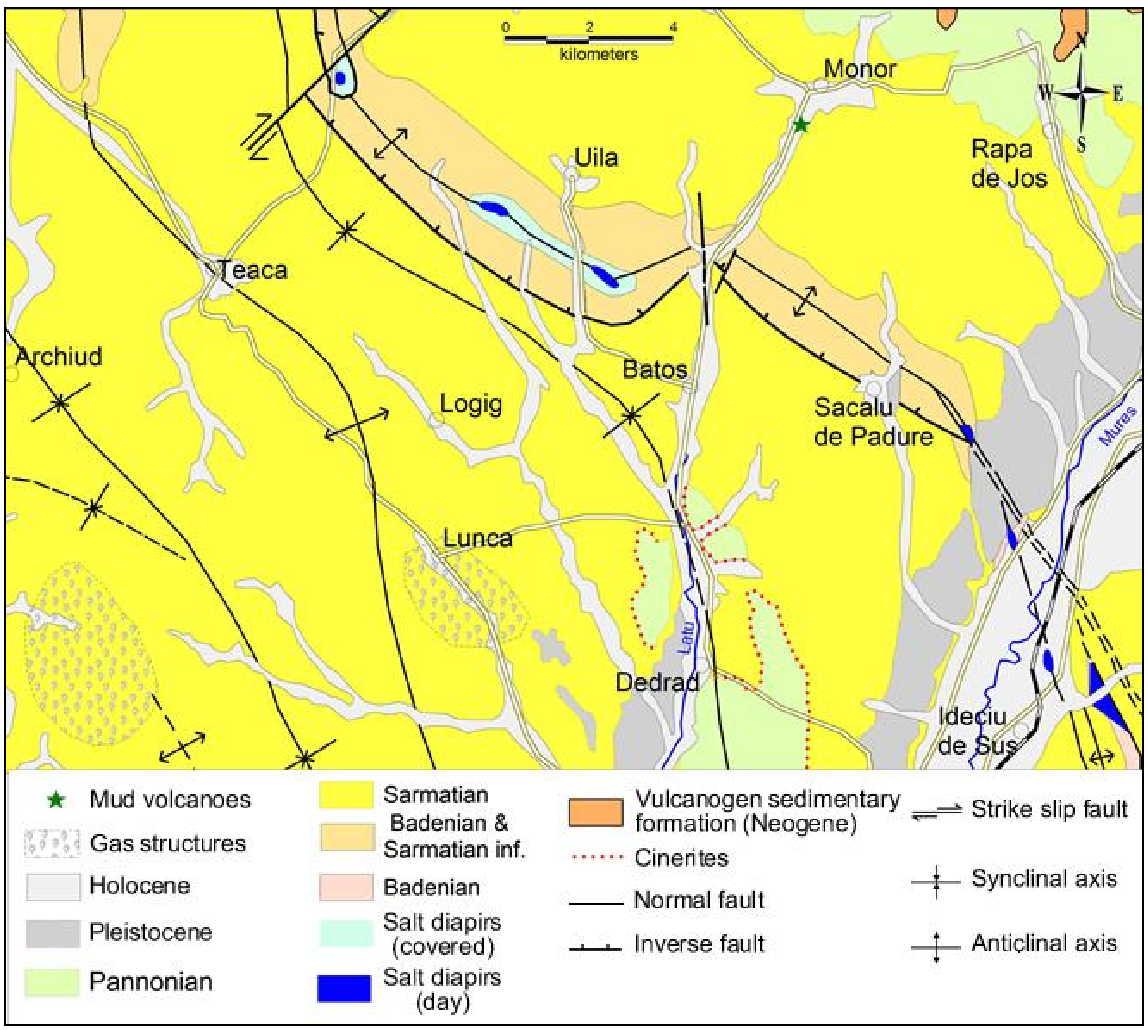

Fig. 6.4.1 Geologic situation in the Monor area (modified after the geological map 1:200000, Foaia Bistriţa, RĂILEANU ET. AL., 1967)

This gas perimeter is located approximately 13 km from Monor. Tectonically speaking, in the middle of the distance between Monor volcanoes and the Lunca gas structure we encounter an anticline with Badenian deposits on the top of the sequence; salt glaciers influenced by normal and reverse faults.

Site characterization

Mud volcanoes from "La Gloduri", in Monor, as known by the villagers, are protected by law through the geological reservation "Vulcanii noroioşi la Gloduri", Monor, Bistriţa-Năsăud.

They are easy to spot, situated at the entrance in Monor village from Reghin, on the right side close to the confluence between Pârg and Lut creeks.

Fig. 6.4.2 One of the volcanic cones alignment from Monor and the active crater (medallion) of one of the mud volcanoes 2008

In Monor the mud volcanic structures are organized in two main alignments with successive volcanic cones **Fig. 6.4.2**. Aside these, numerous mud zones with "soil vaulting/arched soil" are present, "trembling when stepped on" **Fig. 6.4.3**.

Overall, the structures have cones that don't exceed 2.5 – 3m in height, and their base diameter goes up to 10 m.

The activity of the volcanoes is slow enough, eruption products being infiltration water and mud leaks reaching 8-9 m in length, more or less evident due to the rapid installation of grass. Salt appears dissolved in water and mud too.

Fig. 6.4.3 Measurements in the area of mud zones with obvious soil vaulting /arched soil due to gas accumulations

Fig. 6.4.4 Inside crack "crevasse" on one of the volcanic structures. These manifestations characterize the instable zones where fluid mud shows up at the surface.

Interpretation of measurements and results

In Monor a number of 66 measurements were performed in normal atmospheric conditions (temperature of 16° C and atmospheric pressure of 966.67 mBar).

The recorded values of methane flux are presented in **table 6.4.1**. The highest values were recorded in the area of oblate structures (mud pools) in m49 **(Fig. 6.4.5)** and m63 (measurement performed by "provoking" the flux). In m63 **(Fig. 6.4.6)**, the methane concentration in chamber reaches ~27000 ppm in 15 seconds and remains at this value until the measurement is finished (1 minute), the estimated flux in this location being ~8.7 Kg m^{-2} day^{-1}.

Table 6.4.1

Measured methane flux, Monor April 2009

No. of Samples	Sample Name	Characteristics	CH_4 Flux (mg m^{-2} day^{-1})
1	m1	V1/top/crater	< 10 ppm
2	m2	V1/crater	< 10 ppm
3	m3	V1/crater	< 10 ppm
4	***m4***	***V1/crater/forced m7***	***< 10 ppm***
5	m5	V1/flank	< 10 ppm
6	m6	V1/flank	< 10 ppm
7	m7	V1/crater	< 10 ppm
8	m8	V1/flank	< 10 ppm
9	m9	V1/crater	< 10 ppm
10	m10	V2/crevasse	1359
11	m11	V2/crevasse	12450
12	m12	V2/crevasse	60626
13	m13	V2/crevasse	3325
14	m14	V2/crevasse	22157
15	m15	V2/dried mud	< 10 ppm
16	m16	V2/dried mud	< 10 ppm
17	m17	V2/dried mud	< 10 ppm
18	m18	V2/dried mud	< 10 ppm
19	m19	V3/top/crater	406929
20	m20	V3/top/crater	28322
21	***m21***	***V3/top/crater/forced m19***	***121088***
22	m22	V4/top/crater	< 10 ppm
23	m23	V4/flank	< 10 ppm
24	m24	V5/top/crater	< 10 ppm
25	m25	V5/top/crater	< 10 ppm
26	m26	V6/top/crater	< 10 ppm
27	***m27***	***V6/top/crater/forced m26***	***10224***
28	***m28***	***V7/top/crater/forced m29***	***18324***
29	m29	V7/top/crater	< 10 ppm
30	m30	V8/top/crater	< 10 ppm
31	***m31***	***V8/top/crater/forced m30***	***11543***
32	m32	V8/flank	< 10 ppm
33	m33	V8/flank	< 10 ppm
34	m34	V9/flank	< 10 ppm

35	m35	V9/flank	< 10 ppm
36	m36	V9/top/crater	6552
37	m37	V9/top/crater	36212
38	m38	V10/top/crater	< 10 ppm
39	m39	V11/top/crater	6052
40	m40	V11/top/crater	< 10 ppm
41	m41	V11/top/crater	2938
42	m42	V11/flank	1914
43	m43	V11/flank	1584
44	m44	V11/flank	1467
45	m45	G12/top	34407
46	m46	G12/top	210549
47	m47	G13/top	45583
48	m48	G14/top	3636
49	m49	G15/top	1794744
50	m50	G15/top	105165
51	m51	G15/top	672239
52	m52	G15/top	25661
53	m53	G15/top	5490
54	m54	G16/top	49510
55	m55	G16/top	12595
56	m56	G17/top	7245
57	m57	V18/top	164315
58	m58	V18/top	315949
59	m59	V18/top	14667
60	m60	G19/top	35213
61	***m61***	***G19/top/m60***	***7188691***
62	***m62***	***G19/top/forced***	***294528***
63	***m63***	***G19/top/forced***	***8762226***
64	***m64***	***G20/top/forced***	***1586665***
65	***m65***	***G20/top/m66***	***2556216***
66	m66	G20/top	33709

Beside the mentioned measurements, several others were taken where the flux was "forced" using a stick of approx. 2 m (**table 6.4.2**). The purpose was to compare the methane flux values obtained in normal conditions, with the values recorded in forced conditions. As expected, almost all the forced measurements (except m19/m21) had recorded high values. *None of the forced measurements (m4: m21; m27; m28; m31; m61; m65; m62; m63) were taken into account in estimating emissions on the investigated areas.*

Table 6.4.2

Measurements taken in the same location for evaluating the flux (Monor)

Measurement	**Normal conditions ($mg\ m^{-2}\ day^{-1}$)**		**Forced ($mg\ m^{-2}\ day^{-1}$)**		**Characteristics**
1	**m7**	< 10 ppm	m4	< 10 ppm	***V1/top/crater***
2	**m19**	406929	m21	*121088*	***V3/top/crater***
3	**m26**	< 10 ppm	m27	10224	***V6/top/crater***
4	**m29**	< 10 ppm	m28	*18324*	***V7/top/crater***
5	**m30**	< 10 ppm	m31	*11543*	***V8/top/crater***
6	**m60**	35213	m61	*7188691*	G19/top
7	**m66**	33709	m65	*2556216*	G20/top
8	-		m62	*294528*	***G19/top/forced***
9	-		m63	*8762226*	***G19/top/forced***
10	-		m64	*1586665*	***G20/top/forced***

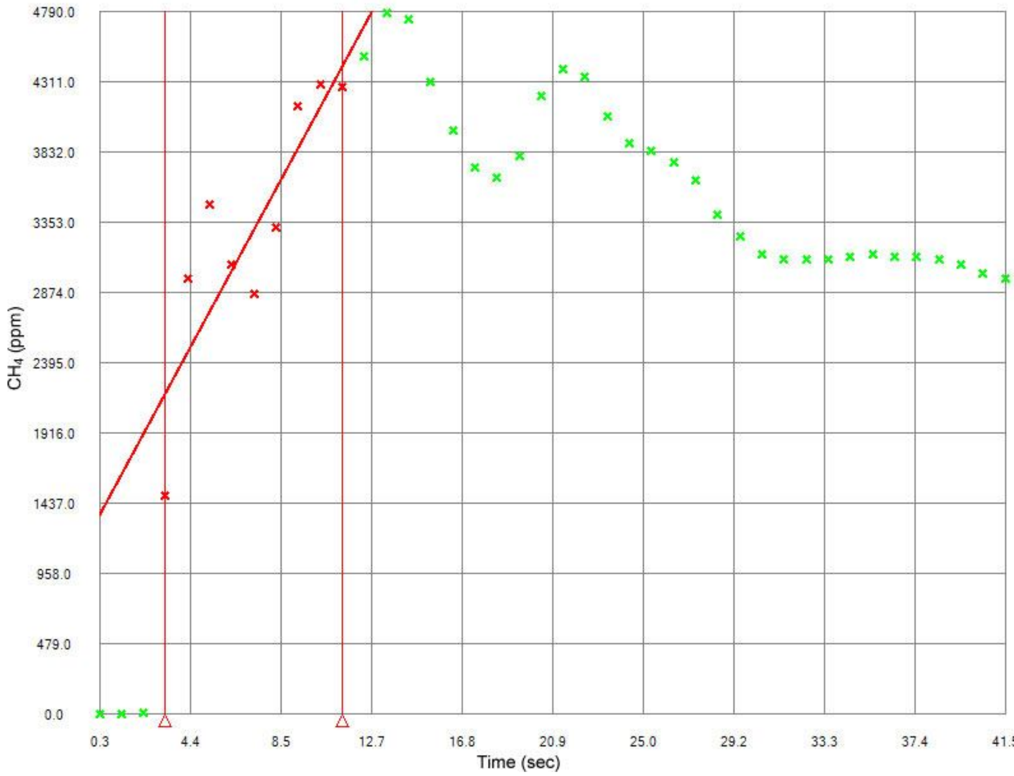

Fig. 6.4.5 Highest recorded flux value (normal conditions) in Monor, m49

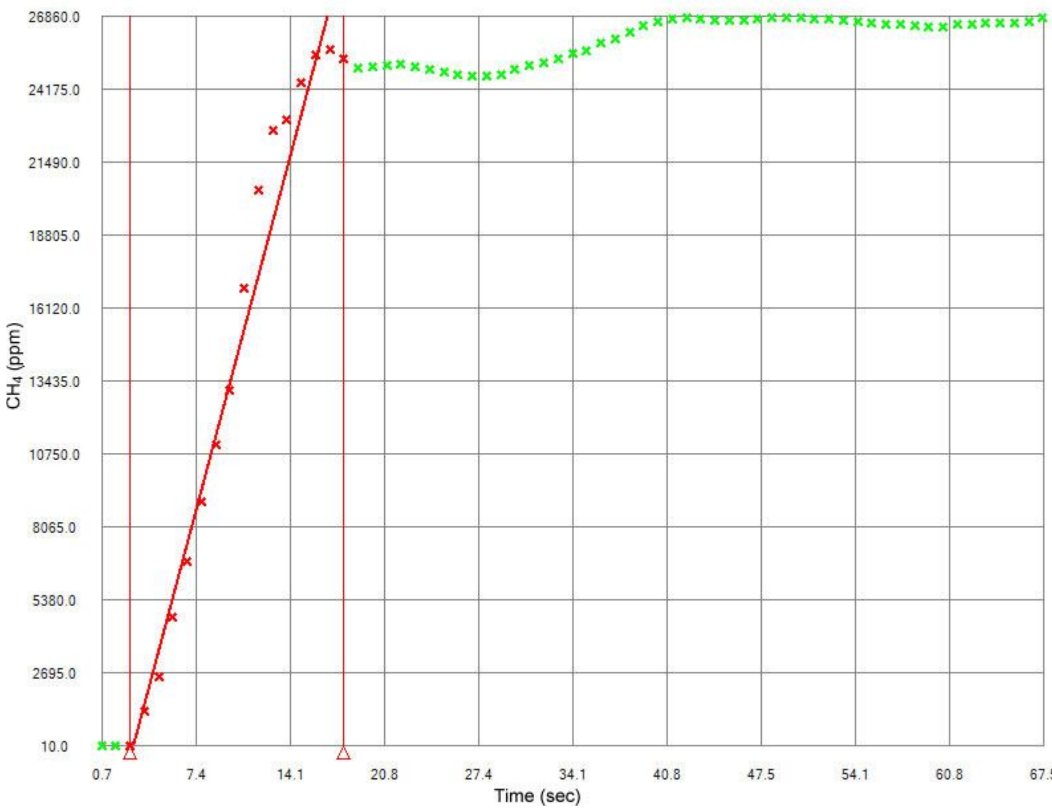

Fig. 6.4.6 Highest recorded flux value (forced) in Monor, m63

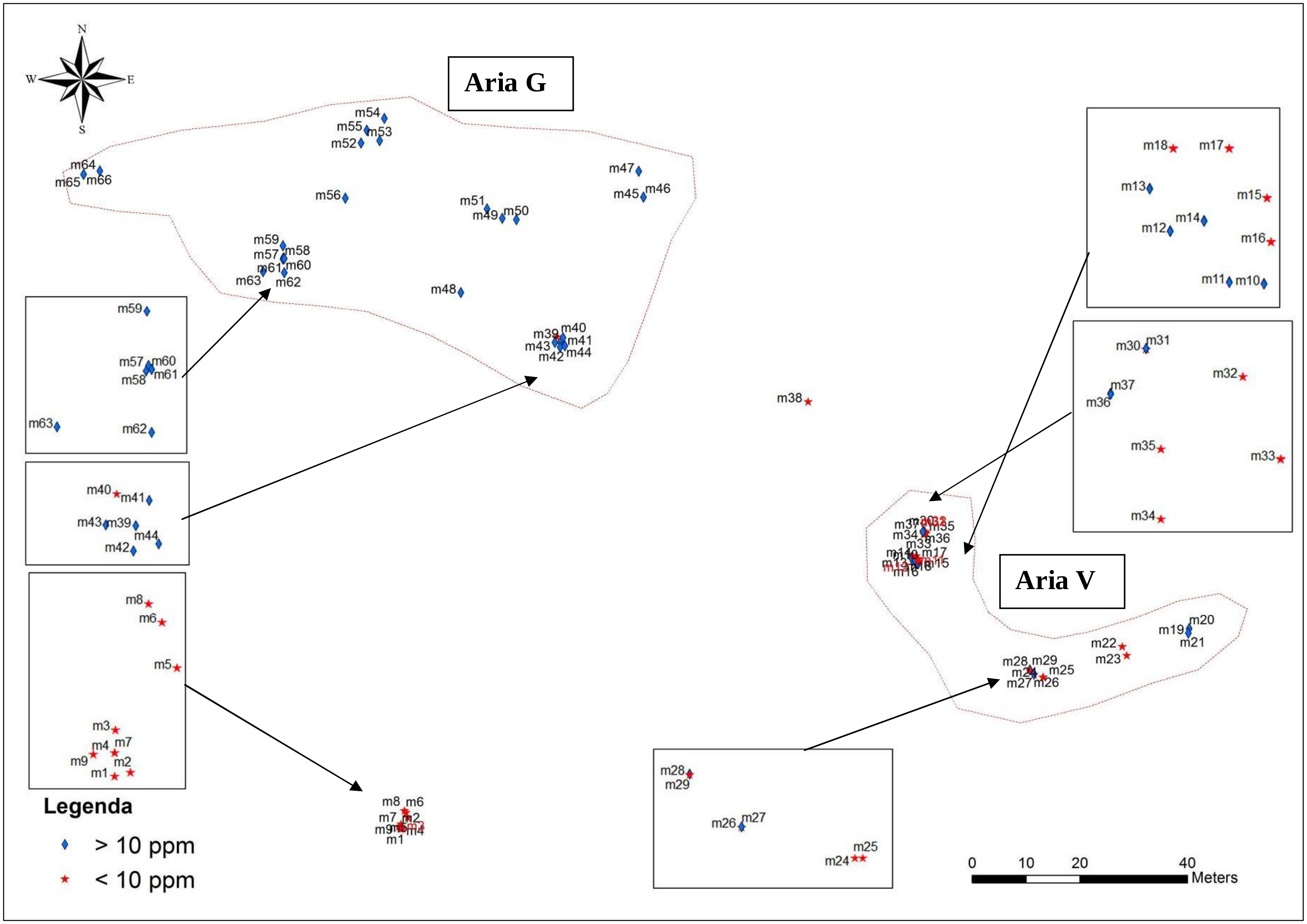

Fig. 6.4.7 The distribution of measurements for the mud volcanoes in Monor, 2009

Two areas for reporting emissions were established in Monor 2009: V area, where risen cone structures are predominant and G area, where flat structures (mud pools) are predominant. Thus, on the V area (approx. 860 m^2) several disposed volcanic structures were investigated with measurements m1-m38, while on the G area 27 measurements were taken.

Measurements m1-m9 were taken at volcano 1, all being under 10 ppm. To calculate the emissions from the V area, 27 measurements were taken into account (m10-m37). The Natural Neighbor interpolation (**Fig. 6.4.8a**) led to a calculated emission of 2.67 t CH_4/y from a surface of 94 m^2. A possible vector modeling of fluxes from zones with higher flux values to those with low values is presented in **Fig. 6.4.8b**.

Methane estimations from the G area (approx. 2600 m^2), were taken separately for micro- and miniemissions (**Fig. 6.4.10a, b**), as well as for the seeps with high fluxes (macroemissions); these were evaluated separately in graphs (**Fig. 6.4.9a, b**). The methane flux from micro- and miniemissions was estimated for an area of 1474 m^2, the resulting emission being 10.8 t CH_4/y. An emission of 2.1 t CH_4/y resulted exclusively from macroemissions measured in 7 flat volcanic structures, distributed on an area of 394 m^2.

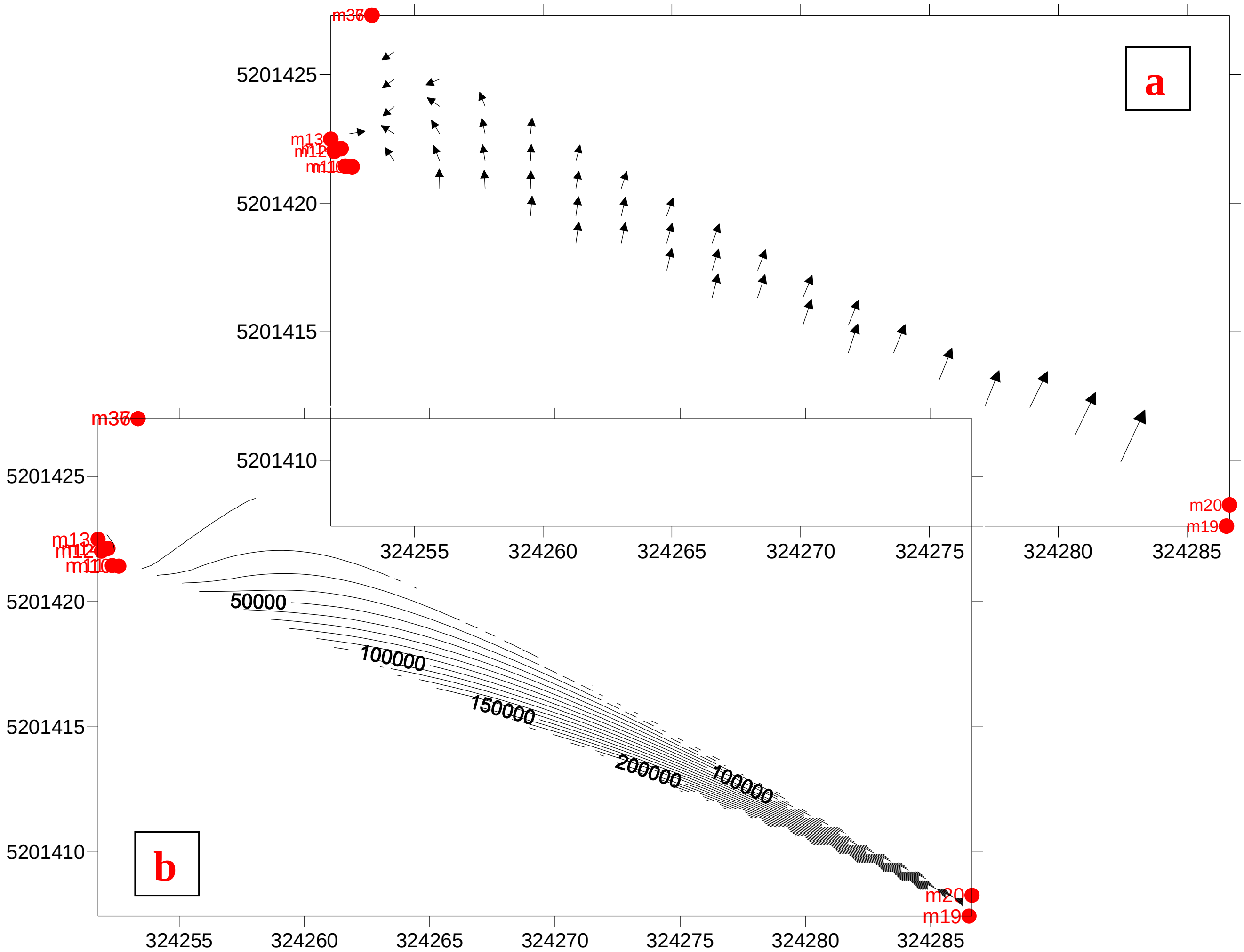

Fig. 6.4.8 The distribution of methane fluxes for the V area, m10-m37 measurements, resulted after the Natural Neighbor interpolation (a); vector modeling (b).

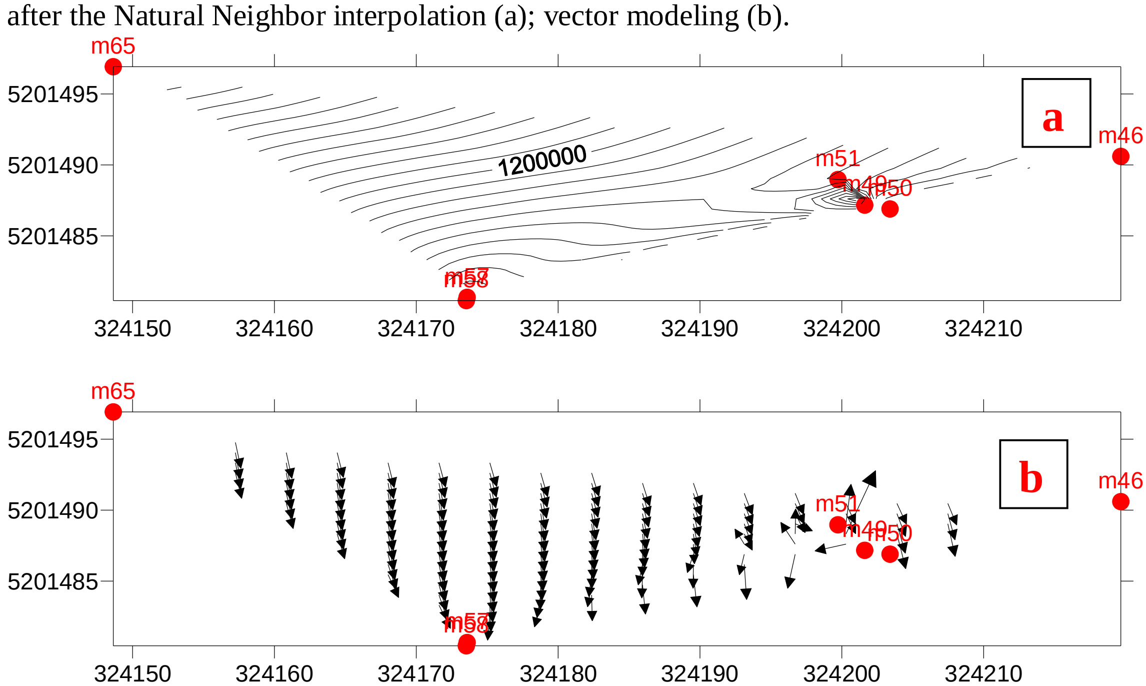

Fig. 6.4.9 The distribution of methane macro-emissions for the G area resulted after the Natural Neighbor interpolation (a); vector modeling (b).

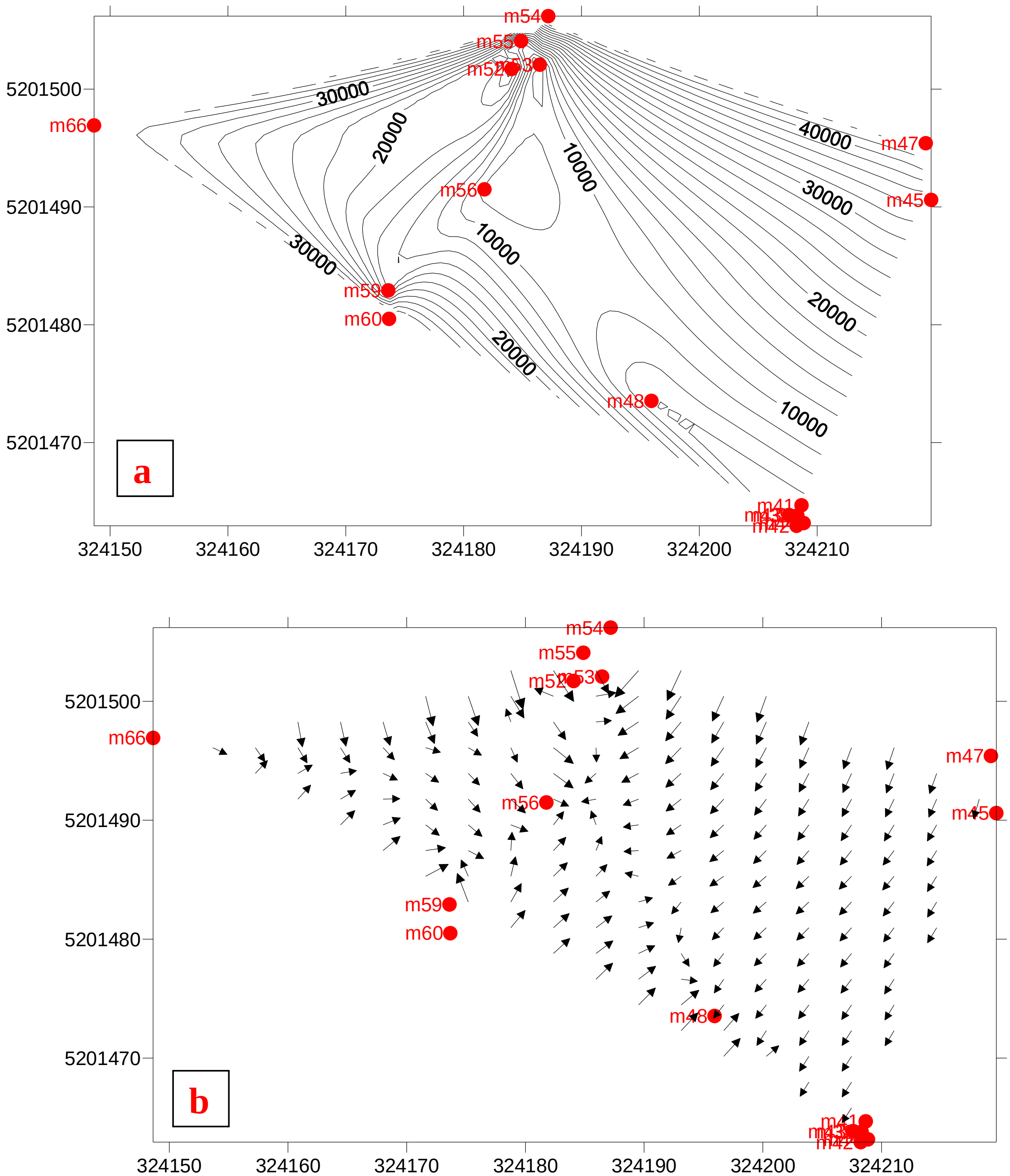

Fig. 6.4.10 The distribution of methane micro-emissions for the G area, m39-m66 measurements, resulted after the Natural Neighbor interpolation (a); vector modeling (b).

The G area (~1870 m^2) where the highest flux values were recorded, had total emissions of 12.9 t CH_4/y, *the highest value reported until now in mud volcanoes from Transylvania.*

Table 6.4.3

Main statistical elements extrapolated from the interpretation of CH_4 emissions from Monor

	Monor V area (2009)	**Monor G area** (2009)
Number of measurements[a]	38	28
Median[b] (mg m^{-2} day^{-1})	22157	29685
Minimum value[b] (mg m^{-2} day^{-1})	1359	1467
Maximum value[b] (mg m^{-2} day^{-1})	406929	1794744
Forced maximum value[b] (mg m^{-2} day^{-1})	121088	8762226
Investigated area (m^2)	860	2600
Emission distribution area - Surfer[b] (m^2)	94	1868
Flux estimations for the total area[b] (t CH_4/year)	2.67	12.9

[a] For all recorded measurements

[b] Values > 10 ppm

Table 6.4.3 shows the essential statistical elements extrapolated from the measurements in Monor, where we can report a methane emission of approximately 16 t CH_4/y from a surface of almost 2000 m^2.

Conclusions

The impact of methane on the environment is universally known on a global scale. The purpose of this thesis was the estimation of methane emissions from geogenic sources in the interior of a hydrocarbon basin (Transylvanian Basin).

For gas measurements visible natural geogenic manifestations were chosen (mud volcanoes, everlasting fires, gas seeps in water) and areas with anthropogenic intervention (gas wells), but also areas that aren't particularly related to gas deposits.

The majority of case studies analyzed in this paper are in correspondence or close to well-known gas structures.

An up-to-date census of mud volcanoes and gas seeps in the Transylvanian Basin is presented, compiled from field and bibliographic data. 73 areas were marked out based on the information from the literature, that were presenting a geogenic source potential (69 mud volcanoes and at least 4 gas seeps in a different form). Methane emissions were measured from 8 mud volcanoes, 1 everlasting fire and 2 gas seeps in water.

Currently, most of the mud volcanoes in Transylvania are inactive or have experimented a prolonged phase of inactivity. Preliminary observations suggest that the reactivation can be tied to meteorological and hydrologic conditions (during rainy periods the appearance of gas bubbles increases in intensity).

Sărmăşel everlasting fires are in the top of the geogenic sources with the highest impact on the environment from Transylvania. A tillage soil that became a waste dump for locals, hosts several chimneys in which due to the powerful seepages from the Sărmăşel deposit, the fire smoulders. This area injects impressive quantities of methane in the atmosphere, evaluated in this paper to 251 t/y, distributed on an area of 1408 m^2 (2007) or 595 t/y from a surface of ~25000 m^2 (2008). Aside from these everlasting fires, no other similar locations are known in the Transylvanian Basin.

Gas and salt water manifestations from Deleni are the result of the degradation for one of the largest gas structures from the Transylvanian Basin (Deleni). Two areas of ~4000 m^2 host gas seeps, mud and salt water. Water basins where gas is bubbling and large muddy areas, surrounded by salty efflorescence, represent the surface image of "depressuring/detensioning" for this deposit. According to this study, total methane emissions were evaluated to 19.55 t/y, reported for a maximum measured surface of 3845 m^2 (2008) or 2.2 t/y, assigned to a smaller surface of only 604 m^2 (2009).

Gas seeps from the Corund (Praid) creek are related to the ascension of gases along the fault lines limiting the salt deposit in its south-west side, or due to relieving the tension of the marginal area of the deposit through drilling wells. Methane measurements recorded are exclusively situated in the macroemission category, with estimated values of 85496 – 592872 mg m^{-2} day^{-1}. High values of CO_2 (>40 $g/m^2/day$), denote the endogen source, reason why this gas was estimated too. CH_4 emissions were evaluated to 4.38 t/y from a surface of 28 m^2, and those of CO_2 to 3.62 t/y from an area of 25 m^2.

Monor's mud volcanoes extend on largest areas, totaling up to 2 hectares, where numerous cones oriented NW-SE and muddy areas with soil vaulting, where the land "trembles when stepped on". Connections with a known deposit from the vicinity are difficult to appreciate for these manifestations. Anyway, the sizes of these cones (2.5 – 3 m high) denote the existence of a geogenic source that maintains and amplifies these phenomena. In Monor the highest methane flux values were recorded, out of those investigated from mud volcanoes in the Transylvanian Basin. A measurement of 8.76 kg $CH_4/m^2/day$ was recorded in "induced" conditions. The highest value recorded in normal conditions reached 1.79 kg $CH_4/m^2/day$ in a mud volcano from the Transylvanian Basin. The total methane emission from the mud volcanoes in Monor was estimated to 15.57 t/y from a surface of 1962 m^2.

The volcanism from Băile Homorod appears on the eastern side of the basin. The activity of the mud volcano and the other 3 salsas depends on the meteorological conditions, intensifying after rainy periods. Small methane quantities were reported several times by different authors through the perspective of being dominantly nitrous. However, investigations from this thesis report emissions for a dry period (2008) of only 0.003 t $CH_4/m^2/day$ for a surface of 10 m^2, but also for a rainy period (2009) of 0.64 t $CH_4/m^2/day$ from a surface of 42.5 m^2. CO_2 fluxes of endogen source were recorded after a rainy period of time in the muddy volcano, leading to a total emission of 0.55 t $CO_2/m^2/day$ for a surface of 18.65 m^2.

Mud volcanoes from Vălişoara overlap on the gas structure from Sânger. Two areas situated at 34 m one from the other, host 2 volcanoes with a moderate activity. In here too the rainy periods influence drastically the activity of the volcanoes. Fluxes are low enough, several recordings from areas with fluid mud were situated between 8860 – 65644 mg CH_4 m^{-2} day^{-1}. A rough estimation of the total methane emission of 0.034 t/y was possible only for a surface of 5.7 m^2.

In Cobăteşti two mud volcanoes were analyzed, one active and the other inactive, both being covered in vegetation. The active volcano from Cobăteşti has a diameter of approx. 8

m, height under 50 cm and the mud flowing surpassed 20 m. Two field measurements between 2008 (dry period) – 2009 (wet period) were performed here. At Cobăteşti in 2008, positive fluxes were recorded in all 10 measurements and led to an emission of 0.25 t CH_4 y^{-1} attributed to a 10 m^2 surface on the active mud volcano cone. For Cobăteşti 2009 the measurements were concentrated also on the active mud volcano on a surface of 94 m^2, leading to estimations of 0.27 t CH_4 y^{-1}.

In Filiaş there are four mud volcano cones, all above 3 m in height. These represent probably the highest volcanic structures in Transylvania. Their activity is very low, mostly influenced by precipitations. The highest flux values (117267 mg CH_4 m^{-2} day^{-1}) were recorded in one volcanic crater presented as a pool with mud, "crater in crater" type. This represents actually a smaller crater with irregular surfaces resulted after the retraction of the main crater due to reduced activity of the mud volcano. Total methane estimations for Filiaş reach the value of 0.39 t CH_4/y, value attributed to a combined surface of ~ 50 m^2.

Porumbenii Mici mud volcanism manifestations are represented by a small volcano with an asymmetric morphology, continuously calm activity and a swampy area (mud pool) with abundant vegetation, located approx. 13 m NE from the volcano. The mud pie is having almost elliptical dimensions with a diameter of approx. 15-20 m and can be considered a muddy area with gas bubbling, water springs and freshly solidified mud. All elements were swept by highly abundant vegetation, difficult to pass through. Flux values measured in both areas at Porumbenii Mici are high (4386-374982 mg CH_4 m^{-2} day^{-1}). The total emission from Porumbenii Mici is 0.47 t CH_4 y^{-1}, reported for a surface of 36.2 m^2.

Boz volcanic manifestations resemble to positive volcanic cones edifices, but also flat structures. More than 12 positive volcanic structures are widespread on a 0.5 ha. The most impressive mud volcano edifice (17 m the base diameter, 2 m in height and 5 m the diameter of the crater) from the Transylvanian Basin, active for at least 50 years, is found in Boz.

The mud volcano from Boz, as state of activity but also because of its dimensions, is the only one from the Transylvanian Basin comparable with some gryphons from the Pâclelor area. Small methane fluxes were found on all active structures from Boz. Conservative estimations of the emissions led to a methane emission estimated to 0.20 t CH_4 y^{-1} for a surface of only 23 m^2.

In the absence of a mud volcanism effect or gas seeps, methane measurements were done in other 12 locations in the Transylvanian Basin, with or without a connection to known gas structures. These measurements were performed in the close vicinity of some wells from

Buneşti (SB); Miheşu de Câmpie (MS); Viforoasa (MS); S67/ European Road E60, section Tg. Mureş - Cluj Napoca; Haşag (SB) or randomly in areas with well known gas structures as those from Sărmaşu (MS), Zău de Câmpie (MS), Cucerdea (MS), Târnăveni (MS), Bazna (SB). Relevant methane fluxes (up to 10^3 mg m^{-2} day^{-1}) recorded in the vicinity of production or exploration wells led to estimating macroemissions. An exceptional value of 14263 mg CH_4 m^{-2} day^{-1} was recorded close to the Viforoasa well.

Measurements performed on soils that have no connection with geogenic methane sources (Cluj, Rădaia, Mihăieşti, Cluj-Napoca (I. Haţieganu park and Raluca Ripan park)) are considered measurements from the category of microemissions and because of that an exact estimation cannot be created for this thesis.

Establishing some intervals for the order of magnitude for CH_4 flux was necessary in order to elaborate criterions for calculating the distribution of flux from areas with high potential towards those with reduced potential. Thus, areas with micro-, mini- and macroemissions were defined.

Methane fluxes from areas with macroemissions and soil can modify seasonally, but annual differences of the medium emission factor are considered minimal.

An estimation of the total general emission, for the investigations presented above in the Transylvanian Basin, leads to a value of ~ 640 t CH_4 y^{-1}. From these, approximately 620 t CH_4 y^{-1} are due to gas seeps (Deleni, Praid, Sărmăşel), 20 t CH_4 y^{-1} due to emissions resulted from 7 mud volcanoes and only 0.10 t CH_4 y^{-1} from soils situated in the vicinity of gas wells.

This total estimation of CH_4 from investigated natural/geogenic sources represent only a small part of the quantity of methane that a hydrocarbon basin introduces annually in the atmosphere.

Conservative preliminary estimations for the entire Miocene gas system (12 000 Km^2), lead to an approximate emission of ~ 680 t CH_4 y^{-1}, including here emissions from all known geogenic sources (mud volcanoes, gas seeps, gas deposits).

The methodology used in this thesis is innovative, until now very few studies based on a similar technique exist. The performance of the "Portable diffuse flux meter for carbon dioxide and methane (WEST Systems)" allows a rapid discovery of new natural or anthropogenic sources of emissions (possible gas accumulations; gas leaks etc.). Fluxes of

CO_2 and CH_4 are calculated directly on the field, leading to the simplification of the data processing stage.

Emissions from geogenic sources assign methane the status of greenhouse gas and only exceptionally that of a pollutant. The negative effect of methane from geologic sources on the inhabited environment and human health is rarely visible. Exceptional cases, when methane emissions reach closed locations, can be due to the lack of initial analysis regarding the concentration of gases in the soil before starting a construction, in the absence of legal background (i.e. the case of the Gherăieşti (BC) ANL houses, located in an area with high methane emissions). In the category of geohazards, by modifying the local geological setting (i.e. ascension of gases due to the faults/fissures), methane from geological sources can appear in inhabited locations.

Contributions regarding the emissions from geogenic sources presented in this paper open new perspectives for performing new studies regarding a better outlining of methane emissions in the Transylvanian Basin.

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