„BABEŞ-BOLYAI” UNIVERSITY CLUJ-NAPOCA
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DOCTORAL SCHOOL ENVIRONMENTAL SCIENCES

GEOGENIC EMISSIONS OF METHANE IN THE MOLDAVIAN PLATFORM AND TRANSYLVANIAN BASIN

— Summary of Doctoral Dissertation —

Scientific coordinator:
Prof. Călin BACIU, Ph.D

Ph.D Candidate:
Ioan-Cristian POP

Cluj-Napoca
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Key words: geogenic emissions of methane, mud volcanoes, Moldavian Platform, Transylvanian Basin

CONTENTS

I. INTRODUCTION

The greenhouse effect represents the phenomenon whereby the terrestrial atmosphere retains the direct solar radiations and radiations from the Earth's surface, due to the presence of gases such as water vapors, CO_2 and CH_4. Among the greenhouse gases, methane ranks third (after water vapors and CO_2) in emphasizing the greenhouse phenomenon (IPCC, 2013).

According to IPCC (2013), after 1750 the atmospheric concentration of CH_4 had increased markedly, reaching 1650 ppb during mid-1980s and 1803 ppb in 2011. Between mid-1980s and mid-2000s the CH_4 concentration growth rate in the atmosphere decreased near to zero, and since 2006 it began increasing again. It cannot be stated whether it is a short-term fluctuation or it represents a new regime for the methane cycle in the atmosphere. The concentration of CH_4 in the atmosphere began to rise along with the industrialization era, that marks an unprecedented intensification of entropic activities (intensive livestock, emissions from the extraction and combustion of fossil fuels, increase of areas planted with rice, etc.), all these representing 50-65% of the total CH_4 sources.

The presence of methane in the atmosphere (both from natural and anthropogenic sources) along with other greenhouse gases (nitrogen oxides, sulfur oxides, chlorofluorocarbons) leads to the greenhouse phenomenon amplification of direct implication on the global temperature increase.

One of the most important natural source of CH_4 is the geogenic emissions. Identification of this type of gas manifestations at soil surface, that may be in the form of mud volcanoes, dry gas emissions or methane-rich springs and quantification of these emissions can provide information in the domain of geology, petroleum explorations, and environmental issues regarding geological hazards and global warming (Etiope et al., 2008).

Mud volcanoes are geological structures resulting from gas emissions, water and sediments at soil surface (Dimitrov, 2003). Mud volcanoes are a significant geological source of methane, having an important role in the atmospheric budget of this gas. On a global scale, dependent on the number of mud volcanoes reported in the literature, various estimates of the annual methane emissions have been made: 10-12 Tg (Dimitrov, 2002), 5-10 Tg (Etiope and Klusman, 2002), 5 Tg (Dimitrov, 2003), 6-9 Tg (Etiope and Milkov, 2004) and 10-20 Tg (Etiope et al., 2011).

Another form of manifestation of gas emissions at soil surface is the dry emissions, whose flows are dependent on the groundwater level or rainfall quantity. A feature of these gas emissions is that they can ignite spontaneously, hence the name “everlasting fires”.

On the basis of information from literature, this thesis aims to identify the gas manifestations in the Moldavian Platform and to quantify for the first time the methane and carbon dioxide emissions and also to complete the existing data on methane and carbon dioxide emissions in the Transylvanian Basin.

Localization of areas with geogenic gas emissions in the two areas involved a thorough documentation from the scientific literature and establishing an effective strategy of verification of the obtained information in the field. During two field research campaigns the points of interest were identified based on data from literature, measurements of gas flows and estimates of methane and carbon dioxide emissions were performed. GPS coordinates were recorded and were noted useful aspects observed in situ, for each point.

This thesis contributes with new information, useful for initiating further investigations in order to obtain more detailed data regarding the area of a potential reservoir. Also the results obtained contribute to outline the methane and carbon dioxide budget on a global scale.

II. THEORETICAL SUBSTANTIATION

Origin of methane

The origin of methane formed in geological environment, called geogenic methane, can be synthesized in two big categories: **biotic**, generated by the decomposition of organic matter by bacteria in the total absence of oxygen and **abiotic**, generated in an inorganic way in volcanic and geothermal systems, or as a result of transformation of ultramafic rocks in serpentine within the Earth's crust (Etiope et.al., 2011c).

Depending on the ways in which it is generated, biotic methane can be **biogenic** or **thermogenic**. Biogenic methane is formed by the action of anaerobic bacteria through sulphates reduction and reduction of albumin, cellulose and lactic acid in sediments. It may also arise by the reduction of carbon dioxide to methane (1) or by the reduction of carbon dioxide by hydrogen (2), in the presence of microorganisms.

$$4CO_2 + 2H_2O \rightarrow CH_4 + 3CO_2 \qquad (1)$$

$$CO_2 + 8H \rightarrow CH_4 + 2H_2O \qquad (2)$$

The temperature for generation of biogenic methane is below 50°C, and the depth of generation is from a few meters up to tens of meters (Beca & Prodan, 1984; Judd, 2000).

Lundegard (2005) considers that biogenic methane can also be generated through acetic acid fermentation resulting from the metabolism of bacterial origin at shallow depths, close to the surface (3):

$$CO_3COOH \rightarrow CH_4 + CO_2 \qquad (3)$$

Thermogenic methane is generated by the decomposition of organic matter in sediments under the influence of physico-chemical factors (temperature, pressure, catalyzers), depth of generation being 1-4 km depending on the geothermal gradient. Thermogenic methane is generated both in catagenesis phase, at temperatures of 200°C and in metagenesis phase at temperatures above 250°C. Transformation of organic matter requires more time, after chemical transformations resulting liquid, solid and gaseous hydrocarbons (Judd et al., 2002).

Atmospheric budget of methane

Estimates of methane emissions were made on a global scale for the last three decades and for 2011 by measuring the CH_4 flow and estimation of CH_4 emissions at source and extrapolate them at regional or national level.

Among the natural sources of atmospheric methane (347 Tg year^{-1} in 2000-2009), the first are wetlands, which represents 62.54% of the total methane emissions, with an approximative emission of 217 Tg CH_4 year^{-1}. Geological sources (including oceans) release annualy about 54 Tg CH_4 year^{-1} representing 15.56%, followed by fresh water (lakes and rivers) that has a contribution of 40 Tg CH_4 year^{-1}, representing 11.53%. Wild animals and termites have an important role in methane emissions, with an emission of 15 and 11 Tg CH_4 year^{-1} respectively, representing 4.32% and 3.17%. Among the natural sources of methane there are also included methane hydrates (1.73%), biomass combustion - spontaneous fires of natural causes (0.86%) and permafrost (0.29%).

Among the anthropogenic sources of methane (331 Tg year^{-1}), production of energy from fossil fuels ranks first with emissions of 96 Tg CH_4 year^{-1}, representing 29% of the total methane emissions. Ruminants is the second important anthropogenic source of methane with emissions of 89 Tg CH_4 year^{-1} representing 26.89%. Microbial activities from landfills have an intake of 75 Tg CH_4 year^{-1}, representing 22.65%. Among the major anthropogenic sources of methane can also be mentioned: rice fields (10.87%) and biomass combustion (10.57%).

Removal of methane from the atmosphere occurs primarily as a result of the reaction with the hydroxyl radical (OH) in the troposphere, the annual consumption of CH_4 equivalent to 90% of all methane emissions from the surface, this total representing 9% of the amount of methane present in the atmosphere (4700-4900 Tg CH_4). The rest of the methane is consumed in the troposphere in reaction with chlorine in the marine environment or in stratosphere in reaction with OH or in soil by the action of methanotrophic bacteria.

Based on the estimation of methane emissions by extrapolating the measured flow at soil surface and on the basis of sources inventory, an emission of 678 Tg CH_4 year^{-1} resulted. Mathematical modeling revealed a global average consumption of 632 Tg CH_4 year^{-1}, resulting in an additional CH_4 of 45 Tg CH_4 year^{-1} in the atmosphere for the period 2000-2011. This surplus was attributed to anthropogenic emissions (IPCC, 2013).

Since 2007, IPCC included CH_4 emissions from geogenic sources in the methane budget. Submarine emissions, mud volcanoes and macro emssions from gas-bearing and oil-bearing basins are considered major sources of geogenic methane, the surface with potential of geogenic emissions representing one third of the Earth’s surface.

Extrapolation of CH_4 emissions globally is difficult to achieve because of the small number of identified and assessed locations (Etiope & Klusman, 2002). Estimates lead to values between 30-70 Tg CH_4 year^{-1}, with an average of 50 Tg CH_4 year^{-1} (IPCC, 2013).

Gas manifestations in geological environments

Gases generated by the decomposition of organic matter in sediments reach the Earth's surface in the form of visible manifestations that alter the soil composition and morphology (macro-emissions) or in the form of invisible emissions (micro-emissions). Macro-emissions can be classified into three categories of gas manifestations: mud volcanoes, springs with gas intake and dry emissions. Micro-emissions are diffuse emissions which occur particularly close to macro-emissions (Etiope et al., 2009).

On the basis of the criterion that a gas manifestation can be named a mud volcano is the existence of three phases: gas, water and sediments. The simplest definition was formulated by Judd and Hovland (2007), who define the mud volcano as a structure that imposes in topography from which a solid material flows or erupts (at least mud, but in general also solid rocks) and fluids (water, gas, oil).

Although there is some similarity between magmatic volcanoes and mud volcanoes regarding surface morphology (i.e. cone structure) or similar activity (eruptions of gas and solid matter), the latter has a different genesis and different eruption products and a reduced manifestation in amplitude.

Dependent on size, mud volcanoes can be complex structures with many craters, peaks and complex exhaust system or simple structures with a single exhaust channel (Judd and Hovland, 2007). Under the mud volcanoes structure there are one or more source-layers (volcano hearth) where the mud material has accumulated and will be expelled through the feed channel.

Mud volcanoes release material originated from sedimentary deposits, in the form of gas, water and solid sediments. The shape and height of mud volcanoes depend on the viscosity, density and grains size of the erupted material, its volume, rate, nature and frequency of emissions: slow or fast (Ivanov et al., 1996; Judd and Hovland, 2007).

If the volcano cone has an angle smaller than 5°, it means they are mud volcanoes with flattened structure. If the crater is filled with mud, the structure formed is called a mud pool.

Another types of macro-emissions

Types of macro-emissions encountered, other than mud volcanoes are (Etiope et al., 2008):

- *Water springs* with CH_4 bubbling. In this case the abundant gas emission is accompanied by water discharge. Water can come from profundity and interacts with the gas in its ascending path to the surface.
- *Dry emissions*, whose main characteristic is the release of a single phase, the gas one, through rock outcrops, soil horizons or beds of rivers and lakes. Gases traversing rocks or dry soil can ignite and burn naturally for longer periods of time (everlasting fires).

Micro-emissions

Micro-emissions are diffuse emissions, slow and continuous characterized usually by small flows and manifestations over wide areas. Micro-emissions were classified into three groups, dependent on the emission factor (Etiope and Klusman, 2010):

- group I, for which the emission factor is >50 mg m^{-2} day^{-1};
- group II, for which the emission factor is between 5-50 mg m^{-2} day^{-1};
- group III, for which the emission factor is between 0-5 mg m^{-2} day^{-1};

The CH_4 flow in case of micro-emissions depends on two factors: the gas amount and pressure in the basin and permeability of rocks and fissures. In areas with seismic activity or active in terms of tectonic, the emission factor can be higher.

Geology of Moldavian Platform

The covering deposited over the crystalline foundation is composed of sedimentary deposits accumulated in three major cycles belonging to the Paleozoic, Mesozoic and Neozoic, having a summed thickness between 2500 m and 6100 m with an increase in thickness from east to west and from north to south (Ionesi, 1994). The oldest rocks that outcrop are the Cretaceous ones.

Geology of the study area in Transylvanian Basin

Opinions on the early formation of the Transylvanian Basin vary from author to author. Vancea (1960) considers Upper Cretaceous - Early Tertiary as a period of the Transylvanian Basin formation and as the completion of the immersion process, the Late Pliocene.

Based on data collected up to that time, Ciupagea et al. (1970) provide a completion, namely that the Transylvanian Basin was formed during five sedimentary cycles: 1 - Upper Cretaceous, 2 - Paleogene, 3 - Lower Miocene (Burdigalian-Helvetian), 4 - Middle Miocene (Badenian) – Upper Miocene (Sarmatian) and 5 - Pliocene.

Krézsek and Filipescu (2005) consider that the evolution of the Transylvanian Basin took place during four stages: Late Cretaceous, Paleogene, Lower Miocene and Mid-Upper Miocene.

Following the tectonic evolution of the Transylvanian Basin, three distinct structures resulted: circular or ellipsoidal domes, diapir folds on the east and west sides and monoclinic in NV, N and S (Săndulescu, 1984).

Natural gas deposits in Moldavian Platform

Gas-bearing structures of the Moldavian Platform occur, in vast majority, in Eocene structures and to a lesser extent in Mesozoic structures (Beca and Prodan, 1983). Through geophysical prospecting, oil-gas-bearing structures of monoclinal type were identified as those in Frasin, Mălin, Valea Seacă, Roman-Secuieni or Mărgineni.

Unlike the folded areas or regions of domes, in the Moldavian Platform hydrocarbon accumulations are in smaller quantities and therefore the exerted pressure is low, resulting in less spectacular gas manifestations, different from the typical mud volcanoes (Peahă, 1965).

Natural gas deposits in the Transylvanian Basin

Most gas deposits were generated in the Miocene (Ciupagea et al., 1970) and are of biogenic origin (Popescu, 1995). Other identified deposits were generated in the Upper Cretaceous - Lower Miocene, as the NV Transylvanian oil-gas-bearing system (Popescu, 1995).

The generating rocks for gas hydrocarbons in the Transylvanian Basin were formed in the Middle Miocene and are of the type of bituminous shales, radiolarian shales and marl packages.

The economic value of some deposits decreased due to the erosion phenomenon: Puini, Strugureni, Sărmăşel, Şincai, Zau de Câmpie, Sânger, Vaidei, because of complications of tectonic nature: Daia, Buneşti, Cristur, Chedea, Şoimuş, Sângeorgiu de Pădure, Ghineşti, Trei Sate, Miercurea Nirajului, Teleac or because of fault structures: Copşa Mică and Noul Săsesc (Paraschiv, 1975; Filipescu and Humă, 1979).

III. RESEARCH METHODOLOGY

Documentation phase

In the scientific literature references were found for 46 locations in the Moldavian Platform and 69 locations in the Transylvanian Basin where there have not been previously made gas flow measurements.

Identification in the field proved to be difficult because of the approximate description of locations, but locals and shepherds proved to be of great help, courtesy of whom most gas manifestations were identified.

Gas manifestations in the Moldavian Platform

During the first field campaign, conducted in the Moldavian Platform in Botoşani, Iaşi and Vaslui counties, 46 locations were investigated selected on the basis of literature data and information from various sources (internet media, personal communications). Among these, active gas manifestations were observed in 11 locations while in one location indications of the existence of inactive manifestations were observed at the time of research. In 34 locations no seeked gas manifestations could be identified.

An active mud volcano was identified which is not mentioned in the literature (Mânjeşti Deal) and an abandoned drilled well with gas emissions in Hlipiceni locality.

The literature records the existence of small gas basins without economic importance in the Moldavian Platform (Paraschiv, 1979). These basins, presumably located at shallow depth, is possible that they have the capacity to generate gas manifestations at the soil surface, that have been studied, at least partially, in the present thesis.

Gas manifestations in the Transylvanian Basin

During the second campaign conducted in the Transylvanian Basin, 69 locations were investigated selected based on literature data and information from various sources (internet media, personal communications). Among these, active gas manifestations were observed in 13 locations while in 3 locations indications of the existence of inactive manifestations were observed at the time of research. In 53 locations no seeked gas manifestations could be identified.

A new point was identified that has not been previously investigated in Boarta locality, represented by an abandoned well from which water flows with gas emissions.

A special case is represented by the geological reservation of Boz, Alba County, where flow measurements have been previously performed at 4 mud volcanoes of the existing 13 (Spulber, 2010). In 2013 measurements have been performed at all volcanoes in the reservation.

Investigation method for the gas flow

Methane and carbon dioxide flow measurements were performed by the closed chamber method, using a portable device developed by West Systems srl Italy. The device is composed of an accumulation chamber, a methane detector and a carbon dioxide detector, a ventilation device of the accumulation chamber, a gas suction pump from the accumulation chamber, filters. Flow calculation is made by a portable computer equipped with a dedicated software. Data reception from detectors is performed through a wireless network.

Mode of operation

The accumulation chamber is placed on the ground up to the limiter and the gas flow is measured by the variation of the gas concentration in a chosen time interval (Etiope, 2008; Spulber et al., 2010).

Data recorded by the detectors are transmitted to the computer via a dedicated software installed (FluxManager) that records in real time the flow curves and calculates the methane and carbon dioxide flows. During measurements, the flow curve, the regression quality factor, the slope (ppm/s) and the minimum and maximum concentration values (ppm) are displayed on the computer screen.

In order to obtain a better flow assessment, a proper selection of the flow curve is required, depending on the measurement duration and the slope. It is recommended that the measurement time is in the range of 120÷360 seconds and the linear regression of the flow curve has the best slope (a).

Method of data interpretation

In order to estimate emissions of methane and carbon dioxide, two methods were used: “natural neighbor” interpolation and emission factor.

a. “Natural neighbor” interpolation method

This method provides the best interpolation for irregular spatial distribution of measurement points, without allocating large flows to sectors where no measurements have been made.

b. Emission factor method

This method consists in dividing the analyzed surface in homogeneous areas with fluxes close in order of magnitude, for which an average flow is determined, the total emission being obtained using the formula (Etiope et al., 2007):

Emission factor method was used in case of a small number of measurement points in relation to the analyzed surface or because of the difficult or impossible access in some parts of the investigated area (usually the central area) and for which interpolation of measured flows leads to an overestimation of gas emissions. Determination of homogeneous areas was based on field observations and according to the flows distribution on the analyzed surface.

The difficulty of the method was to determine the influence of homogeneous areas upon the central area, especially in case of mud volcanoes with large areas and perimeter arrangement of the measurement points. Useful information for this method is regarding the following:

- *Volcano structure*. If it has a dome structure, it is likely that at the maximum height point flows reach the highest values decreasing towards margins. In case of a flat structure, it is difficult to estimate the flow in the central area and framing in one of the homogeneous areas, but for this purpose observations on the presence of water holes in which brawlings or recent traces of sludge leakage are visible may be helpful.
- *Solid material on the surface*. The presence of rock fragments in different environmental uninvestigated areas indicates a probability of emissions. Estimation of gas flows levels and framing in one of the homogeneous areas can be facilitated by comparing these areas with those in which measurements have been performed. If liquid mud or puddles occur in the uninvestigated area, and the study area (perimeter) is covered with a crust of dried mud, it is possible that flows are higher in the uninvestigated area.
- *Crust condition*. If the uninvestigated area is covered with a hardened crust, crossed by cracks, flows diffuse along those. A realistic estimate would be framing of the uninvestigated area in the homogeneous area defined by the flow in the immediate vicinity.

In case of small areas up to 2 m^2 or those completely covered by dry crusts and crossed by cracks, emissions were estimated by calculating the average flow for the whole analyzed area.

Different situations may arise in the field for which a great number of scenarios can be created. A more realistic estimate can be obtained using as much information as possible from the site and on the basis of information from scientific literature. Gas emissions estimation by differentiating data into groups with flows of the same order of magnitude and calculating an average flow for each homogeneous area in part is closer to reality than calculating an average flux attributed to the analyzed surface considered homogeneous or by summing measured flows where the distribution area of emissions is given by the product between the number of measurement points and the surface of the accumulation chamber.

RESULTS AND DISCUSSIONS

Investigation of methane and carbon dioxide emissions in the Moldavian Platform and uninvestigated areas in the Transylvanian Basin represents the experimental part of this thesis.

The Moldavian Platform

Measurements in the Moldavian Platform were performed in a dry period (July 2013), the estimated quantities of methane being generally low. In total, 93 measurements were made of which 67 (72%) recorded flow values below 10 ppm. Higher values of CH_4 flows were recorded punctually in the gas manifestations from Stănileşti (3372 g m^{-2} day^{-1} in point no.6), Pogăneşti MV2 (2116 g m^{-2} day^{-1} in point no.1) and Oțetoaia MV2 (1231 g m^{-2} day^{-1} in point no.1). CO_2 flows measured in individual source points are between 1.45 to 8489 g m^{-2} day^{-1}. Total estimation of emissions from natural sources in the Moldavian Platform reaches 8.99 t/year CH_4 and 55.35 t/year CO_2.

In the case of Hlipiceni site, flow measurements showed values of $13x10^5$ g CH_4 day^{-1} and $4x10^4$ g CO_2 day^{-1}, estimations of emissions reaching 11,08 t/year CH_4 and 0.45 t/year CO_2.

Total overall emissions in the Moldavian Platform form emission sources investigated for the first time in this study show values of 20.07 t/year for methane and 55.8 t/year for carbon dioxide.

In the Moldavian Platform, the rock gas storage is in a region of platform with much lower gas accumulations than in folded regions. This explains the low recorded emanations. In two locations, Pogăneşti and Hlipiceni, a higher gas flow allowed gas sampling for analysis in the laboratory. The results show that in case of the gas manifestation in Pogăneşti, methane has a mixed origin, thermogenic and microbial while in Hlipiceni it has a microbial origin.

No information has been published to date about the existence of hydrocarbons or methane deposits in the Moldavian Platform closely related to methane emissions in the studied areas. Except for the drilled well in Hlipiceni, which allows gas migration to the surface passing through the existent aquifer at a depth of about 200 m. In this case, the very low water flow indicates that a groundwater not being under the pressure of aquifer layers, its flow being caused by the high gas flow (mainly methane and carbon dioxide) that indicates the existence of an underground gas accumulation. Gases can be ignited, the flame reaching 25-30 cm in height.

The obtained results do not provide information about their size and depth, and it can not be stated whether they are economically feasible. The fact that methane emissions have been identified represents a starting point for further investigations in order to obtain more detailed data on the potential reservoir area.

The Transylvanian Basin

In the Transylvanian Basin, 284 measurements were performed out of which 190 (~66%) recorded flow values below 10 ppm. Higher values of CH_4 flows were recorded punctually in gas manifestations from Goagiu (2941 g m^{-2} day^{-1} in point no.1), Blăjel MV4 (512 g m^{-2} day^{-1} in point no.4) and Ţapu MV1 (464 g m^{-2} day^{-1} in point no. 2). CO_2 flows measured in individual source points range between 2.88-2941 g m^{-2} day^{-1}. Total estimation of emissions of gas manifestations from natural sources in the Transylvanian Basin reaches the value of 20.15 t/year CH_4 and 57.08 t/year CO_2.

In the case of Boarta probe (anthropogenic emissions), flow measurements showed values of 41547 g CH_4 m^{-2} day^{-1} and 551 g CO_2 m^{-2} day^{-1}, emissions estimates reaching 1.11 t/year CH_4 and 0.059 t/year CO_2.

Data obtained in the geological reservation of Boz, Alba County represent a completion to measurements performed in 2009 by Spulber. Gas flows measured in 85 individual source points range between 0.13-205 g CH_4 m^{-2} day^{-1} and 8.08-2490 g CO_2 m^{-2} day^{-1}; total estimation of emissions reaches the value of 3.76 t/year CH_4 and 24.19 t/year CO_2 for an emission distribution area of 208.89 m^2. CH_4 estimates obtained by Spulber led to a methane emission of 0.20 t/year CH_4 for an emission distribution area of 23 m^2.

Investigation of gas manifestations at Băile Homorod in 2014 revealed a change of the conditions recorded in 2009 by Spulber. Gas manifestations recorded in 2009 became inactive and three new emission points were identified. Estimates in 2014 led to values of 0.01 t/year

CH_4 and 0.23 t/year of CO_2, indicating a decrease of methane and carbon dioxide emissions in comparison to 2009.

Total estimated overall emissions in the Transylvanian Basin form emission sources investigated for the first time in this study show values of 21.26 t/year for methane and 57.13 t/year of carbon dioxide.

Similar international studies

In the past 50 years numerous studies have been performed on mud volcanoes and gas emissions areas (e.g. Jakubov et al., 1971; Barber et al., 1986; Kopf, 2002), more than 10000 such gas manifestations being estimated (Clarke and Cleverly, 1991), out of which only a small number have been investigated directly: over 1150 gas manifestations in 84 countries.

Measurements of methane emissions from geogenic sources – macro-emissions were measured in five countries in Europe (including Romania). Measurements performed in Italy led to an estimate of emissions of 3203 t CH_4 year^{-1} corresponding to an investigated area of 1.53 km^2. In Greece, in an investigated area of 0.04 km^2, estimated emissions lie around 17.6 t CH_4 year^{-1}. In Scotland, on the investigated 0.0025 km^2, emissions were estimated at 400 t CH_4 year^{-1}. In Switzerland, for which the investigated area was not reported, estimated emissions are 71 t CH_4 year^{-1} (Etiope, 2008).

In Azerbaijan, on the investigated 5.9 km^2, flows of 55-560000 mg m^{-2} year^{-1} were recorded, with total emissions of 1392 t CH_4 year^{-1} and emission estimates were performed on an area of 2000 km^2 resulting methane emissions of 300,000-900,000 t year^{-1} (Etiope, 2008).

Micro-emissions (except for mud volcanoes or areas near macro-emissions) represent a source of methane with an impact on the atmospheric budget of this gas, the estimates indicate a contribution of more than 10 Tg year^{-1} (Etiope and Klusman, 2010).

According to the data published so far, Romania investigated 2,275 km^2, the estimated total emissions exceeding 2100 t CH_4 year^{-1} (Etiope, 2009; Spulber, 2010). Contributions in this thesis regarding emissions form geogenic sources provide the first information about emissions areas in the Moldavian Platform and is a completion of CH_4 emissions in the Transylvanian Basin. However, information published in this thesis on gas emissions in the Moldavian Platform represents the preliminary data in the case of conducting prospecting in the investigated areas.

All data obtained in this thesis will contribute to a more accurate outline of CH_4 budget at global scale.

CONCLUSIONS

- The literature studied for writing this thesis mentions the existence of 46 locations with gas manifestations in the Moldavian Platform and 69 locations in the Transylvanian Basin.
- As a result of investigations in the field, 11 locations with active gas manifestations were identified in the Moldavian Platform (mud volcanoes and areas with emissions) and indications of the existence of an emission manifestation in a location, but inactive at the time of research. Emissions estimated on the basis of the results obtained from the 93 flow measurements performed in the investigated locations in the Moldavian Platform show values of 20.07 t/year for methane and 55.8 t/year of carbon dioxide.
- In the Transylvanian Basin, 13 locations with active gas manifestations were identified (mud volcanoes and areas with emissions) and indications of the existence of inactive manifestations at the moment of research in 3 locations. Emissions estimated on the basis of the results obtained from the 284 flow measurements performed in the investigated locations in the Transylvanian Basin show values of 21.26 t/year for methane and 57.13 t/year for carbon dioxide.
- Currently no information has been found on the existence of deposits or reservoirs of methane or regarding initiation of prospecting in the investigated areas of the Moldavian Platform.
- Gas manifestations investigated in the Moldavian Platform represent the surface evidence of natural gas occurrence, without giving information about their size and depth. At this stage of the investigation it can not be stated whether the identified natural gas accumulations are economically feasible. The importance of these investigations is that they can be a starting point for further investigations in order to obtain more detailed data on the potential reservoir area.
- In the Transylvanian Basin, the performed investigations complete the existing data on methane and carbon dioxide emissions obtained by Baciu (2007) and Spulber (2010).
- This thesis investigated for the first time the emissions of methane and carbon dioxide in the Moldavian Platform and in uninvestigated areas with emissions in the Transylvanian Basin, contributing to the completion of the data published to date on emissions in Romania and to the completion of the global database.

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