Synthesis scientific report

on the implementation of the project between October 2011 – December 2013

GEOGENIC EMISSIONS OF GREENHOUSE GASES FROM GEOTHERMAL AND PETROLEUM SYSTEMS-
APPLICATION TO ROMANIA

PN-II-ID-PCE-2011-3-0537

The main activities of the project between January-December 2012 were mainly focused on work packages 1, 2, 3 and 4.

WP1 – State-of-the-art

This work package started in the first year of implementation of the project, and continued the first 3 months of the second year. In this stage, we continued our activities regarding the synthesis of information regarding the natural emissions of GHG on national and international level. More than 300 publications were analysed in total. The data regarding Romania were synthesized in an international database which contains more than 574 manifestations, and 823 of molecular and isotopic analyses. This package was completed during the first 6 months of the present project (October 2011 and April 2012).

The gas accumulations on the Romanian territory can be attributed to two major categories, based on the geological systems in which they can be found.

1. Petroliferous systems (predominantly with methane emissions) – from this areas the following regions have been investigated: Transylvanian Basin, some regions from the Carpathian Foreddeep, eastern part of the Pannonian Basin (where methane and carbon dioxide emission both are present);

2. Geothermal/volcanic systems (predominantly with carbon dioxide emissions) – the regions to be investigated are: Eastern Carpathians, some areas of the Apuseni Mountains and Southern Carpathians (with uncertain geothermal character: Herculane-Mehadica, Calimanesti-Caciulata, areas with hyper-alkaline rocks from the Danube region.

It is little known, that at international level Romania was the first country to extract petroleum at an industrial level, with the first registered production rate of 1719 barrels in 1857. It must be underlined that this happened one year before the first well of William at Oil Springs, and two years prior Drakes discovery in Pennsylvania (moment which is considered the start of the petroleum industry).

Although Romania has a variety of gas sources and types, a great scientific investigation potential, and important economic potential of hydrocarbons, very few geochemical studies were published before 2000. It is worth mentioning the book of Filipescu and Huma published in 1979, which is an excellent synthesis on the state of the art of that period for the Romanian territory. The two authors describe in detail and very precisely the chemical characteristics of the gases, the reservoir structures in the geological systems. In this book and in other publications of the time, the characterization of gases was done only regarding the molecular composition of the gases. Isotopic analyses are an important key to determine the origin of
gases. A systematic approach for the characterization of the gases was started after the year 2000, within the collaboration between UBB (Calin Baciu) and INGV Roma (Giuseppe Etiope). Studies were performed in different locations in Transylvania and the extra-Carpathian areas, which lead to a database, containing chemical and isotopic analyses, and fluxes of the greenhouse gases (GHG).

The isotopic/molecular analyses were performed in prestigious international laboratories, with the help of INGV Roma, without any financial support. This is the reason why the database has a relative small number of investigated sites. But there are perspectives for upgrading/updating the database during the present project. The research performed by the above mentioned group was published in the international scientific literature (Baciu et al. 2005, 2007, 2009; Etiope et al. 2002, 2003, 2004a, 2004b, 2009, 2010, 2011). In these works the flux of GHG was quantified, first of all the methane of geologic origin, between the lithosphere/soil and atmosphere. It is worth mentioning that some of these articles gave new insights on an international scale regarding: the existence of microseepage in the area of gas manifestations; characterization of areas with strong degradation of petroleum; it also helped calculating the total output regarding GHG emissions to the atmosphere.

Similar to the petroleum systems, the geothermal systems are also insufficiently studied, regarding their gas geochemistry. A reference paper was published by Vaselli et al. in 2002. This article describes a geochemical transect in the southern part of the Eastern Carpathians. Most of the gases have high CO2 content, sometimes with significant amount of nitrogen. In the present study the isotopic ratio of carbon from CO2, and helium were measured. The results show that the CO2 originates from the thermo-metamorphism of the carbonate rocks. Some samples indicate that CO2 derives from the degradation of organic materials.

**WP2 – Field investigations and laboratory analyses**

The investigations connected to the present work package were performed between November 2011 and October 2013, but due to financial modifications it will continue until the last year of the project. Until now the areas marked in fig 1 were investigated.

![Figure 1](image-url)

**Fig. 1.** Investigated areas: violet – 2011, red – 2012, green – 2013.
The good weather condition allowed us to perform a first field campaign, in the western part of the Southern Carpathians, namely the Orsova-Tisovita-Eibenthal area in November 2011. A field campaign was undertaken and several samples were collected. In parallel another location was also visited, the geothermal springs from Mehadica, where gas and water samples were collected. In the field, water pH and temperature were measured with a multi-parameter, and we tried also to detect some gas fluxes with the closed chamber technique (for CH4 and CO2, West System Fluxmeter; and with a Hubert hydrogen detector).

In 2012 the following regions were investigated: the central and southern part of the Eastern Carpathians, the Transylvanian Basin and the Banat region.

In the Eastern Carpathians, multiple field campaigns were undertaken, in order to evaluate the carbon dioxide flux. The main locations were: Corund, Balvanyos, Sugas, Turia, Ciomadu, Homorod, Craciunel, Madicsa, Sancraieni, Vrabia, Lazaresstii, Bancu, Frumoasa, Rodna, Anies, Lunca Ilvei. Also gas samples were collected for molecular and isotopic analysis. The samples were sent to the Nuclear Research Institute ATOMKI from Debrecen.

As carbon dioxide appears as free and dissolved gas in water, a special attention was given to the mineral water springs. At the springs the gas fluxes were measured, and waters and gas samples were collected, for molecular and isotopic analyses. Another field campaign was performed in the western part of the Eastern Carpathians, for sampling sparkling mineral waters. Thanks to collaboration with INGV Palermo, the samples were analysed for: ion-chromatography, gas-chromatography, helium content, carbon-13, oxygen-18, and deuterium. The PhD student Kis Boglarka undertook a 4 month long internship at INGV Palermo, in which she is analysing and interpreting the data obtained from the above mentioned samples.

In summer 2012 another field campaign was performed for investigating the everlasting fires from the flysch part of the Eastern Carpathians and the Carpathian Foredeep. We investigated the following locations: Andreiasu, Raiuti, Lopatari, and Lepsa. These manifestations are quite frequent in the Eastern Carpathians, but quite rare on a European level. The methane and carbon dioxide fluxes were measured on the sites; gas sample were collected which were analysed at Isotech Illinois. The data are currently being prepared for an international publication.

The Banat area was also investigated for carbon dioxide emission in the location of Fibis, and gas samples were collected for isotopic analyses.

During 2013 the Moldavian Plateau, the southern part of the Carpathian Foredeep, the southern part of the Transylvanian Basin, the springs from Slanic-Moldova, a few spring from Bihor County were investigated.

In the Moldavian Plateau a series of locations were investigated, indicated in the scientific literature, which describe some gas manifestations. Flux measurements where performed in the following locations: Cotnari, Gorbani, Poganesti, Stanilest, Otetoiia, Berezeni, Coznesti, Leosti, Musata, Curteni. The most interesting structures where found near the Manjesti Lake (VS), where mud pools have been identified having a few meters in diameter. The mud is fluid, and has a dry crust, which in some cases can withstand the weight of a person. The crust vibrates intensely when a shock is applied. In Hlipiceni, the so called “burning spring” was also investigated. The highest emissions where found at Chersacosu and Hlipiceni sites.
In the southern part of the Carpathian Foredeep, a series of springs were investigated. At some spring we could observe macroscopic bubbles, while for others the presence of methane was only detected by analytical instrumentation. A total of 55 water samples were collected. Almost all samples contain methane in larger or smaller amounts, which open new perspectives for research. The samples which contained larger amounts of dissolved methane were sent to INGV Roma, for molecular (FTIR) and carbon-13 from methane (Piccaro) analysis.

In the scientific literature a lot of sites are mentioned in the southern part of the Transylvanian Basin, where mud volcanoes can be found. More than 40 sites where investigated, out of which approximately half show a methane flux. The locations where larger or smaller fluxes of methane were found are the following: Blajel, Boarta, Boz, Sangatin, Sorostin, Tapu and Veseud. Tauni was also investigated, where the methane emissions are very intense.

Also the springs from Slanic-Moldova where investigated, and samples were collected, in order to identify the dissolved gases. Also some artesian and sulphur springs where sampled in Bihor County. The analyses are in progress for detecting the dissolved gases.

For the field measurements and laboratory analyses the following equipment was used:

1. West Systems Portable Fluxmeter (Italy), with a CH4 and CO2 detector, linked wireless with a palmtop computer. The methane detector contains a semiconductor (range of 0 to 20000 ppmv, detection limit 1 ppmv, and resolution of 1 ppmv), catalytic detector (2000 ppmv until 3% v/v) and a thermal conductometer (range of 3-100%). The carbon dioxide detector is an infrared laser sensor (LI-COR). The CO2 sensor has the following parameters: measuring range of 0 to 20000 ppmv, accuracy of 2%, and repeatability of ±5 ppmv.

2. FTIR Gasmet DX-4030 (Gasmet, Finland) with a standard spectral library, for rapid semi-quantitative detections of 13 gases: CH4, CO2, Co, H2O, C2H4, C2H6, C3H8, n-C4H10, i-C4H10, n-C5H12, i-C5H12, C6H6, COS and SO2. The FTIR has the following parameters: accuracy 10-20%, detection limit of 1 ppmv.

3. For isotopic analyses performed in Rome, an isotopic analyser for carbon-13 from methane, working on the principle of Cavity Ring Down Spectroscopy (CRDS), Picarro G2112-I (accuracy <0.7‰ at 1.8 ppmv of CH4, 5 minutes, 1σ, <0.4‰ at 20 ppmv, 5 minutes, 1σ).
WP 3 – Geochemical interpretations

Work package 3 is dedicated to the geochemical interpretation of isotopic and molecular analyses of the gases.

The first data regarding the isotopic composition of a natural gas reservoir in Romania were published relatively recent (Baciuc et al. 2008). The total available data in publication, regarding seeps in petrolierous areas in Romania, are only for 11 seeps, which are the work of the present project team.

The most unusual gas composition can be found in Homorod (BV). Small mud volcanoes were found at Homorod, which release nitrogen above 90%, CO2 approximately 5% and very low concentrations of methane, and above 1% of helium. These are the highest recorded nitrogen and helium content from any onshore mud volcano. Also the deuterium ratio of methane is the highest ever measured (+124‰) in natural gas. These results were published in the journal Chemical Geology (Etiope et al. 2011). In the present project we will try to extend the research regarding the gases with high nitrogen, and helium content, and also with unusual isotopic ratios.

Fig. 2. Interpretive diagram for the genetic classification of gases in Romania, based on the ratio of deuterium and carbon-13 from methane (Schoell-diagram).
Fig. 3. Schoell-diagram for investigated gases from Romania, calibrated for vitrinite reflectance.

Fig. 4. Bernard diagram for the everlasting fires investigated in the Eastern Carpathians.

The geochemical interpretations use compositional diagrams, combining either isotopic ratios (like the Schoell diagram fig 2 and 3) or isotopic ratios with molecular ratios (like the Bernard-diagram, fig. 4 and 5). For the collected samples the analyses and interpretations are in progress. As preliminary results it can be stated that the gas manifestations that produce everlasting fires in the flysch/molasse areas of the Eastern
Carpathian, have clear thermogenic origin, with the exception of Lepsa which is shifted towards a microbial/thermogenic mix. In the Bernard diagram Andreiasu, Raiuti and Lopatari are clustered, which suggests a genetic similarity. A small mud volcano identified a few hundred meters from the everlasting fires, has different characteristics, especially the higher Bernard ratio \((C_1/(C_2+C_3))\). This is due to the vertical migration of the gas which modifies the ratio between methane and the higher analogues, much like a chromatographic-effect. By plotting the Bernard-diagram for the water samples we can observe a slightly abiotic origin of the gases. This possible abiotic origin of the gases opens new perspectives for future research.

Fig. 5. Bernard diagram for the investigated springs from Oltenia, Caciulata and Baile Herculane.

**WP4 - Georeferenced database of geogenic gas emissions in Romania**

Work package 4 aims to create a georeferenced database for the Romanian geogenic emissions. In this database all locations that have been investigated during the project will be added, containing flux values, isotopic and molecular composition. Based on this a map was created with the gas manifestations (fig 6.). The map is currently under construction, with the database. Until now almost 360 locations where introduced in the data-base and map.
Fig. 6. Screen-shot of the Romanian gas emissions database for Romania (fragment).

Fig. 7. Distribution of the geogenic hydrocarbon manifestations on the Romanian territory

Figure 8 illustrates the activities performed in different sites, in the study areas.
Fig. 8. Field activities: A, B – Lepsa; C, D, U – Andreiasu; E – Raiuti; F – Lopatari; G – Fibis; H – Baile Govora; I – Pausa; J – Sarata Monteour; K – Tauni; L, M – Baile Herculane; N, V – Cotnari; O, X – Manjesti; P, Q – Tisovita; R – Boarta; S – Slanic Moldova; T – Rotaresti; Y – Hlipiceni.
Dissemination activities

The dissemination activities include the participation to scientific conferences and publications in mainstream journals. Within the first two years, the team members have participated to 7 international conferences, and published 6 articles and an abstract in ISI indexed journals. All publications acknowledge the financial support offered by the Romanian government through the IDEI Program.

The activity of the young researchers was very important in the project. Two PhD students involved in the project, Nicolae Frunzeti and Kis Boglarka have finalized and successfully defended their thesis.

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