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FLUX MEASUREMENTS OF ^{222}Rn, CH_4 AND CO_2 ALONG WITH SOIL GAS CONCENTRATIONS (^{222}Rn, CO, NO_2 AND SO_2) OVER A METHANE RESERVOIR IN TRANSYLVANIA (ROMANIA)

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Abstract: The Transylvanian Basin is well known for its large and good quality methane accumulations. In many sites these accumulations are not completely sealed, and methane leaks into the atmosphere through faults or fractures. A soil gas survey was carried out after a rainy season at Sărmăşel, the largest methane seep in Transylvania. This study presents the first results of soil ^{222}Rn concentration measurements in relation with CH_4 flux, in an attempt to better understand the spatial distribution of soil gas concentrations and migration toward the surface in this area. Taking into account the particular situation in the field, the study area was divided in two sub-areas corresponding to the two main seeps with high methane emissions and everlasting fires. Accordingly, two sets of measurements were performed. The first set was distributed on a 36 meters transect with respect to seep 1. The soil gases concentrations (^{222}Rn, CO, NO_2 and SO_2) were measured at 80 cm depth along with CH_4 and CO_2 fluxes. The maximum values of ^{222}Rn concentration from soil was found at 17.5 $kBq \cdot m^{-3}$ and quite high concentrations of other gases, such as 19 ppm of CO, 1 ppm of SO_2 and 0.7 ppm of NO_2. The results suggest that concentrations of CO, NO_2 and SO_2 correlate with CH_4 and CO_2 fluxes. Radon concentration in soil seems to be more dependent on soil permeability than on the CH_4 flux. For the second set of measurements, the CH_4 and ^{222}Rn fluxes were randomly distributed around the main vents. It was observed a relatively high ^{222}Rn flux with a maximum value of 119.3 $mBq \cdot m^{-2} \cdot s^{-1}$ and an average of 58.4 $mBq \cdot m^{-2} \cdot s^{-1}$, over an area with high CH_4 emission.

Keywords: gas geochemistry, methane, radon, soil permeability

1. INTRODUCTION

The importance of soil gas monitoring has been widely demonstrated in numerous applications in volcanology (Gal & Gadalia, 2011), petroleum exploration (Link, 1952; Abrams, 2005), and geophysics (Lombardi & Voltattorni, 2010; Papp et al., 2010). The gas migration toward the surface is strictly related to the existence of a gas reservoir, and the existence of a preferential pathway for degassing such as fractures or faults (Etiope & Martinelli, 2002). The variation of pressure, temperature, mechanical stress, and other tectonic factors lead to gas migration. Geogenic gasses include mainly CO_2, H_2O, H_2S, NH_3, H_2, N_2, CH_4 and heavier hydrocarbons, but also inert gases like He, ^{222}Rn or Ar. In sedimentary basins, the geogenic gas is mainly composed of CH_4 (very often up to 90-99 %) followed by some trace amounts of other gases. The studies performed during the last decades, suggest that during the gas migration towards the surface, the large amount of CO_2 in volcanic-geothermal systems and CH_4 in sedimentary basins act as carrier gasses (Durrance & Gregory, 1990; Morner & Etiope, 2002).

Radon (^{222}Rn) is a radioactive gas, chemically inert, which originates from the decay of the uranium (^{238}U) series. In general, soil ^{222}Rn has a near surface origin as its half-life is 3.82 days. But there are many cases when it may indicate the presence of an area where the advection or diffusion of other gasses like CO_2 or CH_4 occurs. Nazaroff (1992) estimated an average ^{222}Rn flux of about 22 $mBq \cdot m^{-2} \cdot s^{-1}$ in an area without uraniferous formations. In the presence of a

carrier gas, the radon flux may be higher. The physical properties of the soil, especially the permeability, may also influence the ^{222}Rn flux. Despite of the progress in understanding the theoretical processes controlling the release of ^{222}Rn from soil to the atmosphere (Porstendorfer, 1994), the lack of studies of radon flux and its distribution over the earth is still under question. Gas emission very much depends also on external factors such as atmospheric pressure, temperature, soil humidity, etc (Schumann et al., 1994; Toutain & Baubron, 1999).

Geogenic methane is predominantly released by natural seepage systems in sedimentary and petroleum basins (Etiope & Milkov, 2004; Frunzeti et al., 2012; Spulber et al., 2010).

The Transylvanian Basin is well known for its large and good quality methane accumulations, being one of the most important hydrocarbon-bearing basins in Europe (Popescu, 1995). In many sites, these accumulations are not completely sealed and methane leaks into the atmosphere through faults or fractures (Baciu et al., 2007). Sarmasel region (Fig. 1), which represents the study area of this work, is considered to be the largest methane seepage in Transylvania (Spulber et al., 2010).

The current study presents the first results of soil gas concentration measurements (^{222}Rn, CO, NO_2 and SO_2) at Sarmasel seep. The measurements were performed along with ^{222}Rn, CO_2 and CH_4 fluxes, in an attempt to better understand the spatial distribution of gas concentrations in soil and migration toward the surface. Conclusions regarding the ^{222}Rn flux dependency by respect to CH_4 flux and soil permeability have also been drawn.

2. GEOGRAPHICAL AND GEOLOGICAL SETTINGS

The study area is located in the NW part of the Transylvanian Basin, at 325 m a.s.l. Burning flames up to 20-30 cm high may be observed over an area of tens of m^2 (Fig. 2.b). The total area of visible methane emission (everlasting fires and lack of vegetation) is about 2000 m^2, but the diffuse emission of methane may be found on a total surface of about 25 000 m^2 (Spulber et al., 2010). Sarmasel seep is located above the Sarmasel gas reservoir; a N-S oriented brachianticline with 15 productive horizons (Paraschiv, 1979).

The gas bearing sandy horizons are Sarmatian and Badenian in age (Paraschiv, 1975). The wells drilled in the area at the beginning of the XX^{th} century suggest that the gas reservoir is placed between 281 and 1173 m depth. The rocks between the gas-bearing horizons consist of sands and marls, intercalated with sandstones, dacitic tuffs and clays. At more than 2000 m depth, the gas bearing complex is underlain by the salt formation that may exceed 900 m of thickness. The deepest drills have reached the Dej tuff, middle Badenian in age, at almost 3000 m (Paraschiv, 1979).

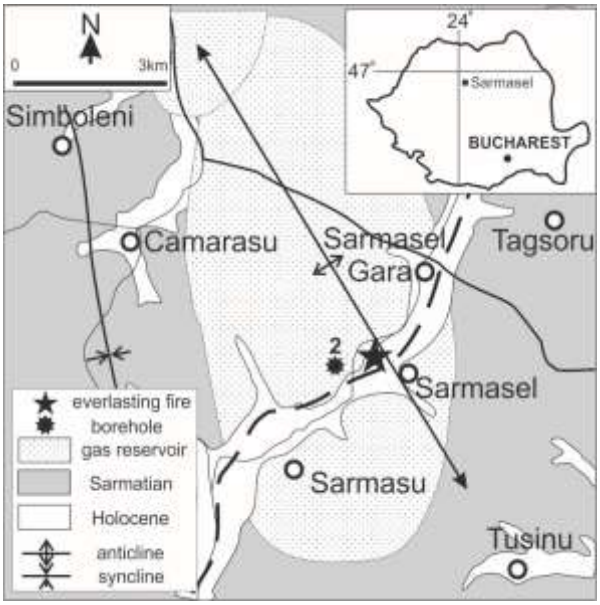

Figure 1. Geological map of Sarmasel area (after Răileanu et al., 1967)

3. METHODOLOGY

The closed chamber technique was applied for CH_4 and CO_2 flux measurements (Fig. 3.b), by using a portable diffuse flux meter (West Systems srl, Italy), as described in Spulber et al., (2010); Frunzeti et al., (2012).

For soil ^{222}Rn concentration measurements, the LUK 3C detector was used. The soil gas was collected by inserting a probe at 80 cm depth in soil and pulled up approximately 5 cm (Fig. 3.a). Detailed description of the methodology may be found in Papp et al., (2010). The ^{222}Rn flux was measured by using the RAD7 radon monitor (Durridge Company Inc.), based on semiconductor detection technique. The instrument draws air from an accumulation chamber (with a volume of 0.005 m^3) through a desiccant (drierite) filter and an inlet filter, into the detection chamber. The mothodology is described in Tuccimei & Sanio, (2008).

Gas concentration measurements for CO, NO_2 and SO_2 were performed with a portable gas analyser (OLDHAM multigas monitor MX 21 PLUS). The measurements were performed after connecting the device to the soil probe inserted in

Figure 2. a) overview of the study area; b) everlasting fire from Sarmasel seep; the numbers correspond to the distance measured in meters from the main vent

soil at 80 cm depth. Soil permeability was measured with a method based on the gravitational flowing out of a water column from a bottle (at the bottom part of the bottle) (Cosma et al., 2013).

The water content from soil at 10 cm depth was determined for the area without vegetation, by collecting three soil samples and analysing the loss of mass by drying in an oven at 40ºC for 72 hours.

4. RESULTS

As gas emissions depend not only of the soil characteristics but also on atmospheric conditions, it is worth considering the meteorological conditions that prevailed while the measurements were taken.

Figure 4 presents the meteorological parameters (temperature, rain amount, atmospheric pressure and air humidity) for the last 10 days prior to the measurements with values recorded at every 3 hours.

It is worth to notice that it was a rainy season, with almost daily precipitations and a total of 75 mm in the last 10 days (Fig. 4.b).The average value of soil humidity at 10 cm depth in the area without vegetation was 26.9 %. The statistics of the gas fluxes and concentrations are reported in table 1.

4.1. Flux measurements of CH_4 and ^{222}Rn

At seep 2, three measurements for both CH_4 and ^{222}Rn fluxes were performed. Another measurement for these fluxes was performed at seep 1. These measurements were performed at approximately 0.5 m from the main vents. The values of ^{222}Rn fluxes were relatively high, which ranged from 17.3 $mBq \cdot m^{-2} \cdot s^{-1}$ to 119.3 $mBq \cdot m^{-2} \cdot s^{-1}$, with an average of 58.4 $mBq \cdot m^{-2} \cdot s^{-1}$. As it may be observed,

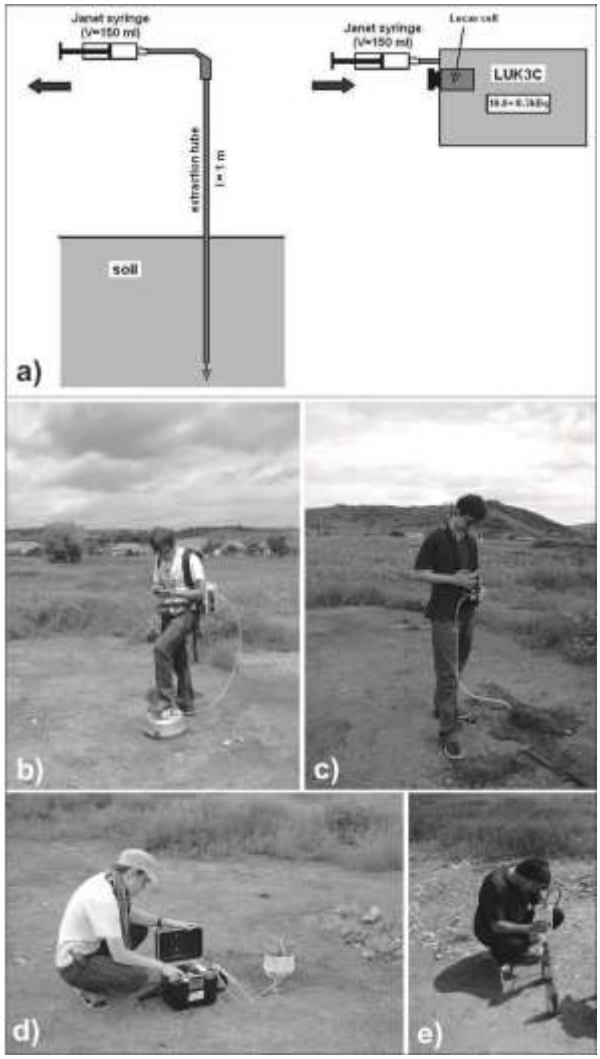

Figure 3. a) the schemes for soil air sampling and its insertion into the Lucas cell of LUK 3C detector for ^{222}Rn activity concentration measurements; b) the closed chamber technique for methane and carbon dioxide flux measurements; c) gas concentration measurements with OLDHAM; d) ^{222}Rn flux measurement with RAD7; e) soil permeability measurement.

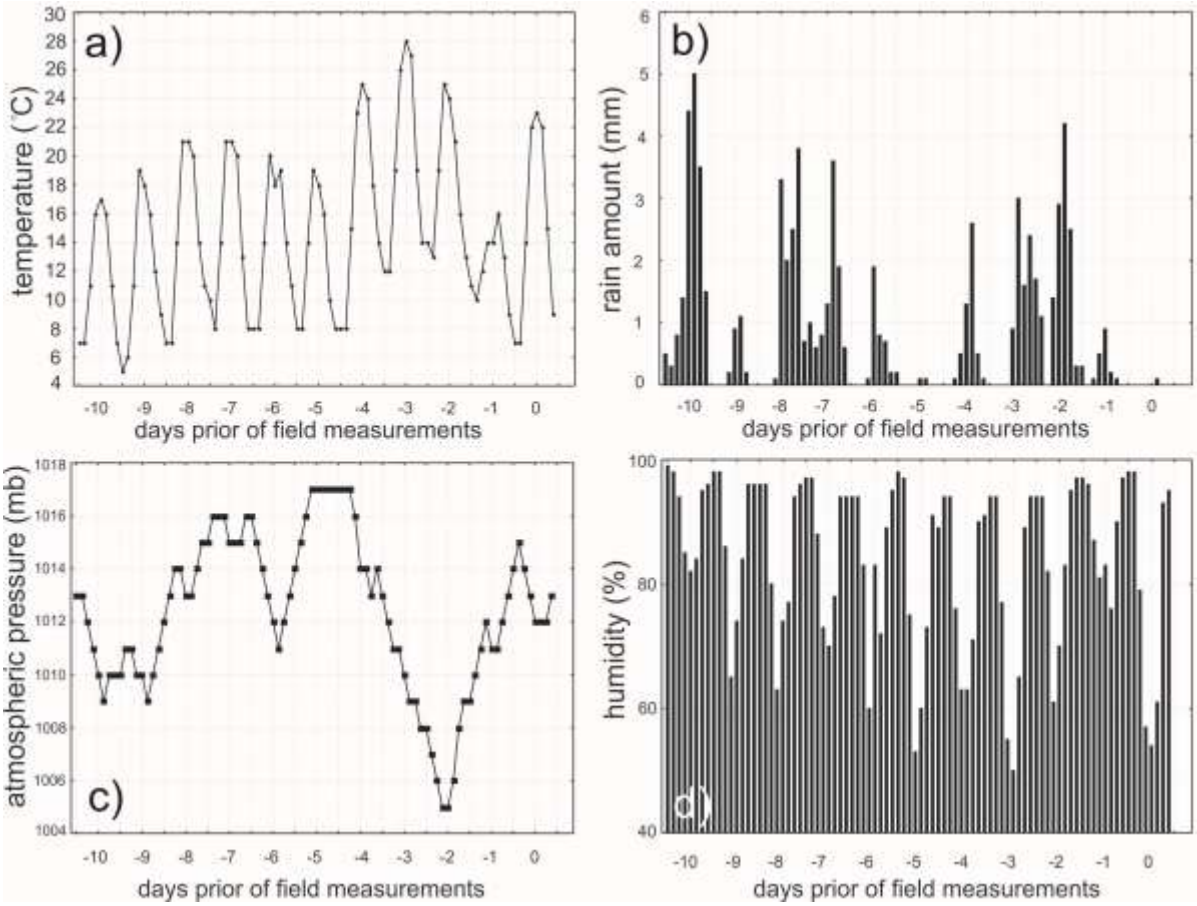

Figure 4. a) Temperature, b) rain amount, c) atmospheric pressure and d) humidity in the last; 10 days prior of field measurements, values recorded at every 3 hours

the average value of ^{222}Rn flux seems to be higher than the estimated value of 22 mBq m^{-2} s^{-1}, which corresponds for areas without uraniferous rocks (Nazaroff, 1992). Methane flux at the same places ranged from 0.23 mg·m^{-2}·s^{-1} up to 129.8 mg·m^{-2}·s^{-1} with an average of 69.3 mg·m^{-2}·s^{-1}.

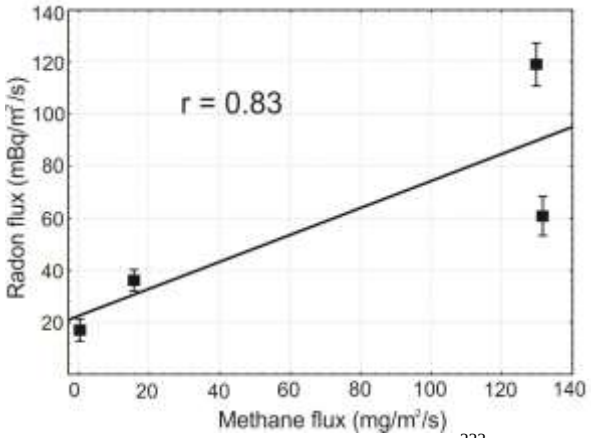

Figure 5. Relation between CH_4 and ^{222}Rn flux

As it may be observed in figure 5, a good correlation between these two fluxes was noticed, which may indicate that CH_4 flux act as carrier gas also for ^{222}Rn, but the origin of ^{222}Rn is poorly understood.

It may have the same origin as the methane but it may also have a shallower origin, such as different layers composed of sands and clays. However, the correlation amounts to 0.83, but is premature to consider ^{222}Rn flux a proxy of CH_4 flux. Some studies reports high ^{222}Rn fluxes up to 20 m distance from the main gas discharges areas (Perrier et al., 2009).

4.2. Transect measurements

The measurements performed on the transect reveal high values of CH_4 flux (with a maximum of 1.6×10^6 mg·m^{-2}·s^{-1}) and quite low values of CO_2 flux (with a maximum of 1.2×10^5 mg·m^{-2}·s^{-1}). As the CO_2 flux is low (CH_4 concentration up to 99% v/v) the extra CO_2 may suggest a small quantity of geogenic origin, or just an accumulation of the biogenic CO_2 from different depths (not related to the gas reservoir).

In the last case, CO_2 acts as a trace gas and not as carrier gas (not a component of the geogenic gas).

Also the gases concentrations at 80 cm depth were rather high with an important peak value for CO (up to 19 ppm). For other gases such as SO_2 (up to 1 ppm) and NO_2 (up to 0.7 ppm) it is worth noticing that although the values are low, they may be considered anomalous as they were recorded only over an area with high methane emission. When CH_4 flux was low, these gases were not detectable. Even if CO, SO_2 and NO_2 occur at 80 cm depth, their origin is poorly understood. They could be a product of biogenic processes in the soil, or may have a geogenic origin, resulting from the gas reservoir. In relation with the carrier gas, these gas species seem to be dependent on the CH_4 flux, as their maximum values correspond to the high CH_4 flux (no. 0 and 6 of the transect) or in the vicinity of high CH_4 flux (Fig. 6.a). On the other hand, ^{222}Rn concentration at the same depth seems to be more dependent on the soil permeability (Fig. 6.b.) than related to the methane flux. Methane (carrier gas) flux seems to be high even when soil permeability is low. This may confirm that methane migration towards the surface is restricted by the existence of a fault or fractures, and not related to soil permeability.

We may conclude that ^{222}Rn may have a shallower origin and not to be related to the gas reservoir. The well drilled in the area reveal some layers of clays and sands (Paraschiv, 1975), a possible source of ^{222}Rn.

5. CONCLUSIONS

Sarmasel seep represents one of the most important seepage of Transylvania (Romania), where large amounts of methane escape into the atmosphere, and contribute to the atmospheric methane budget, with implications in climate change. This paper tries to establish the relation between CH_4 flux and the concentration of other gases such as ^{222}Rn, CO, NO_2, SO_2 and CO_2 and ^{222}Rn fluxes.

Soil gas geochemistry reveals that ^{222}Rn activity concentration (up to 17.5 kBq·m^{-3} at 80 cm depth) and ^{222}Rn flux (up to 119 mBq·m^{-2}·s^{-1}) might be slightly higher than values corresponding for areas without uraniferous or radium formations. High values of CH_4 emission which act as carrier gas may intercept some extra ^{222}Rn from different layers composed of clay and sands.

A 36 m transect was setup and a good correlation was found between CH_4 and CO_2 fluxes, and the concentrations of CO, NO_2, SO_2 at 80 cm depth., but the origin of these gases is poorly understood. They may have the same origin as CH_4, as their maximum values were recorded where CH_4 flux was high. Their migration towards the surface seems to follow the same path of CH_4, and to be restricted by the existence of a fault or fracture.

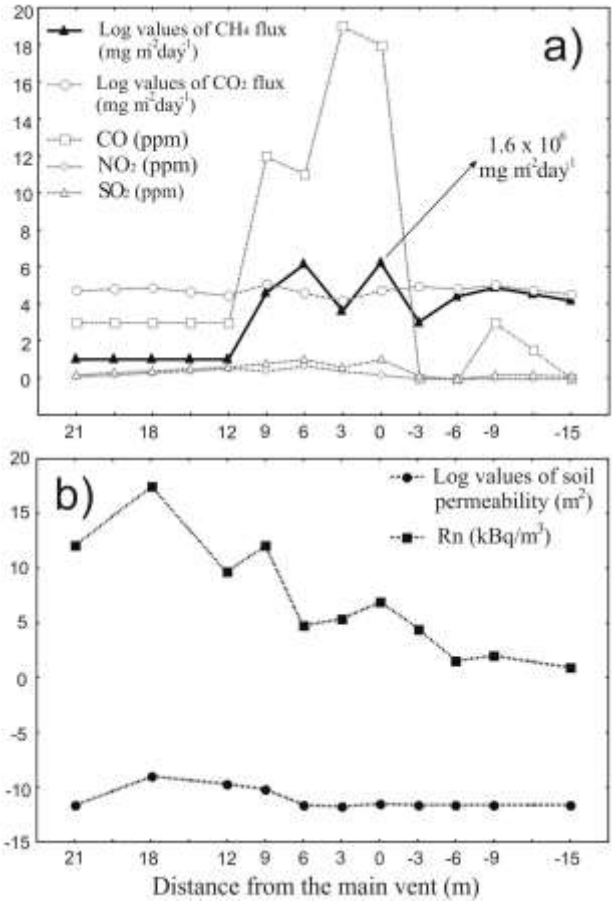

Figure 6. a) Values of the gas concentration for NO_2, SO_2 and CO and flux measurement for CO_2 and CH_4 on the transect; b) Values of ^{222}Rn concentration and soil permeability on the transect

On the other hand, ^{222}Rn concentration seems to be more dependants on the soil permeability in comparison to the other gases. This may suggest a shallower origin of ^{222}Rn than all the other gases.

Despite of the weak correlation between the CH_4 flux and ^{222}Rn concentration in soil, a good correlation was found between the CH_4 and ^{222}Rn fluxes for the measurements located close to the main vents. However, we consider that is premature to conclude the ^{222}Rn flux as a proxy for CH_4 flux and more measurements need to be performed in order to assess the relation between these two fluxes.

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Table 1. Statistics of the gas fluxes and concentrations

Type of measurement	CH_4 flux ($mg\ m^{-2}\ d^{-1}$)	^{222}Rn flux ($mBq\ m^{-2}\ s^{-1}$)	CO_2 flux ($mg\ m^{-2}\ d^{-1}$)	^{222}Rn concentration ($kBq\ m^{-2}$)	CO (ppm)	Soil permeability (m^2)	NO_2 (ppm)	SO_2 (ppm)
Number of measurements	14	4	14	10	10	10	10	10
Max.	1.6×10^6	119.3	125×10^3	17.52 ± 0.846	19	8.78E-10	0.7	1
Min.	0	17.3	25×10^3	1.56 ± 0.062	0	1.72E-12	0	0
Mean	1.9×10^6	59.4	60.5×10^3	7.63	6.5	1.03E-10	0.23	0.45

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