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SOIL RADON AND THORON ACTIVITY CONCENTRATIONS AND CO_2 FLUX MEASUREMENTS IN THE NEOGENE VOLCANIC REGION OF THE EASTERN CARPATHIANS (ROMANIA)

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Abstract. Our study is based on soil radon and thoron activity concentration measurements along with CO_2 flux measurements, performed in the area of the mofettes and mineral water springs occurrences in two locations: Bálványos-Bai (Bodoc Mts.) and Sugás-Bai (Baraolt Mts.) of the Eastern Carpathians (Romania). During the fieldwork, the existence of presumed fault systems was examined (which controls the occurrence of the mofettes and water springs), across selected profiles (normal to the assumed fault direction). Soil radon and thoron activity-concentration measurements were performed by the LUK3C radon and thoron detector (with Lucas cells), and the CO_2 flux measurements at soil surface were performed by using a closed chamber technique. Results of radon and thoron concentrations were in the range from several $kBq \cdot m^{-3}$ to tens of $kBq \cdot m^{-3}$, having distributions with maximum values for both cases (up to 25 $kBq \cdot m^{-3}$ for radon and up to 40 $kBq \cdot m^{-3}$ for thoron). Results of the CO_2 fluxes were in the order of thousands of $g \cdot m^{-2} \cdot day^{-1}$ in case of Bálványos-Bai (at Turia) and of tens of $g \cdot m^{-2} \cdot day^{-1}$ in case of Sugás-Bai, having distributions with maximum values up to 9300 $g \cdot m^{-2} \cdot day^{-1}$ in case of Bálványos-Bai, and up to 20 $g \cdot m^{-2} \cdot day^{-1}$ in case of Sugás-Bai. The distributions of ^{222}Rn, ^{220}Rn and CO_2 are consistent with the hypothesis that the gas migration occurs along the fault system, and consequently, the maximum values indicate a more precise location and direction of the fault line.

Keywords: soil radon, soil thoron, CO_2 flux, faults, dry mofettes, mineral springs.

1. INTRODUCTION

The upward migration of the geo-gases as CO_2, CH_4, H_2S carrying out radioactive gases, as radon (Rn) and thoron (Tn) is facilitated and controlled by tectonic faults. Depending upon local geological and hydro-geological conditions, the upward gas may appear at the surface either as dry CO_2 emanation (mofette) or as CO_2-rich mineral water. There are many occurrences of dry CO_2 emanations along the Neogene Calimani-Gurghiu-Harghita post-volcanic range (Eastern Carpathians, Romania). (Vaselli et al., 2002; Fielitz & Seghedi, 2005; Szakács & Seghedi, 1995). Radon (^{222}Rn; with a half-life of 3.82 days) and thoron (^{220}Rn; with a half life of 55.6 sec) are present in both atmospherically and soil air, and originates from the decay series of uranium (^{238}U; with a half-life of $4.47 \cdot 10^9$ years) and thorium (^{232}Th; with a half life of $14.1 \cdot 10^{10}$ years), which occurs in trace amounts through the Earth crust (Cosma et al., 1996). Both radioactive gases produced continuously in the Earth's crust migrate towards the surface mainly by diffusion and advection processes, or accompanying carrier gases such as CO_2, CH_4, H_2S, etc. (Etiope & Martinelli, 2002).

Faults serving as pathways for ascending gases can be identified by detecting high radon and thoron activities in the soil. Due to the short half-life of thoron (55 sec), the detection of high thoron activities in soil-gas would require a nearby source or a fast migration mechanism from a distant source. High soil-gas thoron activities may indicate a fast gas migration processes, which is possible only in the presence of a carrier gas (e.g. CO_2) which typically occurs along faults and fractured rocks. Gas-emitting tectonic structures can then be mapped with a combination of radon and thoron data, supported by CO_2 measurements as it was the case in the moffetic halo of the East Carpathian volcanic range (Néda et al., 2008; Papp et al., 2010).

1.1. The aim of the study

The aim of the study was to identify and to locate, through systematic measurements of soil radon and thoron activity concentrations along with CO_2 flux measurements, the possible location of the fault zones which controls the occurrence of the mineral springs and mofettes in the study areas.

The present study reports radon and thoron activity concentration measurements along with CO_2 flux measurements, performed along direction normal to the direction which connects areas without vegetation and mofettes occurs at Bálványos-Bai (Bodoc Mts.) or connects mineral water springs and mofettes in Sugás-Bai (Baraolt Mts.), in the Eastern Carpathians (Romania).

1.2. Geographic and geologic background of the studied locations

The studied locations (Bálványos-Bai and Sugás-Bai) are located in the Eastern Carpathians (Romania). Bálványos-Bai village is situated at the foot of Bodoc Mts. (N 46°06'37", E 25°57'32"), at an altitude of 1050 m. The origin of water springs and gas emanations in the resort are from Upper-Cretaceous sandstones. Closed to the resort is the Turia "stinky-cave" (at 6 km SE) which emanates high amounts of sulphurous gas in the atmosphere (mainly CO_2 and H_2O by a rate of 1980 m^3 daily) (Szabó, 1978). Sugás-Bai is situated at SE part of the Baraolt Mts. (N 45°53'51", E 25°42'32") at an altitude of 750 m. Slightly radioactive carbonated mineral waters (with amounts of calcium, magnesium, iron) emerge from Lower Cretaceous flysch deposits (Szabó, 1978) (Fig. 1).

The chemical composition of the mineral waters in Bálványos-Bai (i.e. CO_2 rich gas pool) [in mg/L] are: Na-20000; Cl-12000; HCO_3-9870; SO_4-9790; Ca-7380; Mg-2580; K-920; NH_4-46; Li-268.9, and the *pH*=5.82. The emanated gas composition from Turia cave are: CO_2-98.2 %; N_2-0.9 %; CH_4-0.8 %; Ar-0.02%; O_2-0.04 %; H_2S-0.01 % (Vaselli et al., 2002). The chemical composition of the mineral waters in Sugás-Bai [in mg/L] are: HCO_3-1232.2; CO_2-1909.6; Ca-276.1; Na-150.4; SO_4-39.9; Mg-25.9; Cl-25.5; Fe-11.8; K-6.7 and the *pH*=5.8, and the composition of the mofetta gases are: CO_2-80.7 %; O_2-2.9 %; N_2-16.4 % (Szabó, 1978).The average temperature of the mofette air is 21 °C, and the relative humidity of 83 %. The ^{222}Rn gas concentration in the mofette air is high, with a mean value of 9.1 kBq·m^{-3} (Szabó, 1978).

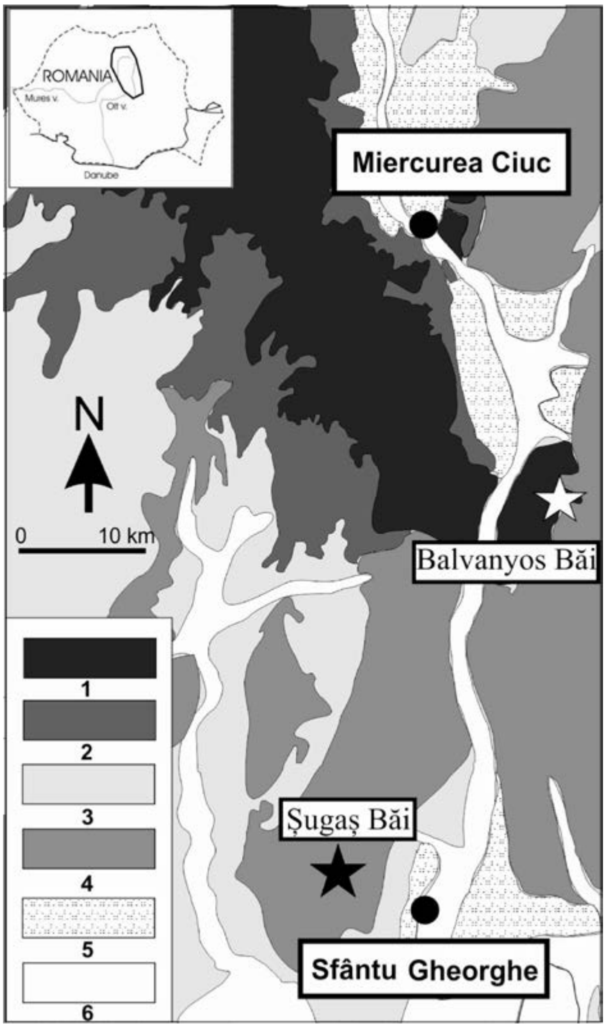

Figure 1. The locations of the investigated areas: Bálványos-Bai (between Miercurea Ciuc and Sfântu Gheorghe municipality) and Sugás-Bai (closed to Sfântu Gheorghe municipality). (Legend: 1. Neogene-Quaternary volcanic rocks: central and cone facies, 2. Neogene-Quaternary volcanic rocks: volcani-clastic facies, 3. Neogene sedimentary rocks of the Transylvanian Basin, 4. Dacide and inner Carpathian nappes, 5. Pliocene-Quaternary sedimentary rocks of the intramountain basins, 6. Quaternary alluvial formations).

2. MEASUREMENT METHODS

Measurements were performed along a well-determined profile line, normal to the direction that connects the mineral water springs and mofettes in the two locations. For accurate location and for the identification of geo-coordinates, we used a Garmin GPS. To determine the direction of the faults and the orientation of the related normal profiles we used a common geological compass.

2.1. Soil radon and thoron measurement method

The method used for radon and thoron measurements in soil was based on sampling of the soil gas and detection of both gases. Radon and thoron activity concentrations from the soil gas were measured using a LUK3C radon and thoron detector (based on scintillation detection technique with Lucas cells). This detector was developed for radon measurements in soil and determines the radon gas concentration relative quickly (direct from the alpha decay of radon and progenies). The principle of the measurement method and the efficiency of the detection used by this detector are described in (Plch, 1997; Barnet et al., 2008; Cosma et al., 2010).

For soil gas sampling a Janet Syringe with a 145 ml volume was used, connected to a steel sampling probe with 1 cm diameter and 1 m length. The probe was inserted into the soil to a certain depth. After this, the soil gas sample was introduced into the detection chamber with the help of a preliminary vacuum technique (Fig. 2).

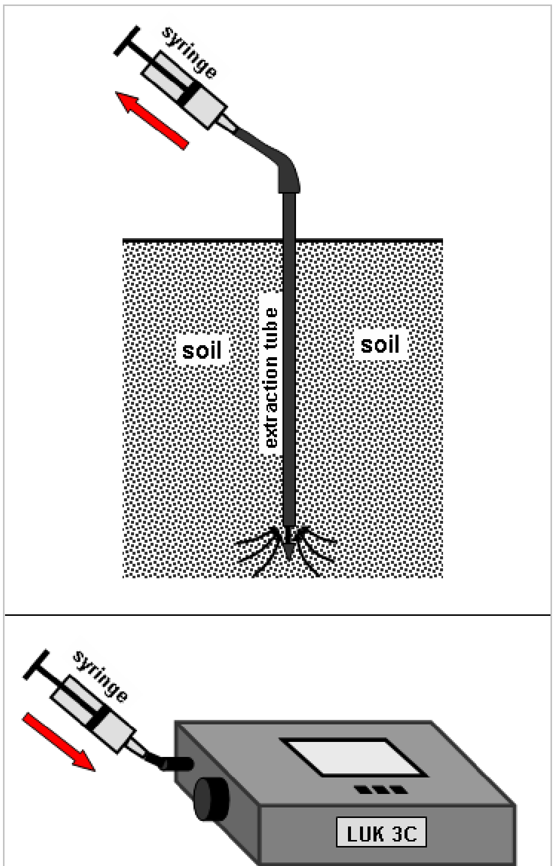

Figure 2. The schemes for sampling of soil gas (on top) and insertion into the Lucas cell of the LUK3C detector for Rn and Tn concentration measurement (on bottom) (according to the method from Papp et al., 2010).

The depth for soil gas sampling was 60 cm in the two locations (Bálványos and Sugás-Bai), which results from a trial soil radon profile from 30 to 80 cm depth interval, closed to the mofettes in Harghita-Bai. The results of these measurements show that the value of the Rn activity concentration at 60 cm (4.6 kBq·m^{-3}) does not change significantly below this depth (Papp et al., 2010).

2.2. The CO_2 flux measurement method

The CO_2 flux measurements were performed using a portable flux meter (West System, srl.), which measure CO_2 and CH_4 fluxes on the soil surface. The same device was used for diffuse CO_2 emission whithin the area of the Călimani-Gurghiu-Harghita Mountains (Frunzeti & Baciu, 2012). The device consists of an accumulation chamber (type C), a CO_2 and a CH_4 sensor and a PDA palmtop for data communication, evaluation and storage (Fig. 3). Details about the CO_2 detector and the CH_4 sensor are described in Portable flux meter handbook, 2007.

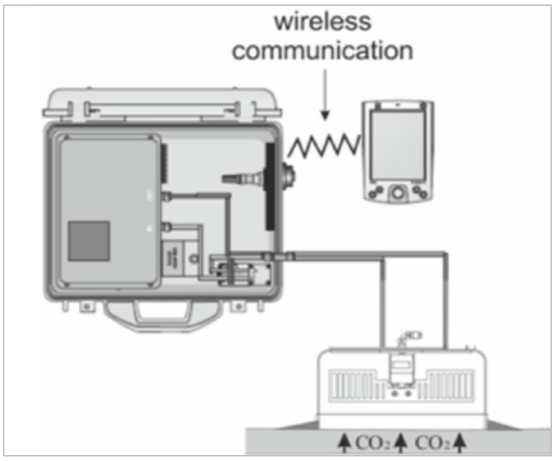

Figure 3. The scheme of CO_2 flux measurement by the WEST FLUX portable flux meter.

The method of the CO_2 flux determination based on the measuring the rising concentration versus time in terms of [ppm·s^{-1}] (Portable flux meter handbook, 2007). If the gas concentration rate inside the chamber is constant, linear regression can be used to calculate the gas flux F [g·m^{-2}·day^{-1}] by the equation (Livingston & Hutchinson, 1995):

$$F = \frac{V_c}{A_c} \cdot \frac{c_2 - c_1}{t_2 - t_1} \qquad (1)$$

where, V_c[m^3] and A_c[m^2] is the volume (3.0 L) and the area (0.03 m^2) of the chamber, c_1 and c_2 [mg·m^{-3}] are gas concentrations at time t_1 and t_2 [sec].

3. RESULTS AND DISCUSSIONS

The Rn and Tn activity concentration measurements along with CO_2 flux measurements in the area of the mineral water springs and mofettes at Bálványos and Sugás-Bai were performed in 2011 summer time, when relatively dry conditions prevailed in the area. Climatic conditions in the time of measurements was 27°C air temperature and 909hPa air pressure at Bálványos-Bai and 20°C air temperature and 929hPa air pressure at Sugás-Bai.

3.1. Measurements at Bálványos-Bai

The Rn and Tn concentration measurements by CO_2 flux measurements were performed in the area of Bálványos-Bai, closed to the Turia "stinky-cave" (cca. 320 m from the cave), along a well-determined profile line that was normal to a direction which fall on a soil surface without vegetation and the Turia cave. This phenomenon of the area without vegetation occurs frequently in the area of high CO_2 emanations (i.e. the Neogen volcanic region of the Eastern Carpathians). The measurements were made in 11 points (labelled from T1 to T11) along a profile line that is normal to the assumed fault direction (strike 60° from N to E). The coordinates (latitude and longitude) of the points recorded by GPS are presented in table 1, and the locations of the points are shown in figure 4. The line connecting the measurement points is normal to the direction of the presumed fracture zone. The distances between the measurements points were 2m, therefore the distance between the end points of the profile T1-T11 was 20m. The results (i.e. the distribution of the measured values) are shown in figure 5 (for Rn and Tn values) and in figure 6 (for CO_2 fluxes).

From the measured values (i.e. the Rn and Tn concentrations and CO_2 fluxes) it can be observed that the values of the Rn concentrations fall within a large interval, between 5.4 and 26.3 $kBq \cdot m^{-3}$, having a maximum in point T2 (26.3 $kBq \cdot m^{-3}$), and the values of the Tn concentrations were found to lie within the same large domain, between 0.3 and 71.9 $kBq \cdot m^{-3}$, which contains also a single maximum in the same point T2 (71.9 $kBq \cdot m^{-3}$). The values of the CO_2 fluxes were found in a range between 25.7 and 9301.9 $g \cdot m^{-2} \cdot day^{-1}$, having a maximum in point T8 (9301.9 $g \cdot m^{-2} \cdot day^{-1}$).

3.2. Measurements at Sugás-Bai

The measurements of Rn and Tn concentrations along with CO_2 flux measurements were performed in the area of the mineral water springs and mofette at Sugás-Bai, along a profile line normal to the direction that connects the mineral water springs and the mofette in the area, while the assumed fault direction having a strike 50° from N to E. The measurements were performed in 11 points along the profile line.

Table 1. The coordinates and elevations (a.s.l.) of the Turia „stinky-cave", and the coordinates of the extremity points of the measurement profile.

Place		**N**	**E**	**ALT [m]**
The Turia „stinky-cave"		46 °07'12.0"	25°56'53.0"	1285
Extreme points of the profile	T1	46°07'08.3"	25°56'39.4"	1031
	T11	46°07'08.9"	25°56'39.0"	1023

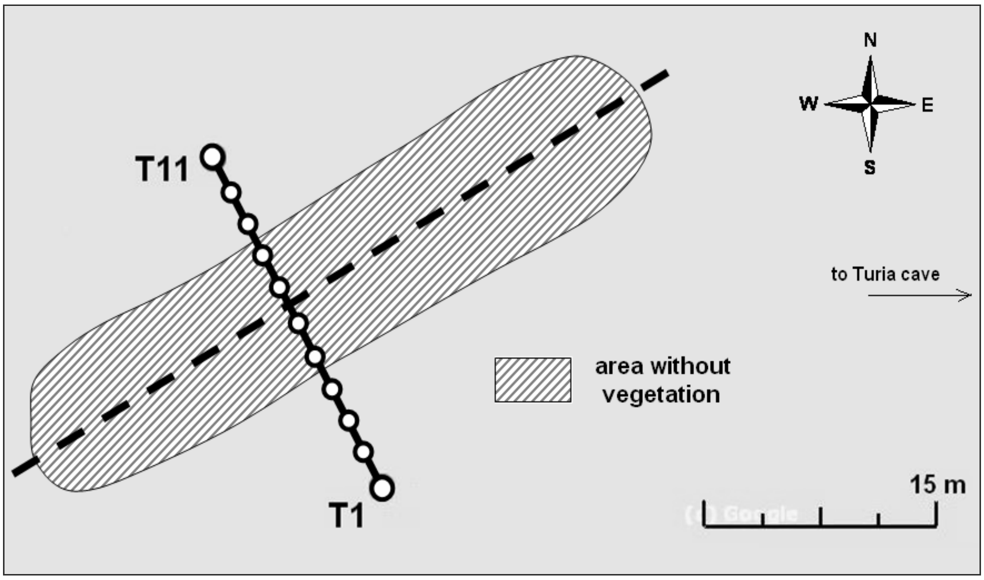

Figure 4. The locations of the measurement profile (T1; T11) and of the area without vegetation (shaded area) at Turia (Bálványos-Bai). The Turia cave is at right from the measurement profile. The T1-T11 segment is the measurement profile and the broken line (normal to the profile) is the direction of the presumed fault zone.

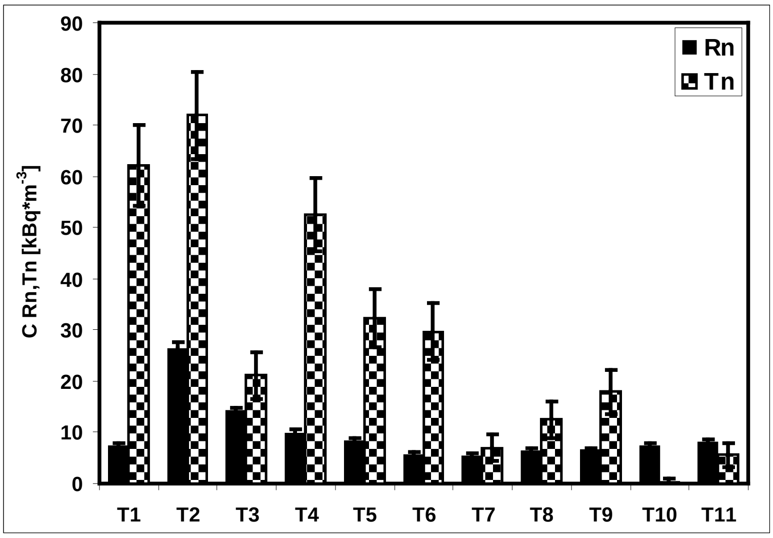

Figure 5. The distribution of the measured Rn and Tn concentrations of the profile at Turia (Bálványos-Bai) (black columns are C(Rn), and the patterned columns are C(Tn))

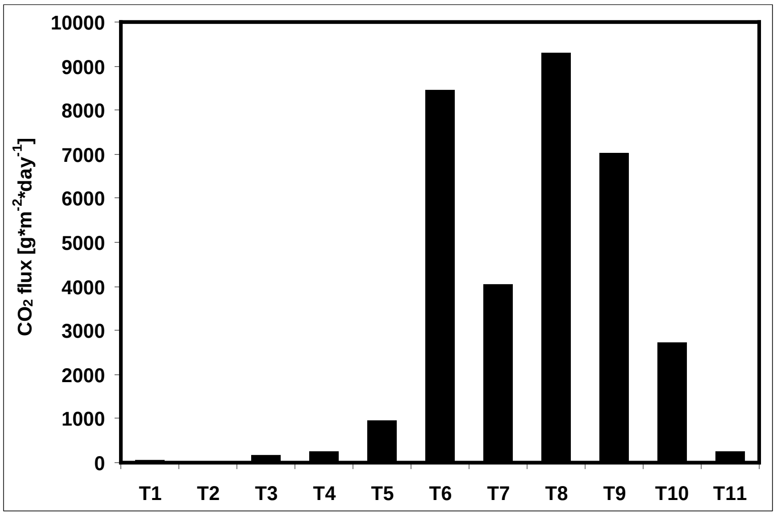

Figure 6. The distribution of the CO_2 fluxes of the profile at Turia (Bálványos-Bai).

The measurement points are labelled from S1 to S11. The coordinates (latitude and longitude) of the points recorded by GPS are presented in table 2, and the locations of the points are shown in figure 7. The distances between the end points of the profile (S1-S11) was 70m, and the distances between the measurement points were: 10m (S1-S2-S3); 5m (S3-S4-S5-S6-S7-S8), and 10m (S8-S9-S10-S11). The results (i.e. the distribution of the measured values) are shown in figure 8 (for Rn and Tn values) and figure 9 (for CO_2 fluxes).

Table 2. The coordinates and the elevations (a.s.l.) of the mineral water springs and mofettes in Sugás-Bai, as well as the coordinates of the extremity points for the measurement profile.

Place		**N**	**E**	**ALT [m]**
SS1 (Sugás spring 1)		45°53'45.4"	25°42'19.4"	788
SS2 (Sugás spring 2)		45°53'45.5"	25°42'19.3"	785
SS3 (Jenő spring)		45°53'46.4"	25°42'21.7"	770
SM (Sugás mofette)		45°53'47.2"	25°42'23.8"	764
SS4 (The main spring)		45°53'50.0"	25°42'30.0"	770
SS5 (Ferike spring)		45°53'51.7"	25°42'33.5"	766
Extreme points of the profile	S 1	45°53'44.6"	25°42'15.8"	746
	S 11	45°53'42.3"	25°42'17.2"	834

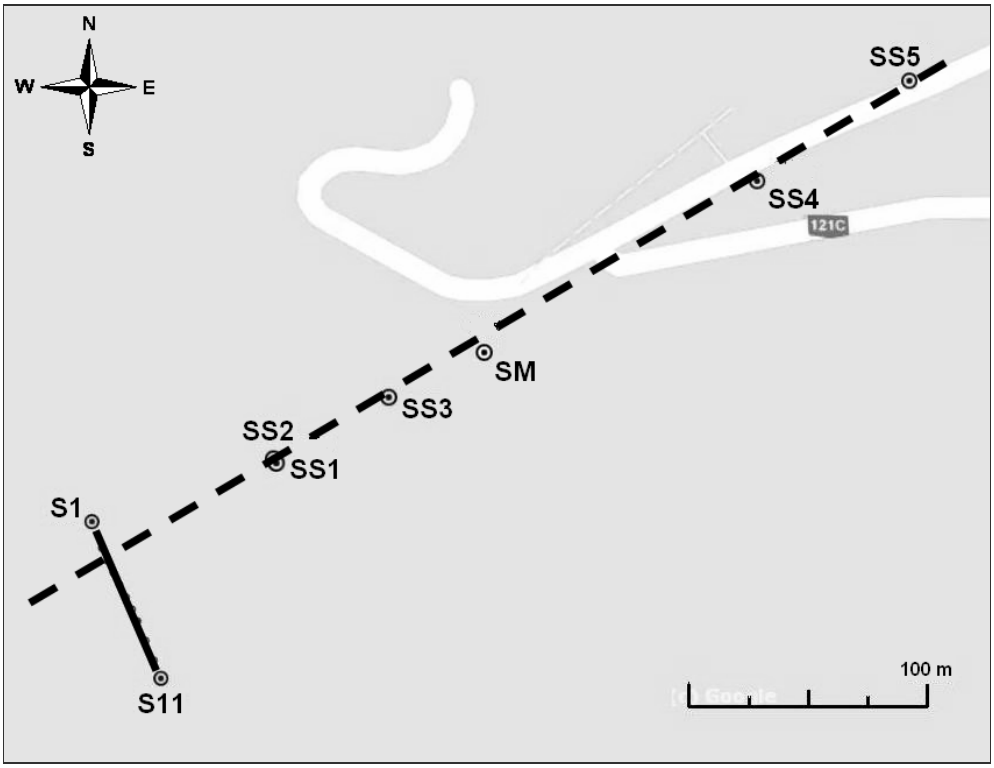

Figure 7. The locations of the mineral water springs (SS1-SS5) and the mofette house (SM) from Sugás-Bai, and the end points of the measurement profile (S1; S11). The S1-S11 segment is the measurement profile and the broken line (normal to the profile) is the direction of the fault zone.

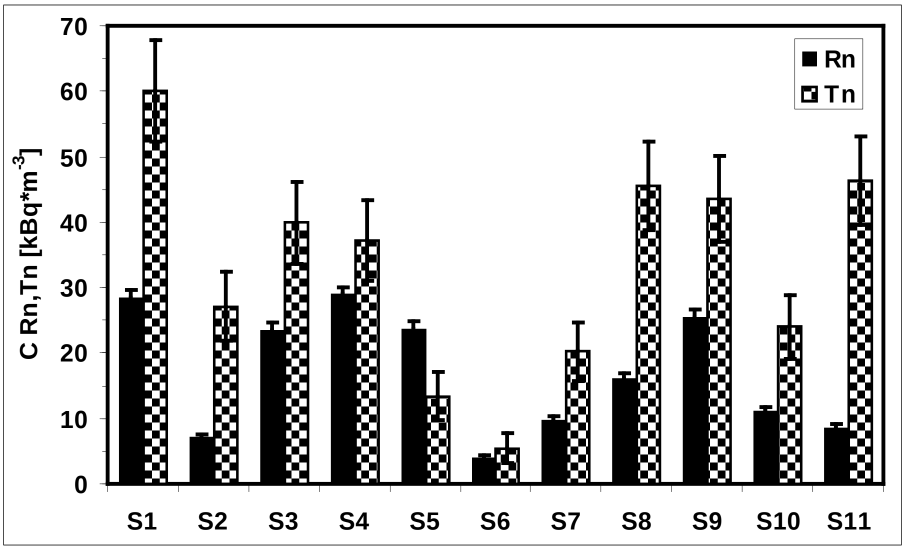

Figure 8. The distribution of the measured Rn and Tn concentration values of the profile at Sugás-Bai (C(Rn) represents the black columns, and C(Tn) represents the patterned columns).

From the measured values (Rn and Tn concentrations and CO_2 fluxes) it can be seen that the values of the Rn concentrations fall within a same large interval (as at Turia, Balványos-Bai), between 4.0 and 29.0 kBq·m^{-3}, having two maxima in point S4 (29.0 kBq·m^{-3}) and in point S9 (25.53 kBq·m^{-3}), except the first point S1 (28.4 kBq·m^{-3}). The values of the Tn activity concentrations were found to lie within the same large domain, between 5.4 and 60.0 kBq·m^{-3}, containing also two maxima in point S3 (40.0 kBq·m^{-3}) and in point S8 (45.6 kBq·m^{-3}), except the extremity points (S1 and S11 of 60.0 and 46.3 kBq·m^{-3}) with higher concentrations then maxima. These results agree with the results obtained before by Papp et al., (2010). The values of the CO_2 fluxes were found between 3.4 and 20.1 g·m^{-2}·day^{-1}, having one maximum values in point S6 (20.1 g·m^{-2}·day^{-1}).

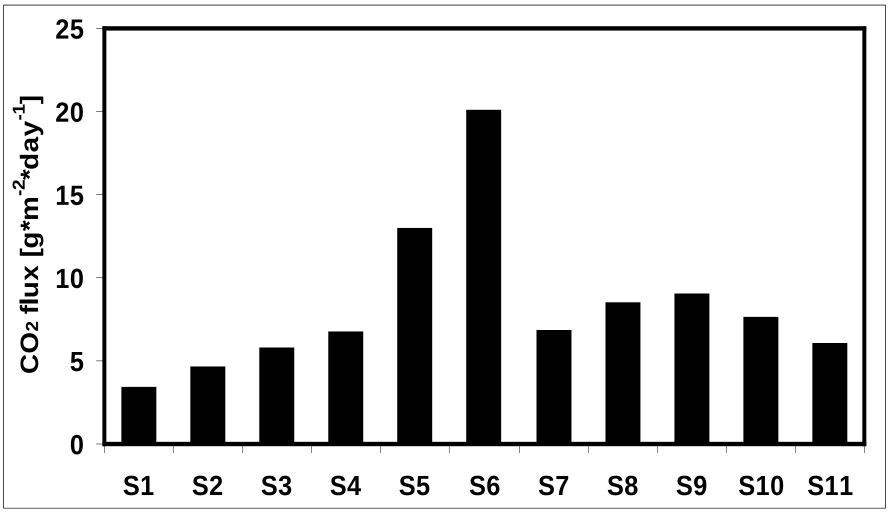

Figure 9. The distribution of the CO_2 flux of the profile at Sugás-Bai.

From soil Rn and Tn measurements (i.e. distributions of the measured activity-concentration values) the Rn and Tn maximum concentrations were systematically different to those found at neighbouring points. In case of Turia (Bálványos-Bai) the Rn and Tn maximum concentrations was found in a same point T2, while in case of Sugás-Bai the Rn maximums were found in points S4 and S9, and the Tn maximums were found in points S3 and S8 (except the extremities). The interpretation is that these faults lies between the points of Rn and Tn maximums, perhaps closer to the Tn maxima than to the Rn maxima due to the shorter diffusion length of Tn as compared to Rn. These faults are not necessarily represented by a single-plane tectonic feature, but rather it is a fracture zone that contains multiple parallel fault planes within a wider zone with variable permeabilities. Another possibility is that these faults are inclined, and that the Tn maxima represent its intersection with the surface, while the more diffusive Rn maximum represents its average location.

The maximum values of the CO_2 fluxes does not correspond with the maximum values of the Rn and Tn concentrations, although in both cases (Turia and Sugás-Bai measurements) the same increasing tendency was observed. The CO_2 flux starts to increase from minimal values tends to a maximum, after decreasing to a minimal value. In case of Turia profile, CO_2 maxima were found in point T8 and in case of Sugás-Bai profile in point S6. A little difference was observed from the decreasing tendency, by 70 % from the expected value in point T6 (in case of Turia profile) and by 20% from the expected value in point S7 (in case of Sugás-Bai profile). This is done probably because of different soil characteristics such as soil permeability or some rocks which does not permit the upward migration of the gas toward the surface. In conclusion, from the comparison of the Rn and Tn concentration values with CO_2 flux values it can be seen that in case of the increasing Rn and Tn concentrations the CO_2 fluxes decreasing. By this, the minimum Rn or Tn concentration correspond to maximum CO_2 flux, and vice versa.

4. SUMMARY AND CONCLUSIONS

The soil radon and thoron measurements, as well as the CO_2 flux measurements performed in the area of the high CO_2 emanations at Turia (Bálványos-Bai) and in the area of the mofettes and mineral water springs at Sugás-Bai have relatively good representations. The measurement results are in contact with the existence and the presumed position of the NNE fault zones (in both cases) along which are connects the mineral water springs and mofettes, as previously stated. For the studied cases, the measurement results displayed normal distributions for the activity concentrations of Rn and Tn (with one or two maxima values) and also for the CO_2 fluxes (with one maximum value). From the comparison of the Rn and Tn concentrations with CO_2 fluxes, by the increasing of Rn and Tn concentrations the CO_2 fluxes decreasing. Although, to the minimum Rn or Tn concentration correspond maximum CO_2 flux, and vice versa.

The distributions shows that the main fault zone crosses through the points corresponding to maximum values of Rn and Tn concentrations, and to the maximum value of the CO_2 fluxes, also. The results obtained during the investigations also suggest a direction for further studies in evaluating the influence of fault inclination on the distribution of Rn and Tn concentrations in soil, and on the distribution of CO_2 fluxes at the surface.

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