SPATIAL VARIABILITY OF SOIL SURFACE CO_2 FLUX DENSITY IN EXCEPTIONALLY HIGH GEOGAS UPWELLING AREAS

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1. Introduction

Carbon dioxide seepages related to post-volcanic activity can be a potential source of danger in themselves, which is further enhanced by the fact that in the near-surface layers these deep origin gases can be significantly enriched with radon gas. The knowledge of nature and behaviour of these subsurface gas flows is the basis for effective protection against them.

In this work we measured the ground surface flux density of carbon dioxide gas in two areas characterized by exceptionally high flux densities, on the one hand, in Mátraderecske, in the surroundings of the Carbon Dioxide Spa; on the other hand, in the areas of the city of Kovászna (Transylvania) most affected by carbon dioxide leakage. We measured the flux density at hundreds of measurement points at both locations. The purpose of the measurements is primarily the statistical characterization of the spatial variability of the carbon dioxide flux density at the soil surface from a scale of 10 cm to a scale of a few kilometers, as well as the use of these results to formulate the conceptual model of the deterministic (partial differential equation system) transport models of near-surface geogas flows and to convert them into mathematical form. In the case of the carbon dioxide flux density measurements in Mátraderecske, a comparison was made with the results of the radon flux density measurements. According to our experience, the radon flux density (radon exhalation) is affected by the radon content of the soil gas at least as much as the flux density of the carrier gas.

2. Site descriptions

The measurements were carried out in the vicinity of the Darnó fault line running through Mátraderecske, Hungary and in the so called Mátraderecske Carbon Dioxide Spa, which is one of Hungary's most famous mofette. Covasna area is situated in the inner part of the Carpathians bend, merely 50 km far from one of the most active seismic zones in Europe, the so called Vrancea region.

2.1. Mátraderecske

Mátraderecske is a small village situated at the northern foot of the Mátra Mountain which is one of the largest units of the calc-alkaline Inner Carpathian volcanic arc, additionally the largest Tertiary volcanic range of Hungary. The so-called Darnó line is a few km wide seismically active tectonic zone, which crosses the North Hungarian Central Range. Mátraderecske is located in the region of this line, which is one of the most mobile crustal parts of Hungary (Czakó, Zelenka, 1981).

Underneath the village at a depth of about 600 meters the basement consists of Triassic limestone. Upper Eocene subvolcanic andesite intruded into this carbonate bedrock. Over the 0.4 km thick andesite a few meters thick layer of clay has been accumulated by the Oligocene sea. The fragmented Triassic limestone serves as a karstic aquifer. The water is saturated with gas (10–16 m^3 gas/m^3 water), containing mostly carbon dioxide (cca. 95%) (Szilágyi, 1992). From this karst water reservoir at ~1000 m depth deep origin geogas migrates upwards along the faults and fractures within the andesite. It escapes to the surface mainly where the Oligocene sediment is thin enough to let the gas through, or is completely missing (Vásárhelyi et al., 1997; Csige et al., 2002). As the results of carbon isotope ratio study done by Hertelendi et al. (see in Szilágyi, 1992) have shown CO_2 has geological origin. Due to the high heat flow coming from the intrusion of andesite magma during the process of contact metamorphism (also called thermal metamorphism) CO_2 is created by thermal dissociation of limestone.

In this region radon is produced from the uranium content of tuffite layer accumulated under the clay sediment. The enrichment is due to the process that sea waves flushed out the lighter materials from tuffite, while the heavier minerals, such as uranium, remained (Tóth et al., 1996).

2.2. Covasna

Covasna area is situated on the middle course of the Olt River in the arc of Neogene volcanic range of the Eastern Carpathians. It is referred to as the land of mofettes, table waters and spas. The city is well-known for its mineral waters and richness in carbon dioxide seepages (Gyila et al., 2017). The Covasna area is made up of Palaeocene and Cretaceous sedimentary deposits (Néda et al., 2008 a). The geogenic CO_2 is derived from both mantle derived processes and thermometamorphism of recently subducted limestones (Vaselli et al., 2002).

3. Methods

Both for radon and carbon dioxide flux measurements we have used the accumulation chamber methods. However, because of the sampling period of measurements was 10 minutes for radon and 1 second for carbon dioxide, the mathematical derivation of the fluxes from the measured concentrations differs significantly.

3.1. Radon flux measurements

Radon (^{222}Rn) is a colourless, odourless, tasteless radioactive noble gas with a half-life of 3.8 days. This naturally occurring inert gas is a decay product of radium, which can be found in rocks and soils, and part of the uranium decay chain. Despite its relatively low concentration, it can be easily measured due to its radioactivity, so radon can be a good natural tracer of some subsurface flow processes.

Radon concentrations were measured with AlphaGUARD PQ2000 ionization chamber radon detector in diffusion mode for 10 minutes integration periods. Based on the response of AlphaGUARD PQ-2000 to sudden changes in the radon concentration, theoretical calculations are used to determine the response of the detector to the time-varying radon concentrations in the collection vessel during the measurement. In the case of specific measurements, we estimate the value of radon exhalation by fitting the parameters of the resulting response function to the measurement data.

Measurement process: To be used, the ionization chamber must be placed on the surface and covered with a closed container. The rim of the so called collection container have to be pressed into the ground at least 5 cm deep and the soil around the rim have to be compacted to minimize ventilation. Make sure that the outlet openings are open so that overpressure does not develop in the collection container. After placing the collection container in its final state, the outlet openings are closed and a low-power fan is operated during the measurement in order to evenly mix the air.

We assume that the Φ ($\frac{B_q}{m^2 s}$) ^{222}Rn flux density under the measuring vessel is constant over time. v (s^{-1}) is the ventilation rate of the measuring vessel. Thus the activity concentration of ^{222}Rn in the measuring vessel changes according to the following equation:

$$C_E(t) = C_{E0} + \frac{\phi}{vh}(1 - e^{-vt})$$

Where C_{E0} is the activity concentration of ^{222}Rn in the measuring vessel at t = 0 and "h" is the height of the measuring vessel. ^{222}Rn can enter the ionization chamber of AlphaGUARD by diffusion. The change in the ionization chamber can be determined with the following differential equation:

$$\frac{dC_1(t)}{dt} = k\big(C_E(t) - C_1(t)\big),$$

where k (s^{-1}) is a transmission factor. By expressing this differential equation for the problem of exhalation measurement, we can get the following expression as a result:

$$C_1(t) = C_{E0} + \frac{\phi}{vh}\left(1 - \frac{k}{k-v}e^{-vt}\right) + \left(C_{I0} - C_{E0} + \frac{\phi}{h(k-v)}\right)e^{-kt}$$

where C_{I0} is the ^{222}Rn activity concentration in the ionization chamber at t = 0.

AlphaGUARD measures the average ^{222}Rn activity concentration in its ionization chamber in the i-th measurement cycle:

$$\bar{C}_{li} = C_{E0} + \frac{\phi}{vh} + \frac{\phi}{v^2 hT}\frac{k}{k-v}(1 - e^{vT})e^{viT}$$
$$- \frac{1}{kT}\left(C_{l0} - C_{E0} + \frac{\phi}{h[k-v]}\right)(1 - e^{kT})e^{-kiT}$$

where T (s) is the length of the measurement cycle. Let y_i be the ^{222}Rn activity concentrations measured in the i-th measurement cycle and let σ_i be their errors. Then the values of the parameters Φ, v, C_{E0} can be obtained by minimizing the following weighted sum of squares:

$$S(\phi, v, C_{E0}) = \sum_i \frac{(y_i - \bar{C}_{li})^2}{\sigma_i^2}$$

The transmission factor k of AlphaGUARD was determined by measurements carried out in a radon chamber (using a 140-liter plastic barrel). After placing the AlphaGUARD and the constant intensity ^{222}Rn source in the barrel, the barrel is sealed at the start of a measurement cycle. According to the measurements, the ^{222}Rn time series measured in the barrel by AlphaGUARD could be described with a model close to the above

3.2. Carbon dioxide flux measurements

Diffusion of CO_2 gas from the soil was carried out with an EGM-5 Portable CO_2 Gas Analyser. The device handles several accessories that characterize different parameters of the soil, so that diverse information can be obtained from them.

The open circuit design of the instrument enables continuous, unsupervised air sampling, as the pump continuously supplies fresh air to the sample gas testing component, IRGA (infrared gas analyser), which forms the core of the measuring system. The term non-dispersive infrared (NDIR) refers to the transmission of broadband infrared wavelengths.

The mathematical model of the measurement:

The instrument determines the amount of carbon dioxide flow according to the following equation.

$$F_{CO_2} = \frac{(C_n - C_0)}{Tn} \times \frac{V}{A}$$

where:

F_{CO2} is the soil respiration rate, the flux density of carbon dioxide, $\left[\frac{g}{m^2 s}\right]$

C_0 is the concentration of CO_2 at time 0

C_n is the concentration at time Tn

A is the surface area of the test soil [m^2]

V is the total volume of the system (respiration chamber + holding cylinder)

The following formula can be used to determine the flux:

$$F_{CO_2} = \frac{dC}{dT} \times \frac{P}{1013} \times \frac{273}{273 + T_{air}} \times \frac{1\,mol}{22,414} x \frac{Vm^3}{Am^2} \times \frac{10^3 L}{m^3}$$

where:

$\frac{dC}{dT}$ change of carbon dioxide at the instant of time

P air pressure [hPa]

T_{air} air temperature in ^{o}C

V is the volume of the measuring cylinder [m^3]

A is the area covered by the cylinder [m^2]

4. Results

As an example Figure 1 shows the highly variable carbon dioxide flux ranges in relatively small areas on the main square of Covasna. On the upper part of the picture the 1–2 g/(m^2 d) flux values can be considered as the biological background. Living organisms in the soil usually produce carbon dioxide the exhalation of which is in this

order of magnitude. Significantly higher fluxes (up to about 500 g/(m² d) can be observed just a few meters away along the line between the "Pokolsár" and the spring of Covasna.
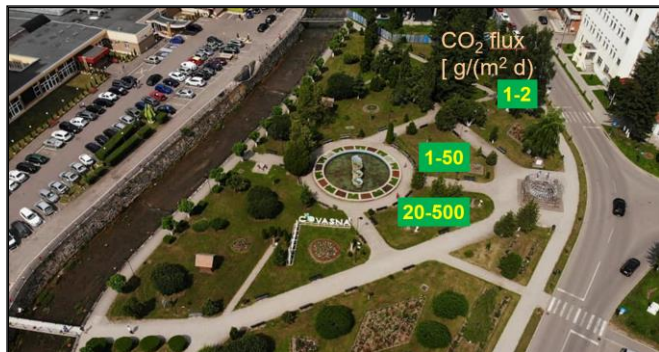

Figure 1 – Aerial view of the main square of Covasna with ranges of measured carbon dioxide fluxes

In order to get an idea of spatial variability of carbon dioxide flux we have measured it with ever greater spatial resultion at the Mátraderecske test area. The results shown in Figure 2 suggest that the variability does not change with the scale ranging from 10 cm-s to some 10 meters. This feature makes extremely difficult to design appropriate sampling technique in order to estimate larger area average fluxes.
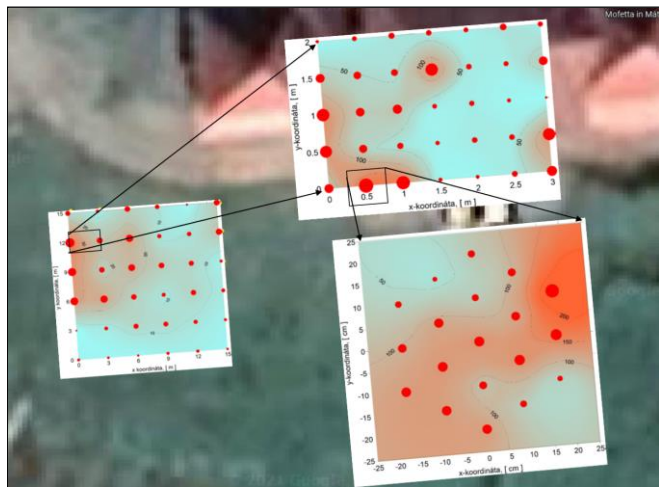

Figure 2 – Areal distribution of measured carbon dioxide fluxes at three different scales

Finally Figure 3 shows that we have not found strong correlation between radon and carbon dioxide fluxes at the Mátraderecske area. This result is again difficult to interpret as higher flux of carbon dioxide was supposed to carry radon with it. One possibility is that these fluxes of carbon dioxide is mainly driven by concentration gradient diffusion but advection.
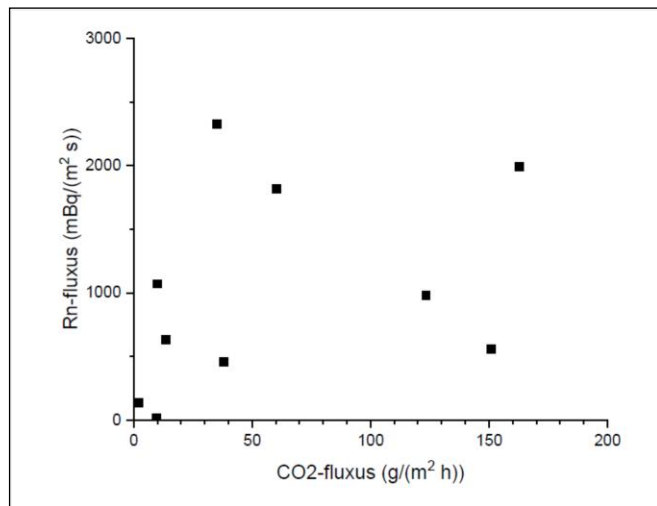

Figure 3 – Comparison of radon and carbon dioxide fluxes at the Mátraderecske test site

Acknowledgements

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