*Proceedings*

# Atmospheric and Soil Methane Concentrations Integrating a New Gas Detection Technology †

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**Abstract:** Cities are major contributors to greenhouse gas emissions (GHG) due to the high density of urbanization, numerous industrial centers, and intensive agricultural activities. This study focused on soil methane and radon gas measurements in the subsurface, as well as in the atmosphere. Measurements were conducted using new gas detection instrumentation and as low-cost devices for methane gas concentrations. Maximum soil radon gas concentration was observed to be approximately 1770 ± 582 Bq/m$^3$ at a depth of 1 m below the ground surface. The soil comprised of 64.31% sand, 20.75% silt, and 14.94% clay, and 0.526 ppm of uranium. The maximum concentration of methane was about 0.06%, at a depth of 1 m into the soil, characterized by 83% sand, 8.96% silt, and 7.89% clay. Moreover, this study focused on a better understanding of the advantages and disadvantages of new soil gas detection technology. The results and findings of environmental data obtained from the soil gas survey were shared with the community, whose involvement was critical in the data acquisition process.

**Keywords:** community; citizen science; greenhouse gas; methane; radon

## 1. Introduction

Gas migration through wellbore failure, from abandoned wells, is identified as the highest risk mechanism from multiple sources in literature [1,2]. The relative importance of monitoring wellbore failure is highlighted by the occurrence of accidents in the natural gas storage industry, including the recent wellbore blowout and sustained $CH_4$ venting of the Aliso Canyon underground gas storage facility in California [3]. Methane is a greenhouse gas (GHG) and its oxidation produces ozone ($O_3$) that degrades the air quality and adversely impacts human health, agricultural yields, and ecosystem productivity [4]. In comparison to $CO_2$, methane has a 25-time higher global warming potential for a 100-year time horizon [5]. Abandoned oil and gas wells provide a potential pathway for subsurface migration and emissions to the atmosphere of methane and other fluids [6]. Air quality has a tremendous effect on public health and the environment [7]. Air quality and the vadose zone were subject to a monitoring system in Minerbio city, located close to a natural gas storage site. Measurements taken close to the near-surface vadose zone are ideal for multiple reasons. Firstly, the vadose zone is quick and easy to sample, as it represents the bounding zone between subsurface storage and the atmosphere [8]. In this study, soil radon gas was investigated as well. 222Rn is a radioactive gas that is produced by the decay of radium (226Ra) within the uranium (238U) decay series. Typical soil air Rn values in Italian sedimentary basins, up to 15 Bq/L, are related to the content of parent radionuclides in the surface rocks (with 1–2 ppm of U) [9]. However, some surface radon anomalies can be related to the upward migration of gas along fault zones [10]. The short half-life of

222Rn (3.85 days) limits its migration distance in the subsoil, and thus, radon measured in the soil air cannot be produced at great depth unless it is lifted upward by a relatively fast-flowing carrier gas, such as $CO_2$, $CH_4$, or $N_2$ [11,12].

## 2. Material and Methods

A soil gas survey was conducted nearby a natural gas storage site. This study would not have been possible without community approval. Before starting the soil gas survey, a few presentations and kick-off meetings were conducted at each house surveyed. The environmental issues and solutions were presented to the community. The measurements were carried out in July, August, and September 2016 in Minerbio (BO), Italy. Air–soil samples were taken at 14 locations, as shown in Figure 1. Fifteen soil samples were collected at 10 cm and 1 m below the ground surface, to determine the soil texture and soil chemical properties.

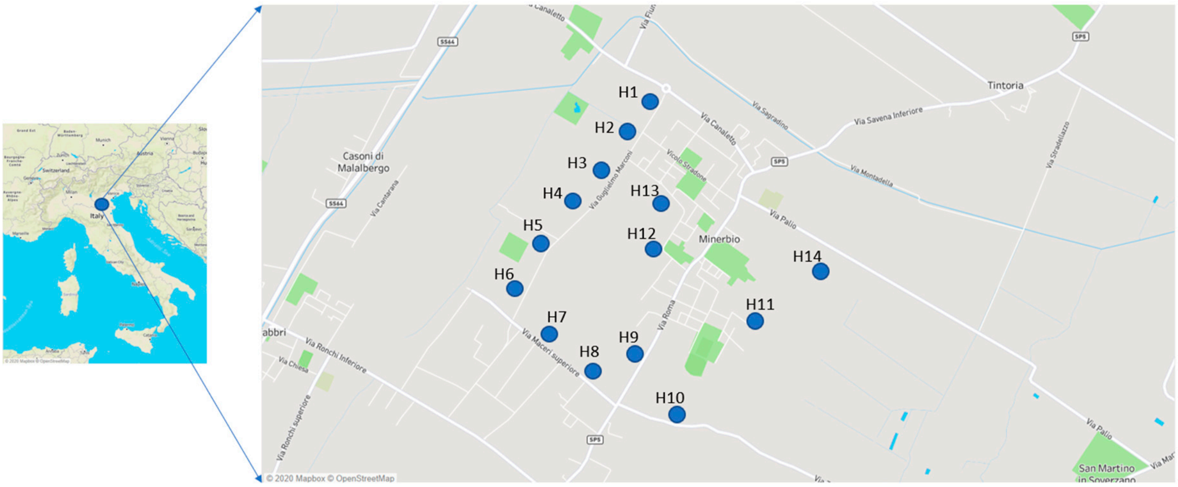

**Figure 1.** Soil gas survey study area.

As the first procedure for texture analysis, the sandy fraction was filtered out from the muddy fraction through wet sieving (net light of 63 µm). A further division of the sands was determined by using a mechanical quencher to obtain a fraction of 2.8–3 g. Instrumentation based on the principles of Stokes law and Sedimcol software were used to elaborate Folk and Ward [13] textural parameters, to determine the relative percentages of the granulometric classes based on the size scale of Wentworth [14]. The X-ray Sedigraph product by Micromeritics (Model 5100) was used to analyze the mud fraction with a dimensional range from 0.0884 mm to 0.00049 mm and a value standard of the density of about 2.7 g/cm$^3$. Inductively coupled plasma mass spectrometry (ICP-MS) analysis technology was conducted through a Thermo Electron Corporation X series spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to obtain the uranium and thorium soil concentrations. Private well water sampling was conducted at each soil gas survey location. Parameters like temperature, the potential of hydrogen (pH), electrical conductivity (EC), oxidation-reduction potential (ORP) were determined in situ using a Hanna device. A stainless-steel probe with a diameter of 6.4 mm was used for the soil gas monitoring to a depth of 10 cm and 1 m below the surface for methane, carbon dioxide, and oxygen measurements, as shown in Figure 2. Radon soil gas survey was conducted at 1 m below the ground surface.

ETG BioGas devices measured $CO_2$% and $CH_4$% gas by using an infrared sensor (with an accuracy of 1.5%) and $O_2$% gas using an electrochemical $O_2$ sensor (with an accuracy of 1%). Devices were provided with an internal air pump to draw the soil gas at a rate of 1 L/min and before each measurement the devices were purged with dry air for 15 min using drierite desiccant. RAD7 Durridge® alpha spectrometry instrument was used for the 222Rn-220Rn soil gas survey. The main study goal was to determine methane concentrations based on soil depth and investigate any discrepancies between the atmosphere and soil gas values.

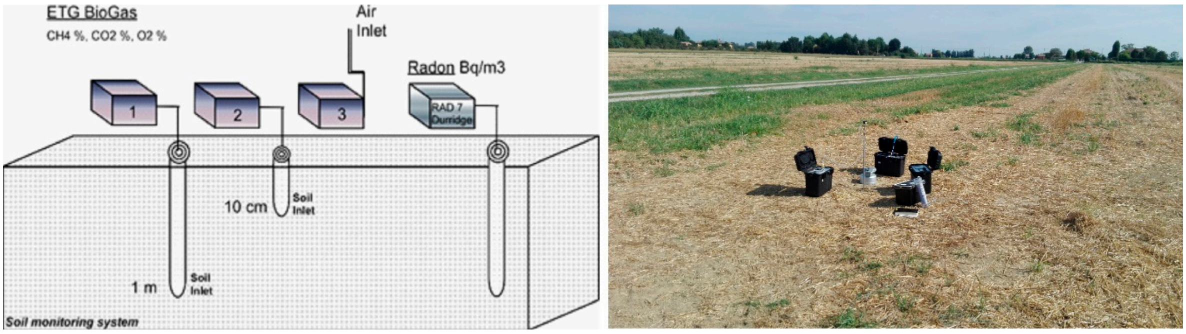

**Figure 2.** Design of the gas monitoring system.

The gas survey helped in a better understanding of the new gas technology, as well as understand the challenges faced during the field activities.

## 3. Results and Discussion

### *3.1. Soil Analysis*

Soil texture and chemical analysis were conducted on 15 soil samples. Percentages of sand, silt, and clay were determined for each soil sample. Shepard diagram was used, where percentage limits of sediment were defined. M06 sandy soil, M03, M07, and M12 silty sand, and the other remaining samples of loam are shown in Figure 3.

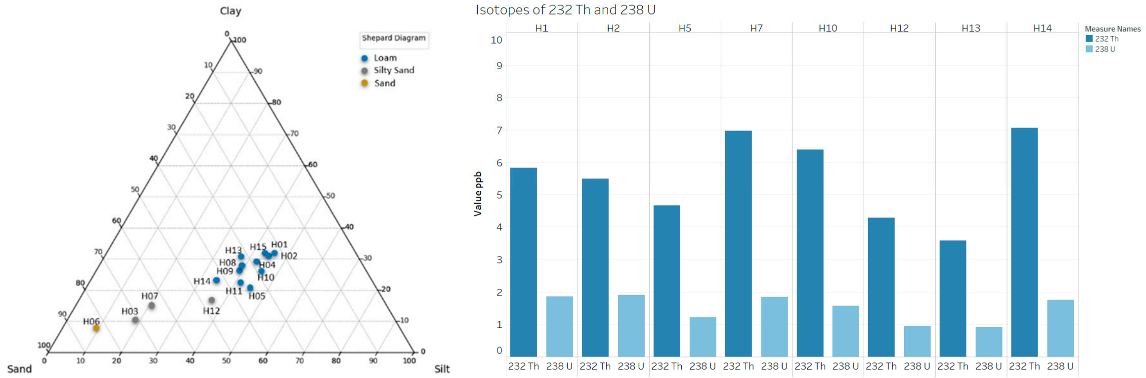

**Figure 3.** Shepard diagram and isotopes of Th and U for each soil sample.

The samples M03, M06, and M07 were sand-based soils, estimating the highest permeability, which allows more gas to migrate from the shallow soil to the surface. Higher concentrations of thorium and uranium were found to be in clay-silt based soils. These lithological units may potentially be the cause of soil radon concentrations. Soil texture and isotope composition give a better understanding of the soil gas dynamics and migration from greater soil depths. Soil texture of these samples (sandy soil, silty sand, loam) refers to the proportion of sand-, silt-, and clay-sized particles that compose the mineral fraction of the soil. The soil water content, the water movement through the soil, and gas migration depend on soil texture. Sandy soil has a high infiltration rate, while clay soil has a lower infiltration rate, which might affect the soil gas concentrations.

### *3.2. Soil Gas Survey*

Atmospheric methane gas concentrations were found to be lower than soil methane gas concentrations. Atmospheric methane gas concentrations depend on the local weather conditions, especially wind speed and direction. Studies have shown greater $CH_4$ soil emissions under high $CO_2$ [15] and elevated temperature [16,17]. Typically, surface ground methane gas concentration varies between 0.2 and 1.6 ppm (mean concentration in air), with no external source of $CH_4$, and the concentration is not expected to exceed 0.1% *v/v* [18]. In the study area, methane concentrations were found to be around 0.020–0.030% at 1 m below the surface. Anaerobic decomposition of organic matter produces large quantities of methane in the soil. Methane soil gas concentrations depend on the relative rates of methanogenic and methanotrophic soil activity, as well as on pH, Eh, temperature, and soil moisture content. A temperature rise stimulates microbial activity in submerged soils, which may lead to a higher rate of $CH_4$ production [19]. Increased soil moisture under elevated $CO_2$ reduces the rate of diffusion and therefore decreases $CH_4$ oxidation in the soil [20,21]. However, if the rising temperature due to the global climate change makes the soil drier, $CH_4$ oxidation may be enhanced [22]. In Figure 4, the corresponding value on the Y-axis is the monthly average concentration of $CH_4$ % *v/v* with the locations monitored during the month, labeled on the X-axis. In July, the soil methane concentrations were observed to be higher than the atmosphere by about 0.03%. In August, the methane concentrations were found to be highest in the atmosphere, with a maximum concentration of about 0.05%. Soil methane gas concentrations were higher at a depth of 1 m than at 10 cm, due to the atmospheric conditions affecting the surface soil. However, the study area was not characterized by soils rich in organic matter and it might explain the low concentrations found on methane soil gas. The study area was characterized by alluvium sediments that consisted of silt, clay, and sand. The highest methane concentration was found to be around 0.06% in sand-based soil. A better understanding of the methane gas process in the soil would require a carbon isotopic analysis to determine initially the methane sources, biogenic or thermogenic.

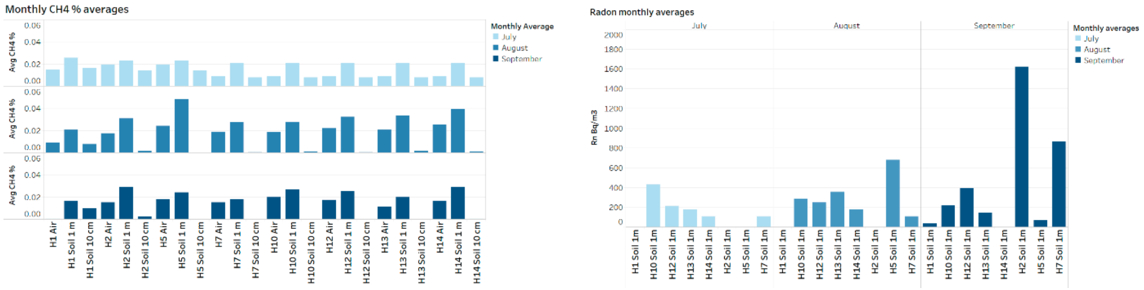

**Figure 4.** Monthly $CH_4$ % and Rn averages for each location.

Regarding the soil gas radon, at a depth of 1 m below the ground surface, the maximum concentration was about 1770 ± 582 Bq/m³, with soil consisting of 64.31% sand, 20.75% silt, and 14.94% clay, and 0.526 ppm of uranium. The short half-life of $^{222}Rn$ (3.85 days) limits its migration distance in the subsoil, and thus, radon measured in the soil air cannot be produced at great depth unless it is lifted upward by a relatively fast-flowing carrier gas, such as $CO_2$, $CH_4$, or $N_2$ [11]. Three main factors are known to predispose elevated radon levels. First, the regional and local geochemical and geological characteristics of the soil/rock will establish the in-situ conditions. For example, uranium ($^{238}U$, $^{235}Th$) and radium ($^{226}Ra$) content will control the amount of radon generated [23]. Second, environmental conditions will control the rate of movement of soil radon toward the surface. The escape of radon atoms at the grain scale is controlled by porosity, water content, and grain size, whereas migration toward the shallow environment is controlled by large-scale geological features like rock thickness, permeability, fractures, and karst [24,25].

Private well water sampling was conducted at each soil gas survey location. Water parameters can be linked to high methane concentrations dissolved in water. Parameters like temperature, the potential of hydrogen (pH), electrical conductivity (EC), and oxidation-reduction potential (ORP) were determined in situ using a Hanna device and no outliers were identified. In the study area, the pH values ranged between 6.69 and 8.2, while the temperature values ranged between 10 °C and 22 °C. In a few water samples, positive oxidation and negative reduction ORP values were observed.

## 4. Conclusions

The main goal of this study was to better understand soil methane gas dynamics using ETG devices as a new low-cost gas-sensing technology. Soil gas dynamics were related to soil texture, organic matter content, and structural features, which affected the soil gas concentration. The maximum soil methane concentration was about 0.06% with a soil characterized by 83% sand, 8.96% silt, and 7.89% clay. The values from the soil gas survey lay in the range of 0.01% to 0.03% CH4. A continuous monitoring system was conducted after this field campaign using new low-cost gas sensors and water sensors, and using pH and electrical conductivity sensors, parameters that can be linked to high methane concentrations dissolved in water [26]. The new system was built to address the issues faced during the field activities using the ETG portable gas monitoring devices. As an example, heavy cases were not used on the new prototype and the air pump was not located inside the sensor box to prevent the influence of increasing temperature and its impact on sensor readings. The data were saved on an SD card and integrated into a database created with a raspberry pi, which was not feasible on the ETG devices. ETG portable devices were not suitable for continuous monitoring since the battery life was about 5 h, thus it was not possible to determine diurnal patterns of soil methane gas concentrations at each location. Meteorological parameters like wind, barometric pressure, and relative humidity were not included in the ETG devices, however, they should be a part of the gas survey since it might affect the gas migration from the soil to the atmosphere. The stainless-steel soil probe was configured first with tubing for drierite desiccant to reduce the soil moisture by at least 60%. Regarding the stainless-steel probe, it was difficult to bore a hole down into a clay-based soil, and it had several soil gas access holes for the gas to flow in. The soil gas access holes were getting clogged with the surrounding soil affecting the gas volume sampled. It is recommended to use a mesh on the soil gas access holes to let the gas flow out with the specific volume requested by the pump itself. More information on the soil conditions and suitable instruments, soil gas monitoring components, tubing, and pumps for the study purposes is required at each location for a better performance of the soil gas sampling. At the end of each soil gas survey, insights gathered from the data were disseminated to the community. This process helped the community get a better understanding of the surveyed area and get trained on the environmental safety issues like methane gas leakage into the soil or groundwater.

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