



Using groundwater monitoring wells for rapid application of soil gas radon deficit technique to evaluate residual LNAPL

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ABSTRACT

The application of the ²²²Radon (Rn) deficit technique using subsurface soil gas probes for the identification and quantification of light non-aqueous phase liquids (LNAPL) has provided positive outcomes in recent years. This study presents an alternative method for applying this technique in the headspace of groundwater monitoring wells. The developed protocol, designed for groundwater monitoring wells with a portion of their screen in the vadose zone, is based on the use of portable equipment that allows rapid measurement of the Rn soil gas activity in the vadose zone close to the water table (i.e., smear zone) where LNAPL is typically expected. The paper first describes the step-by-step procedure to be followed for the application of this method. Then, a preliminary assessment of the potential of the method was carried out at two Italian sites characterized by accidental gasoline and diesel spills into the subsurface from underground storage tanks. Although the number of tests conducted does not allow for definitive conclusions, the results obtained suggest that, from a qualitative point of view, Rn monitoring in the headspace of monitoring wells is a promising, fast, and minimally invasive screening method that could also potentially reduce the costs associated with field data acquisition. This method proves to be suitable for detecting the presence of LNAPL in both the mobile and residual phases with results consistent with the other lines of evidence available at the sites, such as groundwater and soil gas monitoring. Future efforts should be directed toward evaluating the accuracy of this method for a quantitative assessment of residual LNAPL saturations.

1. Introduction

The occurrence of light non-aqueous phase liquids (LNAPL) in the subsurface is a significant issue in hydrocarbon-contaminated sites (Newell et al., 1995). LNAPL primarily originates from releases of fuels and oils, and its wide range of components is among the most frequently encountered organic contaminants in the subsurface environment (CL: AIRE, 2014). The assessment of petroleum-contaminated sites has progressed over time, improving efficiency in terms of time and cost (Sweeney and Ririe, 2017). However, it is still common that the evaluation of the presence and distribution of LNAPL at these sites relies on traditional methods like the collection of soil cores for laboratory analysis, and the installation of groundwater monitoring wells to observe the apparent thickness of the floating free product (US EPA, 2004). However, these methodologies are insufficient to provide

exhaustive information for a comprehensive site assessment and the planning and monitoring of effective remediation activities (ITRC, 2019, 2018; Mineo, 2023). To overcome such technological and economic barriers, several technologies have been introduced and tested in the field over the last few decades. These include Electrical Resistivity Tomography (ERT), Ground-Penetrating Radar (GPR), Laser-Induced Fluorescence (LIF) and the Optical Imaging Profiler (OIP) (Bertolla et al., 2014; McCall et al., 2018; Shao et al., 2019; Teramoto et al., 2019; García-Rincón et al., 2020; Lu et al., 2021; Meng et al., 2022; Mineo, 2023). Many of these methods, although promising, require further investigation to ensure their efficiency in the field, as the achievement of reliable results is often conditioned by the site characteristics (ITRC, 2019; Mineo, 2023). Among the available alternatives, the use of tracer techniques is another way to characterize and monitor LNAPL and assess the efficacy of in-situ remediation technologies implemented for LNAPL

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source zone remediation (Rao et al., 2000). The use of ^{222}Rn (Radon (Rn), a natural partitioning tracer that selectively partitions into the NAPL, has been explored in recent years within this context (Mineo, 2023). Rn is a naturally occurring radioactive gas, resulting from the decay of $^{226}\text{Radium}$, as an intermediate step in the radioactive decay chain of $^{238}\text{Uranium}$ (Ball et al., 1991). A portion of the Rn atoms produced in soil grains and rocks is released from the solid matrix into the pore space (Nazaroff and Nero Jr, 1988). Within the pore volume, Rn partitions among the different phases in the subsurface, being consequently present in the soil as sorbed to the soil grains, dissolved in water and dispersed in the soil gas, reaching a site-specific equilibrium concentration (Nazaroff, 1992). The presence of LNAPL in the subsurface causes Rn to preferentially partition into this additional phase, resulting in a change in the equilibrium concentration value that would be observed compared to that in the absence of contamination (ITRC, 2000). Indeed, studies have shown that Rn activities in soil gas or water in areas containing LNAPL are lower than those obtained from adjacent areas without LNAPL (background Rn value) (e.g., Hunkeler et al., 1997; García-González et al., 2008; Ponsin et al., 2015; Schubert, 2015). Therefore, it is possible to identify and quantify LNAPL in the subsurface by monitoring Rn in soil gas or water and determining the Rn deficit between the two zones (e.g., Semprini et al., 2000; Schubert et al., 2002; Fan et al., 2007; Castelluccio et al., 2018). Theoretical and practical aspects of this method, known as Rn deficit technique (Semprini et al., 2000; Schubert et al., 2001), were studied through laboratory experiments (e.g., Davis et al., 2002; Schubert et al., 2005, 2007a; De Simone et al., 2015; Cohen et al., 2019; Le Meur et al., 2021), modeling approaches (e.g., Semprini et al., 2000; Höhener and Surbeck, 2004; Davis et al., 2005; Cohen et al., 2019; Barrio-Parra et al., 2022; Cecconi et al., 2022, 2023), and field experiences (e.g., Schubert et al., 2001; García-González et al., 2008; Yoon et al., 2013; Barbosa et al., 2014; Cohen et al., 2016; De Simone et al., 2017; De Miguel et al., 2018, 2020; Mattia et al., 2020; Barrio-Parra et al., 2021). These latter applications involved different configurations, starting with Rn analysis in groundwater samples collected from wells installed at sites with known NAPL contamination (Cho et al., 2020). The aim of these activities was to detect NAPL in the saturated zone and to estimate its saturation using Rn analysis in groundwater samples. In this context, Rn activity in groundwater samples collected on site is typically measured not in the field, but through laboratory analysis (Hunkeler et al., 1997; Davis et al., 2002; Fan et al., 2007; Yoon et al., 2013), although field-based techniques that enable the direct analysis of collected samples can also be used (Schubert et al., 2007b; Wang et al., 2019). Furthermore, the Rn deficit technique has also been used to evaluate the presence of residual LNAPL in the vadose zone and the smear zone (Schubert et al., 2002; García-González et al., 2008; Barbosa et al., 2014; Mateus and Pecequilo, 2015; Castelluccio et al., 2018; De Miguel et al., 2018, 2020; Barrio-Parra et al., 2021). In this case, Rn activity can be analyzed directly in the soil gas, using different configurations depending on the equipment employed, the sampling method selected, and the features of the site being studied. The prevailing technique for soil gas sampling involves the use of temporary soil gas probes, which consist of stainless-steel hollow rods equipped with free, sharpened lower ends ("lost" tips). These probes are inserted into the ground, either manually or with equipment such as electric drill hammers, to a depth of 0.7–1 m (Schubert et al., 2001; García-González et al., 2008; Castelluccio et al., 2018; De Miguel et al., 2018; Barrio-Parra et al., 2021). This is the typical sampling depth range when using temporary probes, and it is dictated primarily by the need to sample soil gas at a depth that minimizes the impact of atmospheric variables (e.g., temperature, atmospheric pressure, wind speed). On the other hand, it is important to consider the practicality of temporary probe installation (Neznal et al., 2004), as the insertion of a hollow probe to greater depths may not be possible depending on the characteristics of the soil or in the presence of underground infrastructures (García-González et al., 2008). For other applications such as vapor intrusion studies, permanent soil gas probes

can also be used for soil gas monitoring. These probes consist of PVC or stainless-steel pipes, inserted into the unsaturated soil to the desired depth, using direct push drilling techniques (ASTM, 2012) or using previously excavated boreholes (ITRC, 2006). The borehole is then packed with filler material, consisting of clean sand near the probe tip, and of a sealing material, such as bentonite, for the rest of the borehole length (CalEPA, (California Environmental Protection Agency Department of Toxic Substances Control), 2015). Probes are typically equipped with a *gas-tight fitting* that can be connected to the sampling tube. This configuration is usually not cost-effective and does not offer significant advantages in terms of data quality compared to the temporary probe approach, for the application of the soil gas Rn deficit technique, which requires a relatively large number of monitoring points to delineate the LNAPL source. In this view, an alternative to the traditional method was proposed by De Miguel et al. (2020) who employed PVC pipes directly inserted into the ground, with the bottom perforated to allow soil gas to enter the probe, and equipped with an air-tight outlet valve that is only opened during purging and sampling. In all the above-mentioned configurations, soil gas is pumped directly into Rn detectors via external or instrument built-in pumps. Another approach is to use solid-state, nuclear track detectors, which are passive, low-cost and compact devices that do not require a power supply or suction systems. Schubert et al. (2005) and Mateus and Pecequilo (2015), among others, tested this method by placing the detectors inside special diffusion chambers within 1 m long PVC tubes buried in the soil. The detectors are exposed for a variable period (days or weeks) before being analyzed to determine the average Rn activity for the exposure period. In spite of the favorable outcomes observed with each of the above-mentioned configurations, certain limitations still exist concerning the applicability of the Rn deficit technique in the soil gas, which is the focus of this work. A crucial aspect emphasized by several authors (Cohen et al., 2016; De Miguel et al., 2020; Cecconi et al., 2023) is the vertical distance up to which NAPL contamination at a certain depth can be indirectly detected using the Rn deficit in soil gas as an indicator. This distance depends on various factors, such as soil texture characteristics, NAPL saturation of soil pores and Rn diffusion coefficient in the soil. In dry, sandy soils, Rn diffusion length can reach approximately 2 m (Schubert et al., 2001), but it can be significantly smaller in finer, wetter materials (Cecconi et al., 2022). Additionally, a heterogeneous geological setting can complicate the interpretation of the collected Rn data (Cohen et al., 2016; Cho et al., 2020). Therefore, if gas transport in the soil is purely diffusive, the technique's application would be limited to cases where the distance between NAPL contamination and the depth at which the soil gas samples are taken falls within the range of the Rn characteristic diffusion length in the soil (Schubert et al., 2001; De Miguel et al., 2020; Cecconi et al., 2022). Furthermore, Cecconi et al. (2023) highlighted that performing Rn measurements in soil gas at a depth close to the LNAPL source zone can enhance the method's performance also in the occurrence of local advective fluxes, due to groundwater level fluctuations, or methanogenesis phenomena that may occur in the proximity of LNAPL, which can complicate the interpretation of Rn data for the application of the Rn deficit technique. In this view, it is worth considering that a common characteristic of the LNAPL-contaminated sites being investigated is the presence of monitoring wells, typically screened across part of the vadose zone, through the smear zone and some portion of the aquifer (Lenhard and Parker, 1990; Steffy et al., 1995; CalEPA, (California Environmental Protection Agency Department of Toxic Substances Control), 2014; Sweeney and Ririe, 2017). However, installing the soil gas probes at the depth of the smear zone is not technically feasible as close to the water table, as low-flow conditions might be encountered due to the high moisture content (CalEPA, (California Environmental Protection Agency Department of Toxic Substances Control), 2015). In light of these observations, Jewell and Wilson (2011) developed a method that allows for soil gas sampling to be carried out using monitoring wells without the need for invasive installation of soil gas probes. Sweeney and Ririe (2017) proposed some

modifications to the method, which have been applied by other authors (Sookhak Lari et al., 2017; Smith et al., 2021; Ririe and Sweeney, 2022) to investigate phenomena such as vapor intrusion and natural source zone depletion (NSZD). It is worth noting that, although this method proved to be promising, it still must undergo further validation and obtain regulatory acceptance.

The objective of this study was to develop and evaluate a methodology for the application of the Rn deficit technique in soil gas by using the headspace of groundwater monitoring wells screened across the smear zone, installed at sites with LNAPL presence. In this work, we first defined the developed field protocol and then employed it at two Italian sites characterized in the past by accidental gasoline and diesel spills in the subsurface from underground storage tanks. At the first site, the developed protocol was compared with the results obtained using soil gas probes. The campaign carried out at the second site involved the use of groundwater monitoring wells to evaluate Rn data over a more significant number of monitoring points, also examining the temporal variability of Rn gas activity values through repeated measurements within the same day. Based on the obtained results, general recommendations on the use of monitoring wells for the application of soil gas Rn deficit technique to evaluate residual LNAPL are provided.

2. Materials and methods

2.1. Field protocol

This section describes a simple procedure developed for a rapid application of the Rn deficit technique in soil gas, to assess LNAPL contamination, analyzing the headspace of groundwater monitoring wells using portable equipment. This application can be suitable for sites with wells installed both in an area with presumed, or proven, presence of LNAPL, as well as in an area considered uncontaminated, to determine also the background value of Rn activity, necessary for the interpretation of the data. Note that, as for groundwater sampling, proper design and installation of the well is crucial to ensure the quality of the soil gas data obtained with the protocol outlined below. Considering the possible deterioration of the well's materials over time, conducting regular checks on the well's integrity and visual inspections can help ensure conformity with this last aspect. Note also that the method is best suited to typical LNAPL distributions in the subsurface, where the contamination is mainly found in the area comprising the shallower portion of the aquifer, the capillary fringe and some portion of the vadose zone, where the presence of LNAPL-gas interfaces allows the Rn deficit in the soil gas to be observed. Therefore, the protocol is suitable for groundwater monitoring wells that have a portion of their screen in the vadose zone. The configuration of the procedure follows some of the aspects proposed by Sweeney and Ririe (2017), in a modification of the US EPA protocol (Jewell and Wilson, 2011) for soil gas sampling from the headspace of monitoring wells. Fig. 1 shows a schematic representation of the method. For each monitoring point, both in the contaminated and the background area, the following steps can be followed:

- The well protective cap of the well is opened, and a sampling tube (typically of the size of 1/2 inch, of materials such as Tygon®, nylon or HDPE) is dropped into the well under investigation to a depth of approximately 1 m above the top of groundwater or LNAPL in the well. To ensure measurement in the gas phase without reaching the liquid interface, the liquid phase level should be measured ideally immediately before the sampling tube is inserted. In this case, the sampling tube can be brought even closer to the groundwater level to ensure the reliability of the monitored data. It is suggested that the end of the sampling tube, being flexible, is attached to a reinforcement that allows the tube to be extended to the desired depth.
- The wellhead is sealed with a well cap, fitted with an opening for the sampling tube, to prevent the ingress of air and the dilution of the soil gas to be sampled.

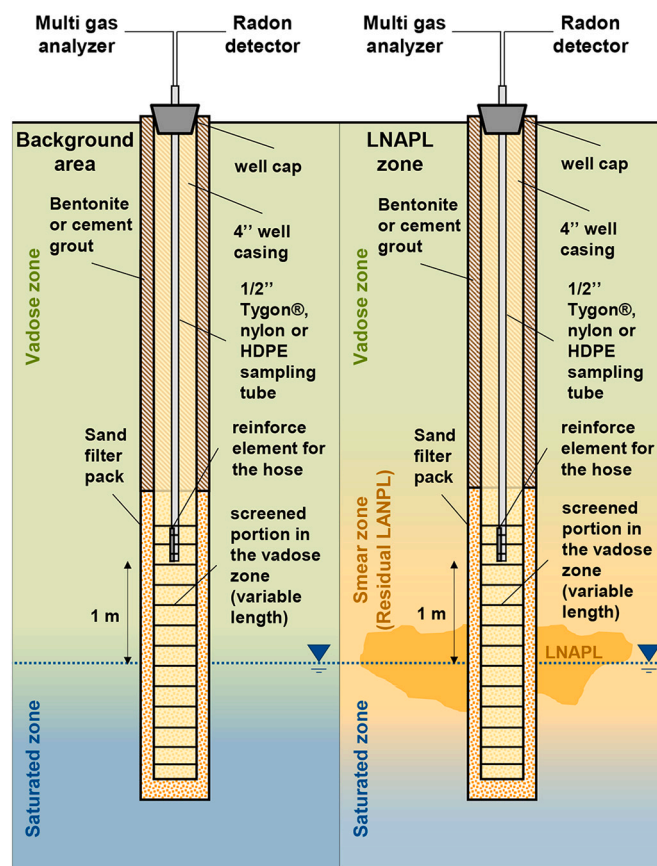


Fig. 1. Schematic of the method for the application of the Rn deficit technique in monitoring wells, located both in the LNAPL area and background zone.

- The purge of the system can be carried out with the built-in pump of a portable gas detector or with an external pump. Using the gas detector to purge the system is considered the simplest approach and also provides an analysis of the soil gas sample from the well immediately after the purging phase (Sweeney and Ririe, 2017). The time for this phase can be calculated by dividing the purge volume by the flow rate of the instrument used, typically 0.5–1 L/min if field gas detectors are used. The purge volume can be considered as the sum of the internal volume of the well and of the sampling and connection tubes.
- A multi-gas detector is used immediately after purging for a first sampling phase, for the analysis of CH₄ and CO₂, to provide supplementary information on the composition of the soil gas pumped from the bottom of the vadose zone and to highlight any ongoing attenuation processes of LNAPL sources (ITRC, 2009). High concentrations of CH₄ and CO₂ may be indicative of biodegradation phenomena. Measurements can be taken for approximately 5 min, after the monitored concentrations stabilize.
- The gas detector is then disconnected from the sampling line and replaced by a portable, active Rn gas detector (e.g., RAD7 manufactured by DURRIDGE or AlphaGUARD, manufactured by Bertin Instruments). To select the best setting and time for Rn analysis, reference must be made to the specific characteristics of the Rn monitor used and, if available, to the manufacturer's instructions for analysis in soil gas.
- At the end of the survey, the sampling tube is removed, and the well is closed with its own cap before proceeding to the following monitoring point and repeating the procedure.

The procedure should be followed, following the protocol described, for both groundwater wells located in the LNAPL-impacted area and in

the background area.

2.2. Interpretation of Rn data

From the ratio of the Rn activity detected in the LNAPL area and background zone, the Rn deficit, D (–), can be derived using the following relationship:

$$D = \frac{Rn_{LNAPL}}{Rn_{background}} \quad (1)$$

where Rn_{LNAPL} is the Rn concentration in the monitoring point in the LNAPL zone and $Rn_{background}$ is the Rn activity detected in the monitoring point located in the background area. Note that the term deficit indicates a depletion ratio of Rn activity, so that the greater the value of the deficit, the greater the difference between the background values and those in the LNAPL area.

It is then possible to estimate the fraction of LNAPL in the subsurface based on the observed Rn deficit, using different approaches. To take into account the vertical distance of the measurement point from the LNAPL source, the method proposed by Cecconi et al. (2022, 2023) can be used, assuming respectively diffusive and diffusive-advective transport. If Rn measurements are carried in proximity of the LNAPL source (as in the case proposed here) more simplified approaches based on the assumption of equilibrium conditions can be used. Schubert et al. (2001) developed an equation to describe the equilibrium Rn activity in the soil gas within a volume of NAPL-contaminated soil, Rn_{LNAPL} (Bq/m³):

$$Rn_{LNAPL} = \frac{\varepsilon C_{Ra} \rho_s}{\theta_t (k_{w/g} S_w + S_g + k_{N/g} S_N)} \quad (2)$$

where ε (–) is the Rn emanation coefficient, C_{Ra} is the ²²⁶Ra concentration of the solids (Bq/kg), ρ_s is the dry soil bulk density (kg/m³), θ_t is the soil porosity (–), $k_{w/g}$ (–) is Rn water-gas partition coefficient, $k_{N/g}$ (–) is Rn NAPL-gas partition coefficient and S_w (–), S_g (–) and S_N (–) are respectively the water, gas and NAPL saturations in the soil in the area impacted by LNAPL. Note that the following equation applies:

$$S_g = 1 - S_w - S_N \quad (3)$$

Based on Eq. (2), the equilibrium activity of Rn in the soil gas in the background zone, i.e. in the absence of LNAPL, $Rn_{background}$ (Bq/m³), can be derived:

$$Rn_{background} = \frac{\varepsilon C_{Ra} \rho_s}{\theta_t (k_{w/g} S_{w,b} + S_{g,b})} \quad (4)$$

where $S_{w,b}$ (–) and $S_{g,b}$ (–) are respectively the water and gas saturations in the soil in the background area, related to each other as follows:

$$S_{g,b} = 1 - S_{w,b} \quad (5)$$

From the ratio of Eq. (2) to Eq. (4) (i.e., Eq. (1)), the Rn deficit, D (–), is obtained:

$$D = \frac{1 + S_{w,b} (k_{w/g} - 1)}{1 + S_w (k_{w/g} - 1) + S_N (k_{N/g} - 1)} \quad (6)$$

Note that Rn might have a different partitioning behavior within soil pores and inside the well casing, which could lead to a potential dilution of the soil gas within the well casing. This potential dilution factor DF is represented by the ratio of the Rn concentration in soil gas to that in the well headspace, and can be expressed as the ratio of the total headspace volume of the well, V_{HS} (L), to the volume aspirated for Rn detection, as indicated by Eq. (7):

$$DF = \frac{V_{HS}}{Q \cdot t} \quad (7)$$

where Q (L/min) is the flow rate of the Rn detector's pump and t (min) is the soil gas sampling duration for Rn measurement. This could be accounted for in the interpretation of Rn data. As will be shown later, for the typical flow rates and duration adopted for Rn monitoring the expected dilution factor is relatively small and thus can be neglected.

From Eq. (6), it is then possible to derive the relationship for estimating the fraction of LNAPL in the subsoil, S_N (%), based on the observed Rn deficit:

$$S_N = \frac{(1 - D) + (S_{w,b} - D \cdot S_w) \cdot (k_{w/g} - 1)}{D (k_{N/g} - 1)} \cdot 100 \quad (8)$$

The LNAPL saturation can also be expressed in terms of total petroleum hydrocarbons (TPH) concentration, C (mg/kg), using the following relation (Brost and De Vaull, 2000):

$$C = \frac{\theta_t \cdot \rho_N \cdot S_N}{\rho_s} \cdot 10^6 \quad (9)$$

where ρ_N is LNAPL density (g/cm³) and S_N (%) is expressed in percentage.

2.3. Field tests

To test the performance of the method described above, the protocol was applied in two field campaigns, conducted between March 2021 and June 2022, at two contaminated sites located in Italy.

2.3.1. First campaign (site 1)

The first site, located in central Italy, was characterized in the past by accidental spills of diesel from an underground storage tank with a consequent contamination of the unsaturated soil and groundwater by hydrocarbons. A portion of the site was previously affected by the presence of free LNAPL in groundwater, which is located about 3–4 m below ground surface, with an aquifer thickness of about 3 m. The site is characterized by a rather homogeneous geology, with the presence of a layer of silty sands at the most superficial layer and weakly silty sands at greater depth, up to approximately 7 m from the surface, overlying a layer of clays.

The field test at the first site was conducted in March 2021. The activities consisted of the application of the Rn deficit technique in two groundwater wells and two soil gas probes to verify the feasibility of the proposed method. The operating procedure followed for gas analysis in the headspace of the monitoring wells is the described in the previous section. For the two soil gas probes, the instruments (see Section 2.3.3) were instead connected directly to the sampling tube of the probes, installed to a depth of 1.2 m. The monitoring points were selected based on the contamination present at the site. In particular, free LNAPL was found in the past at the monitoring well named MW-L, in proximity of the soil gas probe SGS-L and were therefore selected for the application of the method. The area near the monitoring well MW-B and the soil gas probe SGS-B, instead, was always uncontaminated, and was considered suitable to obtain the Rn background activity expected in the absence of contamination, also considering the stratigraphic homogeneity of the site. Table 1 shows the characteristics, in terms of water table depth, screening and contamination, of the 4" monitoring wells selected for the first site.

2.3.2. Second campaign (site 2)

The second site, located in central Italy, was characterized in the past by accidental spills of gasoline from an underground storage tank with consequent contamination of the unsaturated soil and groundwater by light ($C \leq 12$) and heavy ($C > 12$) hydrocarbons. A portion of the site was previously affected by the presence of free LNAPL in groundwater, which is located about 4–6 m below ground surface. The site is

Table 1

Characteristics of the monitoring wells (MW) selected at site 1. The monitoring well indicated with the letter B (MW-B) is in the background area, while the one indicated with the letter L (MW-L) is in the contaminated zone. TPH = Total Petroleum Hydrocarbons.

Monitoring point	Water table depth (m from surface) March 2021	Top of the MW screen (m from surface)	Free LNAPL thickness (mm)		Groundwater TPH tot (µg/L) June 2020
			Min - Max value 2018–2020	Last measure March 2021	
MW-B	3.5	2	–	–	< 30
MW-L	3.1	2	0–40	sheen	16,100

characterized by a heterogeneous stratigraphy that presents a more superficial layer of backfill sands and gravels (up to about 2 m from ground level) and a layer of compact silts or clays with possible inclusions of medium-fine sand and gravel layers (up to about 12 m from the surface), laying on a layer of clays. The water table lies on average at a depth of 4–6 m below ground surface.

The investigation conducted at the second site aimed to evaluate the applicability of the proposed method in a larger number of monitoring points, as well as to assess the temporal variability of Rn activity. The groundwater wells were selected based on the contamination found in different areas of the site, on the local stratigraphy, and on the possible presence of skimmers or pumps in the wells. In particular, MW-B1 and MW-B2, located upgradient of the contamination source zone with respect to the direction of the groundwater flux, were chosen as background monitoring points. These two monitoring points showed no evidence of contamination during the characterization and the concentrations of hydrocarbons in groundwater were always below the detection limit. Instead, the groundwater wells MW-L1, MW-L2, MW-L3 and MW-L4 were chosen as monitoring points for the LNAPL area. Specifically, they were chosen for the presence of free product (or high concentrations of hydrocarbons and a sheen of LNAPL). Note that the monitoring wells with installed total fluid or electric submersible pumps were excluded from the test. The background point MW-B2 and the contaminated point MW-L3 were selected to assess how the daily variability of Rn emissions from the subsurface may affect the estimation of LNAPL concentrations, repeating the procedure for three times within the same day. The characteristics of the selected monitoring wells, all with a diameter of 4", are summarized in Table 2. It is worth noting that in the wells MW-L1 and MW-L3 the skimmers were turned off the early morning of the test date, so that possible interference with the activities could be minimized.

2.3.3. Instruments used in the field campaigns

The instrument used for both the purging of the well and the subsequent sampling phase was the portable multi-gas detector Eagle 2 (RKI Instruments Inc., California, USA). The purge was carried out with a flow rate of 0.9 L/min for 10 min. For the analysis of CH₄ and CO₂ the measurements were taken at the stabilization of the monitored concentrations, at a maximum of 5 min after the purge.

For the analysis of Rn activity an electronic active Rn monitor (RAD7, DURRIDGE Company Inc., Massachusetts, USA) was used. The

detector is equipped with a built-in pump to collect a gas sample at a flow rate of 0.8 L/min, that decays inside the instruments chamber, producing positively charged progeny, used by a solid-state alpha detector to determine Rn activity. The Rn detector was connected to a small tube containing 30 g of drierite (provided by DURRIDGE Co.), a desiccant that reduces the moisture content of the gas sample before it is pumped into the Rn monitor. Before the connection to the sampling line, a warm-up of the instrument of about 10 min is required, during which the internal pump runs continuously. As suggested by the RAD7 instrument manual for soil gas analysis, the "Sniff" protocol was set for the measurements. This protocol involves readings (hereinafter referred to as cycles) of Rn activity every 5 min and the continuous operation of the instrument's pump. The 5 min measurement cycles were repeated for each well until a stabilization of the detected Rn activity was reached, for a total measurement duration for each point of about 30 min. To obtain a representative value of Rn activity at the investigated well, the first two five-minute readings were excluded, following the instrument manual's recommendation, while the last three measurement cycles were averaged.

3. Results and discussion

3.1. First campaign (site 1)

Table 3 provides a summary of the results obtained from the first field campaign carried out at site 1, in which the proposed method was applied in two monitoring wells and, for comparison, in two soil gas probes. Specifically, for each monitoring point, the detected soil gas concentrations of CH₄, CO₂ and Rn are provided. The Rn activity reported in the table refers to the average activity obtained in the last three measurement cycles (the first two measurement cycles, as suggested by the manufacturer of the Rn instrument, were discarded). The standard deviation and the associated coefficient of variation of the three Rn measurement cycles are also reported as a reference. The Rn deficit (*D*) in the probes and monitoring wells was calculated based on the ratio of average activity obtained in the two areas using Eq. (1). The expected dilution factor was evaluated using Eq. (7). Considering sampling times of approximately 30 min for Rn measurement, with a flow rate of 0.8 L/min, and considering the geometry of site's wells (i.e., 4" diameter, and 3.5 m height above the water table level), it was estimated a dilution factor of about 1.2, which was considered negligible. LNAPL saturation

Table 2

Characteristics of the monitoring wells (MW) selected at site 2. Monitoring wells indicated with the letter B are in the background zone, those indicated with the letter L are in the contamination zone. TPH = Total Petroleum Hydrocarbons.

Monitoring well	Water table depth (m from surface) Dec 2021	Top of the MW screen (m from surface)	Free LNAPL thickness (mm)		Groundwater TPH tot (µg/L) Dec 2021	Active measures
			Min - Max value 2021	Last measure Dec 2021		
MW-B1	4.4	3	–	–	< 30	–
MW-B2	4.2	3	–	–	< 30	–
MW-L1	4.3	3	0–220	2	not sampled (Free LNAPL)	skimmer
MW-L2	4.1	3	0–2	2	not sampled (Free LNAPL)	–
MW-L3	6.2	3	0–608	13	not sampled (Free LNAPL)	skimmer
MW-L4	4.5	3	0–0.5	–	1600	–

Table 3

Results of the first campaign carried out on site 1. The Rn mean activity and the standard deviation was calculated considering the results of the last three 5-min Rn measurement cycles. The mean Rn deficit was calculated using Eq. (1), LNAPL saturation and the relative TPH concentration in the soil were calculated using Eq. (8) and Eq. (9), respectively. The method of uncertainty propagation was used to derive the uncertainty values for Rn deficit, LNAPL saturation and TPH concentration.

Parameter	Symbol	Unit	Soil gas probes		Monitoring wells	
			SGS-L	SGS-B	MW-L	MW-B
CH ₄ concentration	CH ₄	% _{vol}	0.05	0	0.05–0.1	0.05
CO ₂ concentration	CO ₂	% _{vol}	0.2–0.3	0.1	0.7	0.7–0.8
Radon mean activity	Rn	Bq/m³	7604	8206	6362	7768
Radon standard deviation	σ Rn	Bq/m ³	1819	1058	406	560
Radon coefficient of variation	CV Rn	%	24	13	6	7
Radon deficit	D	–	0.93 ± 0.34		0.82 ± 0.11	
LNAPL saturation	S	%	0.5 ± 2.53 (K_{N/w} = 60)		0.78 ± 0.59 (K_{N/w} = 60)	
			1.09 ± 5.45 (K_{N/w} = 30)		1.68 ± 1.26 (K_{N/w} = 30)	
			1071 ± 5376 (K_{N/w} = 60)		1656 ± 1243 (K_{N/w} = 60)	
TPH concentration	C	mg/kg	2307 ± 11,580 (K_{N/w} = 30)		3567 ± 2678 (K_{N/w} = 30)	

(S_N) and the relative TPH concentration in the soil (C) were calculated using Eq. (8) and Eq. (9), respectively. To derive the uncertainty values for Rn deficit, LNAPL saturation and TPH concentration the uncertainty propagation method was used.

In this campaign, the analysis of the gases associated with LNAPL depletion did not yield relevant information on the subsurface contamination, either in the probes or the wells. This can be an indication of the absence of significant free-phase LNAPL in the monitored area, as this would result in higher concentrations of CO₂ or CH₄ due to hydrocarbon degradation processes. Consequently, the soil gas measurements did not exhibit distinctive patterns that would indicate the extent of contamination. However, Rn measurements proved to be informative in this regard, as it was observed that the Rn activities detected in the contaminated area were, on average, lower than those measured in the background zone. The deficit was approximately 90% in the soil gas probes and around 80% in the monitoring wells. Note that accounting for the standard deviation, the deficit values obtained in the soil gas probes result close to the unit or even higher, indicating that there is no statistically significant difference between the Rn activity values obtained from the background zone and the NAPL zone. The observed difference between the results obtained with the two systems could be attributed in part to the variation in contamination levels at the two measurement points (SGS-L and MW-L are approximately 10 m apart) and to the fact that Rn measurements in the wells reflect Rn activity at the depth likely to be affected by the presence of LNAPL (smear zone), whereas measurements in the soil gas probes were taken at a vertical distance of nearly 2 m from the source zone. At this distance, the effect of Rn adsorption in the LNAPL could have been partially obscured due to Rn emissions from the clean soil layers between the impacted zone and the probe depth, also considering the typical characteristic diffusion length of Rn (Schubert et al., 2001; Cohen et al., 2019; De Miguel et al., 2020; Cecconi et al., 2022). It should also be noted that the data obtained from the wells exhibited smaller coefficients of variation (6–7%) compared to those measured in the soil gas probes (13–24%), indicating lower variability.

The fraction of LNAPL in the subsoil was estimated based on the observed Rn deficit, using Eq. (8).

The latter equation requires site-specific measurements of water saturation in the NAPL-affected area. Since for site 1 this site-specific information is not available, an average literature value of water saturation, based on soil type, was used. This implies that the same level of water saturation was assumed for both the background zone and the LNAPL-impacted zone (i.e. $S_w = S_{w,b}$). Specifically, for the application of Eq. (8) in the soil gas probes, a water saturation (S_w) of 0.144, determined as the ratio of soil moisture ($\theta_w = 0.054$) to soil porosity ($\theta_t = 0.375$) for a sandy soil (US EPA, 2004), was used. For the application of Eq. (8) in the groundwater monitoring wells, a water saturation (S_w) of 0.675, representative of the value expected in the capillary fringe for a sandy soil ($\theta_w = 0.253$ and $\theta_t = 0.375$), always according to the values

provided by US EPA (2004), was instead adopted. Note that while this assumption may provide a reasonable estimate, it may not fully account for the variations in water saturation between the two zones, leading to some level of uncertainty in the results, i.e., assuming that water saturation in the contaminated area is reduced due to the presence of LNAPL, leading to a slight overestimation of LNAPL saturation. The Rn water-gas partition coefficient ($k_{w/g}$) was assumed equal to 0.25 (calculated at 20 °C from Kiliari and Pashalidis (2008)). The Rn NAPL-gas partition coefficient ($k_{N/g}$) was calculated as the product of $k_{w/g}$ and the NAPL-water partition coefficient $k_{N/w}$. Regarding the value of this last parameter, it should be noted that $k_{N/w}$ does not have a unique and recognized value. For LNAPL with a typical diesel mixture composition, Hunkeler et al. (1997) found a value of 40 ± 2.3 . Schubert et al. (2007a) proposed a value of 60 ± 1.3 , and Le Meur et al. (2021) also found similar values (60.7 ± 6.1) for fresh diesel. Höhener and Surbeck (2004) used a value of 11.7 for the partition coefficient between diesel and air ($k_{N/g}$), which, considering a Henry's constant of 4.4 (Wilhelm et al., 1977) results in a $k_{N/w}$ of about 51.5. Furthermore, considering the potential physical phenomena that can lead to an alteration of the diesel mixture (e.g., evaporation and UV-degradation) values ranging from 25.1 ± 2.5 to 74.8 ± 7.5 were found by Le Meur et al. (2021) for the diesel mixture studied. Similarly, for LNAPL with a typical gasoline mixture composition, Schubert et al. (2007a) proposed a value of 38.9 ± 0.9 . Le Meur et al. (2021) also found similar results for fresh gasoline (37.4 ± 5.6) and observed a certain variability due to the above-mentioned degradation phenomena, finding $k_{N/w}$ values ranging between 30.8 ± 4.6 and 37.4 ± 5.6 . Considering the data mentioned above, it was deemed appropriate to choose a range of values for $k_{N/w}$ between 30 and 60 for both diesel and gasoline, as also suggested by Le Meur et al. (2021). Based on these assumptions, the estimated average LNAPL fraction (S_N) was found to be between 0.5% and 1%, according to the results obtained in the soil gas probes. Note that, as shown in Table 3, the variability of the Rn measurements for the soil gas probes brought to a high uncertainty in the estimation of LNAPL saturation and TPH concentrations. The S_N estimated from the average Rn data obtained for the monitoring wells was between 0.8 and 1.7% (see Table 3). TPH concentrations in the range of 1500–3500 mg/kg (see Table 3) were then obtained using Eq. (9), assuming a soil bulk density of 1.66 g/cm^3 (US EPA, 2004) and NAPL density of 0.94 g/cm^3 (density of a diesel mixture provided by Brost and De Vaull (2000)). These concentrations are higher than the saturation concentration (C_{sat}) typically expected for diesel contamination, which is in the range of 18 mg/kg (Brost and De Vaull, 2000). However, considering the residual concentration (C_{res}) value suggested by Brost and De Vaull (2000) for diesel and sandy soil, which is around 7700 mg/kg, it can be inferred that the concentrations estimated using the Rn deficit technique are below this threshold. This result is consistent with the other field investigations (see Table 4). No measurable product thickness was indeed detected in MW-L with the water-oil probe, although traces of sheen were observed in the well

Table 4
Comparison of different lines of evidence on LNAPL contamination at well MW-L at site 1.

Free LNAPL thickness (mm)		Groundwater TPH ($\mu\text{g/L}$) June 2020	TPH from soil samples (mg/kg) 2012	CO ₂ (%vol) March 2021	CH ₄ (%vol) March 2021	LNAPL saturation from Rn deficit (%) March 2021	TPH from Rn deficit (mg/kg) March 2021
Min - Max value 2018–2020	Last measure March 2021						
0–40	sheen	16,100	~ 4800	0.7	0.05 -	0.78 ± 0.59 ($K_{N/w} = 60$)	1656 ± 1243 ($K_{N/w} = 60$)
					0.1	1.68 ± 1.26 ($K_{N/w} = 30$)	3567 ± 2678 ($K_{N/w} = 30$)

water samples collected with a bailer, indicating the possible presence of residual immobile LNAPL in the saturated zone. Furthermore, soil samples taken during the site characterization (conducted prior to this work) in the survey carried out for the installation of MW-L, revealed concentrations of hydrocarbons C < 12 of approximately 4000 mg/kg and hydrocarbons C > 12 of approximately 800 mg/kg, thus with a TPH concentration of about 4800 mg/kg. These values are consistent, although slightly higher, with those estimated from Rn deficits for the monitoring wells.

3.2. Second campaign (site 2)

The results obtained in the second campaign, using the proposed protocol in the headspace of the six selected monitoring wells of site 2, are presented in Table 5 and Table 6. As for the first campaign, the tables show the detected soil gas concentrations of CH₄, CO₂ and Rn activity for each monitoring point. It should be noted that the Rn activity values measured at site 2 are about one order of magnitude higher than those measured at site 1. The background Rn activity in soil gas can vary considerably between different locations, as it is the result of several mechanisms, all influenced by site-specific parameters. In particular, the main mechanisms that can affect Rn activity in soil gas, excluding migration processes in soil pores, are Rn generation from the decay of radium (influenced by radium content in rocks and soil and by its distribution), Rn emanation process (influenced e.g., by moisture, temperature and grain size), and Rn partitioning process between the soil phases (Nazaroff, 1992). This emphasizes the importance of measuring Rn activity in a background area for the application of the Rn deficit technique, as this value is strongly site-specific. For this site as well, considering a well diameter of 4" and a height of about 5 m above the water table, and considering the use of the same Rn detector with the same protocol as for site 1, the dilution factor from Eq. (7) is about 1.5 and can therefore be considered negligible.

Table 5 and Table 6 also show the deficits obtained for each monitoring point with contamination, in relation to the background Rn activity found in the background wells (see Eq. (1)), together with the corresponding LNAPL saturation (see Eq. (8)). For the determination of these latter value, values representative of a sandy clay were considered, since site-specific data were not measured. As for site 1, the same value

of water saturation was assumed for both the background and the LNAPL-impacted zone. Specifically, a water saturation (S_w) of 0.92, determined as the ratio of soil moisture of the capillary fringe ($\theta_w = 0.355$) to soil porosity ($\theta_t = 0.385$) for a sandy clay soil (US EPA, 2004) was used. The Rn water-gas partition coefficient ($k_{w/g}$) was assumed equal to 0.25 (calculated at 20 °C from Kiliari and Pashalidis (2008)) and the Rn NAPL-gas partition coefficient ($k_{N/g}$) was calculated as the product of $k_{w/g}$ and the NAPL-water partition coefficient $k_{N/w}$. As discussed in the previous section, $k_{N/w}$ was ranged between 30 and 60. Finally, a soil bulk density 1.63 g/cm^3 (US EPA, 2004) and a NAPL density of 0.78 g/cm^3 were used.

Referring to the results of the investigations performed in the background well MW-B1 and in the MW-L1, MW-L2 and MW-L4 wells in the contaminated zone (Table 5), it can be observed that some traces of CH₄ and CO₂ were observed in the wells located in the impacted zone, thus providing first evidence on the presence of LNAPL in these monitoring points. More robust evidence for the presence of LNAPL was instead provided by the average Rn activity found in the contaminated area, which resulted significantly lower (approximately half) than that found in the background. The TPH concentrations estimated from the Rn deficit (3000–9000 mg/kg) are in line with the residual concentration (Cres) of 10,000 mg/kg, indicated by Brost and De Vaull (2000) for silt to fine sand soil type contaminated by gasoline. Therefore, these results indicate the presence of residual LNAPL and potential free-phase LNAPL in the selected wells. This result is consistent with the investigations carried out in wells MW-L1 and MW-L2 (see Table 7), in which the occasional presence of mobile product was observed during the previous conventional groundwater monitoring (a few millimeters in the most recent).

Table 6 shows Rn activity and the concentrations of the other gases detected in the three measurements repeated within the same day in the headspace of the groundwater wells MW-B2 (background area) and MW-L3 (LNAPL zone). Elevated levels of CH₄ were observed in MW-L3, reaching up to approximately 1.3%vol, indicating the potential occurrence of methanogenesis processes commonly associated with areas contaminated with LNAPL. Note that also MW-B2 showed the presence of CH₄, although in lower concentrations compared to MW-L3. This suggests that petroleum hydrocarbons may be present even in areas considered not impacted by the contamination, which could result in an

Table 5

Results of the first campaign carried out on site 2. The Rn mean activity and the standard deviation was calculated considering the results of the last three 5-min Rn measurement cycles. The mean Rn deficit was calculated using Eq. (1), LNAPL saturation and the relative TPH concentration in the soil were calculated using Eq. (8) and Eq. (9), respectively. The method of uncertainty propagation was used to derive the uncertainty values for Rn deficit, LNAPL saturation and TPH concentration.

Parameter	Symbol	Unit	MW-B1	MW-L1	MW-L2	MW-L4
CH ₄ concentration	CH ₄	%vol	0.05	0.2	0.1	0
CO ₂ concentration	CO ₂	%vol	0	0.8	0.3	0
Radon mean activity	Rn	Bq/m³	85,167	48,867	43,000	43,400
Radon standard deviation	σ Rn	Bq/m ³	4336	3686	1732	2946
Radon coefficient of variation	CV Rn	%	5	8	4	7
Radon deficit	D	-	-	0.57 ± 0.07	0.50 ± 0.05	0.51 ± 0.06
LNAPL saturation	S	%	-	1.64 ± 0.49 ($K_{N/w} = 60$) 3.52 ± 1.04 ($K_{N/w} = 30$)	2.16 ± 0.4 ($K_{N/w} = 60$) 4.65 ± 0.86 ($K_{N/w} = 30$)	2.12 ± 0.51 ($K_{N/w} = 60$) 4.57 ± 1.11 ($K_{N/w} = 30$)
TPH concentration	C	mg/kg	-	3015 ± 894 ($K_{N/w} = 60$) 6494 ± 1925 ($K_{N/w} = 30$)	3980 ± 733 ($K_{N/w} = 60$) 8573 ± 1579 ($K_{N/w} = 30$)	3906 ± 946 ($K_{N/w} = 60$) 8413 ± 2038 ($K_{N/w} = 30$)

Table 6

Results of the second campaign, carried out on site 2, for the wells MW-B2 and MW-L3. The Rn mean activity and the standard deviation was calculated considering the results of the last three 5-min Rn measurement cycles. The mean Rn deficit was calculated using Eq. (1) and LNAPL saturation was calculated using Eq. (8). The method of uncertainty propagation was used to derive the uncertainty values for Rn deficit and LNAPL saturation.

Parameter	Symbol	Unit	1° measure (morning)		2° measure (mid-day)		3° measure (afternoon)	
			MW-L3	MW-B2	MW-L3	MW-B2	MW-L3	MW-B2
CH ₄ concentration	CH ₄	% _{vol}	1.2	0.1	1.3	0.15	0.65	0.35
CO ₂ concentration	CO ₂	% _{vol}	0.7	0.5	0.8	0.3	0.4	0.1
Radon mean activity	Rn	Bq/m³	3840	77,967	7367	92,267	9723	97,933
Radon standard deviation	σ Rn	Bq/m ³	173	7315	220	7433	585	2875
Radon coefficient of variation	CV Rn	%	5	9	3	8	6	3
Radon deficit	D	–	0.05 ± 0.01		0.08 ± 0.01		0.10 ± 0.01	
			42.53 ± 6.21		25.39 ± 3.05		19.99 ± 1.99	
			(K_{N/w} = 60)		(K_{N/w} = 60)		(K_{N/w} = 60)	
LNAPL saturation	S	%	91.6 ± 13.38		54.69 ± 6.56		43.05 ± 4.28	
			(K_{N/w} = 30)		(K_{N/w} = 30)		(K_{N/w} = 30)	

Table 7

Comparison of different lines of evidence on LNAPL contamination at site 2.

Well	Free LNAPL thickness (mm)		Groundwater TPH (µg/L) Dec 2021	Active measures	CO ₂ (% _{vol}) 2022	CH ₄ (% _{vol}) 2022	LNAPL saturation from Rn deficit (%) 2022
	Min - Max value 2021	Last measure Dec 2021					
MW-L1	0–220	2	not sampled (Free LNAPL)	skimmer	0.8	0.2	1–4
MW-L2	0–2	2	not sampled (Free LNAPL)	–	0.3	0.1	2–5
MW-L3	0–608	13	not sampled (Free LNAPL)	skimmer	0.1–0.8	0.6–1.3	20–90 (Free LNAPL)
MW-L4	0–0.5	–	1600	–	0	0	2–5

inaccurate assessment of the Rn background values for the area. The repeated measurements carried out during the day revealed a considerable Rn variability, with a tendency to increase during the day. This could be related to the increase in atmospheric temperature during the daytime hours, in agreement with observations by other studies (Minkin and Shapovalov, 2016; De Miguel et al., 2020; Barrio-Parra et al., 2021), who found a positive correlation between air temperature and Rn exhalation. This resulted in variability in the Rn deficit by a factor of about 2, with a value of 0.05 detected in the morning sampling compared to the value of 0.1 detected in the afternoon. It is first observed that these deficit values are rather pronounced. This could be due to the fact that the Rn measurements in the headspace of the wells were carried out at greater depth, closer to the area with LNAPL, compared to the more shallow measurements typically carried out with soil gas probes. Furthermore, measuring Rn in the headspace of a well that shows a layer of free product, could lead to a modification of Rn partition behavior. In particular, the observed deficit could be also influenced by the presence of free product in the well besides the residual saturation in the surrounding vadose zone. The pronounced deficit values detected have indeed led to the estimation of very high LNAPL saturations, especially in the first measurement in the morning (S_N estimates even exceeding 90%), that suggest that mobile LNAPL is present in the area of MW-L3. This conclusion is also supported by the elevated methane values detected in well MW-L3, as well as by the results of previous water monitoring campaigns (see Table 7).

4. Conclusions

The method proposed in this study has the potential to offer a rapid and low invasive approach for the application of the Rn deficit technique, using portable equipment to sample the soil gas in the headspace of groundwater monitoring wells already present at LNAPL-contaminated sites. The protocol described is suitable for groundwater monitoring wells presenting a portion of the screen through the aquifer and in the overlying vadose zone (smear zone), so that gas can be sampled in the unsaturated zone closest to the groundwater table, where

LNAPL is usually found. The proposed method can be applied using various Rn detectors and multi-gas analyzers and is not affected by the depth of the aquifer, but only requires adjustments to the depth of the measurement point based on aquifer depth. For this reason, it is recommended to measure the water table depth before the beginning of the protocol activities. A simple method for estimating LNAPL saturation and TPH concentration was also provided based on the measured Rn deficit. The equations were derived from previous works that are based on Rn equilibrium conditions (Schubert et al., 2001). Note that these relations may be inaccurate in cases where the probe to LNAPL vertical distance increases, and in such cases methods that account for the Rn transport in the subsurface (e.g., Cecconi et al., 2022, 2023) may be more appropriate. Also, the lack of site-specific data on water saturation in the investigated area can affect the accuracy of the results.

To provide an initial insight into the method's potential as a tool for the detection of LNAPL, the proposed protocol was tested at a first site, in comparison to the more traditional application in soil gas probes, yielding overall positive results from a qualitative point of view, and no complications related to the proposed configuration. In the second site, the method was applied in a more significant number of wells, showing results consistent with other lines of evidence, such as groundwater and soil gas monitoring. Overall, from these first evaluations, the proposed method has shown potential for a qualitative identification of LNAPL in the subsurface. Compared to the more traditional technique using soil gas probes, the proposed method has indeed the potential to offer several improvements, providing a rapid and non-invasive approach and eliminating the need to install additional gas probes at sites. Furthermore, although this sampling method is yet to be validated and is not yet regulated, the use of the headspace of monitoring wells may allow for gas sampling in the unsaturated zone, closest to the water table, where both free and residual phase LNAPL may be present (smear zone). This may allow for a more representative Rn measurement at the zone of interest, without the limitations associated with Rn diffusion distance, and reducing the potential errors caused by local advective phenomena. Furthermore, the proposed method has the potential to provide quantitative information on the subsurface contamination concentrations.

Therefore, future investigations could be oriented to collect additional data to assess the accuracy of this approach for a quantitative assessment of LNAPL. In this view, it is worth recalling some limitations typically associated with the methods based on the Rn deficit technique. For instance, the almost instantaneous nature of the measurements may provide a Rn activity value strongly tied to the sampling moment without considering temporal fluctuations in Rn emissions, which could affect the estimation of the actual subsurface contamination (Winkler et al., 2001; Neznal et al., 2004; De Miguel et al., 2020). Moreover, as highlighted by several authors, the heterogeneity of the soil matrix can have a significant impact on the distribution of Rn in the soil gas, independently of the presence of LNAPL (Fan et al., 2007; Cohen et al., 2016; De Miguel et al., 2018; Cho et al., 2020). Therefore, spatial and temporal variability of contamination and Rn emissions from the subsurface implies that a higher spatial density of measuring points and a higher frequency of field campaigns are necessary for accurate determinations. These aspects should be addressed in future research efforts to advance the understanding and application of LNAPL detection using the soil gas Rn deficit.

CRedit authorship contribution statement

Alessandra Cecconi: Methodology, Data curation, Formal analysis, Investigation, Writing – original draft. **Iason Verginelli:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Renato Baciocchi:** Writing – review & editing, Supervision. **Camilla Lanari:** Methodology, Writing – review & editing. **Federico Villani:** Writing – review & editing, Supervision. **Guido Bonfedi:** Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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