

Using radon-222 in soil gas as an indicator of subsurface contamination by non-aqueous phase-liquids (NAPLs)

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RESUMEN

Se estudia la dependencia de la concentración de radón del suelo con su contaminación por líquidos en fase no-acuosa (NAPLs). La contaminación subterránea por NAPLs es uno de los mayores problemas relacionados con la limpieza de sitios industriales contaminados. Una de las razones es el número limitado de estaciones de muestreo de suelo que dificulta el trazado de la extensión de la contaminación. Con la finalidad de estudiar plumas de NAPLs, se desarrolló un método nuevo de detección indirecta. El método utiliza la mayor solubilidad que tiene el radón en NAPLs, lo cual permite que estos últimos acumulen el radón presente en los poros del suelo. Este enriquecimiento de los NAPLs en radón provoca simultáneamente una disminución de la concentración del radón del suelo en la vecindad de la zona contaminada con NAPLs. Por lo tanto, los valores mínimos de radón podrían utilizarse para localizar indirectamente las plumas de NAPLs. Los resultados de esta investigación sugieren que la concentración de radón del suelo pueden utilizarse potencialmente como una herramienta complementaria para la detección de contaminación subterránea por NAPLs, junto con métodos convencionales de investigación.

PALABRAS CLAVE: NAPL, contaminación del suelo, radón, gas del suelo, método de detección, remediación de sitios.

ABSTRACT

The dependence of the soil gas radon concentration on ground contamination by non-aqueous phase-liquids (NAPLs) was studied. Subsurface NAPL contamination is known as one of the major problems concerning the clean-up of polluted industrial sites. One reason is the mostly limited number of soil sampling locations, which makes adequate tracing of the extent of contamination difficult. With the aim to enable a more detailed assessment of NAPL plumes a new *indirect* method for NAPL detection has been developed. The method uses the good solubility of radon in NAPLs which enables the NAPLs to partly accumulate the radon available in the soil pores. Radon enrichment in the NAPL causes a local decrease of the soil gas radon concentration in the vicinity of the NAPL contamination. Thus radon minima can be used to localize NAPL plumes indirectly. The results of the present investigation suggest that the radon concentration in soil gas may be used as a complementary tool for the detection of subsurface NAPL contamination together with conventional investigation methods.

KEYWORDS: NAPL, soil contamination, soil gas, radon, detection method, remediation.

INTRODUCTION

One of the major problems facing prior-remediation risk assessment at abandoned and/or polluted industrial sites, military bases and petrol stations is ground contamination by non-aqueous phase-liquids (NAPLs) such as fuels or mineral oils. Before appropriate clean-up measures can be designed, the distribution of the contaminants in the subsurface has to be explored and its extent traced.

A possible approach to meet the demands is an investigation based on the *direct* detection of organic carbons, such as BTEX, in the soil gas (Marrin and Kerfoot, 1988; Kerfoot, 1987). That method can, however, only be put to use in the case of ground contamination with volatile NAPLs. It can hardly be used for the investigation of e.g. diesel fuel, kerosene, or heavy mineral oil contamination.

Another method which has also been suggested and applied since several years is the exploration and mapping of NAPL derivatives such as CO₂ and CH₄ and their use as NAPL tracers (Marrin, 1987). Methane vapor concentrations generated within a NAPL contaminated soil zone can be within the percent range, and correlate directly with the NAPL plume. However the generation of NAPL derivatives depends on bioactivity in the ground which can hardly be expected in case of fresh contamination.

Therefore on-site activities usually begin with drive point profiling, the actual examination points being located either close to the contamination source or, if known, inside the zone that covers the plume of the contamination. However, because of the given local infrastructure or due to low investigation budgets, the number of such soil sampling points is often limited. Consequently it is hardly ever possible to

satisfactorily trace the shape of subsurface NAPL contamination, and this may cause wrong decisions concerning the remediation action. To obtain a sufficiently detailed picture of ground contamination, a complementary more uncomplicated detection method which allows a denser network of monitoring points would be desirable.

The radioactive noble gas radon, a naturally occurring component of soil gas, exhibits very good solubility in a wide range of NAPLs (Barton, 1991; Lewis *et al.*, 1987; Schubert *et al.*, 2000). Consequently, and given the problems outlined above, the idea was put forward that subsurface NAPL contamination partly traps the soil gas radon, resulting in a local reduction of the soil gas radon concentration in the vicinity of the contaminated soil volume (Figure 1). Provided this “NAPL-Effect” is significant, a NAPL contamination could be indirectly localized by carrying out a straightforward radon survey on a sampling grid covering the suspected area.

The aim of the investigation that will be described in this paper was to assess the significance of the impact of a subsurface NAPL contamination on the local soil gas radon distribution pattern – and hence to see whether anomalous radon concentration can be used as an indicator of NAPL contamination. Related research has been carried out by Hunkeler *et al.* (1997) and Semprini *et al.* (2000) whose activities were focused on changes in ground water radon concentration rather than radon in soil gas.

METHODS

The radon solubility in NAPLs can be quantified for each NAPL with an individual NAPL/air partitioning coefficient ($K_{\text{NAPL/AIR}}$). The partitioning coefficient $K_{\text{NAPL/AIR}}$ is one of the most influential parameters governing the decrease in the soil gas radon concentration in the presence of NAPLs. The aim of the **laboratory experiments** was to determine the radon partitioning coefficients for environmentally relevant complex NAPL mixtures. Whereas the partitioning coefficients for a wide range of pure NAPLs have been published, hardly any data for environmentally significant NAPL mixtures such as gasoline, diesel fuel or kerosene are available. Since these three NAPL mixtures are among the most relevant ones for clean-up activities, their partitioning coefficients were determined in the laboratory as part of the investigations discussed here.

As a first step the NAPL/water partitioning coefficients ($K_{\text{NAPL/W}}$) of the mentioned NAPLs were determined. For that purpose a 1 liter glass bottle was filled with 0.5 liters of water enriched in radon and 0.5 liters of the (virtually radon free) NAPL of concern. The radon activities of the water and the NAPL were determined previously. The bottle was

shaken for 3 hours at a temperature of 20°C. After shaking a period of 1 hour was allowed for the aqueous and the non aqueous phase to separate. Thereafter a virtually complete separation of the two phases could be observed. The two phases were decanted into 2 separate flasks and a further period of 3 hours was allowed to ensure an equilibrium between radon and its short-lived progenies ^{214}Pb ($T_{1/2}=26,8$ min) and ^{214}Bi ($T_{1/2} = 19,9$ min). At last the radon activities of the 2 phases were measured indirectly by gamma spectroscopy by determining the activity concentrations of ^{214}Pb and ^{214}Bi . The values for $K_{\text{NAPL/W}}$ were obtained by dividing the radon activity of the NAPL by the radon activity of the water. Eventually $K_{\text{NAPL/AIR}}$ was determined by multiplying the achieved values for $K_{\text{NAPL/W}}$ with the radon partitioning coefficient between water and air $K_{\text{W/AIR}}$, the latter being assumed to be 0.25 at 20°C (Clever, 1979).

The aim of the **field experiments** was to test the suitability of using radon on-site as an indicator of subsurface NAPL contamination. Three NAPL contaminated sites were chosen and each was covered with a grid of soil-gas sampling points. To exclude the possibility of significant influences of diurnally changing meteorological conditions such as air pressure, wind speed, or temperature on the radon concentration of the soil gas samples, the samples were taken from a depth of 0.7 m. Findings of experiments carried out earlier had shown that the results of a radon survey are not affected by the *diurnal* alterations of these meteorological

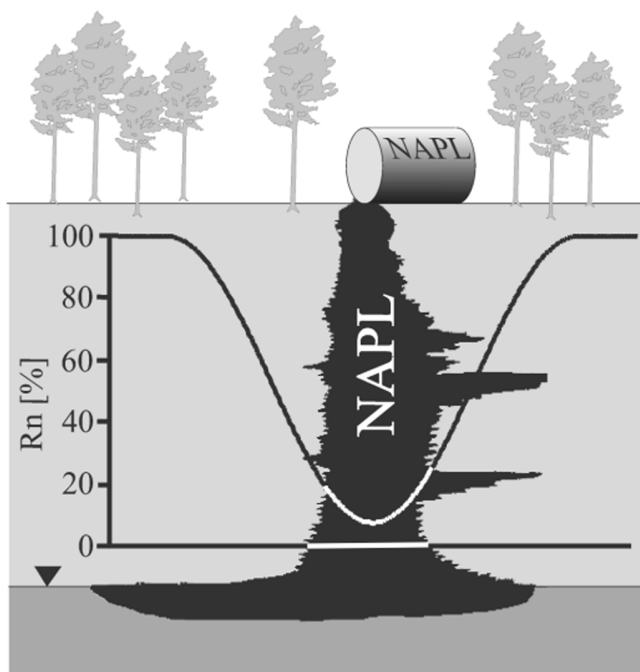


Fig. 1. Schematic sketch of the principle of the local reduction of the soil gas radon concentration in the vicinity of the contaminated soil volume.

parameters if the soil gas samples are taken from a depth of > 0.7 m. Since permeable sands had been used for this previous investigation their results can be considered as representative for a wide range of soils (Schubert and Schulz, 2002). Rain however can affect the soil gas radon concentration at even larger depths (Schery *et al.*, 1984; Lindmark and Rosen, 1985; Nazaroff, 1992). Yet, since the influence of rain on the radon exhalation is known and principally understood we did not concentrate on that effect in the study described and discussed here.

On each of the three investigated sites the lateral radon distribution pattern was mapped. The soil-gas radon concentration was measured with the mobile radon monitor AlphaGUARD PQ 2000¹. It allows radon concentrations to be measured in a range between 2 Bq/m³ and 2000 kBq/m³ with a precision of $\pm 3\%$. The soil gas samples were taken with a special AlphaPUMP which is part of the AlphaGUARD equipment. The pump was connected to the soil gas probe STITZ S2388². After the soil gas sample had been pumped into the ionization chamber of the AlphaGUARD, a waiting period of 10 min was allowed before the radon concentration was recorded. As a result, it could be ensured that all thoron (²²⁰Rn, $T_{1/2} = 55.6$ sec) present in the soil gas sample had decayed and the monitored α -decays represented only radon (²²²Rn, $T_{1/2} = 3.82$ d).

The achieved lateral radon distribution patterns were compared to the extent of the NAPL contaminations of the three sites that had been previously recorded with conventional, much more expensive research methods (laboratory analysis of soil samples taken by drive point profiling) and the correspondence of the results of the two methods was assessed.

RESULTS

The results of the **laboratory experiments** clearly show the strong affinity of radon to the NAPL mixtures examined (Table 1). The achieved partitioning coefficients correspond to those which have been published for pure NAPLs (Clever, 1979) and are thus in the range of expectations.

To illustrate the results of the **field experiments** one of the three surveyed sites will in the following paragraphs be looked at more closely. The discussed test of the method was carried out at an abandoned air strip with a geological situation characterized by a homogenous sandy soil and a groundwater table at about 4 m below the surface. Exploration had revealed a free floating layer of kerosene with a thickness of about 0.1 – 0.5 m as well as a considerable contamination of

Table 1

Radon partitioning coefficients $K_{\text{NAPL/W}}$ and $K_{\text{NAPL/AIR}}$ between NAPLs and water or NAPLs and air respectively

NAPL	$K_{\text{NAPL/W}}$	$K_{\text{NAPL/AIR}}$	No. of experiments
gasoline	50,9 +/- 5,8	13,2 +/- 1,5	7
diesel fuel	43,8 +/- 4,6	11,4 +/- 1,2	10
kerosene	40,6 +/- 8,3	10,6 +/- 2,1	4

the unsaturated soil above. The old kerosene storage tanks which have been taken out of the ground as part of a remediation scheme are assumed to be the main source of the contamination.

Figure 2 shows the results of the radon survey. The minimum radon concentrations found (caused by the accumulation of the radon in the NAPL) closely match the extent of NAPL contamination detected by conventional means.

DISCUSSION

The results of the field experiments indicate that the soil gas radon concentration can potentially be used as an appropriate tool to localize sub-surface NAPL contamination. The investigation showed that NAPLs in the ground give rise to anomalous low radon concentrations of the soil gas in the close vicinity of the contaminated soil volume. That is due to the good solubility of radon in NAPLs which could be confirmed by the lab experiments and which enables the NAPLs to accumulate part of the radon available in the soil pores and thus to act as a radon trap.

Up to which distance NAPL contamination can be indirectly detected using decreased radon concentrations as indicator depends on the NAPL saturation of the soil pores, on the gas permeability of the soil, and on the diffusion coefficient of the soil. The more dense or/and moist a soil is, the shorter is the distance up to which the soil gas radon concentration will be influenced by the NAPLs.

Despite the potential suitability of radon surveys as a tool for investigating subsurface NAPL contamination, the detection method presented also has its limitations. Because of the similarity of the partitioning coefficients of a wide range of NAPLs, especially non volatile NAPLs cannot be

¹ http://www.genitron.de/products/alpha_slides.html

² <http://www.stitz-gmbh.de>

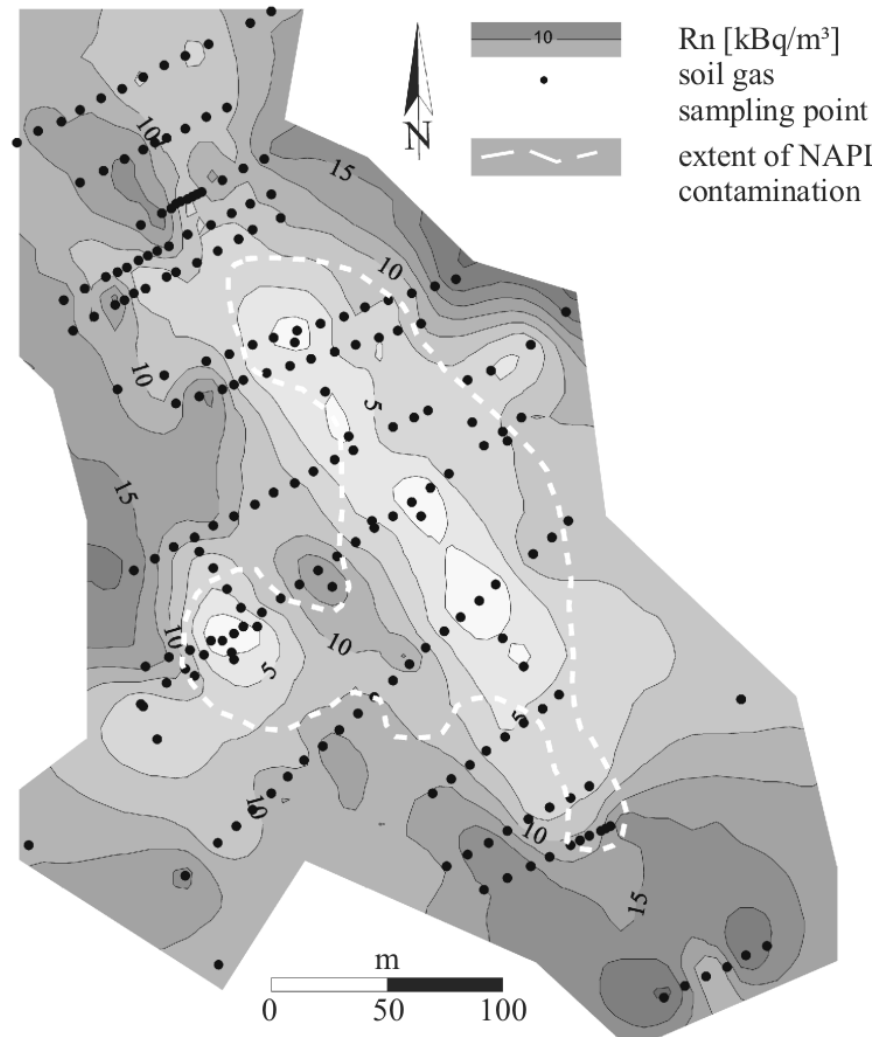


Fig. 2. Anomalous low radon concentrations of the soil gas in the close vicinity of a NAPL-contaminated soil volume.

identified without also taking a few soil samples and analyzing them conventionally. Moreover, a complex geological situation can complicate the interpretation of the radon data gathered. Furthermore, it has to be mentioned that the method is limited to NAPL contaminations which sit in a depth that is within the range of the diffusion length of radon in soil (plus the depths from which the soil gas samples are taken from). The diffusion length of radon in soil is about 2 meters in dry and sandy soils and even less in more dense/moist materials. Since the diffusion length of radon in water amounts to just a few centimeters, NAPL contamination in aquifers (i.e. below the water table) cannot be detected by the discussed method.

The results of the experiments suggest that the radon concentration of the soil gas can potentially be used as a complementary tool for the preliminary evaluation of NAPL contaminated sites to be joined with conventional investigation methods such as drive point profiling or the direct

detection of organic carbons and their derivatives in the soil gas.

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