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PRELIMINARY RESULTS OF NAPL CONTAMINATION IN A DISUSED INDUSTRY IN THE CITY OF SÃO PAULO, BRAZIL, BY RADON EVALUATION WITH CR-39 DETECTORS

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ABSTRACT

Contaminated sites by NAPL (Non-Aqueous Phase-Liquids) may lead to safety risks to human health and to ecosystems, restrictions to urban development and decrease of real estate value. This work used the radon gas as an indicator for the analysis of subsurface soil gas, once this noble gas presents good solubility in a wide range of NAPL, being partially retained in the NAPL contamination. Therefore, a decrease of the activity of radon in the contaminated soil gas can be expected, due to the high capacity of partitioning of radon in NAPL, which allows that the NAPL retain part of the radon previously available in the soil pores. The survey was carried out at a disused industry, contaminated by low volatile NAPL, located at east of São Paulo city, in March/2015. Radon was evaluated by passive detection methodology with CR-39 solid state nuclear track detectors (SSNTD). Radon concentrations for the eight monitoring stations at non-contaminated locations in March/2015 varied from 16.4 ± 1.2 $kBq.m^{-3}$ to 55 ± 4 $kBq.m^{-3}$. For the two monitoring stations assumed as contaminated locations in March/2015, radon concentrations were 1.17 ± 0.08 $kBq.m^{-3}$ and 4.2 ± 0.3 $kBq.m^{-3}$, diminished in a range from 92% to 98% when compared with the results for the non-contaminated areas.

1. INTRODUCTION

The contamination of soil and groundwater is a growing concern in industrialized countries. This environmental problem becomes more serious in industrial urban centers. For Sanchez, the existence of contaminated sites not only creates obvious problems, such as the occurrence or the possibility of explosions and fires, but also may lead to safety risks to human health and ecosystems, caused by processes which appear mostly in the long-term, resulting in: increased incidence of disease in people exposed to chemicals from groundwater collected from wells; dermal contact and ingestion of contaminated soil by children or workers; inhalation of vapors and consumption of contaminated food [1]. In December 2013, CETESB (São Paulo state Environmental Protection Agency) registered 4771 contaminated and rehabilitated sites in São Paulo state, 91.5% of which presented potential risk of contamination by NAPL (Non-Aqueous Phase-Liquids) [2]. Hydrocarbons can be considered as "residents" contaminants because they are part of most industrial activities [3]. In the metropolitan region of São Paulo, Brazil's leading industrial region, old abandoned industrial sites are being used for new purposes such as residential or commercial, indicating the need to develop techniques that save time and investment in the identification of contamination and subsequent remediation.

The approach discussed in this work is based on the analysis of the soil gas using radon as a NAPL indicator, once ^{222}Rn has a good solubility in a wide range of NAPL [4, 5]. For this work, radon or ^{222}Rn represent indistinctly the radionuclide ^{222}Rn. The effectiveness of the use the radon activity concentration in soil gas to locate NAPL contamination was confirmed by field tests with monitor Genitron AlphaGUARD®, [6-9] and monitor SARAD® RTM 2100 current-ionization alpha-particle spectrometer [10].

Radon is a noble gas, characterized by its electronic stability, and emanates from soils or minerals. ^{222}Rn originates from the alpha decay of ^{226}Ra in the natural ^{238}U radioactive series and is the only gaseous element of this long series [11]. Radon is naturally present in the soil gas and can migrate toward the NAPL contamination through the pores of the soil, without undergoing reaction. Clever and Schubert [4, 5] states that radon has affinity with benzene, toluene and other organic compounds. Therefore, due to the high capacity of partitioning of radon in NAPL, which allows that the NAPL retain part of the radon previously available in the soil's pores, a decrease in the content of radon in the soil gas is expected. Currently, in Brazil, the most common SGS (soil gas survey) technologies use portable gas chromatographs PID detectors and sensors by catalytic oxidation. The catalytic oxidation technique is effective for the measurement of volatile organic compounds (VOC); however, there is not useful in contaminations by non-volatile NAPL, such as diesel or hydraulic oils.

The aim of this work was to develop an alternative method using CR-39 detectors for radon measurements in the investigation of environmental contamination by NAPL.

2. MATERIALS AND METHODS

2.1. Study site

In this work, a partnership was made with the ConAm Environmental Consulting Company that provided data from environmental investigation by conventional techniques and allowed access to the study site for radon measurements in soil gas.

The study site (**Fig. 1**) is located at east of São Paulo city and integrates the Continental Rift of Southeast Brazil [12]. Recent alluvial deposits composed by quartz sand, gravel, silt, clay and, locally, peat, are prevalent in the site and its genesis is associated with alluvial plains of the rivers Tamanduateí and Tiete [13]. The water table is between two and three meters deep.

Figure 1: Location of studied site at east of São Paulo city.

The assessed site, with 3786.70 m², is located in an urban area, which is composed of commercial area and residences. In 1970s was used as glass industry and the place will be remediated for construction of residential buildings [13].

Preliminary environmental investigation studies [13] identified free-phase contamination (dark oil), TPH (Total Petroleum Hydrocarbons), antimony and arsenic in the soil contaminated and aluminum and iron in the groundwater contaminated. The free-phase, present in the monitoring wells, is LNAPL (Light Non-Aqueous Phase-Liquids) type, because contaminant density lower than water density. This dark and viscous oil, was possible used as fuel in furnaces of glass industry, was found impregnated on the soil in most of the drillings.

2.2. Experimental procedure

The method used in this study is the passive detection with CR-39 (polyallyl diglycol carbonate) Solid State Nuclear Track Detectors (SSNDT). According to Schubert [8] field experiments confirm that SSNTD can be used as adequate and less costly means, when compared with alpha spectrometry, for the determination of radon distribution patterns in the upper soil.

Figure 2 shows the schematic description of the used monitoring station adapted from literature [14, 15].

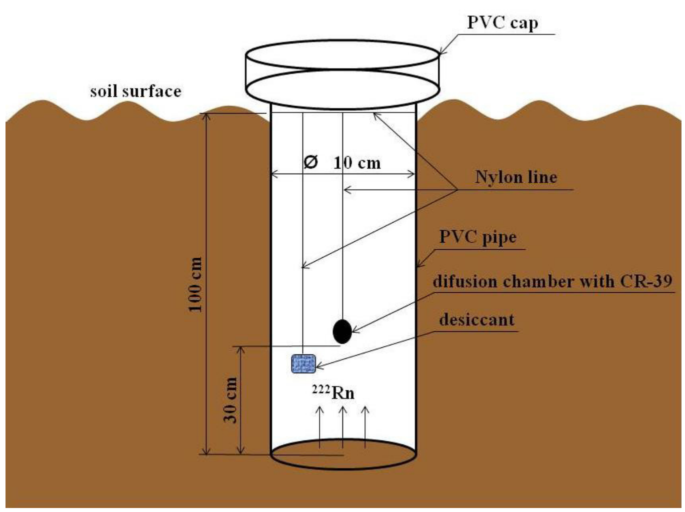

Figure 2: Diagram of the monitoring station used for radon measurements in soil gas.

Each monitoring station is a 10 cm diameter PVC pipe, buried 100 cm in the soil. The CR-39 detector, inside a NRPB/SSI diffusion chamber, was hanged inside the PVC pipe, remaining at 70 cm depth in the soil and 30 cm from the bottom. A permeable bag with 65 g of silica gel, was hanged inside the PVC pipe, to prevent moisture [16], as droplets of water on the surface of the SSNTD detector can complicate the alpha particles interactions.

After 20-days exposure, the detectors were retrieved to the Environmental Radiometric Laboratory, IPEN, São Paulo, etched during 5.5 hours with a KOH 30% solution at 80°C in a temperature-stabilized water-bath. The track densities were read under a Zeiss optical microscope coupled to a video camera and a personal computer. The radon tracks density (tracks.cm^{-2}) were determined with Axiovision Zeiss image analysis software [17].

Data presented were acquired during the summer (March/2015) at ten monitoring stations distributed in a non uniform mesh, covering both the contaminated and the NAPL free areas (**Fig. 3**).

Figure 3: Location of radon monitoring stations in the studied site.

2.3. Calculation of radon activity concentration

The radon activity concentration in air was determined using Eq. (1) [18].

$$C_{Rn} = \frac{D}{k.t} \qquad (1)$$

Where

C_{Rn} = radon activity concentrations in air (kBq.m^{-3})

D = net tracks density (tracks.cm^{-2})

k = calibration factor (tracks.cm^{-2}/kBq.m^{-3}.h)

t = exposure time (h)

The calibration factor adopted was [19]:

$$k = (2.8 \pm 0.2) \text{ (tracks.cm}^{-2}\text{/kBq.m}^{-3}\text{.h)}$$

The uncertainty associated with the radon concentration was calculated using Eq. (2) [20]:

$$\sigma_{C_{Rn}} = \sqrt{\left(t^{-1}\right)^2 . \left(\frac{D}{k}\right)^2 . \left[\frac{\sigma_D{}^2}{D^2} + \frac{\sigma_k{}^2}{k^2}\right]} \qquad (2)$$

3. RESULTS

Figure 4 shows the monitoring wells with and without NAPL contamination, resulting from classic monitoring techniques: soil gas survey, monitoring wells installation and drilling for groundwater and soil. The results of that environmental investigation [13] identified the presence of two NAPL plumes, which consist of a dark oily. The NAPL plume has an area of 250 m^2 and was confirmed that the NAPL is delimited within the study site, not reaching neighboring areas. The soil impregnated with oil is represented by the NAPL estimated plume presented.

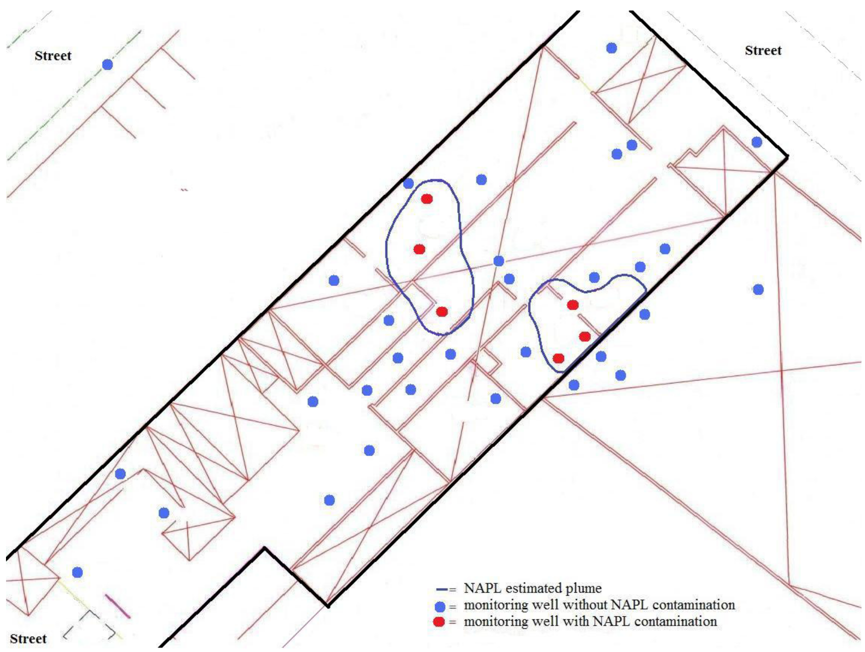

Figure 4: Location of NAPL estimated plume by conventional techniques in studied site.

Analysis of TPH were performed in soil and groundwater samples by ConAm. A TPH value was reported above the limits set by CETESB (4584.74 mg.kg^{-1} in soil). Two other results also showed detectable TPH values, but below the applicable limit. The highest TPH concentrations occurred in Carbon 36, corresponding to the lube oil range [13].

That particular LNAPL is composed of long chain carbonic, indicates contamination little-volatile or non-volatile. The environmental investigation by soil gas survey (volatile organic compounds) is not functional in that case.

The results of the radon analyses for soil gas are show in **Table 1** and plotted in **Fig. 5** for better understanding. The radon concentrations for the eight monitoring stations at non-contaminated locations varied from 16.4 ± 1.2 $kBq.m^{-3}$ to 55 ± 4 $kBq.m^{-3}$. For the two monitoring stations assumed as contaminated locations, radon concentrations were 1.17 ± 0.08 $kBq.m^{-3}$ and 4.2 ± 0.3 $kBq.m^{-3}$, diminished in a range from 92% to 98% when compared with the results for the non-contaminated areas.

Table 1: ^{222}Rn activities concentrations and uncertainties with CR-39 detectors in a disused industry in the city of São Paulo, Brazil.

Monitoring station	^{222}Rn ($kBq.m^{-3}$)
A	16.4 ± 1.2
B	34.6 ± 2.5
C	55 ± 4
D	50 ± 4
E	17.3 ± 1.2
F	18.8 ± 1.3
G	1.17 ± 0.08
H	4.2 ± 0.3
I	20.6 ± 1.5
J	24.3 ± 1.7

The radon lowest activity concentration was found in monitoring station G indicating a potential NAPL contamination (**Fig. 5**). However, it is not within the NAPL estimated plume by classical environmental investigation techniques [13].

Currently excavation services are carried out with complete removal of the soil from the region with NAPL presence for proper disposal [13]. During excavation in the G monitoring station area, the presence of oil-impregnated soil was evidenced, confirming the results of the radon monitoring technique used in this work.

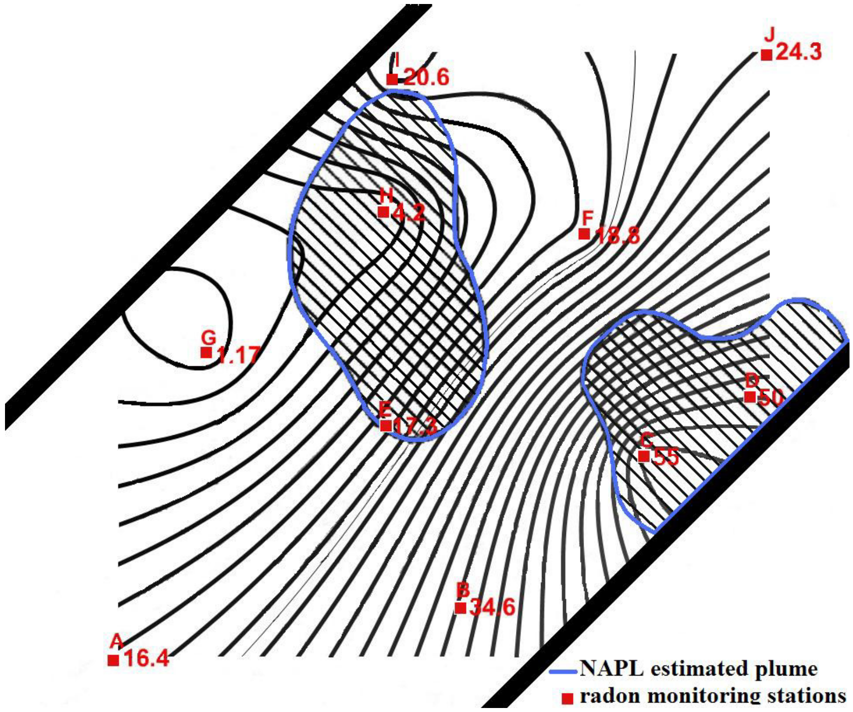

Figure 5: Spatial distribution of the radon activity concentration in a disused industry in the city of São Paulo, Brazil.

4. CONCLUSIONS

The preliminary survey of radon activity concentrations in soil gas at a disused industry locate of São Paulo city was performed. The results showed the method used in this work was consistent with conventional environmental investigation techniques for the most of radon monitoring stations measurements.

In the future, the radon results for all other measurements from June/14 to April/15 will be assessed and compared with results from classic monitoring techniques (SGS, monitoring wells installation and drilling for groundwater and soil) applied to the site. Monitoring of excavation measures, assessing the actual condition of the soil on the site is important to confirm the technique efficiency, and is currently being held. The uranium and thorium analysis of site soil samples may also help to understand the correlation of the NAPL contamination with radon concentrations observed in the monitoring stations.

Finally, this method will contribute effectively to better locate NAPL contamination in the site, reducing duration and costs of an environmental investigation.

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