DETERMINATION OF RADON PARTITION COEFFICIENTS BETWEEN WATER AND DIFFERENT KINDS OF NAPLs FOR USE IN ANALYSIS OF RESIDUAL SOIL NAPLs

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ABSTRACT

Different studies indicate the applicability of natural radon as a tracer in the determination of contaminated environments by Non-Aqueous Phase Liquids (NAPLs). Such use being due to the non-homogeneous distribution of this element between water, air and NAPL. Thus, it is known that the concentration of radon in a given soil / aquifer and in a given area may indicate that such site is contaminated by NAPL. However, the simple measurement of radon concentration activity allows only a qualitative evaluation of the area contaminated in study. For a quantitative estimate of the NAPL saturation in the pore space, it is necessary to know the radon partition coefficients between the coexisting phases, considering the kind of NAPL present. The present study, the radon partitioning coefficients between air, water and diverse types of NAPL mixtures, such as gasoline, diesel fuel, alcohol, kerosene and olive oil was measured. In a closed system, was applied an analytical method based on the distribution of the radon between the present phases with the use of a system of Flow Injection Analysis (FIA). The measurement of the specific activity of radon was performed by using an AlphaGUARD monitor. It is observed that, in the presence of NAPL, the concentration of radon in water and air is significantly lower than in its absence, indicating a negative correlation and allowing the evaluation of the contamination of the area by NAPL.

1. INTRODUCTION

One of the major problems related to contamination of soils and groundwater in the world is due to the production, storage and handling of fuels. In this way, such contaminations are caused by complex mixtures of organic liquids, the NAPLs (Non-Aqueous Phase Liquids). In the search for a correct risk assessment and remediation plan for sites contaminated by NAPL, it is necessary to know the precise location as well as the quantitative estimate of the residual NAPL source in the studied environment. The NAPL contamination doesn't follow a pattern in all localities, it spreads irregularly and erratically, conventional means such as soil extraction with laboratory analysis of samples are limited ways of knowing the contamination in order to ensure the correct remediation [1].
Radon has great affinity for NAPL, as it has an affinity for organic substances such as benzene, toluene and octane, so an area contaminated by NAPL presents a radon deficit in relation to the concentration observed in the rest of the investigated region. Considering this property of radon in solubilizing in the NAPL phases, it can be used as a partition marker in the location of areas contaminated by organic liquids. However, the use of radon as a marker depends on two relevant factors: the saturation of residual NAPL in the pore space and the radon partition coefficient specific for the NAPL present. The knowledge of the partition coefficient for the NAPL in question, not only allows to locate the contamination zone, but also to perform a quantitative estimation of NAPL saturation in the pore space [1].

There is a large amount of radon partition coefficient data for pure organic compounds, however, little information is available regarding these coefficients for complex NAPL mixtures (gasoline, diesel oil, lubricating oil, etc.). With the objective of studying the behavior of radon gas in a NAPL contaminated environment, and knowing that most of the environmental contamination by these types of compounds are found in gas stations, military installations and refineries areas, it is of significant importance the calculation and knowledge of the radon partition coefficients between complex NAPLs and water [1].

2. THEORETICAL BASIS

2.1. Natural radioactivity

The main source of radiation received by the human body is from natural radioactivity. Much of this radioactivity comes from soils and rocks, which are composed of radionuclides that do not belong to the series of natural decay (\(^{40}\)K) or that belong (\(^{232}\)Th, \(^{235}\)U and \(^{238}\)U), called primordial radionuclides and that form a family of radioactive decay. Another part of the radiation comes from the interaction of the cosmic radiation with atoms that compose the terrestrial atmosphere originating radionuclides called cosmogenic [2].

Radionuclides contribute to the dose received by the human body in about 55.8% by \(^{226}\)Ra, 14% by \(^{232}\)Th, 13.8% by \(^{40}\)K and about 15% for cosmogenic. Exposure can occur by external or internal irradiation, the first by gamma emission from the process of radioactive decay of natural radionuclides and cosmic radiation, and the second by ingestion or inhalation of radionuclides such as radon and daughters [2].

Radon is an inert, natural and radioactive gas, it belongs to the series of natural decay of uranium and thorium and is produced from the alpha decay of the radio in the mineral fraction of the soils. It is present in virtually every place and, because it is a gas, has the property of accumulating in closed places. The most stable isotope is \(^{222}\)Rn, which is a half-life alpha emitter 3.83 days and, along with its daughters \(^{218}\)Po and \(^{214}\)Po, it accounts for about 50% of the equivalent effective dose produced by natural ionizing radiation [3].

Radon is distributed in space according to lithological, pedological and geochemical characteristics, so large variations in the concentration of radon at a location indicates a non-standard condition, such as contamination by some type of NAPL. The concentration of radon in an uncontaminated environment can be calculated according to Eq. 1, where \(A_{Ra}\) is the
activity of the radium in the matrix rock, \( \varepsilon \) is the radon emanation of the soil, \( n \) is the porosity of the place and \( \rho_d \) is the apparent density of the mineral matrix [4].

\[
C_\infty = \frac{\varepsilon A_{Ra} \rho_d}{n} \quad (1)
\]

2.2 Partition coefficient and the Hildebrand parameter

The partition coefficient, or distribution, is a quantity that informs the tendency of a solute to be distributed between two non-miscible phases, that is, it indicates the preferential tendency of a solute \( X \) to dissolve in one phase or another. The magnitude is defined as the ratio of the concentration of the solute in a phase \( A \) by the concentration thereof in a phase \( B \). Considering the radon as the solute and the phases of NAPL and water as the phases by which it will distribute, the equation for distribution coefficient is [5]:

\[
K_{\text{NAPL}/w} = \frac{C_{\text{NAPL}}}{C_w} \quad (2)
\]

Where \( K_{\text{NAPL}/w} \) is the partition coefficient, \( C_{\text{NAPL}} \) is the concentration of radon in the NAPL phase and \( C_w \) is the concentration of radon in the water phase [4].

It is known that the radon concentration in the portion of the aquifer contaminated with NAPL is clearly lower than in uncontaminated water, as already mentioned above. This concentration decreases depending on the residual saturation of NAPL in the pore space (\( S_{\text{NAPL}} \)), the radon partition coefficient between the phases (\( K_{\text{NAPL}/w} \)) and common factors such as radon concentration in an aquifer such as radon emanation coefficient, Porosity, radio activity in the matrix and apparent density of the matrix. Thus, the partition coefficient can contribute to the determination of the contamination of an aquifer and thus the concentration of radon in a water contaminated by NAPL is given by [4]:

\[
C_w = \frac{\varepsilon A_{Ra} \rho_d}{n (1 - S_{\text{NAPL}} + K_{\text{NAPL}/w} S_{\text{NAPL}})} \quad (3)
\]

Although inert, the radon gas presents good solubility in NAPL, being about 40 times more soluble in NAPL than in water, when in the same temperature conditions. This solubility of radon in NAPL can be explained quantitatively using the Hildebrand parameter, which is defined as the square root of cohesive energy per unit volume [6]:

\[
\delta = \frac{1}{2} [Pa^{-\frac{3}{2}}] \quad (4)
\]

Wherein \( c \) (cohesive energy density) is given by:

\[
c = \frac{\Delta_l U_g}{V}, [Pa] \quad (5)
\]

Where \( (\Delta_l U_g) \) is the molar vaporization energy, i.e. the energy required to vaporize one mole of a substance, and \( V \) the volume of the substance. Using the molar enthalpy of vaporization and knowing that \( R \) is the general gas constant and \( T \) is the temperature, the calculation of the Hildebrand parameter is [6]:

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\[ \delta = \sqrt{\frac{\Delta H_g - RT}{V}} \]  

(6)

The higher solubility of radon in NAPL than in water can be explained by the Hildebrand parameter, however, it is important to emphasize that this parameter is a property of the liquid state of matter, so when there are gaseous substances, it must be treated as hypothetically liquid solutes at atmospheric pressure. A substance with a high Hildebrand parameter requires greatest dispersive energy when mixed with a low-parameter substance, which results in immiscibility, but two substances of similar Hildebrand parameters have sufficient dispersive energy to solubilize [6].

Understanding the Hildebrand parameter, it is possible to relate it to the radon partition coefficient between NAPL and water which, as already mentioned, indicates the tendency of a solute to solubilize in one or another phase. This relationship can be visualized in Fig. 1, where it is observed that substances with similar Hildebrand parameters tend to be miscible.

![Figure 1: Hildebrand parameter for some NAPLs and water at 20 °C versus the partition coefficient of radon $K_{NAPL/air}$ and $K_{W/air}$ (for water) [6].](image)

It is observed that the substances with the highest radon partition coefficient between them and air (L - Oswald's coefficient), that is, the radon dissolves preferentially in them, have the Hildebrand parameter close to 18 MPa$^{1/2}$, already that the radon has a parameter of 18.1 MPa$^{1/2}$. Such solubility of radon is not verified in water due to its high Hildebrand parameter, that is equal to 47.9 MPa$^{1/2}$ [7].
3. METHODOLOGY

As previously mentioned and shown in Eq. 3, it is of fundamental importance the knowledge of the radon partition coefficient between NAPL and water, since it contributes to the knowledge of the real contamination of a source zone of NAPL. In this sense, experiments were carried out with distinct types of NAPLs (gasoline, fuel alcohol, diesel, kerosene and olive oil), which allowed the calculation of the partitioning between water and these mixtures of NAPL [1].

For the calculation of the partition coefficient, it was first necessary to measure the radon concentration in well water (rich in radon) without and with the presence of the NAPLs studied. For this measure the AlphaGUARD equipment was used, it is a portable device that measures the alpha particles emitted by radon from the air through the total charge produced by the ionization of a gaseous environment, in addition, it provides information of temperature, humidity and atmospheric pressure, because it has integrated sensors. The data obtained through the measurements were collected and processed in the DataExpert software and Excel, respectively.

3.1 Ionization Detectors

An ionization detector measures the ionization that a particle produces when it crosses some site. Detection is a measure of the energy deposited in the material and is performed by the number of electrons and ions detected. Thus, a basic ionization detector consists of a chamber with a chemically stable gas and possible to be ionized, in this chamber there is a cathode and an anode maintained at a high potential difference [8].

When a charged particle crosses the sensitive region of the detector the site is ionized and then electron-ion pairs are produced because of the potential difference, the electron migrates to the anode and the ions to the cathode, producing an electric current passing through a resistor and an amplifier. The amplified signal is analyzed by obtaining a pulse height that is associated with the amount of ionization produced and depends on the energy and charge of the incident particle [8].

In the ionization chamber detector, the voltage in the recombination region is increased by generating a signal that reflects the number of ionizations produced, in which the field is sufficiently high allowing all charged particles to be collected and measured [8]. The AlphaGUARD used in this work has an ion chamber type detector, which detects the alpha particles, through the total charge produced by the ionization of a gaseous site.

3.2 Assembling the experiment

For the determination of the radon partition coefficients between water and the NAPL mixtures, a closed system has been assembled as shown in Fig. 2. The measurement of the radon concentration was based on the measurement of its concentration in air, removing it from the water and measuring the air in the closed system, after stabilization, the NAPL was intercalated and the measurements were carried out until a new stabilization.
In the circuit was placed a gas pump (maintained at a constant flow of 0.5L/min), a radon monitor in the air (AlphaGUARD - operating in 1min-Flow mode), a 600mL vessel for water, a 150mL safety vessel and plastic hoses, which ensured minimal loss of radon from the system by diffusion. To ensure that no drop of water or NAPL impaired the integrity of the AlphaGUARD and the air pump, the safety vessel was added to the system.

450mL of well water was placed in the water vessel and the concentration of radon, drawn from the water, was measured in the air up to the stability of the system. After stabilization, a 300mL vessel was added with NAPL (Fig. 3). 200mL of NAPL was placed in it and, again, expected that the system was to reach a new stability with respect to the radon concentration. Such procedure was repeated several times for each of the NAPL mixtures analyzed.

![Figure 2: Closed system mounted for analysis of radon concentration.](image)

![Figure 3: Assembly of the closed system after adding the NAPL to the circuit.](image)
4. RESULTS AND DISCUSSIONS

After performing the experiments and removing the data obtained from the DataExpert software, the results were treated in Excel. As a part of the results, graphs were generated, in which the significant decrease in the radon concentration in the system after the addition of the vessel with NAPL (Fig. 4) can be seen. This reduction happens due to the dissolution and preferential accumulation of radon in the volume of NAPL added. The equilibrium concentration of radon removed from the water in the air ($C_{\text{air}}^{*}$) and the equilibrium concentration of radon in the air after passing through NAPL ($C_{\text{air}}^{**}$) were calculated by averaging the measurements during equilibrations as shown in Fig. 4.

![Figure 4: Radon concentration in the air of the closed system, with and without NAPL, during the experiment.](image)

The calculation of the radon partition coefficient for NAPL and water depends on the partition coefficient between water and air (Coefficient of Oswald.), which is a function of temperature. The temperature considered was 20°C, which was the temperature of the system during the measurements, thus, the $K_{w/air}$ used in the calculations was 0.23. The mean values of the concentrations ($C_{\text{air}}^{*}$) in the first phase of the experiment (equilibrium of the water) were converted into a radon inventory of the closed system used by SCHUBERT et al. by the following equation:

$$I = C_{\text{air}}^{*} (V_{\text{air}}^{*} + K_{w/air} V_{w})$$  \hspace{1cm} (7)

Where $V_{\text{air}}^{*}$ is the volume of air in the system, which this moment was 1010mL (0.00101m$^3$), and $V_{w}$ the volume of water, which was 450mL (0.00045m$^3$). For the second phase of the experiment (after addition of NAPL) the mean value of radon concentration in the air of the system ($C_{\text{air}}^{**}$) was used to determine the radon partition coefficient between NAPL and water.
using the inventory previously calculated and the following formula used by SCHUBERT et al.:

\[
K_{\text{NAPL/w}} = \frac{I}{V_{\text{NAPL}}K_{\text{w/air}}C_{\text{air}}^{**}} - \frac{V_{\text{air}}^{**}}{V_{\text{NAPL}}K_{\text{w/air}}} - \frac{V_{\text{w}}}{V_{\text{NAPL}}} \quad (8)
\]

Where \( V_{\text{NAPL}} \) is the volume of NAPL in the system, which was 200mL (0.0002m\(^3\)), \( V_{\text{air}}^{**} \) is the air volume at this stage of the experiment, which is 1144mL (0.001144m\(^3\)).

For each type of NAPL, 4 measurements were performed, all results were treated as described above, were obtained similar values of \( K_{\text{NAPL/w}} \) and, therefore, the coefficients of each of the analyzed NAPLs were obtained by calculating the mean of the measurements and the associated error. The following partition coefficient values were obtained:

**Table 1: Results of the radon partition coefficients between water and the diverse types of complexes NAPL.**

<table>
<thead>
<tr>
<th>NAPL</th>
<th>Gasoline</th>
<th>Ethanol</th>
<th>Olive oil</th>
<th>Diesel fuel</th>
<th>Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partition coefficient</td>
<td>32.7 ± 2.0</td>
<td>37.1 ± 2.0</td>
<td>106.9 ± 6.8</td>
<td>81.3 ± 2.6</td>
<td>82.4 ± 0.9</td>
</tr>
</tbody>
</table>

Analyzing the results was observed that the deviations associated with the measurements remained within an acceptable margin of error for experimental data. Olive oil had the highest mean standard deviation, however, most of the measurements showed a reliability above 95%, indicating good precision of the results.

The analysis of the Hildebrand parameter to the data obtained, was used the parameter calculated by Schubert et al. for the studied NAPLs as shown in Table 2. With the \( K_{\text{NAPL/w}} \) and the Hildebrand parameter was created a graph with this data, for distinct types of simple NAPLs and for the complexes NAPLs studied (Fig. 5). It was observed that NAPLs that present Hildebrand parameter close to that of radon also show a high \( K_{\text{NAPL/w}} \) value, which confirms the higher solubility of radon in NAPL. On the other hand, the water that presents parameter of Hildebrand high has low coefficient of partition for the radon and, in this way, tends to have low concentration of the same one.

**Table 2: Parameter of Hildeband of the NAPLs under study.**

<table>
<thead>
<tr>
<th></th>
<th>( K_{\text{NAPL/w}} )</th>
<th>( \delta \text{ (MPa}^{1/2})</th>
<th>(SCHUBERT et al, 2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>32.68</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>37.12</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Olive oil</td>
<td>106.88</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>81.32</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>Kerosene</td>
<td>82.39</td>
<td>15.8</td>
<td></td>
</tr>
</tbody>
</table>
5. CONCLUSION

In general, the results obtained were satisfactory demonstrating the great preference of radon to dissolve in NAPL, which will contribute to further work in the analysis and determination of areas contaminated by NAPLs, such as gasoline, diesel and ethanol. The AlphaGuard equipment demonstrated good reproducibility, which contributed to results with good reliability. However, new tests should be performed considering the exact compositions of the NAPLs studied and the exact temperatures.

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