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Radon as a naturally occurring tracer for the assessment of residual NAPL contamination of aquifers

Michael Schubert*, Albrecht Paschke, Steffen Lau, Wolfgang Geyer, Kay Knöller

UFZ Centre for Environmental Research, Permoserstrasse 15, 04318 Leipzig, Germany

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The paper presents the theoretical concept and experimental results which confirm the applicability of naturally occurring radon for assessing residual NAPL contamination of aquifers.

Abstract

The noble gas radon has a strong affinity to non-aqueous phase-liquids (NAPLs). That property makes it applicable as naturally occurring partitioning tracer for assessing residual NAPL contamination of aquifers. In a NAPL contaminated aquifer, radon dissolved in the groundwater partitions preferably into the NAPL. The magnitude of the resulting radon deficit in the groundwater depends on the NAPL-specific radon partition coefficient and on the NAPL saturation of the pore space. Hence, if the partition coefficient is known, the NAPL saturation is attainable by determination of the radon deficit. After a concise discussion of theoretical aspects regarding radon partitioning into NAPL, related experimental data and results of a field investigation are presented. Aim of the laboratory experiments was the determination of radon partition coefficients of multi-component NAPLs of environmental concern. The on-site activities were carried out in order to confirm the applicability of the "radon method" under field conditions.

Keywords: Radon; NAPL; Contamination; groundwater; Partitioning tracer

1. Introduction

Subsurface contamination with non-aqueous phase-liquid (NAPL) is a common problem at sites such as gas stations, airports, military bases, tank farms, or industrial plants. While the actual contamination source is usually found close to the surface (leaking pipelines, pumps or storage tanks), a frequent result of NAPL entering the subsurface is contamination not only of the vadose zone of the soil but also of the aquifer. In particular, dense NAPL (DNAPL) is likely to migrate into the groundwater-saturated zone due to its density ($\rho_{\text{NAPL}} > 1$ g/cm^3). But also light NAPL (LNAPL, $\rho_{\text{NAPL}} < 1$ g/cm^3) does not necessarily remain floating on the groundwater table. LNAPL and groundwater usually form a two phase system occupying the capillary fringe and the upper aquifer whereby the relative saturation of each phase changes gradually with depth. In addition, seasonal fluctuations of the groundwater table or extensive groundwater pumping may result in a "NAPL smear zone", which potentially extends over several meters below the groundwater table.

In any case, migration of NAPL into an aquifer results in a certain amount of NAPL being retained in the aquifer mineral matrix forming a "NAPL source zone". NAPL source zones generally comprise small, disconnected residual blobs of organic liquid, typically between 1 and 10 pore throats in length, which are entrapped in the mineral matrix by capillary forces. In a source zone, residual NAPL can occupy up to 20% of the pore space available (Mercer and Cohen, 1990).

Generally, due to the relatively low water solubility of NAPL, source zones have to be considered as long term sources of dissolved organic contaminants. That implies that site management and remediation planning at NAPL contaminated sites require adequate assessment of residual NAPL contamination

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* Corresponding author.
E-mail address: michael.schubert@ufz.de (M. Schubert).

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of the aquifer. Regardless of the technique chosen for source zone treatment (excavation, flushing, stabilization, or containment), the central points of interest at planning stage are a sufficient identification of the spatial distribution of the source zone and an estimation of the NAPL quantities present in the subsurface, i.e. of the specific pore volume occupied by residual NAPL. In particular the latter plays a decisive role for the choice of remediation strategy and hence for the cost and duration of remediation activities.

Direct examination of the NAPL saturation of the aquifer pore space by means of soil coring and subsequent laboratory analysis of the sampled aquifer material is expensive and time consuming. Moreover, while such conventional technique provides precise data for very selective spatial areas (point values), its use for characterizing a larger aquifer domain is limited. Hence, groundwater sampling and analysis is commonly used as a supplementary tool to allow for a more integrative source zone assessment. Spatial concentration patterns of dissolved organic contaminants, such as BTEX, are used for the characterization and approximate localization of residual NAPL. However, this information is of rather qualitative nature and hence not suitable for the quantification of the NAPL quantities present.

With the aim to perform more accurate quantitative NAPL source zone assessment and based on experiences with aquatic tracers used for the hydrodynamic characterization of aquifers, several innovative tracer techniques have been developed and applied during the last decade (Rao et al., 2000). New approaches include, e.g. the use of interfacial tracers, which tend to accumulate at the NAPL/water interface. The magnitude of tracer concentration decrease during displacement through the investigated aquifer domain is employed for the quantification of the fluid/fluid interfacial area (Kim et al., 1997). Another innovative tracer method is the application of biochemical tracers, which are used for the investigation of specific microbial activities in the aquifer rather than for physical source zone assessment. Within the contaminated aquifer portion the microbial community present converts injected biologically reactive components into various products, the breakthrough functions of which allow for an estimation of the respective reaction kinetics (Istok et al., 1997).

A third innovative approach is the application of tracers, which partition preferably into NAPL and can therefore be applied for the determination of the residual NAPL saturation of the aquifer pore space. The partitioning of such tracers into the residual organic phase causes a retardation of the respective tracer with respect to the concentration of a conservative tracer injected simultaneously. The degree of retardation is used to obtain quantitative information on the residual NAPL saturation of the pore space (Jin et al., 1995).

Partitioning tracers commonly used for NAPL source zone characterization, such as SF_6 (Wilson and Mackay, 1995) or alcohols (Istok et al., 2002), have to be injected into the aquifer. While tracer injection requires in general additional technical expenditure and may cause technical or even legal problems, the application of a partitioning substance that occurs as a natural constituent of the groundwater would allow for a more convenient approach.

The use of radon as naturally occurring indicator for residual NAPL contamination has been suggested for the vadose soil zone (Schubert et al., 2001; Höhener and Surbeck, 2004) as well as for saturated aquifers (Hunkeler et al., 1997; Semprini et al., 2000; Davis et al., 2005). However, whereas the theoretical background of the partitioning of artificial tracers into NAPL was subject of several publications (e.g. Dwarakanath and Pope, 1998), the high solubility of radon in organic liquids, as key parameter for its partitioning behavior, has not been discussed as comprehensively, especially from the thermodynamical point of view. Furthermore and in contrast to data on pure NAPLs (Clever, 1979), reliable quantitative information concerning the partitioning of radon into multi-component NAPL mixtures of environmental concern is rare (Hunkeler et al., 1997). Also, and maybe most importantly, the number of field-scale results published so far is unsatisfactory, a fact which might give rise to concerns to potential users with regard to the reliability and effectiveness of the ‘‘radon method’’.

Hence, the aims of the presented paper are as follows: (i) to give a concise thermodynamical explanation of radon partitioning into NAPL, (ii) to present radon partition coefficients of selected multi-component NAPLs of environmental concern, and (iii), as main objective, to discuss a field experiment, the results of which confirm the general applicability of radon as naturally occurring partitioning tracer for the characterization of NAPL source zones.

2. Materials and methods

2.1. Theoretical background

2.1.1. The ubiquitous presence of radon in groundwater

Radon (^{222}Rn) is continuously produced via α-decay of its parent nuclide radium (^{226}Ra), which is commonly found in soil and aquifer material. Hence, radon is a ubiquitously occurring natural component of groundwater, occurring as dissolved gas. The aquifer specific equilibrium radon concentration in groundwater (C^{∞}) can be quantified as follows (Andrews and Wood, 1972).

$$C^{\infty} = \frac{\varepsilon A_{\mathrm{Ra}} \rho_{\mathrm{d}}}{n} \, [\mathrm{Bq/m^3}] \tag{1}$$

Eq. (1) shows that the equilibrium radon concentration in groundwater is governed by just a few aquifer characteristics. The radium activity concentration of the aquifer matrix (A_{Ra}, [Bq/kg]) determines the total amount of radon produced in the mineral matrix. The dimensionless emanation coefficient (ε) quantifies the share of the produced radon atoms that emanate into the pore space. The two matrix parameters porosity (n, [m^3/m^3]) and dry density (ρ_{d}, [kg/m^3]) are influential because a higher porosity at a given density results in a lower radon concentration in the pore space (Tanner, 1964). Equilibrium radon concentrations in groundwater normally range between 10 and 100 Bq/l (Cothern and Smith, 1987).

2.1.2. Partitioning of radon into NAPL – thermodynamic aspects

In liquid phase, strong cohesive interactions exist between the molecules. A whole range of cohesion parameters can be employed for describing and quantifying the extent of these interactions. Cohesion parameters are a general measure for the internal energy of a liquid phase compared to its respective ideal vapor at the same temperature (Barton, 1991, 1997).