



γ -Ray spectrometry of radon in water and the role of radon to representatively sample aquifers

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ABSTRACT

Measurement of radon in water by γ -ray spectrometry using a HPGe detector has been investigated to determine aquifer characteristics. The radon activity concentration is determined by taking the weighted average of the concentrations derived from γ -ray lines associated with ²¹⁴Pb and ²¹⁴Bi decay. The role of accurate radon data to representatively sample aquifers was also investigated by studying a semi-cased borehole. A simplified physical model describing the change of radon concentration with the pumping time, reproduces the data and predicts the time for representative sampling of the aquifer.

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1. Introduction

Radon (²²²Rn) is an inert, noble gas generated in the ²³⁸U decay series. It is found virtually in all types of rock, soil and groundwater. Radon in water is predominantly measured with:

- *Liquid-scintillation counting (LSC)*: In this method, the radon concentration is determined by detection of scintillation light generated by α -particles emitted by ²²²Rn and its short-lived progeny, ²¹⁸Po and ²¹⁴Po (Barnett et al., 1995; Hamanaka et al., 1998; Prichard and Gesell, 1977; Vitz, 1991).
- *γ -Ray spectrometry*: Radon concentrations are derived from the γ -rays emitted following the decay of the radon progeny ²¹⁴Pb and ²¹⁴Bi, after reaching secular equilibrium with ²²²Rn (Countess, 1976; Erlandsson et al., 2001; Povinec et al., 2006; Sánchez et al., 1995; Shizuma et al., 1998).
- *α -Particle spectrometers* (Burnett et al., 2001; Dulaiova et al., 2005): An example of this method is continuous radon monitoring using RAD7 (Lee and Kim, 2006). The RAD7 system method involves detecting α -particles emitted by the radon progeny ²¹⁸Po and ²¹⁴Po, using a planar silicon α -detector.

Radon is a natural tracer for studying hydrological transport processes. It is transported without substantial adsorption in the

matrix. Radon in water measurements has been used to study aquifer-flow rates, estimate recharge rates and residence times of groundwater (Snow and Spalding, 1997), and study the interaction between groundwater and surface water through discharge and mixing processes (Schwartz, 2003). The application to aquifers requires representative sampling of groundwater. For boreholes, optimal flushing before sampling commences is required (Zereshki, 1983; Freyer et al., 1997) to remove stagnant water, in which radon has decayed.

In a study of aquifer properties the emphasis is on precision and reproducibility rather than accuracy. In view of the uncertainties in geological and hydrological description of radon-generation properties of aquifers, an accuracy of 25% (systematic uncertainties) for the method is more than sufficient. The aim of this work is to optimize the measurement of radon in water via γ -ray spectrometry and model the time evolution of radon concentrations during sampling. It involves the investigation of statistical and systematic uncertainties due to sampling, measurement and analysis.

2. Materials and methods

Sampling of aquifers was investigated by a long-term (about one year) study of a semi-cased borehole (volume ~ 1.2 m³, cased with steel up to a depth of 45 m and screened between 15 and 45 m depth, whereafter it is opened through hard rocks to a final depth of ~ 62 m). The borehole is located at iThemba LABS, 30 km east of Cape Town, South Africa. This borehole taps the Cape Flats

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aquifer, which is a sandy, primary and unconfined aquifer. Water from the borehole was pumped from depths of 8.0 and 28.5 m. Ten pumping tests, PT1–PT10, were made. The pump speed, date of pumping and the sampling depth for each of these pump tests are given in Table 2. During the first 2 h of each pumping test, samples were collected at short intervals (5–15 min) because the ^{222}Rn concentration increases rapidly. The reason is that as pumping continues, more radon-rich groundwater flows from the aquifer into the pumping zone and mixes with the stagnant water. For the remainder of each pumping test samples were collected at convenient intervals (1–7 h).

In this study radon in water was measured in a counting geometry of a screw-top Marinelli beaker (AEC-Amersham, code NQB2205, volume ~ 1.3 L) filled to the top. The γ -ray spectra were measured with a Canberra p-type HPGe detector (model GC4520 of 45% relative efficiency, and 2.2 keV FWHM resolution at 1.33 MeV) encased in a lead castle (10 cm thick) and equipped with standard nuclear electronics to process the detector signals. Radon concentrations were derived from the intensity of six γ -lines emitted by radon progeny: $E_\gamma = 295$ and 352 keV from ^{214}Pb , and $E_\gamma = 609$, 934, 1120 and 1764 keV from ^{214}Bi . Measurements commenced after radioactive equilibrium between radon and its short-lived progeny had been established (3 h). Each sample was counted for 2 h. In addition, at least three samples from each of the pumping tests were sealed for 3 weeks, to measure the radon in-growth from ^{226}Ra , and counted for a minimum of 7 h.

Fig. 1 shows three partial spectra: for an empty Marinelli, Marinelli beaker filled with tap water for background correction, and of a groundwater sample. From the figure, it is clear that the radon-related γ -rays dominate the groundwater spectrum. Moreover, there is no difference between the spectrum obtained with an empty Marinelli beaker and with one filled with tap water. This implies that the tap water does not contain any significant amount of radon. For this set-up the minimum detectable activity (MDA), based on the $E_\gamma = 352$ keV γ -line and a counting time of 2 h, was found to be 0.2 Bq/L (3σ). This value is one to two orders of magnitude lower than the measured values.

The reported radon concentration is the weighted average for the concentration of the individual γ -lines. The quoted uncertainties are external uncertainties (see e.g. Debertin and Helmer, 2001).

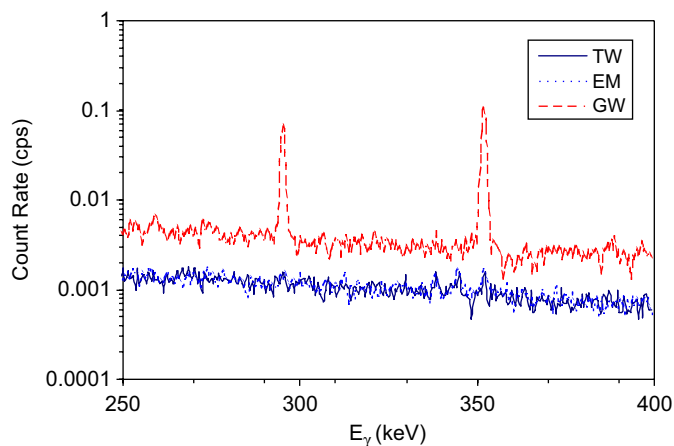


Fig. 1. A small part (including two radon related γ -ray peaks, 295 and 352 keV) of three spectra to illustrate that radon in tap water used for background correction is insignificant. The three spectra were obtained by measuring an empty Marinelli beaker (EM), a beaker filled with tap water (TW) and a beaker filled with groundwater (GW).

Table 1

Average ratio (1σ) of concentrations obtained by applying the simulated efficiencies to the 34 measurements of groundwater samples

E_γ (keV)	Mean of ratio
295	0.99 ± 0.03
352	0.99 ± 0.01
609	0.94 ± 0.03
934	1.02 ± 0.10
1120	0.97 ± 0.06
1764	1.07 ± 0.06

Each ratio was calculated from the radon concentration derived from one γ -line divided by the weighted average of concentrations derived from four γ -lines 295, 352, 934 and 1764 keV, which are not significantly affected by coincident summing.

The detector-efficiency calibration was carried out according to the method reported by Croft and Hutchinson (1999). The relative, full-energy peak (FEP) efficiencies of $E_\gamma = 295$, 352, 609, 934, 1120 and 1764 keV were determined from groundwater samples of unknown ^{222}Rn concentration. This procedure involves the listed branching ratios (Firestone et al., 1996) and the assumption that coincident summing is negligible; see Section 3 and Table 1. The absolute FEP efficiencies are based on the intensity of the 1460 keV γ -line of ^{40}K in a sample with a known amount of KCl dissolved in tap water.

Some of the γ -lines that were used to derive the radon concentrations, as for example 609 and 1120 keV from ^{214}Bi , are reported to have been associated with systematic effects such as coincident summing-out. (Garcia-Talavera et al., 2001). Coincident-summing effects for the geometry of our 1 L Marinelli beaker were investigated by simulating the efficiencies of the six γ -lines of interest. This simulation was based on the Monte Carlo code MCNPX 2.6 b. The parameters of the HPGe detector used for the simulations were optimized in a previous study (Damon, 2005). It is found that the simulated efficiencies are in good agreement with their counterparts obtained by the KCl method. The simulated efficiencies were then applied to 34 water samples, with various radon concentrations, and the radon concentration was derived from each of the six γ -lines separately. A weighted average of radon concentration from the four γ -lines 295, 352, 934 and 1764 keV, which are not expected to be affected significantly by coincident summing, was determined. The ratio between the concentration derived from each line and the weighted average was calculated. The average ratios for the 34 samples are given in Table 1, which is discussed further in Section 4. The conclusion of this exercise is that coincident summing does not play a significant role in the present analysis. The overall systematic uncertainty of a few percent in the absolute activity concentration is considerably smaller than the anticipated accuracy.

3. Pumping model description

Based on the borehole measurements, a simplified physical model has been developed to describe the radon concentration as a function of pumping time and pumped volume. It is assumed that the borehole samples a primary and homogenous reservoir (aquifer) with radon activity concentration C_1 (Bq/L). Effective sampling starts when the dynamic water level begins to stabilize. Considering the mass balance of the water pumped and the resultant change of ^{222}Rn concentration in the water column, one finds

$$C(t) = (C_1 - C_0)(1 - e^{-\mu t}) + C_0 \quad (1)$$

where $\mu = v_p/V_{wf}$, v_p represents the pump speed, V_{wf} is the water-filled volume of the borehole and C_0 is the ^{222}Rn concentration when sampling commences. From the procedure described above, the time at which sampling commences introduces an uncertainty which is reflected in the value of C_0 . Therefore C_0 may differ from test to test.

4. Results and discussion

4.1. Coincident summing

The results of applying the simulated efficiencies to the measurements of the 34 samples are presented in Table 1. The average ratio of radon concentrations derived from the 609 keV γ -line indicates that the effect of coincident summing for this particular γ -ray is $6 \pm 3\%$. In view of the uncertainties in the ratios for the other γ -rays the overall effect on the weighted average is at maximum a few percent.

The HPGe radon measurements were checked further in two ways. The first involved extracting the ^{222}Rn decay constant, λ . For this, four water samples were measured several times over 4 days using the HPGe detector. Depending on the ^{222}Rn concentration, the measurement time for these samples ranged between 7 and 10 h. The decay of the ^{222}Rn concentrations was fitted with an exponential decay curve. The ^{222}Rn decay constants for the four samples were found to be $(2.51 \pm 0.05) \times 10^{-6}$, $(2.11 \pm 0.02) \times 10^{-6}$, $(2.08 \pm 0.11) \times 10^{-6}$ and $(2.27 \pm 0.10) \times 10^{-6} \text{ s}^{-1}$, with a weighted average of $(2.16 \pm 0.08) \times 10^{-6} \text{ s}^{-1}$, which is consistent with the known λ -value of $2.10 \times 10^{-6} \text{ s}^{-1}$. This implies that there is no significant ^{222}Rn loss during the measurement process.

To validate these results, radon concentrations were also measured by α -spectrometry using the continuous radon monitor, RAD7 DurrIDGE. Water samples were collected in large volume containers ($\sim 3 \text{ L}$), split into sub-samples, and decanted into Marinelli beakers and glass vials for the HPGe and the RAD7 measurements, respectively. The radon concentrations ranged from 1 to 45 Bq/L and the correlation factor between the HPGe and the RAD7 results was found to be 98%. This result also supports the insignificance of coincidence-summing effects for this study.

4.2. Pumping model

The model parameters for Eq. (1) are derived from the 10 sets of pumping test data presented in Table 2. Two examples are plotted in Fig. 2 (PT5) and Fig. 3 (PT10); they correspond to pumping depths of 8.0 and 28.5 m, respectively. Figs. 2 and 3 demonstrate that the radon concentration initially increases with the water volume pumped out. After pumping out about 4 m^3 of

water the radon concentration remains steady until about 100 m^3 before the radon concentration increases to a higher plateau (Fig. 3). The increase of radon concentration may indicate that water from another reservoir starts to be sampled. This pattern of time evolution of radon concentrations during sampling is consistent with Zereszki (1983) and Freyer et al. (1997).

Table 2 shows the model (Eq. (1)) parameters for the 10 pumping tests. C_0 , the ^{222}Rn concentration when sampling commences, varies between the various PTs as sampling starts at different pumping time. The weighted average of μ yields a value of $\mu = (1.32 \pm 0.12) \times 10^{-2} \text{ min}^{-1}$ and a reduced chi-squared (χ_v^2) value of 3. Since there is obvious change in the μ value by switching pumping speeds, the χ_v^2 value most likely reflects systematic uncertainties introduced by correlations between μ

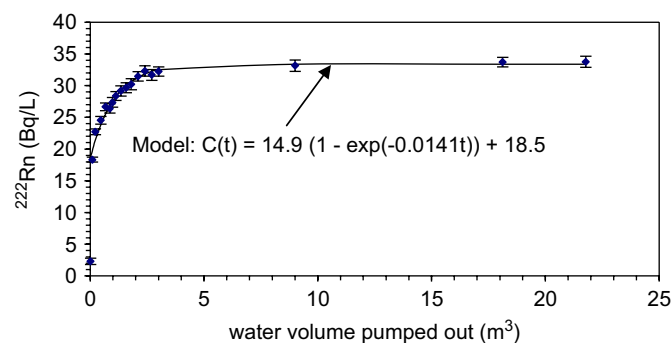


Fig. 2. ^{222}Rn concentration for test PT5 ($\sim 24 \text{ h}$ duration) at a pumping rate of $0.015 \text{ m}^3/\text{min}$. The solid line is the model fit.

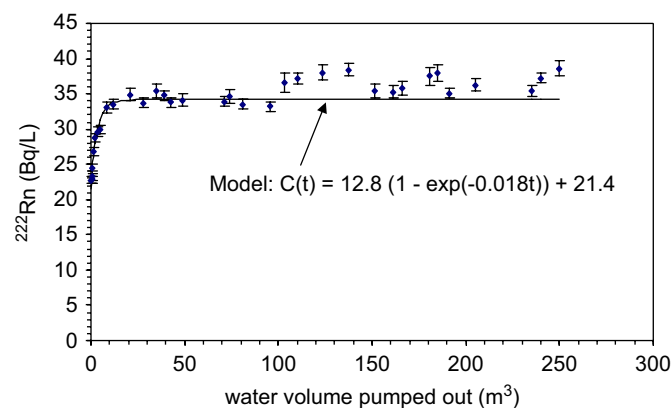


Fig. 3. ^{222}Rn concentration for test PT10 (72 h duration) at a pumping rate of $0.060 \text{ m}^3/\text{min}$. The model (solid line) parameters were extracted from the data for the first 24 h of pumping (corresponding to $V_{\text{out}} = 85 \text{ m}^3$) and then extrapolated through the remaining data of the 72 h.

Table 2

Details of pumping tests (PT) and the model parameters extracted by least squares regression

Pumping test	Date conducted	Pumping depth (m)	Pump speed (L/min)	μ ($\text{min}^{-1} \times 10^{-2}$)	C_0 (Bq/L)	C_1 (Bq/L)
PT1	2005/12/12	8.0	14.6 ± 0.4	1.4 ± 0.4	10.3 ± 1.0	29.6 ± 2.1
PT2	2006/01/26	8.0	14.5 ± 0.5	1.4 ± 0.4	8.5 ± 1.1	33.5 ± 2.0
PT3	2006/02/16	8.0	13.9 ± 0.8	1.3 ± 0.4	4.0 ± 1.5	29.6 ± 1.5
PT4	2006/03/02	8.0	15.0 ± 0.8	1.0 ± 0.4	22.3 ± 1.0	32.8 ± 1.9
PT5	2006/04/19	8.0	14.9 ± 1.2	1.41 ± 0.13	18.5 ± 0.6	33.4 ± 1.3
PT6	2006/06/28	28.5	12.6 ± 1.1	0.9 ± 0.3	20.7 ± 1.2	33.3 ± 1.4
PT7	2006/08/14	28.5	38.5 ± 1.0	2.0 ± 0.7	23.3 ± 0.7	33.2 ± 1.6
PT8	2006/11/15	28.5	59.1 ± 1.2	3.4 ± 1.2	23.4 ± 0.8	33.5 ± 2.0
PT9	2007/01/09	28.5	58.2 ± 1.8	2.2 ± 0.9	21.7 ± 1.2	33.5 ± 1.7
PT10	2007/03/09	28.5	59.8 ± 0.8	1.8 ± 0.6	21.4 ± 1.2	34.2 ± 1.1

The weighted average of $\mu = (1.32 \pm 0.12) \times 10^{-2} \text{ min}^{-1}$ and of $C_1 = (32.9 \pm 0.5) \text{ Bq/L}$ with χ_v^2 values of 3 and 12, respectively. Uncertainties reported with μ and C_1 are external.

and C_0 . The weighted average of C_1 is $C_1 = (32.9 \pm 0.5) \text{ Bq/L}$ with a χ_v^2 value of 12. This higher than expected value of χ_v^2 most likely represents the fact that C_1 is not a real constant but changes after some time (see Fig. 3).

The time window between pumping out 4 and 20 m³ of water appears to be the optimal time for representative sampling for this borehole. The measurement of radon concentration with the pumping time or the pumped volume evolution of an unknown aquifer may provide insight into the extent of the initial reservoir and the optimal flushing time before sampling.

It should be noted that, for this pumping model, it is assumed that there is no significant radon in-growth from dissolved ²²²Ra (supported radon). During this study the average ²²⁶Ra concentration from the in-growth measurements of the borehole water was found to be only $0.7 \pm 0.3 \text{ Bq/L}$; almost two orders of magnitudes lower than the plateau radon concentrations.

5. Conclusion and outlook

In this work, a model has been described that uses the time evolution of radon concentration in borehole water to indicate the pumping time required for sampling an aquifer. To be able to measure the radon concentration accurately and with the precision required for such applications, the measurement of radon by γ -ray spectrometry using an HPGe detector and Marinelli beakers has been investigated. The results show that the radon concentration in water can be found with good precision (5%) in a reasonable time by taking the weighted average of radon concentrations derived from six γ -lines associated with ²¹⁴Bi and ²¹⁴Pb decay. The absolute accuracy of the method is a few percent.

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