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Measuring radon in water using a portable liquid scintillation counter

Groundwater Resources Programme

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Measuring radon in water using a portable liquid scintillation counter

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Front cover

Radon sampling site at Westbrook Farm near Boxford [NGR 4428 1722]

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Summary

This report describes the development of a method that measures radon in waters using the portable liquid scintillation counter Triathler^{TM} (HIDEX Oy, Turku). The work is presented in six parts. Part 1 provides some background to this study and outlines its objectives. Part 2 describes the instruments and methods that were used during method development, including field-based as well as laboratory-based techniques. In part 3, the results of this study are presented for two extraction methods. Problems that were encountered during the sample collection, preparation and analysis are discussed and the methods are evaluated in the context of potential hydrogeological applications. Part 4 to 6 of the report outline the limitations of the method, give recommendation for future work and summarise the findings and final conclusions.

1 Introduction

Radon is a natural radioactive noble gas that is produced in rocks and soils by radioactive decay of radium. It has three naturally occurring isotopes, ^{219}Rn, ^{220}Rn and ^{222}Rn, which are daughters of ^{223}Ra, ^{224}Ra and ^{226}Ra, respectively. Since the half-lives of ^{219}Rn and ^{220}Rn are very short (less than a minute), these are not considered in this report and the term "radon" as used hereafter refers solely to ^{222}Rn, which has a half-life of 3.8 days.

The presence of radon in the environment is of increasing interest mainly because of the health risks associated with radiation exposure. The main health hazard arises through inhalation of radon. However, radon is a relatively soluble gas and increased exposure through high concentrations in drinking water also increases the risk of developing stomach cancer (Kendall and Smith, 2002). Therefore, recommendations have been passed by the European Union (European Commission, 2001) for public and private water supply stating that remedial actions should be considered at radon levels above 100 Bq l^{-1} and 1000 Bq l^{-1}, respectively.

Radon can emanate from radium-bearing mineral grains into surrounding pore spaces and subsequently dissolve in and be transported by groundwater. As a result, most groundwaters are enriched in radon compared to surface waters. This contrast, together with radon's unique characteristic of being chemically and biologically inert, has made it a valuable tracer for surface water–groundwater interactions (Genereux et al., 1993; Cook et al., 2006).

It was the interest in this application that has prompted the work described in this report. The focus of the work described here has been to develop a method that allows the measurement of radon in surface water and groundwater samples. Two methods were investigated, a small-volume extraction method (SV) and a large-volume extraction method (LV). Since the samples for the radon analysis were collected from an existing study site, the following research aspects were also investigated:

- Is there sufficient contrast in radon concentrations between river water and groundwater at the study site to make Rn a suitable tracer for surface water–groundwater interactions?
- Can radon concentrations in the groundwaters at the study site be used to determine groundwater flow velocities at different depths within the aquifer?

The methods described in the following sections are developed specifically for radon analysis in water using a portable liquid scintillation counter (LSC) (Triathler^{TM}, model 425-034) with integrated α/β pulse shape discriminator (HIDEX Oy, Turku, Finland).

2 Instruments and methods

A number of analytical techniques are available to determine ^{222}Rn in water. These include:

1. Emanations methods: stripping radon from the sample by a carrier gas and analysis using a Lucas cell (Lucas, 1957)
2. Counting by liquid scintillation spectrometry (LSS) (ASTM, 1998; Pates and Mullinger, 2007)
3. Counting of radon daughters by gamma-ray spectroscopy.

The methods have different advantages/disadvantages and are frequently selected to suit the available resources and research aims of a particular study. Emanation methods, for example, achieve very low detection limits and are widely used in studies where low-level ^{222}Rn concentrations are expected. Gamma counting methods have the advantage of using widely available instrumentation (NaI or Ge detectors). LSS is the most widely used method for Rn analysis in water, probably because sampling and sample preparation methods are comparatively easy. Two methods are available for measuring ^{222}Rn in water by LSS:

1. The direct method (homogenous gel)
2. The extraction method (two-phase sample).

The direct method is applied by mixing a defined volume of sample with a water-miscible LSC cocktail (e.g., AquaLight, UltimaGold XR) to form a homogeneous gel. This stable emulsion allows immediate counting of the radon together with its progenies. The extraction method, in contrast, takes advantage of the fact that Rn is more soluble in organic solvent than in water. It utilises a water-immiscible cocktail (e.g. Mineral Oil scintillator, toluene-based scintilator, MaxiLight, Ultima Gold F) to efficiently extract ^{222}Rn from the water. The method requires about 3 hours for the α-emitting daughters ^{218}Po and ^{214}Po to equilibrate with ^{222}Rn. However, the extraction method has the advantage that ^{222}Rn can be extracted from a much larger volume of water (e.g. 500ml), hence increasing the sensitivity of the analysis. Furthermore, the method only measures radon, i.e. other radionuclides and solutes remain in the water, thereby reducing inaccuracies related to background and quenching. The direct method is generally quicker as counting can be started immediately after preparation. It also has the advantage that collection (extraction) and counting is carried out in the same vial. However, the extraction method is more sensitive and provides a better lower limit of detection (LLD). In this study, the extraction method is favoured over the direct method as good detection limits are necessary for measuring ^{222}Rn in surface waters and in the groundwaters from the Chalk aquifer where concentrations are low.

Sample analysis, as described in this report, was carried out using a portable LSC (Triathler^{TM}, model 425-034) with integrated α/β pulse shape discriminator (HIDEX Oy, Turku). The instrument employs a single photomultiplier tube (PMT) to measure multiphoton scintillation events. It uses a multichannel analyzer (MCA) to distinguish the scintillation signal from unwanted single photon thermal noise and luminescence pulses. The instrument also incorporates a dual MCA technology which simultaneously measures pulse amplitude and duration. Since alpha particles generate electronic pulses of longer duration (length) than beta particles, this is used to perform pulse shape analysis (PSA) and to separate the alpha from the beta particle signals. The latter allows the selection of an appropriate counting window which excludes betas, thereby reducing the background (noise) for alpha counting.

2.1 SAMPLE COLLECTION

2.1.1 Sampling site

Water samples were collected at the former LOCAR site at Westbrook Farm, north of Boxford [NGR 442800 172250]. The site is located at the River Lambourn and has been established as one of BGS's prime study sites for surface water – groundwater interactions. The site consists of a series of boreholes and piezometers located in the riparian zone adjacent to the river as well as perpendicular to the river. The piezometers are completed to different depths within the underlying aquifer, allowing access to the shallow groundwaters that flow within the alluvial aquifer as well as to the deeper groundwaters from the underlying Chalk aquifer. This makes it a suitable sampling location for this study as the differences in aquifer lithology between the gravels and the Chalk are expected to result in a range of groundwater radon concentrations. Furthermore, the site allows easy access to the river, including a river stilling well and piezometers installed at different depths within the river bed.

2.1.2 Sample collection

A total of 12 samples was collected at the Westbrook Farm site including samples from the alluvial aquifer (piezometers P [NGR 442813 172295] and Q [NGR 442837 172296]), the Chalk (piezometer A1 [NGR 442823 172294]) and the river (RWBF, [NGR 442671 172261]). Samples were collected using a submersible pump and after the borehole has been purged for 3-5 borehole volumes. Samples were collected into Duran® borosilicate-glass bottles with a nominal capacity of 500 ml (actual capacity is approximately 600ml). To avoid degassing of the sample (i.e., to minimise loss of radon), a sampling technique similar to the displacement method used for the collection of CFC and SF_6 atmospheric tracers was adopted. The abstracted water was pumped directly into the sample bottle which had been placed into a 10-L bucket. Sample bottle and bucket were then filled and the bucket was allowed to overflow for about one bucket volume. The bottle was then tightly capped (while still under water) before being withdrawn from the bucket. For collecting the river sample, the pump was installed at about 10 cm above the bottom of the river and samples were collected as previously described. All samples were collected in triplicate and stored in a cool box until being transferred to the refrigerator on return to the laboratory.

At borehole P, an additional set of samples was collected for the determination of groundwater flow velocities. This was done prior to the main sample collection by sampling the borehole before and after purging. The unpurged samples were collected by lowering the pump tube to a position just above the screened interval and abstracting a sample at a very slow pumping rate. A peristaltic pump was used in order to achieve sufficiently low flow rates at which only water from within the well but not from the adjacent aquifer was abstracted. Sample collection included collecting sets of large-volume (500-ml) samples (triplicates) and small-volume (10-ml) samples (triplicates) prior to and after purging. Large-volume samples were collected as described above. Small-volumes samples were collected by drawing a 10ml sample into a gas-tight syringe and injecting it directly into a pre-weight vial containing 10ml of scintillation (water-immiscible) cocktail. The vial was capped and the sample was shaken by hand for 5 minutes. The borehole was then purged and large-volume and small-volume sampling was repeated following the methods described above.

An additional set of samples was collected at Rowbury Farm [NGR 443800 175100] to be used as working standards. This source is a constantly- pumped borehole about 4 km from Boxford abstracting from the Chalk aquifer and considered to have a stable groundwater composition (George Darling, personal communication). Samples were collected in 500ml-Duran® borosilicate-glass bottles following the method described above.

2.2 SAMPLE ANALYSIS

2.2.1 Sample preparation

All sample extractions were carried out using a non-evaporating, water-immiscible scintillation cocktail (MaxiLight) with di-isopropyl naphthalene solvent. The samples were prepared individually rather than in batches. After removing the lid, a volume of approximately 60 ml was removed from each bottle and 50ml of MaxiLight cocktail were added. The bottle was then capped tightly and shaken for 20 minutes on a rattle shaker. The samples were allowed to equilibrate for a minimum of 4 hours before 7ml of cocktail were transferred to LS Minivials for counting. The vials used in this study are made of frosted, low potassium Wheaton 180 borosilicate glass and are specifically designed to improve the alpha resolution of the method by decreasing light losses due to internal reflections in the vial wall (Hidex, 2008).

The small-volume (10 ml) method did not require any further sample preparation and samples were measured directly in the 20-ml vials.

Background samples were prepared by filling a 500ml bottle to the brim with de-ionised (DI) water. A volume of 60ml of water was removed from the bottle and replaced by 50ml of MaxiLight cocktail. The bottle was capped and shaken for 20 minutes on a rattle shaker. After equilibrating for (a minimum of) 4 hours, 7ml of cocktail were transferred to a LS Minivial and the background sample was counted alongside the other samples. One background sample was made up per 10 field samples.

2.2.2 Sample analysis

Sample analysis was carried out using a portable LSC (Triathler$^{\text{TM}}$, model 425-034) with integrated α/β pulse shape discriminator (HIDEX Oy, Turku).

INSTRUMENT SETTINGS

Instrument settings applied during sample analysis are summarised in Table 1. They include details on the label and measurement protocol that was used for sample counting, the size of the counting windows, the background count rate, counting time and units as well as settings for the alpha / beta separation.

Table 1 Instrument settings for radon analysis with Triathler$^{\text{TM}}$

Label (measurement protocol)	<Rn222>
Measurement time (min)	
Small-volume method	60
Large-volume method	30
Measurement units	CPM
Background count rate	0
Alpha window	
Lower limit	299
Upper limit	1000
Pulse length Index	365

Counting window and alpha/beta settings were adjusted based on visual data provided by initial sample runs. For setting the counting window, only the alpha spectrum (Figure 1) was considered and limits were set such that the entire alpha spectrum lay within the counting window except for the initial single photon peak (where observed).

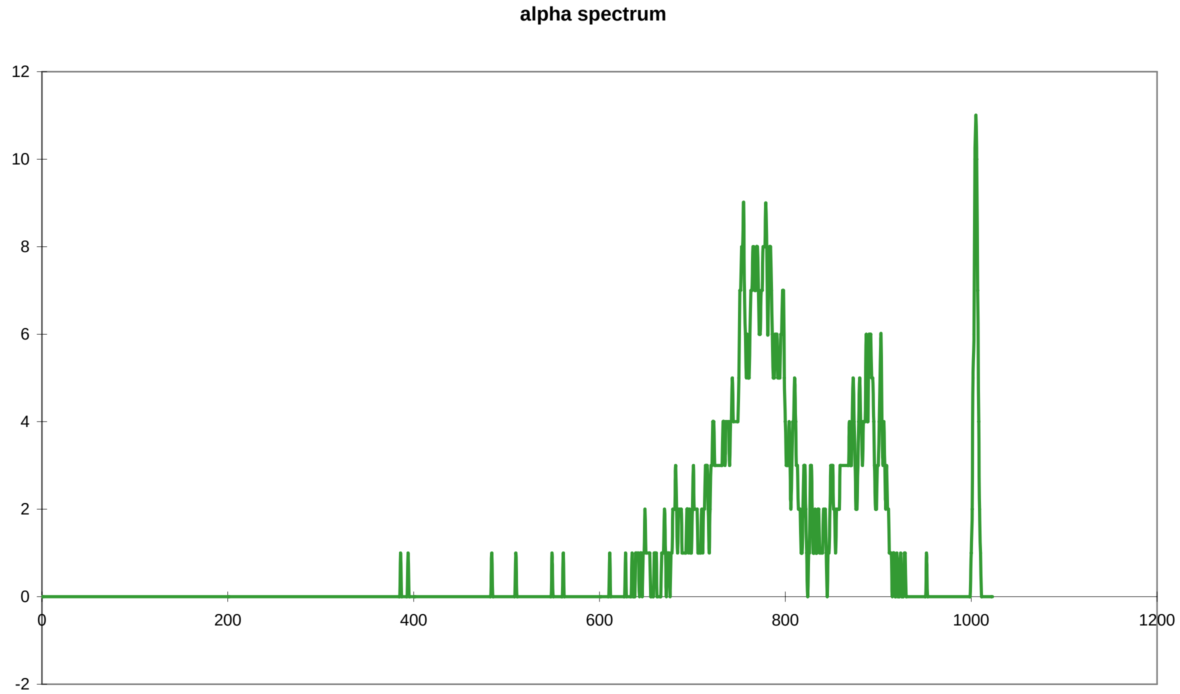

Figure 1 Typical alpha spectrum for groundwater sample analysed in this study

Parameters for alpha/beta separation were set using the 2D-graph provided by the LSC output. A typical graph is given in Figure 2 displaying the pulse-heights (total energy) on the x-axis versus the pulse length on the y-axis. The horizontal line in the middle of the graph is referred to as Pulse Length Index (PLI). All signals (pulses) measured above this line are registered as alpha counts, the ones below as beta counts. In this example, the PLI value is slightly too high as the alpha clusters do not completely fit the alpha window.

PLI values and window settings were adjusted in an iterative way and for a range of samples until the settings were adjusted adequately. The final settings are given table and a 2D graph for these settings is displayed in Figure 3. The beta window settings were kept at default values as these were not of interest in this study.

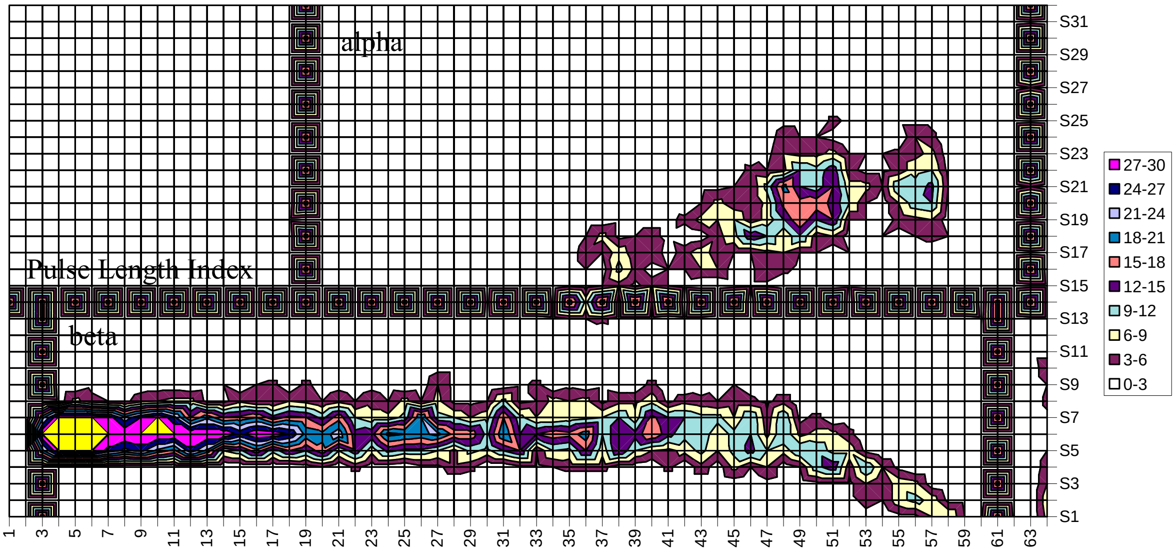

Figure 2 Typical 2D-graph of pulse-heights (x-axis) versus pulse length (y-axis) for groundwater sample analysed in this study (for further explanation see comments in text

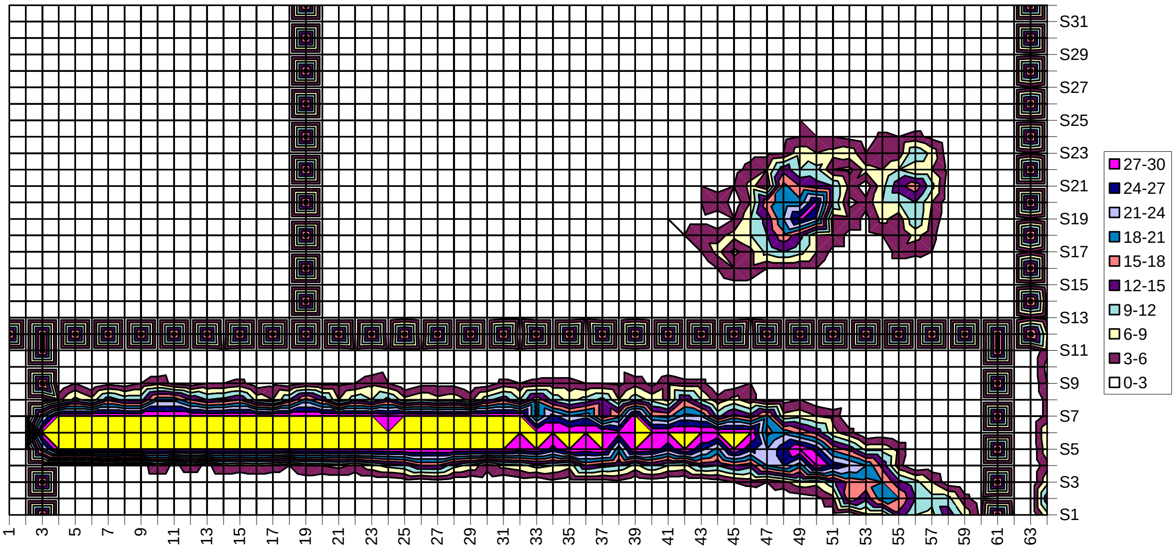

Figure 3 2D-graph of pulse-heights (x-axis) versus pulse length (y-axis) with final window and PLI settings (note this graph is for a different water sample than the one above)

QUENCH CORRECTIONS AND STANDARDS

Quench is a common interference in scintillation counting that produces a reduction in the sample's apparent activity. Its effect on the measured concentrations is usually assessed by measuring a series of standards in which the absolute radioactivity (DPM) per vial is constant and the amount of quench increases from vial to vial (quench curve). However, the solvent extraction approach is generally less prone to variable quenching problems and quench corrections are not frequently used in alpha counting (Timo Oikari, HIDEX Oy, personal communication). Therefore, quench correction options are not provided for the Triathler^{TM} protocol <Rn222> and were not applied in this study.

Samples containing known concentrations of a solute are usually measured prior to, or alongside, the samples to allow instrument calibration and/or make comparison measurements. In the case of ^{222}Rn analysis, such calibration standards are usually made up by adding a known activity of ^{226}Ra tracer to de-ionised water and storing it for 30 days until ^{222}Rn (and its progenies) and ^{226}Ra are in secular equilibrium. This requires the laboratory and/or the person preparing and measuring the standard solutions to have a licence for handling open-source radioactive materials. Alternatively, one can use a working standard, which is a measurement calibrated from a primary or secondary standard that can be used to calibrate other devices or make comparison measurements.

In this study, working standards were used to compare and correct the measurement results. For this, two sets of triplicate samples were collected from the groundwater source at Rowbury Farm (see above). The first set was prepared and analysed as part of this study alongside the other samples. The second set was send to an external laboratory (Stuart Black at the School of Human and Environmental Sciences, Reading University) for radon analysis. The samples were analysed using a Durridge RAD 7 scintillation detector and results were decay-corrected to the time of sampling.

SAMPLE COUNTING

The samples were analysed using the <Rn222> protocol with a counting time of 30 minutes (60 minutes for the small-volume method). This counting time was a compromise between the sensitivity of the method and the time available for the analysis of all collected samples. However, the resulting limit of detection (LDD) of 0.04 Bq l^{-1} (as estimated in Section 2.3.3) is considered to be sufficient for the low radon concentrations that are expected in the surface waters.

Working standards were counted alongside the groundwater and surface water samples and one background sample was included for every 10 samples.

2.3 DATA PROCESSING

2.3.1 Conversion from CPM to Bq l^{-1}

The results provided by the Triathler were given in alpha counts per minute (CPM) and were converted to its specific activity in Becquerels per litre (Bq l^{-1}) using the following equations provided by the manufacturer (Timo Oikari, personal communication):

$$Bq / L = alphaCPM * \frac{1}{E * V * T * P * 60} \qquad \text{(Equation 1)}$$

with

alphaCPM: alpha counts per minute

E: fractional alpha counting efficiency (~ 2.8)

V: water volume (L)

T: radon extraction efficiency (~0.7 for 10:1 water/cocktail ratio)

P: proportion of cocktail in vial.

For the methods used in this study the resulting factor average around 0.12 (large-volume method) and 0.06 (small-volume method), yielding

$$Bq / L = alphaCPM * 0.12 \qquad \text{(Equation 2)}$$

and

$$Bq / L = alphaCPM * 0.06 \qquad \text{(Equation 3)}$$

for calculating the specific activities. The specific activity is directly related to the concentration of a particular radionuclide and therefore, it is referred to hereafter as concentration.

2.3.2 Decay correction

The decay of a radionuclide can be expressed as:

$$A_t = A_0 e^{-\lambda t} \qquad \text{(Equation 4)}$$

with

A_t:	activity at time = t
A_0:	initial activity (time = 0)
λ:	decay constant
t:	time.

Based on this equation, the measured count rates C_t were decay corrected to the time of sample collection. The count rate at the time of sampling C_0 was calculated by multiplying C_t with the correction rate $\frac{1}{e^{-\lambda t}}$ with $t = t_c - t_0$ (t_c = time at which sample counting was completed and t_0 = time of sample collection) and using the widely-accepted literature value of λ=0.18129 d^{-1} (Lederer and Shirley, 1978).

2.3.3 Lower limit of detection

The sensitivity of the method was estimated by calculating its lower limit of detection based on the following equation provided by Haaslathi et al. (2006):

$$LLD(Bq / L) = \frac{3.29 * \sqrt{R * \left(\frac{1}{t(b)} + \frac{1}{t(s)} \right)}}{E * V * 60} \qquad \text{(Equation 5)}$$

where

R:	background count rate (CPM)
$t(b)$:	background counting time (min)
$t(s)$:	sample counting time (min)
E:	fractional counting efficiency (~ 2.8)

V:		water volume (l).

The water volume V refers to the extracted water volume multiplied by the ratio of cocktail phase in the counting vial and the total amount of cocktail added for extraction. For the large-volume method it is calculated as $V = \frac{7}{50} * 0.54l = 0.0756l$ and for the small-volume method it is $V = \frac{10}{10} * 0.01l = 0.01l$.

Assuming a counting efficiency of 280% (Timo Oikari, HIDEX Oy, personal communication) and using the measured background count rate of 0.4 CPM , the detection limits for the large-volume (LV) and the small-volume (SV) methods are calculated as $\mathrm{LLD}_{\mathrm{LV}} = 0.04$ Bq l^{-1} and $\mathrm{LLD}_{\mathrm{SV}} = 0.3$ Bq l^{-1}.

3 Results and discussion

3.1 LARGE-VOLUME EXTRACTION METHOD

The measured radon concentrations for the different samples are given in Table 2. Included in the table are the radon concentrations for the working standards (analysed by an external laboratory) as well as literature data from radon surveys in the Lambourn catchment carried out by Mullinger et al. (2007, in press-a). All data are given as decay-corrected means in units of Becquerel per litre. The quoted uncertainties are standard deviations of triplicate samples.

The table shows that the results from the radon analysis using the Triathler$^{\text{TM}}$ are in very good agreement with data obtained by other studies at the Westbrook Farm site and elsewhere within the Lambourn catchment (Mullinger et al., 2007, in press-a) (Table 2). This suggests that the results are directly comparable to data derived from other counting methods as was previously suggested by Moebius (2002).

Table 2 Radon concentrations measured at the Westbrook Farm site

		BGS data[1]		**Working standards[2]**		**Literature values[3]**	
Field ID	**Description**	**Triathler$^{\text{TM}}$**	**±2s**	**RAD 7 detector**	**±2s**	**Westbrook Farm site**	**Lambourn catchment**
		Bq l^{-1}	***Bq l^{-1}***	***Bq l^{-1}***	***Bq l^{-1}***	***Bq l^{-1}***	***Bq l^{-1}***
P	**Gravels/alluvial aquifer**	4.50	0.23	16.15	4.64	3 to 5	3-12
Q		3.25	0.26				
A1	**Chalk aquifer**	1.67	0.37	9.58	3.57	< 3	<3
STA[4]		2.04	0.19	9.46	4.35		
River	**River Lambourn**	0.50	0.04	14.26	3.79	0.2	0.2 to 2

[1] for large-volume method (500ml-bottles), uncertainties quoted are standard deviations of triplicate samples

[2] analysed by external laboratory

[3] Mullinger et al. (Mullinger et al., 2007, in press-a)

[4] Rowbury Farm samples

However, there is considerable disagreement with the results for the working standards that were provided by the external laboratory and measured using a Durridge RAD 7 detector. The reported radon concentrations are 4 to 28 times higher than those measured with the Triathler$^{\text{TM}}$ and seem implausible for many of these samples. For example, radon concentrations of 9-10 Bq l^{-1} are very high for groundwaters from non-mineralised carbonate aquifers, such as the Chalk, which usually have concentrations of <4 Bq l^{-1} (Michel, 1990). Similarly, radon concentrations in the river of 14 Bq l^{-1} are very unlikely, particularly when considering the rapid gas transfer (degassing) that occurs within the river.

A direct comparison of the results from this study with those reported by the external laboratory is given in Figure 4. The plot shows that the differences in results are not due to consistent over- or underestimation, as would be expected for systematic/calibration errors, but seem rather random. Therefore, it would not be possible to determine a consistent correction factor for the calibration of the Triathler data, even if the working standard data were more plausible. Based on these observations, it was decided not to use these working standard data for the method calibration. Calibration is not considered necessary for the ^{222}Rn analysis with the Triathler$^{\text{TM}}$ (Timo Okinari, HIDEX Oy, personal communication) as the alpha counting efficiency of the instrument is nearly 100% and hence, the observed alpha counts per minute are more or less identical to the alpha (radon) disintegration rate per minute.

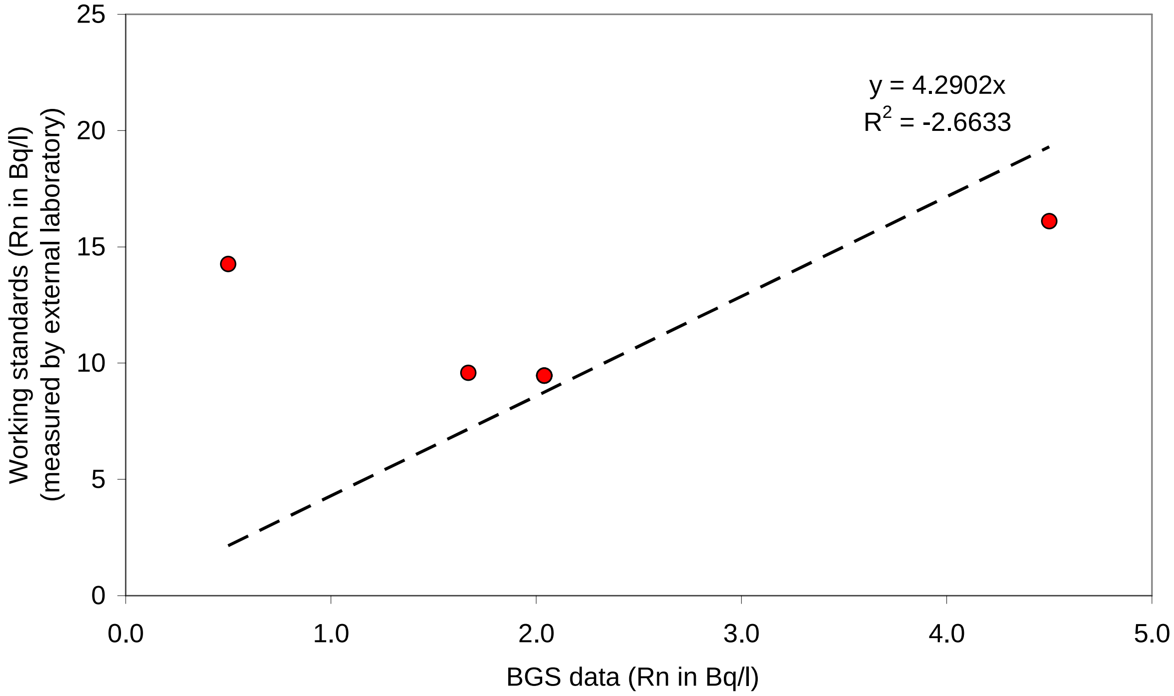

Figure 4 Comparison of results from this study with data provided by the external laboratory for the same samples (replicates collected at same location and time).

3.2 SMALL-VOLUME EXTRACTION METHOD

Four sets of triplicate samples were collected at piezometer P. The sets were collected prior to and after purging of the piezometers, by either using the small-volume (SV) or the large-volume (LV) method. The samples were collected in order to assess the suitability of radon as a tool to estimate groundwater flow velocities in the wells. However, the data are also used to provide an initial assessment of the performance of the small-volume (SV) method, where 10ml of sample water are directly injected into 10ml of water-immiscible cocktail, in comparison to that of the large-volume (LV) method which collects 500ml of sample that is later extracted in the laboratory.

The results for the different sampling sets are displayed in Table 3 and are given as decay-corrected means. The quoted uncertainties are standard deviations of triplicate samples. The data show that the radon concentrations measured by the SV-method are less than those measured by the LV-method. The results differ by about 40-65% although for the unpurged samples this is partly due to fresh aquifer water being drawn into the well, as is discussed in section 2. The difference in results is probably due to the lower sensitivity of the SV method (LLD_{SV} ~0.3 Bq l^{-1}, LLD_{LV} ~0.04 Bq l^{-1}) and the considerably smaller water volume that it uses (V_{SV} = 10ml; V_{LV} = 500ml) for the extraction. These two factors are particularly important in waters where ^{222}Rn concentrations are low. However, greater precision can be acquired by either analysing larger volumes of water (as in the LV method) or by improving the sensitivity of the techniques, which can be achieved by optimising the cocktail-to-sample ratio of the method. Moebius and Salonen (2002), for example, suggests that for radon analysis with the Triathler^{TM} the best LLD is obtained by extracting Rn from 19ml of water into 3ml cocktail and transferring 2ml of the cocktail into a plastic vial for counting.

Table 3 Radon concentrations determined by small-volume (SV) and large-volume (LV) method for piezometers P before and after purging

Piezometer P	**Small-volume method (10ml-sample)**		**Large-volume method (500ml-sample)**	
	^{222}Rn (Bq l^{-1})	***±2s (Bq l^{-1})***	***^{222}Rn (Bq l^{-1})***	***±2s (Bq l^{-1})***
unpurged	1.43	0.02	4.22	1.66
Purged	3.01	0.19	4.50	0.23

Large sample volumes and/or high method sensitivity are required where radon concentrations are low, but are less critical for waters with high radon concentrations (e.g., groundwaters in granite aquifers / mineralised areas). For such waters, the SV-method may be sufficient and has the advantage of requiring less or no additional sample preparation.

However, the assessment of the SV method as part of this study is limited by the sparse data. Therefore, further studies to test and optimise the SV method are required before detailed conclusions on the suitability of this method for determining radon concentrations in different groundwaters (and surface waters) can be drawn.

3.3 RADON METHOD TO DETERMINE FLOW VELOCITIES IN WELLS

Radon has been used to estimate groundwater flow velocities in wells and to locate zones of active groundwater inflow (Cook et al., 1999; Hamada, 2000). The method assumes that radon concentrations in unpumped wells decreases with decreasing flow velocity as radon decays during its residence time in well. Therefore, flow velocity can be estimated from the ratio of radon concentrations in the well to the radon concentrations in the aquifer.

In this study, a sampling method was tested for collecting groundwater samples for radon analysis before and after well purging with the aim to infer groundwater flow rates from the ratio of these two values. The focus of this work was on the actual sampling procedure, rather than on the calculation of flow velocities, and only this aspect of the work is discussed in detail.

Sample collection of the unpurged samples is described in section 2 and differed from the collection of the purged samples in that it used a peristaltic pump rather than the submersible pumps. The peristaltic pump was used in order to achieve sufficiently low flow rates at which only water from within the well but not from the adjacent aquifer was abstracted. This was critical as fresh aquifer water increases the radon concentrations in the sample and as a result, flow velocities in the well are overestimated.

Radon concentrations in piezometer P prior to and after purging are displayed in Table 3. The data show a good contrast between radon concentrations in unpurged and purged samples determined by the SV method. The contrast is less distinct in the samples analysed by the LV method and this is probably due to fresh aquifer water being drawn into the well. The LV method requires much larger water volumes (sample volume + overflow for bucket) than the SV method. Considering the small piezometers diameter (50mm), it is likely that stagnant water was gradually depleted from the well during the collection of the LV samples and progressively replaced by, or mixed with, fresh aquifer water. This is supported by the changing sample composition reflected in increasing Rn concentrations in the triplicate samples (increasing from 3.36 Bq l^{-1} to 5.01 Bq l^{-1}). It also explains the high uncertainty (1.66 Bq l^{-1}) associated with the unpurged LV sample (Table 3).

Assuming that the water within the well is perfectly mixed, the flow velocity was calculated from the following equation by Cook et al. (1999):

$$q = \frac{c}{c_0 - c}\frac{\lambda \pi r}{2} \qquad \text{(Equation 6)}$$

with

q: flow rate in borehole (m d^{-1})

c: radon concentrations in the well/piezometer

c_0: radon concentrations in the aquifer

λ: decay constant for radon = 0.18129 d^{-1} (Lederer and Shirley, 1978)

r: piezometers radius.

The resulting velocities are 0.01 m d^{-1} for the SV method data and 0.1 m d^{-1} for the LV method data and similar velocities were obtained by using equations given in Hamada (2000). These values are considerably lower than the velocities expected in the gravel aquifer which are estimated to lie in the range of 0.3 – 3 m d^{-1} (David Allen, BGS, personal communication). The failure of the method to predict the flow velocity in the well is unlikely to be related to the uncertainty in radon measurements, but is probably due to the fact that the flow rates at the study site are too high. As a result, groundwater residence times in the well are so short that radon decay becomes negligible and no longer controls the radon concentrations in the well. In this case, however, one would expect the radon concentrations in the well to be equal to the concentrations in the aquifer. Alternatively, it is possible that flow velocities in piezometer P vary over the screened interval and that the radon samples were collected from a depth where flow velocities are low, e.g., due to the presence of clay deposits.

From the above discussion it is clear that more and better radon data are needed in order to establish the difference in concentrations in the well and in the aquifer. Therefore, additional sample collection is recommended, which should focus on aquifers/wells with expected groundwater flow velocities of < 40 m $year^{-1}$. Above this velocity, the radon decay method becomes insensitive to changes in groundwater flow (Cook et al., 1999).

To decrease uncertainty in the radon results, samples should be collected using a gas-tight grab sampling device/bailer so that water can be withdrawn without pulling fresh aquifer water into well. Alternatively, the peristaltic pump can be used for abstracting small volumes of water from the well. However, this implies use of the SV method and requires that the sensitivity of the method be improved so that it can provide consistent/good-quality measurements for such low-radon waters.

Furthermore, it is suggested that alternative methods (e.g., point-dilution tests) are considered for determining flow velocities at the Westbrook site. Such data are valuable to confirm that the radon-decay method is not suitable for this study site due to the high flow velocities and to investigate the possibility that flow within the aquifer is locally limited by the presence of clays or other low-flow horizons (as is suggested by the above data).

3.4 RADON AS A TRACER FOR SURFACE WATER-GROUNDWATER INTERACTIONS

Results from the limited radon sampling carried out at Westbrook Farm as part of this study show that radon concentrations are highest in the alluvial aquifer. The aquifer comprises a mixture of clay, sand and flint gravels, which have a high surface area for the release of radon. These gravels probably also contain higher radium concentrations than the Chalk, which is predominantly composed of calcium carbonate. Lowest concentrations are observed in the river, which is expected as radon is rapidly lost from the water when it comes in contact with the atmosphere. The data collected as part of this study suggest that there is sufficient contrast between the radon signatures of the river and the groundwater to make ^{222}Rn a suitable tracer for surface water-groundwater interactions at the Westbrook study site. This has been previously shown by Mullinger et al., (2007, in press-a; in press-b) who also outlined the problems and limitations associated with such an approach. The important implication within the context of this study is, however, that the method developed for the analysis of radon in water using the Triathler^{TM} is sufficiently sensitive to resolve the contrast between these signatures and hence, it can be employed to study surface water – groundwater interactions.

4 Method limitations

The data analysed by LSC (Triathler^{TM}, HIDEX) using the LV method show good agreement with results from other studies which use lab-based instruments (Mullinger et al., 2007). However, the method described in this report, has not been calibrated due to an unresolved problem with the working standards. Calibration is not considered necessary when using the ^{222}Rn protocol of the Triathler^{TM} (Timo Okinari, HIDEX Oy, personal communication), but would facilitate the direct comparison of the results with those from other studies. It would also provide direct measurements of the extraction efficiency of the method as well as of the counting efficiency of the instrument. These parameters are used to calculate the sensitivity (LLD) of the method and to convert counts-per-minute values to Becquerel per litre, respectively. In this study, these parameters were estimated from values provided by the manufacturer (HIDEX Oy, Turku). To confirm that radon concentrations measured by the described methods can be directly compared to those from other studies, it is recommended that these parameters are determined in future studies for each of the methods (small-volume method and large-volume method). This involves the preparation, extraction and analysis of ^{226}Ra standard solutions (Pates and Mullinger, 2007) and will require a licence and facilities for the handling of open-source radioactive materials. The acquisition of such a licence should be considered.

Using the portable Triathler^{TM} for the sample analysis imposes some limits on the number of samples that can be collected during a sampling survey. This is because sample analysis with the Triathler^{TM} is not automated and needs to be carried out manually (e.g., changing-over of samples, starting of a new counting cycle). This has the advantage that the analyst can adjust instrument settings for individual samples, but it also means that the sample throughput is slower and requires more input from the analyst than lab-based instruments. The sample numbers that can be processed vary depending on the radon concentrations in the sample, as lower concentrations require longer counting times to achieve adequate detection limits. These limitations need to be considered when designing the sampling programme, in particular since the time available for sample analysis is limited by the half-life of radon.

5 Recommendations

The discussions in sections 3 and 4 have identified a number of shortcomings and unresolved issues associated with the method for measuring radon in water and its application to specific hydrogeological problems. Recommendations have been made on how to address these issues and how to improve the performance of the method and its applications. These are summarised below:

1. Method development

- Calibrating the SV and LV methods using ^{226}Ra standard solutions (including determination of counting efficiency of the instrument and abstraction efficiency of both methods)
- Improving the sensitivity of the SV method by optimising sample-to-cocktail ratio

2. Method applications

- Testing and adjusting the SV method for use in groundwaters with high radon concentrations
- Testing the radon method to determine groundwater flow velocities in wells in aquifers with low groundwater flow velocities (40 m year-1), verify the results with alternative measurements of groundwater flow velocities (e.g., point dilution tests)

6 Summary and conclusions

A method has been developed to measure radon concentrations in water using the portable LSC Triathler^{TM} instrument (HIDEX Oy, Turku, Finland). The method was sufficiently sensitive to determine radon concentrations in surface waters and low-radon groundwaters. The results showed very good agreement with radon measurements from external studies undertaken in the study area. This suggests that the Triathler^{TM} measurements are directly comparable to those from other studies and techniques. However, this needs to be confirmed by calibrating the method with ^{226}Ra standard solutions.

There were considerable discrepancies in the radon concentrations of the working standards measured in this study compared with those reported by an external laboratory, which appeared to be anomalously high. The reasons for this disagreement are unclear and need to be further investigated. The laboratory has been contacted for clarification and for more detailed information on their methodology and protocols.

The method was applied at the Westbrook Farm site to estimate groundwater flow velocities from the difference in radon concentrations in an unpurged well (piezometer P) and in the aquifer. The predicted velocity did not agree with those expected at this site, probably because the groundwater flow velocity in the well was too high. Further tests are recommended (on different aquifers/wells) to establish the range of flow velocities at which the method can be applied.

Groundwater and river water sampling at the Westbrook Farm site demonstrated that the method was able to measure radon in the different waters even though the concentrations were low. The data also confirmed that the contrast between the radon signatures of the river and that of the groundwater is sufficiently high to make radon a suitable tracer for studying surface water-groundwater interactions at this site. However, the limited sample throughput associated with the proposed method needs to be considered when designing the sampling programme.

The method as presented in this report is still under development and requires further testing and optimisation. However, when established it will provide a relatively inexpensive techniques that can be used for a wide range of hydrogeological and geochemical applications. These include the detection of zones of active groundwater inflow into wells and/or streams and other surface water bodies, measurements of radon concentrations in different aquifers and lithologies (e.g., in granite aquifers or mineralised areas) as well as estimations of groundwater flow velocities in different aquifers/wells.

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