Measuring radon-222 in soil gas with high spatial and temporal resolution

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ARTICLE INFO

ABSTRACT

In order to exploit ^{222}Rn as a naturally-occurring tracer in soils we need to sample and measure radon isotopes in soil gas with high spatial and temporal resolution, without disturbing in situ activity concentrations and fluxes. Minimisation of sample volume is key to improving the resolution with which soil gas can be sampled; an analytical method is then needed which can measure radon with appropriate detection limits and precision for soil gas tracer studies. We have designed a soil gas probe with minimal internal dead volume to allow us to sample soil gas volumes of 45 cm^3. Radon-222 is extracted from these samples into a mineral oil-based scintillation cocktail before counting on a conventional liquid scintillation counter. A detection limit of 320 Bq m^{-3} (in soil gas) is achievable with a 1 h count. This could be further reduced but, in practice, is sufficient for our purpose since ^{222}Rn in soil gas typically ranges from 2000—50,000 Bq m^{-3}. The method is simple and provides several advantages over commonly used field-portable instruments, including smaller sample volumes, speed of deployment and reliability under field conditions. The major limitation is the need to count samples in a liquid scintillation counter within 2—3 days of collection, due to the short (3.824 day) radioactive half-life of ^{222}Rn. The method is not applicable to the very short-lived (55 s half-life) ^{220}Rn.

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1. Introduction

Radon isotopes (^{220}Rn and ^{222}Rn) occur naturally in all soils due to the decay of the parent nuclides ^{224}Ra and ^{226}Ra, which ultimately derive from radioactive decay of ^{232}Th and ^{238}U, respectively. Radon-220 (thoron) and ^{222}Rn (radon) both undergo alpha decay; each gives rise to a series of short-lived alpha- and beta-emitting progeny which can impart significant radiation doses when inhaled. Thus, many studies of radon gas are driven by the need to quantify radiation doses due to the efflux of radon from soil into the atmosphere above, especially when this occurs into buildings. However, radon gas can also be used as a naturally-occurring tracer which can assist in predicting earthquake risk (Papastefanou, 2007) and in quantifying gas transport in soils. Radon flux measurements have previously been used to determine diffusive properties of surface soils (Dorr and Munnich, 1990; Lehmann et al., 2000; Huxol et al., 2013) and also the diffusive

transport characteristics of the near surface atmosphere within short vegetation canopies (Nemitz et al., 2009). There is potential to use radon in a wider range of applications, but we need flexible and easily applied methods to measure activity concentrations in soil profiles. Soils are complex: porosity and tortuosity vary spatially, whereas water content varies both spatially and temporally. Each of these properties exerts a strong influence on the effective diffusivity of gases, including radon, in soils (Rogers and Nielson, 1991). Thus, we need to be able to sample and measure radon isotopes in soil gas with high spatial and temporal resolution, preferably in ways that disturb in situ activity concentrations and fluxes as little as possible.

Numerous methods can be used to sample and measure radon in soil gas. These include detectors such as the Clipperton probe (Monnin and Seidel, 1998), Barasol™ (www.algade.com) or electret ion chambers which can be embedded directly in the soil for periods ranging from days to years (Antonopoulos-Domis et al., 2009). For long term measurements, gas-permeable tubes can be buried in the soil, through which air is circulated and radon measured at the surface using a suitable detector (Lehmann et al., 2000). Shorter-term measurements can be made by driving narrow tube

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samplers into the soil and extracting soil gas under suction at defined depths. Dorr and Munnich (1990) sampled soil gas by driving a narrow (6 mm ⌀) stainless steel tube with a perforated tip into the soil to depths ranging from 5 cm to as deep as 10 m. They extracted 200—300 cm^3 of soil gas by pumping through the tip of the sampler at a rate of 400 cm^3 minute^{-1}. In a soil with air-filled porosity of 40%, a soil gas sample of 300 cm^3 will be drawn from a sphere with 5.64 cm radius, assuming homogeneous and isotropic pore structure. This would give an uncertainty of almost 12 cm on the vertical position of the sample. As soil wetness increases, so does this uncertainty; with an air-filled porosity of 20%, the notional sampling sphere of a 300 cm^3 gas sample has a radius greater than 7 cm and the minimum spacing of adjacent samples is, for all practical purposes, 10 cm. Similarly, the minimum depth of sampling is 10 cm below the soil surface. Reducing the volume of the soil gas sample will increase the spatial precision with which it can be taken (Born et al., 1990). Fig. 1 indicates that, as sample volume is reduced to less than 100 cm^3, the effective sampling radius, hence the positional uncertainty on the sample, falls rapidly. Fig. 1 also shows that the smaller the gas sample, the less the influence of soil wetness (i.e. effective porosity) on the positional uncertainty on the sample. Taking smaller soil gas samples also reduces the risk of drawing air from the above-soil atmosphere between the outer surface of the sampling tube and the soil.

Some field-portable radon monitoring instruments (e.g. RAD7™ and AlphaGUARD™) are able to pump soil gas from sampling tubes, either in one-off volumes or on a continuous cycle in which samples are taken every few minutes for as long as necessary (www.durridge.com; www.saphymo.com). The minimum volumes required for one-off samples are in the order of 2 dm^3, with corresponding sampling radii ranging from 10 to 20 cm, depending on the effective porosity of the soil; some studies using stand-alone radon monitors have used sample volumes as large as 5 dm^3 (Schroth et al., 2012). While such instruments are convenient to use, they are limited in their ability to take samples with high spatial and temporal resolution.

The aim of the current study was to develop and test an alternative method to allow small volume samples of soil gas to be collected with high precision, both spatially and temporally, and for these samples to be analysed for ^{222}Rn with sufficient accuracy and precision for soil gas transport studies.
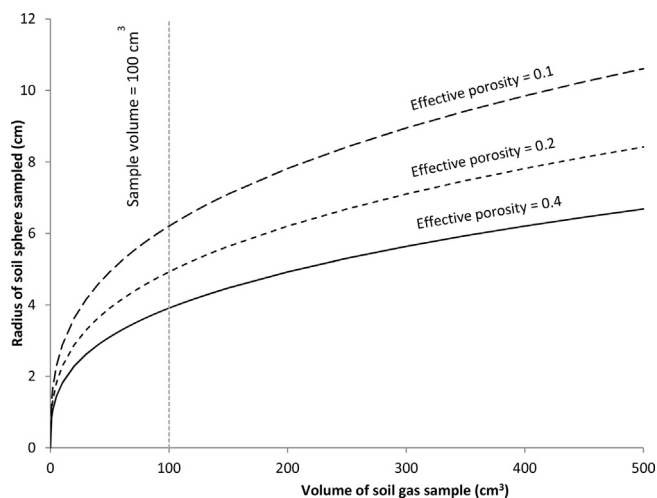
2. Methods

A probe (Fig. 2) was designed to allow small volume samples of soil gas to be taken quickly and conveniently down to soil depths of 1 m. This consists of a length of aluminium tube (8 mm external diameter) with a pointed tip behind which numerous 1 mm holes are drilled over a length of 2 cm. A flexible silicone rubber tube with narrow (0.8 mm) internal bore passes through the external aluminium tube and is sealed into position near the perforated sampling tip with a silicone rubber plug. The design minimises 'dead volume' within the sampler (~0.5 cm^3 in the sampler head and 0.5 cm^3 m^{-1} in the silicone tube). The length of aluminium tube can be varied from 15 cm to 1 m, to suit the required depth of sampling. A brass elbow joint at the upper end of the aluminium tube provides a conduit in which the silicone rubber tube is protected from the pressure needed to push the tube sampler into the soil to the required sampling depth. A plastic tap with a Luer fitting allows a disposable 20 cm^3 syringe to be attached to the end of the silicone rubber tube — this syringe is used to withdraw a gas sample through the sampling probe from the required soil depth.

In practice the first aliquot (<5 cm^3) of soil gas withdrawn from the sampler, which includes the 'dead volume', is discarded. 15 cm^3 of soil gas are then withdrawn and injected into a pre-evacuated glass vial (Exetainer®, www.exetainer.com) through a rubber septum. Each vial (12 cm^3) is prepared by half-filling with 6.6 cm^3 of a liquid scintillation cocktail (Pro-Scint Rn™, Meridian Biotechnologies Ltd.), leaving an evacuated volume of 5.4 cm^3. Injecting 15 cm^3 of soil gas into this volume results in an 'overpressure' of approximately 2 bar. A further two 15 cm^3 aliquots of soil gas are withdrawn from the soil via the sampling probe and injected into separate Exetainer® vials, thus giving triplicate vials for each sampling point and a nominal total of 45 cm^3 of soil gas extracted per sampling point (experimental analysis of Type A error gave an actual value of 44.89 ± 0.03 cm^3). If a vertical profile of soil gas samples is needed, the probe is inserted to the shallowest depth (usually 10 cm from the soil surface) from which triplicate gas samples are withdrawn. The probe is then pushed to the next sampling depth and the procedure repeated until soil gas samples have been taken over the required sequence of depth intervals.

Once injected into the Exetainer® vials, ^{220}Rn and ^{222}Rn are free to partition into the liquid scintillation cocktail. Pro-Scint Rn™ is mineral oil-based and contains 20—40% 'pseudocumene' (1,2,4-trimethylbenzene) as a liquid scintillator. It was chosen for this application as it is specifically formulated to 'extract' radon from water or gas samples with a partition coefficient of approximately 50 (Clever, 1979). The extraction process is facilitated by shaking the vials vigorously by hand before transporting to the laboratory where, after at least 1 h contact time, the liquid contents of the triplicate Exetainer® vials are decanted into a single low-potassium borosilicate glass scintillation vial, giving a 20 cm^3 volume of scintillation cocktail per vial. The scintillation vials are then placed into a liquid scintillation counter (we used a Packard Tri-Carb 2100TR) where they are dark-adjusted for 3 h before counting across an energy range from 0 to 2 MeV. By the time the vials are counted any ^{220}Rn (T½ ~ 55 s) has completely decayed and counts collected should result solely from ^{222}Rn and its short-lived progeny, ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po. With physical half-lives of 3.11 min, 26.8 min, 19.9 min and 0.00016 s, respectively, these decay products need approximately 4 h to achieve secular equilibrium with ^{222}Rn. Thus, the dark-adjustment period, plus the time needed to count a reagent blank 'background' sample (1 h), ensure that the samples contain combined activities of parent and progeny which are representative of the original ^{222}Rn activity in each soil gas sample.

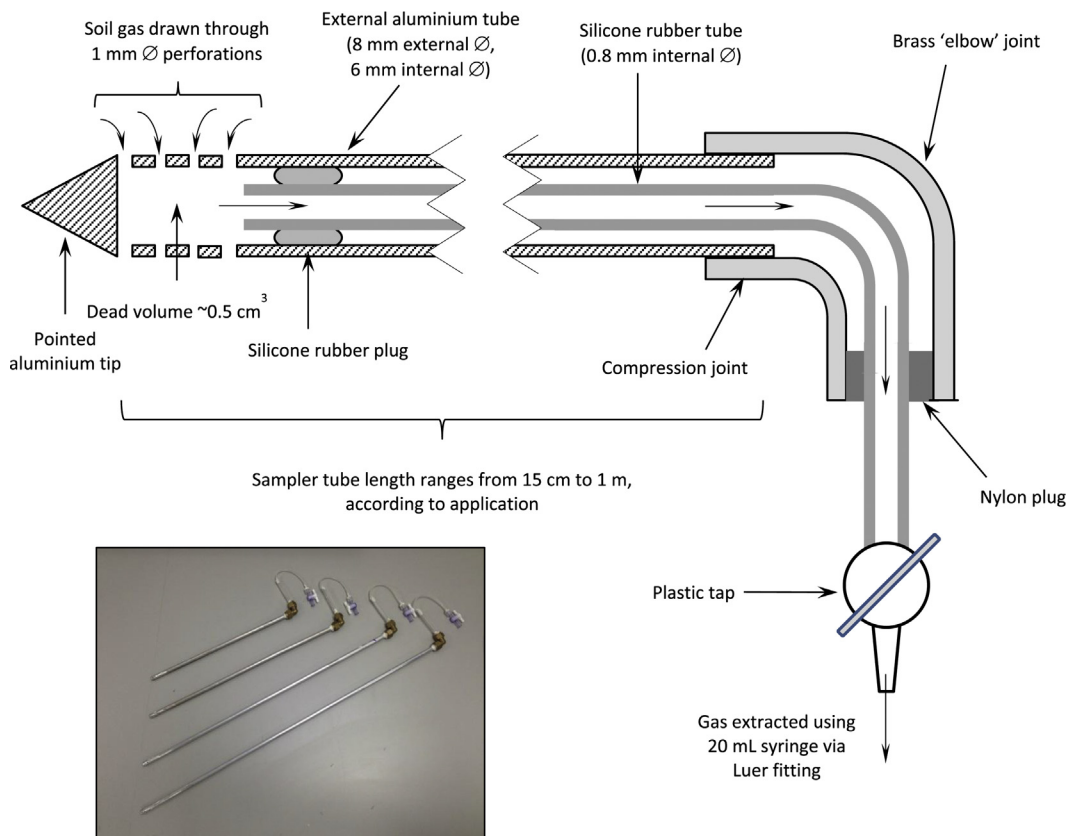Each sample is counted for 1 h and the sample activities

Fig. 1. Influence of soil gas sample volume on effective radius of soil sphere sampled.

Fig. 2. Cross-sectional diagram of soil gas sampling tubes. Sampler head dead volume ~0.5 cm^3; sampler tube dead volume = 0.5 cm^3 m^{-1}. Inset shows samplers of different lengths, from 45 cm to 1 m.

reported in counts per minute after subtraction of background counts (CPM net). A reliable calibration is then needed to convert CPM net values to volumetric activity concentrations (Bq m^{-3}). A small quantity of ^{226}Ra-containing scale (barium-radium sulphate, derived from deposits within an industrial pipe) was placed in a sealed chamber within the laboratory and ^{222}Rn emanating from the physical decay of ^{226}Ra was sampled using the continuous flow mode of a pulse-counting ionisation chamber (AlphaGUARD™ PQ2000 PRO radon monitor; www.saphymo.com) with a stated measurement range from 2–2 × 10^6 Bq m^{-3} for ^{222}Rn. The AlphaGUARD™ is factory calibrated using a NIST standard (SAPHYMO, pers. comm.) and thus provides an accurate baseline of measured ^{222}Rn activity concentrations against which to compare independent measurements using liquid scintillation counting (LSC). During measurement of a wide range of ^{222}Rn activity concentrations (280–1.3 × 10^5 Bq m^{-3}) in the laboratory chamber system, triplicate 15 cm^3 syringe samples of gas were taken directly from the ionisation chamber of the AlphaGUARD™ monitor and treated as previously described for soil gas samples. These samples were analysed using LSC and compared with data obtained using the AlphaGUARD™. The AlphaGUARD™ manufacturer's stated calibration error is 3%, not including the uncertainty on the primary standard which is not provided. We could not, therefore, quantify the complete Type B uncertainty contributed by the primary calibration of the AlphaGUARD™, though the 1-sigma (Type A) counting uncertainties of both the AlphaGUARD™ and LSC methods were tightly constrained, as shown in Fig. 5.

To verify the comparability of ^{222}Rn measurements using both methods in the field, a series of soil gas samples were taken from an experimental plot at Sutton Bonington, UK (52.833°N, 1.249°W).

Samples were taken at 60 cm depth from randomised points within a 15 × 15 m area on seven different days between September and December 2013. Soil gas samples were taken using the sampling probes described above. The soil gas was extracted using an AlphaGUARD™ radon monitor coupled to an AlphaPUMP™, at a rate of 1 dm^3 min^{-1} for 2 min. The volume of the ionisation chamber is 0.62 dm^3, hence approximately two chamber volumes were pumped through to purge the monitor and the third chamber volume was sealed in the ionisation chamber for counting. A time interval of 1 min was used to integrate the counts collected and an overall counting period of 30 min was used for each soil gas sample. As in the laboratory chamber experiment, triplicate 15 cm^3 syringe samples of gas were taken directly from the ionisation chamber of the AlphaGUARD™ monitor and treated as previously described for soil gas samples. These samples were analysed using LSC and compared with data obtained using the AlphaGUARD™ in the field.

The same experimental plot was used to sample soil gas over depth profiles from 10 to 60 cm. These samples were taken at randomly located points within the 15 × 15 m experimental area by inserting the sampling probe in 10 cm increments, as described above. The overall time taken to insert the probe to the required depth and then to extract 3 × 15 cm^3 aliquots of soil gas was approximately 5 min, giving a combined sampling time of 25–30 min per profile. Gas samples were injected into Exetainer® vials, prepared as described above, and taken directly to the laboratory for analysis. A further field test of the method was made by carrying out a survey of the horizontal distribution of ^{222}Rn activity concentrations in soil developed in alluvium above the junction between two rock types in the Peak District, Central England. Soil gas was sampled on Cromford Meadow (53.11°N, 1.55°W) at 15 cm

depth along a transect perpendicular to the boundary between the uraniferous Bowland Shale and Lower Carboniferous Limestone. The approximate location of the boundary was determined using a geological map (BGS, 1963) and magnetic bearing from a visible fault line. Samples were then collected over a distance of 11 m at 1 m spacings. This sampling exercise took less than 1 h.

3. Results and discussion

Minimisation of sample volume is key to improving the spatial and temporal resolution with which soil gas can be sampled although few studies on soil gas sampling specifically address this problem. In a radon detector such as AlphaGUARD™, the volume of the ionisation chamber dictates the minimum soil gas volume which can be measured. When using LSC to measure radon in soil gas there is a balance between the volume of gas sampled and the count rate detected. During development of our method we took gas sample volumes ranging from 10 cm^3 to 20 cm^3, each taken in triplicate to give total sample volumes of 30 cm^3—60 cm^3. The optimum volume was 45 cm^3 (i.e. 3 × 15 cm^3) which increased the count rate obtained from 30 cm^3 samples in a linear fashion (Fig. 3). Larger (60 cm^3) samples further increased the count rate, but the gain in counts was not proportional to the increased gas volume taken.

Liquid scintillation counting of soil gas samples measures the combined contribution from alpha and beta particles from ^{222}Rn and its short-lived progeny. It is not possible from the energy spectrum obtained during LSC to identify the presence of individual emitted particles which might definitively identify the presence of ^{222}Rn. However, due to the fact that its 3.824 day radioactive half-life is considerably longer than the half-lives of its four immediate descendants, it is possible to identify ^{222}Rn as the main source of radioactivity in a sample by comparing the declining count rate over several days with the theoretical physical decay curve for ^{222}Rn. Ingrowth of the much longer-lived ^{210}Pb (T½ = 22.3 years) is too slow to contribute to the count rate over a period of hours to days. Fig. 4 compares repeated counts of the same soil gas sample with the theoretical decay curve for ^{222}Rn, indicating that the counts were indeed due solely to ^{222}Rn and its short-lived progeny. Fig. 4 also indicates that count rates in a typical soil gas sample were achieved with 2-sigma precision ranging from 2 to 10%.

Having established that ^{222}Rn could be identified and counted with good precision in a composite soil gas sample of 45 cm^3, a calibration curve between the AlphaGUARD™ (Bq m^{-3}) and LSC
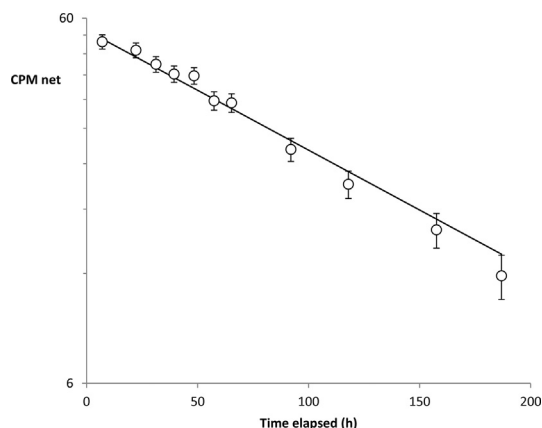
Fig. 4. Radon-222 activity (CPM net) in a liquid scintillation vial counted repeatedly after sampling from soil gas and partitioning into ProScint Rn™ liquid scintillation cocktail. Vertical bars represent 2-sigma counting errors. The solid line shows the curve of declining activity expected if ^{222}Rn and its short-lived progeny are the sole contributors to radioactivity within the vial; the measured and calculated activities were statistically indistinguishable (χ^2 = 1.001, p < 0.001).
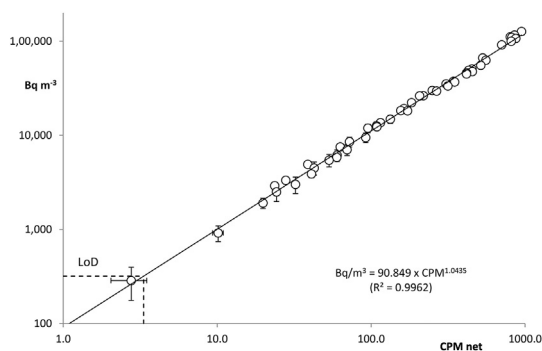
Fig. 5. Radon-222 activities in gas samples obtained using two detection methods: liquid scintillation counting (CPM net) and an ionisation chamber (AlphaGUARD™, Bq m^{-3}). The AlphaGUARD™ was used in 'flow' mode with a 10 min count. Measurements were made using gas samples from a closed chamber system with barium-radium sulphate scale as the source of ^{222}Rn; 45 cm^3 (3 × 15 cm^3) samples for liquid scintillation counting were taken directly from the ionisation chamber of the AlphaGUARD™ instrument. Horizontal and vertical bars are 1-sigma errors; dashed lines show the limit of detection (LoD − 3.33 CPM, equivalent to 320 Bq m^{-3}) which was calculated according to Currie (1968) based on liquid scintillation counting for 60 min in ProScint Rn™.

(CPM net) methods was drawn, based on measurements in a laboratory chamber using barium-radium sulphate as a source of ^{222}Rn. This curve was approximately linear but could be described most accurately, especially at LSC count rates less than approximately 50 CPM, using a power function with an exponent just greater than 1 (1.0435). This weakly non-linear function (the AlphaGUARD™ manufacturer's stated linearity error is <3%) provided a strong fit (R^2 = 0.996) to the experimental measurements over a range of ^{222}Rn activity concentrations spanning almost four orders of magnitude. The limit of detection was calculated (according to Currie, 1968) to be 3.33 CPM net for a 60 min count time; this equates to a ^{222}Rn activity concentration of 320 Bq m^{-3}. Doubling the count time to 120 min would reduce the limit of detection to 2.35 CPM net, equivalent to 220 Bq m^{-3}. The limit of detection may be further decreased by raising the lower energy threshold above zero MeV which would exclude the high background lower energy radiation, thus raising the signal-to-noise ratio (Genereux and Hemond, 1991). Our current detection limit is comparable to LSC methods using other liquid scintillation
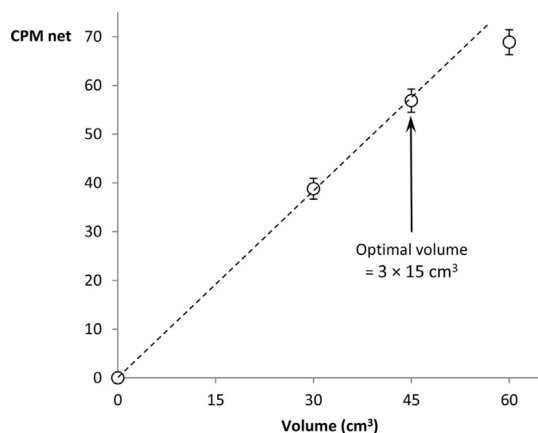
Fig. 3. Radon-222 activity (CPM net) in ProScint Rn™ liquid scintillation vial versus volume of soil gas injected/partitioned in scintillation cocktail. Vertical bars represent 2-sigma counting errors.

counters, including Quantulus™ (Buzinny et al., 2009). It is relatively high compared with some other methods, including instrumental detectors such as RAD7™ and AlphaGUARD™ (typically 20 Bq m^{-3}), but suitable for most soil gas applications; activity concentrations of ^{222}Rn measured in soil gas commonly range from 2000—50,000 Bq m^{-3} (Schubert et al., 2002).

In our field comparison of AlphaGUARD™ and LSC, ^{222}Rn activity concentrations in soil gas ranged from 936 (±780) to 24,004 (±3448) Bq m^{-3} (1-sigma uncertainties from AlphaGUARD™ measurements in parentheses). Fig. 6 shows data from a typical AlphaGUARD™ counting cycle which lasted 30 min, during which counts were integrated over 1 min intervals. An initial peak in activity concentration at 2—3 min is given by the combined counts from ^{220}Rn and ^{222}Rn. After 5 min, the counts from ^{220}Rn have been lost by radioactive decay and counts from ^{222}Rn and its short-lived progeny are collected for the next 20 min before purging the ionisation chamber for 5 min so that the next sample can be collected. The average ^{222}Rn activity concentration for the sample is calculated from the 1 min counts taken between 5 and 25 min. 45 cm^3 gas samples were taken directly from the ionisation chamber to be analysed by LSC and the results of the two methods are compared in Fig. 7. The relationship between AlphaGUARD™ activity concentrations and CPM net by LSC was more strongly log-linear than in the laboratory chamber experiment and could be described using a power function with an exponent of 1.253 (R^2 = 0.859). The predictive accuracy of the calibration curve in Fig. 5 was tested by converting CPM net values from the field samples in Fig. 7 to ^{222}Rn activity concentrations (Bq m^{-3}). These calculated activity concentrations were then compared with those measured directly using AlphaGUARD™ in the field (Fig. 8). Linear regression of the two data sets yielded a coefficient of determination (R^2) of 0.742. A χ^2 test (p = 0) allows us to conclude that the laboratory calibration between the two methods is sufficiently reliable for LSC to be used as a stand-alone method for ^{222}Rn detection in small soil gas samples.

Given the design of the soil gas sampling probe, the method is particularly suitable for measuring ^{222}Rn activity concentrations in soil profiles over a depth range from close to the soil surface (5—10 cm) to 1 m. Two example profiles are shown in Fig. 9, both measured at randomly-located points within the 15 × 15 m experimental plot described above. Several published studies show that ^{222}Rn diffusion in soils can be described by a single effective diffusion coefficient (Nazaroff, 1992). This is convenient since it

Fig. 7. Radon-222 activity concentrations in field samples of soil gas (60 cm depth) measured on seven different days between September and December 2013 using two detection methods: liquid scintillation counting (CPM net) and an ionisation chamber (AlphaGUARD™, Bq m^{-3}). The AlphaGUARD™ was used in 'flow' mode with a 1 min count time following purging of the ionisation chamber with two chamber volumes (total volume sampled ~ 2 L). 45 cm^3 (3 × 15 cm^3) samples were removed directly from the ionisation chamber for analysis by LSC. Vertical and horizontal bars are 1-sigma errors.
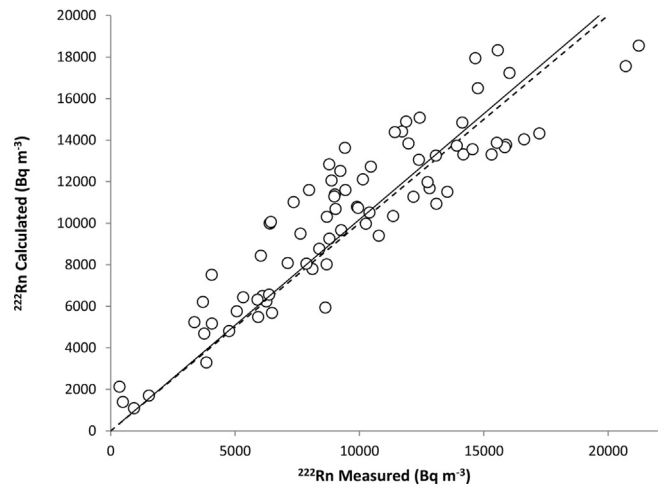
Fig. 8. Comparison of ^{222}Rn activity concentrations in field samples of soil gas (60 cm depth) measured on seven different days between September and December 2013. Measurements were made in the field with AlphaGUARD™ (X axis) and in the laboratory by liquid scintillation counting, using the calibration curve in Fig. 5 to convert CPM (net) to Bq m^{-3}. The dashed line is the line of unity while the solid line is a linear regression (R^2 = 0.742). The measured and calculated values were statistically indistinguishable (χ^2 = 0, p = 0).
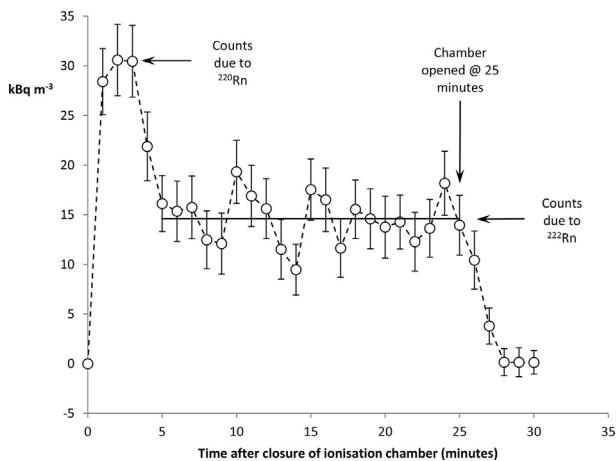

Fig. 6. Typical activity concentration data from a 30 min AlphaGUARD™ counting cycle in the field. The X axis shows time after a soil gas sample is sealed in the ionisation chamber. Vertical bars represent 1-sigma errors on 1 min counts.
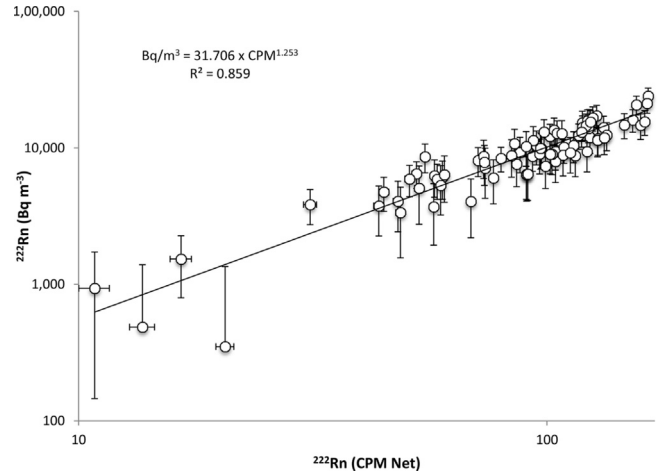
allows ^{222}Rn fluxes at the soil surface to be calculated by fitting an analytical solution of the 1-D diffusion equation. However, it is known that complexities arise in the distribution of radon through the soil profile due to changes in the effective porosity of the soil and the radon emanation rate associated with variations in soil mineralogy and other properties. For example, Antonopoulos-Domis et al. (2009) showed that the radon activity concentration profile in a Greek soil was strongly influenced by a change from sandy to clayey texture. In our study, the shape of the ^{222}Rn activity concentration profiles was not monotonic, but clearly influenced by changes in soil porosity. In Fig. 9 this can be seen at a depth of 30—40 cm where the soil texture changed from sandy loam in the upper part of the profile to sandy clay below. A simple analytical
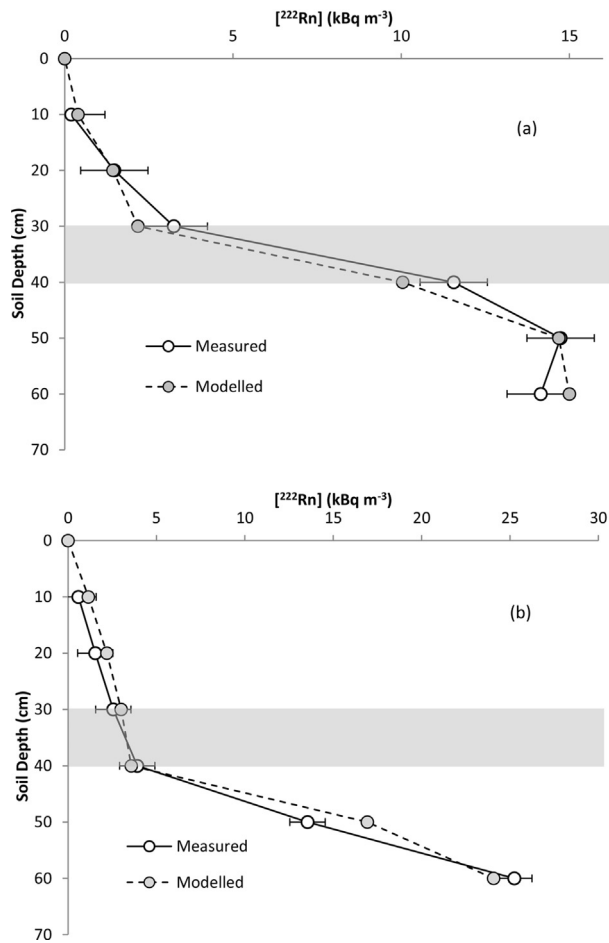
Fig. 9. Two depth profiles of [222]Rn measured within a 15 m × 15 m plot in Sutton Bonington soil. Also shown are modelled curves using numerical solutions of the 1-D diffusion equation (see text for model parameters). The horizontal grey bar indicates the depth at which the soil texture changes from sandy loam to sandy clay, with a consequent change in effective diffusion coefficient for [222]Rn and other gases. Error bars represent 2-sigma counting errors on measured [222]Rn activity concentrations.

solution of the 1-D diffusion equation cannot be fitted to either of the two [222]Rn profiles in Fig. 9 since the effective diffusion coefficient is not constant with depth. It is possible, however, to approximate the shapes of the measured [222]Rn activity concentration profiles with a numerical solution of the 1-D diffusion equation, assuming a vertically uniform [222]Rn production rate (calculated according to Chamberlain, 1991) and discrete diffusion coefficients for different parts of the soil profile. In Fig. 9(a) the [222]Rn production rate was assumed to be 0.056 Bq m^{-3} s^{-1} and the effective diffusion coefficients were 5.25 × 10^{-6} m^2 s^{-1} for the 0—10 cm soil depth, 1.75 × 10^{-6} m^2 s^{-1} for the 10—30 cm soil depth and 1.05 × 10^{-7} m^2 s^{-1} for the 30—70 cm soil depth. For Fig. 9(b) the assumed [222]Rn production rate was 0.1 Bq m^{-3} s^{-1} and the effective diffusion coefficients were 3.5 × 10^{-6} m^2 s^{-1} for the 0—40 cm soil depth and 1.05 × 10^{-7} m^2 s^{-1} for the 40—70 cm soil depth. The diffusion coefficients for both profiles lie within the range of effective diffusion coefficients for [222]Rn in soils presented by Nazaroff (1992). One of the most useful applications of measured soil activity concentration profiles of [222]Rn is to estimate effective gas diffusion coefficients for soils, which can then be scaled to other important soil gases such as CH_4, CO_2 and N_2O whose diffusive behaviour is difficult to estimate directly due to complications including interactions with soil organisms (eg. Born et al., 1990;

Dorr and Munnich, 1990). The fact that different values of effective diffusion coefficients have to be used to model [222]Rn activity concentration profiles, especially in the upper soil layers, underlines the complexity of behaviour of radon gas in soils and the need for high spatial resolution measurements to provide better understanding of the factors which control its distribution and flux.

The second field test of our method involved a horizontal survey of [222]Rn in soil gas in the vicinity of a geological discontinuity which is suspected to result in a localised increase in radon flux at the soil surface due to authigenic uranium within the Bowland Shale (Leeder et al., 1990). The influence of underlying geology on radon activity concentrations in surface soil (10—30 cm depth) soil is expected to reduce with increasing thickness of soil overlying the bedrock. Nevertheless, Fig. 10 shows that, within 2 m of where the boundary was suspected to lie between the Bowland Shale and Carboniferous Limestone, [222]Rn activity concentrations in soil gas at 15 cm depth increased from a baseline of 10,000—15,000 Bq m^{-3} to a peak of 40,000 Bq m^{-3}. The method of soil gas sampling and analysis described in this paper allowed us to identify a band of elevated radon concentration only 3 m wide based on a field survey which took less than 1 h.

The accuracy of the LSC method has been demonstrated by calibration against field and laboratory measurements using an instrumental radon detector (AlphaGUARD™). The LSC method provided much better spatial resolution than the AlphaGUARD™ owing to the smaller gas volumes sampled. Another advantage of the LSC method is that, as long as a soil gas sample can be extracted, it is unaffected by soil moisture, unlike instruments such as the RAD7™. Szabó et al. (2013) have shown that seasonal variation in soil water content has a major influence on radon activity concentrations in soil gas. Our own field studies have shown that, if water content is too high (often the case in winter) then the physical process of extracting a soil gas sample is inhibited, although the analysis by LSC of any gas sample obtained is not compromised. Hence, the LSC method provides a promising way to explore variations in [222]Rn in relation to variable soil moisture contents from very dry to almost fully saturated. A disadvantage of LSC compared with instrumental methods is that it suffers from higher detection limits and so would not be generally suitable for measurements of radon in the free atmosphere unless used in conjunction with a pre-concentration method (Passo and Floekher, 1991; Buzinny, 1996); however, this is not required for most soil gas
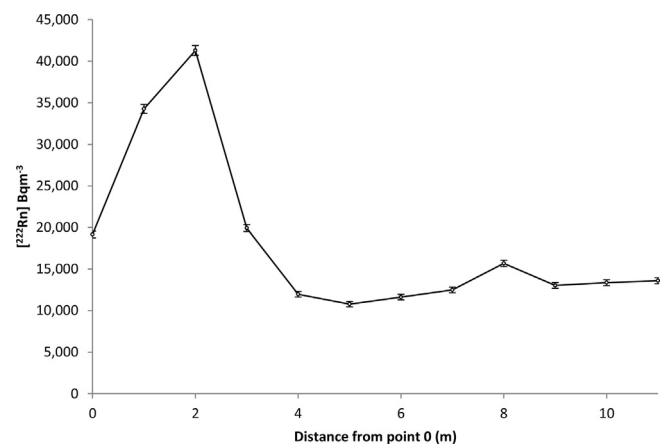

Fig. 10. Radon-222 activity concentrations measured in soil gas sampled at 15 cm depth on Cromford Meadow (UK, 53.110°N, 1.549°W) along a transect perpendicular to the boundary between the uraniferous Bowland Shale and Lower Carboniferous Limestone. Measurements were made using liquid scintillation counting; 2-sigma counting errors are plotted as vertical bars.

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applications.

Another drawback to our method is that it is time-limited by the half-life of ^{222}Rn. For the field studies we have carried out so far, it has been possible to return gas samples to the laboratory within 24 h of collection; in practice, a 2–3 day delay between sample collection and analysis would be feasible. However, samples collected in remote locations may be too far from a LSC facility to allow this method to be used. One other shortcoming of the method is that it cannot be used to measure ^{220}Rn, simply because its 55.6 s half-life is too short. For applications in which dual counting of radon and thoron are needed (e.g. Huxol et al., 2013) instrumental methods such as AlphaGUARD™ and RAD7™ would be needed.

4. Conclusions

We present a method for the sampling and analysis of soil gas for ^{222}Rn activity concentrations. Our primary motivation in proposing this method is to use measured ^{222}Rn activity concentration profiles in soils to improve quantitative understanding of the diffusion of radon and other important gases in soils whilst minimising any disturbance to soil gases *in situ*. To achieve this, our sampler is designed to minimise the volume of soil gas sampled and our preferred analytical method for the gas samples obtained is liquid scintillation counting (LSC). Analysis of soil gas samples by LSC has been rigorously compared with a commercially-available, factory calibrated ionisation chamber (AlphaGUARD™) and found to provide a convenient and appropriate method for the stated purpose.

Acknowledgements

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