

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

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16 **ABSTRACT**

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18 In order to exploit ^{222}Rn as a naturally-occurring tracer in soils we need to sample and measure
19 radon isotopes in soil gas with high spatial and temporal resolution, without disturbing *in situ* activity
20 concentrations and fluxes. Minimization of sample volume is key to improving the resolution with
21 which soil gas can be sampled; an analytical method is then needed which can measure radon with
22 appropriate detection limits and precision for soil gas tracer studies. We have designed a soil gas
23 probe with minimal internal dead volume to allow us to sample soil gas volumes of 45 cm^3 . Radon-
24 ^{222}Rn is extracted from these samples into a mineral oil-based scintillation cocktail before counting on
25 a conventional liquid scintillation counter. A detection limit of 320 Bq m^{-3} (in soil gas) is achievable
26 with a one hour count. This could be further reduced but, in practice, is sufficient for our purpose
27 since ^{222}Rn in soil gas typically ranges from $2,000 - 50,000\text{ Bq m}^{-3}$. The method is simple and provides
28 several advantages over commonly used field-portable instruments, including smaller sample
29 volumes, speed of deployment and reliability under field conditions. The major limitation is the
30 need to count samples in a liquid scintillation counter within 2 – 3 days of collection, due to the
31 short (3.824 day) radioactive half-life of ^{222}Rn . The method is not applicable to the very short-lived
32 (55 second half-life) ^{220}Rn .

33

34 **KEY WORDS**

35 radon-222; ^{222}Rn ; soil gas; tube sampler; liquid scintillation counting; ionisation chamber

36 INTRODUCTION

37

38 Radon isotopes (^{220}Rn and ^{222}Rn) occur naturally in all soils due to the decay of the parent nuclides
39 ^{224}Ra and ^{226}Ra , which ultimately derive from radioactive decay of ^{232}Th and ^{238}U , respectively.
40 Radon-220 (thoron) and ^{222}Rn (radon) both undergo alpha decay; each gives rise to a series of short-
41 lived alpha- and beta-emitting progeny which can impart significant radiation doses when inhaled.
42 Thus, many studies of radon gas are driven by the need to quantify radiation doses due to the efflux
43 of radon from soil into the atmosphere above, especially when this occurs into buildings. However,
44 radon gas can also be used as a naturally-occurring tracer which can assist in predicting earthquake
45 risk (Papastefanou, 2007) and in quantifying gas transport in soils. Radon flux measurements have
46 previously been used to determine diffusive properties of surface soils (Dorr and Munnich, 1990;
47 Lehman et al., 2000; Huxol et al., 2013) and also the diffusive transport characteristics of the near
48 surface atmosphere within short vegetation canopies (Nemitz et al., 2009). There is potential to use
49 radon in a wider range of applications, but we need flexible and easily applied methods to measure
50 activity concentrations in soil profiles. Soils are complex: porosity and tortuosity vary spatially,
51 whereas water content varies both spatially and temporally. Each of these properties exerts a
52 strong influence on the effective diffusivity of gases, including radon, in soils (Rogers and Nielson,
53 1991). Thus, we need to be able to sample and measure radon isotopes in soil gas with high spatial
54 and temporal resolution, preferably in ways that disturb *in situ* activity concentrations and fluxes as
55 little as possible.

56

57 Numerous methods can be used to sample and measure radon in soil gas. These include detectors
58 such as the Clipperton probe (Monnin and Seidel, 1998), Barasol™ (www.algade.com) or electret ion
59 chambers which can be embedded directly in the soil for periods ranging from days to years
60 (Antonopoulos-Domis et al., 2009). For long term measurements, gas-permeable tubes can be
61 buried in the soil, through which air is circulated and radon measured at the surface using a suitable
62 detector (Lehmann et al., 2000). Shorter-term measurements can be made by driving narrow tube
63 samplers into the soil and extracting soil gas under suction at defined depths. Dorr and Munnich
64 (1990) sampled soil gas by driving a narrow (6 mm \varnothing) stainless steel tube with a perforated tip into
65 the soil to depths ranging from 5 cm to as deep as 10 m. They extracted 200 – 300 cm³ of soil gas by
66 pumping through the tip of the sampler at a rate of 400 cm³ minute⁻¹. In a soil with air-filled porosity
67 of 40%, a soil gas sample of 300 cm³ will be drawn from a sphere with 5.64 cm radius, assuming
68 homogeneous and isotropic pore structure. This would give an uncertainty of almost 12 cm on the
69 vertical position of the sample. As soil wetness increases, so does this uncertainty; with an air-filled

70 porosity of 20%, the notional sampling sphere of a 300 cm³ gas sample has a radius greater than 7
71 cm and the minimum spacing of adjacent samples is, for all practical purposes, 10 cm. Similarly, the
72 minimum depth of sampling is 10 cm below the soil surface. Reducing the volume of the soil gas
73 sample will increase the spatial precision with which it can be taken (Born et al., 1990). Figure 1
74 indicates that, as sample volume is reduced to less than 100 cm³, the effective sampling radius,
75 hence the positional uncertainty on the sample, falls rapidly. Figure 1 also shows that the smaller
76 the gas sample, the less the influence of soil wetness (i.e. effective porosity) on the positional
77 uncertainty on the sample. Taking smaller soil gas samples also reduces the risk of drawing air from
78 the above-soil atmosphere between the outer surface of the sampling tube and the soil.

79

80 Some field-portable radon monitoring instruments (e.g. RAD7™ and AlphaGUARD™) are able to
81 pump soil gas from sampling tubes, either in one-off volumes or on a continuous cycle in which
82 samples are taken every few minutes for as long as necessary (www.durridge.com;
83 www.saphymo.com). The minimum volumes required for one-off samples are in the order of 2 dm³,
84 with corresponding sampling radii ranging from 10 - 20 cm, depending on the effective porosity of
85 the soil; some studies using stand-alone radon monitors have used sample volumes as large as 5 dm³
86 (Schroth et al., 2012). While such instruments are convenient to use, they are limited in their ability
87 to take samples with high spatial and temporal resolution.

88

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

92

93 **METHODS**

94

95 A probe (Figure 2) was designed to allow small volume samples of soil gas to be taken quickly and
96 conveniently down to soil depths of 1 metre. This consists of a length of aluminium tube (8 mm
97 external diameter) with a pointed tip behind which numerous 1 mm holes are drilled over a length
98 of 2 cm. A flexible silicone rubber tube with narrow (0.8 mm) internal bore passes through the
99 external aluminium tube and is sealed into position near the perforated sampling tip with a silicone
100 rubber plug. The design minimises 'dead volume' within the sampler (~0.5 cm³ in the sampler head
101 and 0.5 cm³ m⁻¹ in the silicone tube). The length of aluminium tube can be varied from 15 cm to 1
102 metre, to suit the required depth of sampling. A brass elbow joint at the upper end of the
103 aluminium tube provides a conduit in which the silicone rubber tube is protected from the pressure

104 needed to push the tube sampler into the soil to the required sampling depth. A plastic tap with a
105 Luer fitting allows a disposable 20 cm³ syringe to be attached to the end of the silicone rubber tube –
106 this syringe is used to withdraw a gas sample through the sampling probe from the required soil
107 depth.

108
109 In practice the first aliquot (<5 cm³) of soil gas withdrawn from the sampler, which includes the
110 'dead volume', is discarded. 15 cm³ of soil gas are then withdrawn and injected into a pre-evacuated
111 glass vial (Exetainer®, www.exetainer.com) through a rubber septum. Each vial (12 cm³) is prepared
112 by half-filling with 6.6 cm³ of a liquid scintillation cocktail (Pro-Scint Rn™, Meridian Biotechnologies
113 Ltd.), leaving an evacuated volume of 5.4 cm³. Injecting 15 cm³ of soil gas into this volume results in
114 an 'overpressure' of approximately 2 bar. A further two 15 cm³ aliquots of soil gas are withdrawn
115 from the soil via the sampling probe and injected into separate Exetainer® vials, thus giving triplicate
116 vials for each sampling point and a nominal total of 45 cm³ of soil gas extracted per sampling point
117 (experimental analysis of Type A error gave an actual value of 44.89 ± 0.03 cm³). If a vertical profile
118 of soil gas samples is needed, the probe is inserted to the shallowest depth (usually 10 cm from the
119 soil surface) from which triplicate gas samples are withdrawn. The probe is then pushed to the next
120 sampling depth and the procedure repeated until soil gas samples have been taken over the
121 required sequence of depth intervals.

122
123 Once injected into the Exetainer® vials, ²²⁰Rn and ²²²Rn are free to partition into the liquid
124 scintillation cocktail. Pro-Scint Rn™ is mineral oil-based and contains 20-40% 'pseudocumene'
125 (1,2,4-trimethylbenzene) as a liquid scintillator. It was chosen for this application as it is specifically
126 formulated to 'extract' radon from water or gas samples with a partition coefficient of
127 approximately 50 (Clever, 1979). The extraction process is facilitated by shaking the vials vigorously
128 by hand before transporting to the laboratory where, after at least 1 hour contact time, the liquid
129 contents of the triplicate Exetainer® vials are decanted into a single low-potassium borosilicate glass
130 scintillation vial, giving a 20 cm³ volume of scintillation cocktail per vial. The scintillation vials are
131 then placed into a liquid scintillation counter (we used a Packard Tri-Carb 2100TR) where they are
132 dark-adjusted for three hours before counting across an energy range from 0 to 2 MeV. By the time
133 the vials are counted any ²²⁰Rn (T_{1/2} ~ 55 s) has completely decayed and counts collected should
134 result solely from ²²²Rn and its short-lived progeny, ²¹⁸Po, ²¹⁴Pb, ²¹⁴Bi and ²¹⁴Po. With physical half-
135 lives of 3.11 minutes, 26.8 minutes, 19.9 minutes and 0.00016 seconds, respectively, these decay
136 products need approximately four hours to achieve secular equilibrium with ²²²Rn. Thus, the dark-
137 adjustment period, plus the time needed to count a reagent blank 'background' sample (1 hour),

138 ensure that the samples contain combined activities of parent and progeny which are representative
139 of the original ^{222}Rn activity in each soil gas sample.

140

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

160

161 To verify the comparability of ^{222}Rn measurements using both methods in the field, a series of soil
162 gas samples were taken from an experimental plot at Sutton Bonington, UK (52.833°N , 1.249°W).
163 Samples were taken at 60 cm depth from randomised points within a $15 \times 15 \text{ m}$ area on seven
164 different days between September and December 2013. Soil gas samples were taken using the
165 sampling probes described above. The soil gas was extracted using an AlphaGUARD™ radon monitor
166 coupled to an AlphaPUMP™, at a rate of $1 \text{ dm}^3 \text{ minute}^{-1}$ for 2 minutes. The volume of the ionisation
167 chamber is 0.62 dm^3 , hence approximately two chamber volumes were pumped through to purge
168 the monitor and the third chamber volume was sealed in the ionisation chamber for counting. A
169 time interval of 1 minute was used to integrate the counts collected and an overall counting period
170 of 30 minutes was used for each soil gas sample. As in the laboratory chamber experiment, triplicate
171 15 cm^3 syringe samples of gas were taken directly from the ionisation chamber of the AlphaGUARD™

172 monitor and treated as previously described for soil gas samples. These samples were analysed
173 using LSC and compared with data obtained using the AlphaGUARD™ in the field.

174

175 The same experimental plot was used to sample soil gas over depth profiles from 10 to 60 cm.
176 These samples were taken at randomly located points within the 15 × 15 m experimental area by
177 inserting the sampling probe in 10 cm increments, as described above. The overall time taken to
178 insert the probe to the required depth and then to extract 3 × 15 cm³ aliquots of soil gas was
179 approximately 5 minutes, giving a combined sampling time of 25 - 30 minutes per profile. Gas
180 samples were injected into Exetainer® vials, prepared as described above, and taken directly to the
181 laboratory for analysis. A further field test of the method was made by carrying out a survey of the
182 horizontal distribution of ²²²Rn activity concentrations in soil developed in alluvium above the
183 junction between two rock types in the Peak District, Central England. Soil gas was sampled on
184 Cromford Meadow (53.11° N, 1.55° W) at 15 cm depth along a transect perpendicular to the
185 boundary between the uraniferous Bowland Shale and Lower Carboniferous Limestone. The
186 approximate location of the boundary was determined using a geological map (BGS, 1963) and
187 magnetic bearing from a visible fault line. Samples were then collected over a distance of 11 m at
188 1 m spacings. This sampling exercise took less than one hour.

189

190 **RESULTS and DISCUSSION**

191

192 Minimization of sample volume is key to improving the spatial and temporal resolution with which
193 soil gas can be sampled although few studies on soil gas sampling specifically address this problem.
194 In a radon detector such as AlphaGUARD™, the volume of the ionization chamber dictates the
195 minimum soil gas volume which can be measured. When using LSC to measure radon in soil gas
196 there is a balance between the volume of gas sampled and the count rate detected. During
197 development of our method we took gas sample volumes ranging from 10 cm³ - 20 cm³, each taken
198 in triplicate to give total sample volumes of 30 cm³ - 60 cm³. The optimum volume was 45 cm³ (i.e. 3
199 × 15 cm³) which increased the count rate obtained from 30 cm³ samples in a linear fashion (Figure
200 3). Larger (60 cm³) samples further increased the count rate, but the gain in counts was not
201 proportional to the increased gas volume taken.

202

203 Liquid scintillation counting of soil gas samples measures the combined contribution from alpha and
204 beta particles from ²²²Rn and its short-lived progeny. It is not possible from the energy spectrum
205 obtained during LSC to identify the presence of individual emitted particles which might definitively

206 identify the presence of ^{222}Rn . However, due to the fact that its 3.824 day radioactive half-life is
207 considerably longer than the half-lives of its four immediate descendants, it is possible to identify
208 ^{222}Rn as the main source of radioactivity in a sample by comparing the declining count rate over
209 several days with the theoretical physical decay curve for ^{222}Rn . Ingrowth of the much longer-lived
210 ^{210}Pb ($T_{1/2} = 22.3$ years) is too slow to contribute to the count rate over a period of hours to days.
211 Figure 4 compares repeated counts of the same soil gas sample with the theoretical decay curve for
212 ^{222}Rn , indicating that the counts were indeed due solely to ^{222}Rn and its short-lived progeny. Figure 4
213 also indicates that count rates in a typical soil gas sample were achieved with 2-sigma precision
214 ranging from 2 - 10%.

215

216 Having established that ^{222}Rn could be identified and counted with good precision in a composite soil
217 gas sample of 45 cm^3 , a calibration curve between the AlphaGUARD™ (Bq m^{-3}) and LSC (CPM net)
218 methods was drawn, based on measurements in a laboratory chamber using barium-radium
219 sulphate as a source of ^{222}Rn . This curve was approximately linear but could be described most
220 accurately, especially at LSC count rates less than approximately 50 CPM, using a power function
221 with an exponent just greater than 1 (1.0435). This weakly non-linear function (the AlphaGUARD™
222 manufacturer's stated linearity error is <3%) provided a strong fit ($R^2 = 0.996$) to the experimental
223 measurements over a range of ^{222}Rn activity concentrations spanning almost four orders of
224 magnitude. The limit of detection was calculated (according to Currie, 1968) to be 3.33 CPM net for
225 a 60 minute count time; this equates to a ^{222}Rn activity concentration of 320 Bq m^{-3} . Doubling the
226 count time to 120 minutes would reduce the limit of detection to 2.35 CPM net, equivalent to 220
227 Bq m^{-3} . The limit of detection may be further decreased by raising the lower energy threshold above
228 zero MeV which would exclude the high background lower energy radiation, thus raising the signal-
229 to-noise ratio (Genereux and Hemond, 1991). Our current detection limit is comparable to LSC
230 methods using other liquid scintillation counters, including Quantulus™ (Buzinny et al., 2009). It is
231 relatively high compared with some other methods, including instrumental detectors such as RAD7™
232 and AlphaGUARD™ (typically 20 Bq m^{-3}), but suitable for most soil gas applications; activity
233 concentrations of ^{222}Rn measured in soil gas commonly range from 2,000 - 50,000 Bq m^{-3} (Schubert
234 et al., 2002).

235

236 In our field comparison of AlphaGUARD™ and LSC, ^{222}Rn activity concentrations in soil gas ranged
237 from $936 (\pm 780)$ - $24,004 (\pm 3448)\text{ Bq m}^{-3}$ (1-sigma uncertainties from AlphaGUARD™ measurements
238 in parentheses). Figure 6 shows data from a typical AlphaGUARD™ counting cycle which lasted 30
239 minutes, during which counts were integrated over one minute intervals. An initial peak in activity

240 concentration at 2 – 3 minutes is given by the combined counts from ^{220}Rn and ^{222}Rn . After 5
241 minutes, the counts from ^{220}Rn have been lost by radioactive decay and counts from ^{222}Rn and its
242 short-lived progeny are collected for the next 20 minutes before purging the ionization chamber for
243 5 minutes so that the next sample can be collected. The average ^{222}Rn activity concentration for the
244 sample is calculated from the 1 minute counts taken between 5 and 25 minutes. 45 cm^3 gas samples
245 were taken directly from the ionization chamber to be analysed by LSC and the results of the two
246 methods are compared in Figure 7. The relationship between AlphaGUARD™ activity concentrations
247 and CPM net by LSC was more strongly log-linear than in the laboratory chamber experiment and
248 could be described using a power function with an exponent of 1.253 ($R^2 = 0.859$). The predictive
249 accuracy of the calibration curve in Figure 5 was tested by converting CPM net values from the field
250 samples in Figure 7 to ^{222}Rn activity concentrations (Bq m^{-3}). These calculated activity concentrations
251 were then compared with those measured directly using AlphaGUARD™ in the field (Figure 8).
252 Linear regression of the two data sets yielded a coefficient of determination (R^2) of 0.742. A χ^2 test
253 ($p = 0$) allows us to conclude that the laboratory calibration between the two methods is sufficiently
254 reliable for LSC to be used as a stand-alone method for ^{222}Rn detection in small soil gas samples.

255

256 Given the design of the soil gas sampling probe, the method is particularly suitable for measuring
257 ^{222}Rn activity concentrations in soil profiles over a depth range from close to the soil surface (5 – 10
258 cm) to 1 m. Two example profiles are shown in Figure 9, both measured at randomly-located points
259 within the 15×15 m experimental plot described above. Several published studies show that ^{222}Rn
260 diffusion in soils can be described by a single effective diffusion coefficient (Nazaroff, 1992). This is
261 convenient since it allows ^{222}Rn fluxes at the soil surface to be calculated by fitting an analytical
262 solution of the 1-D diffusion equation. However, it is known that complexities arise in the
263 distribution of radon through the soil profile due to changes in the effective porosity of the soil and
264 the radon emanation rate associated with variations in soil mineralogy and other properties. For
265 example, Antonopoulos-Domis et al. (2009) showed that the radon activity concentration profile in a
266 Greek soil was strongly influenced by a change from sandy to clayey texture. In our study, the shape
267 of the ^{222}Rn activity concentration profiles was not monotonic, but clearly influenced by changes in
268 soil porosity. In Figure 9 this can be seen at a depth of 30 – 40 cm where the soil texture changed
269 from sandy loam in the upper part of the profile to sandy clay below. A simple analytical solution of
270 the 1-D diffusion equation cannot be fitted to either of the two ^{222}Rn profiles in Figure 9 since the
271 effective diffusion coefficient is not constant with depth. It is possible, however, to approximate the
272 shapes of the measured ^{222}Rn activity concentration profiles with a numerical solution of the 1-D
273 diffusion equation, assuming a vertically uniform ^{222}Rn production rate (calculated according to

274 Chamberlain, 1991) and discrete diffusion coefficients for different parts of the soil profile. In Figure
275 9(a) the ^{222}Rn production rate was assumed to be $0.056 \text{ Bq m}^{-3} \text{ s}^{-1}$ and the effective diffusion
276 coefficients were $5.25 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for the 0 – 10 cm soil depth, $1.75 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for the 10 – 30 cm
277 soil depth and $1.05 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for the 30 – 70 cm soil depth. For Figure 9(b) the assumed ^{222}Rn
278 production rate was $0.1 \text{ Bq m}^{-3} \text{ s}^{-1}$ and the effective diffusion coefficients were $3.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for
279 the 0 – 40 cm soil depth and $1.05 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for the 40 – 70 cm soil depth. The diffusion
280 coefficients for both profiles lie within the range of effective diffusion coefficients for ^{222}Rn in soils
281 presented by Nazaroff (1992). One of the most useful applications of measured soil activity
282 concentration profiles of ^{222}Rn is to estimate effective gas diffusion coefficients for soils, which can
283 then be scaled to other important soil gases such as CH_4 , CO_2 and N_2O whose diffusive behaviour is
284 difficult to estimate directly due to complications including interactions with soil organisms (eg. Born
285 et al., 1990; Dorr and Munnich, 1990). The fact that different values of effective diffusion
286 coefficients have to be used to model ^{222}Rn activity concentration profiles, especially in the upper
287 soil layers, underlines the complexity of behaviour of radon gas in soils and the need for high spatial
288 resolution measurements to provide better understanding of the factors which control its
289 distribution and flux.

290

291 The second field test of our method involved a horizontal survey of ^{222}Rn in soil gas in the vicinity of
292 a geological discontinuity which is suspected to result in a localised increase in radon flux at the soil
293 surface due to authigenic uranium within the Bowland Shale (Leeder et al., 1990). The influence of
294 underlying geology on radon activity concentrations in surface soil (10 – 30 cm depth) soil is
295 expected to reduce with increasing thickness of soil overlying the bedrock. Nevertheless, Figure 10
296 shows that, within 2 metres of where the boundary was suspected to lie between the Bowland Shale
297 and Carboniferous Limestone, ^{222}Rn activity concentrations in soil gas at 15 cm depth increased from
298 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
299 analysis described in this paper allowed us to identify a band of elevated radon concentration only 3
300 metres wide based on a field survey which took less than one hour.

301

302 The accuracy of the LSC method has been demonstrated by calibration against field and laboratory
303 measurements using an instrumental radon detector (ALPHAGUARD™). The LSC method provided
304 much better spatial resolution than the ALPHAGUARD™ owing to the smaller gas volumes sampled.
305 Another advantage of the LSC method is that, as long as a soil gas sample can be extracted, it is
306 unaffected by soil moisture, unlike instruments such as the RAD7™. Szabo et al. (2013) have shown
307 that seasonal variation in soil water content has a major influence on radon activity concentrations

308 in soil gas. Our own field studies have shown that, if water content is too high (often the case in
309 winter) then the physical process of extracting a soil gas sample is inhibited, although the analysis by
310 LSC of any gas sample obtained is not compromised. Hence, the LSC method provides a promising
311 way to explore variations in ^{222}Rn in relation to variable soil moisture contents from very dry to
312 almost fully saturated. A disadvantage of LSC compared with instrumental methods is that it suffers
313 from higher detection limits and so would not be generally suitable for measurements of radon in
314 the free atmosphere unless used in conjunction with a pre-concentration method (Passo and
315 Floekher, 1991; Buzinny, 1996); however, this is not required for most soil gas applications.

316

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

325

326 **CONCLUSIONS**

327

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

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337

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421 FIGURES

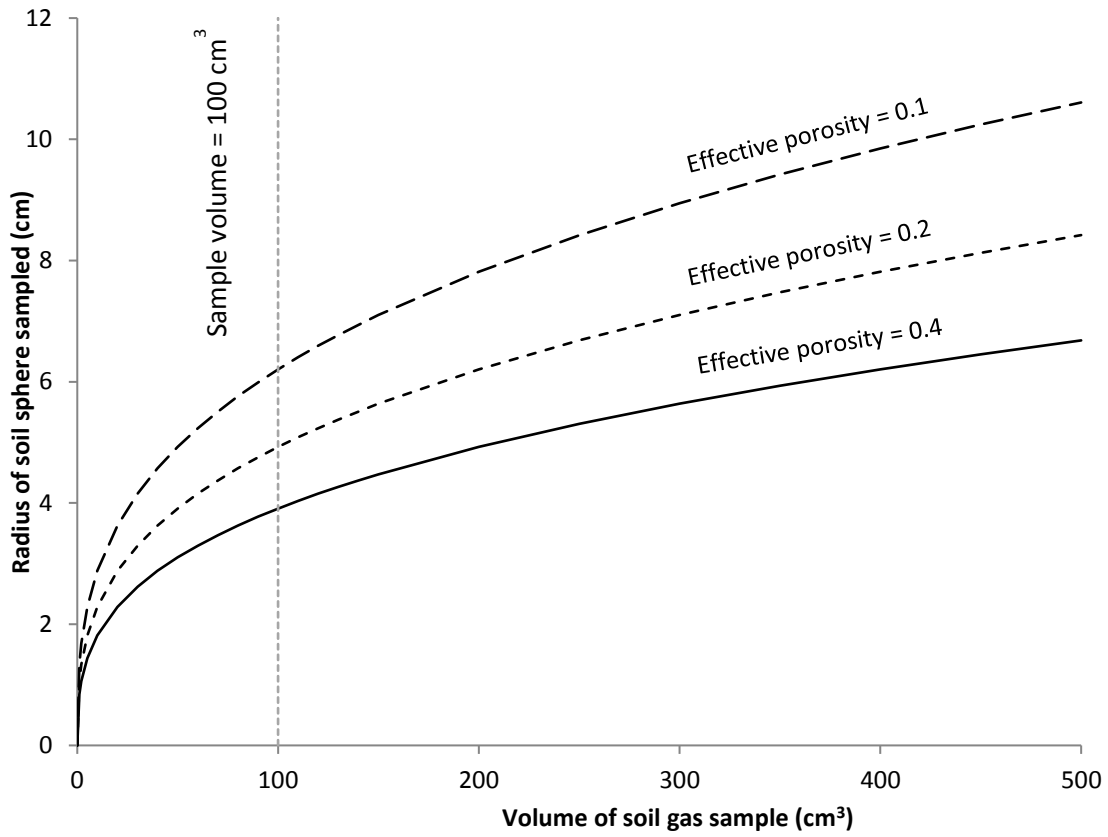
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429 **Figure 1.** Influence of soil gas sample volume on effective radius of soil sphere sampled.

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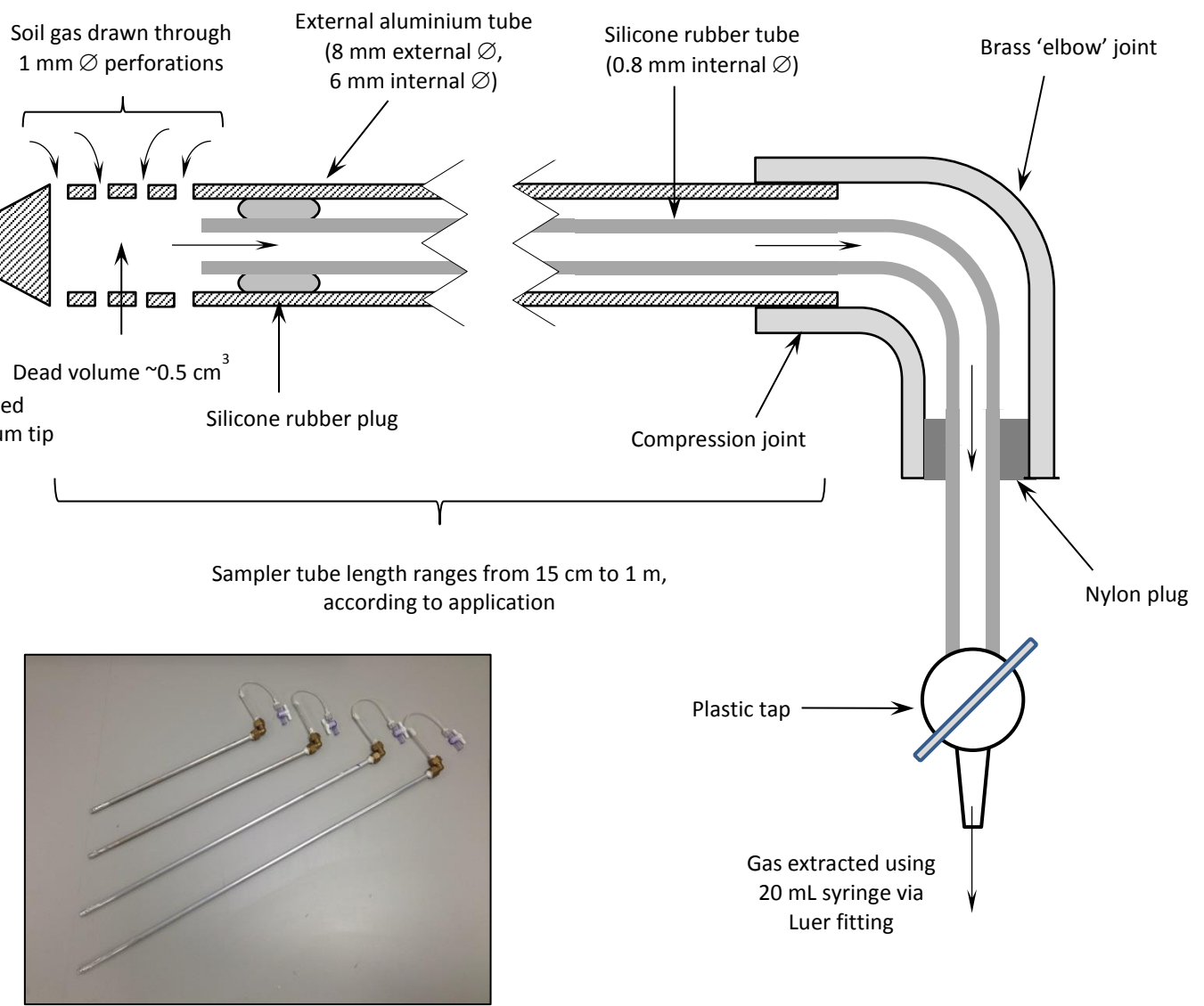
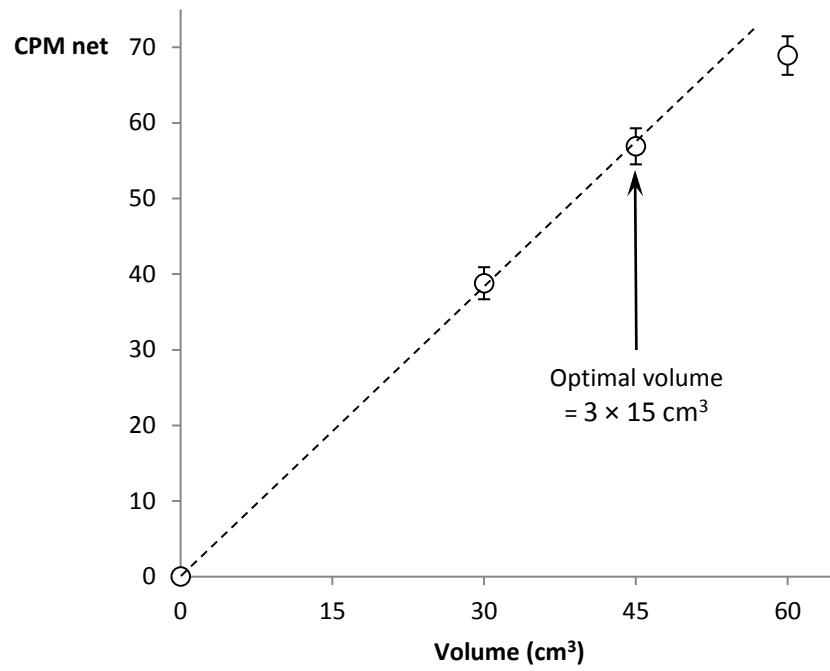


Figure 2. Cross-sectional diagram of soil gas sampling tubes. Sampler head dead volume $\sim 0.5 \text{ cm}^3$; sampler tube dead volume = $0.5 \text{ cm}^3 \text{ m}^{-1}$. Inset shows samplers of different lengths, from 45 cm to 1 m.



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473 **Figure 3.** Radon-222 activity (CPM net) in ProScint Rn™ liquid scintillation vial versus volume of soil
474 gas injected / partitioned in scintillation cocktail. Vertical bars represent 2-sigma counting errors.

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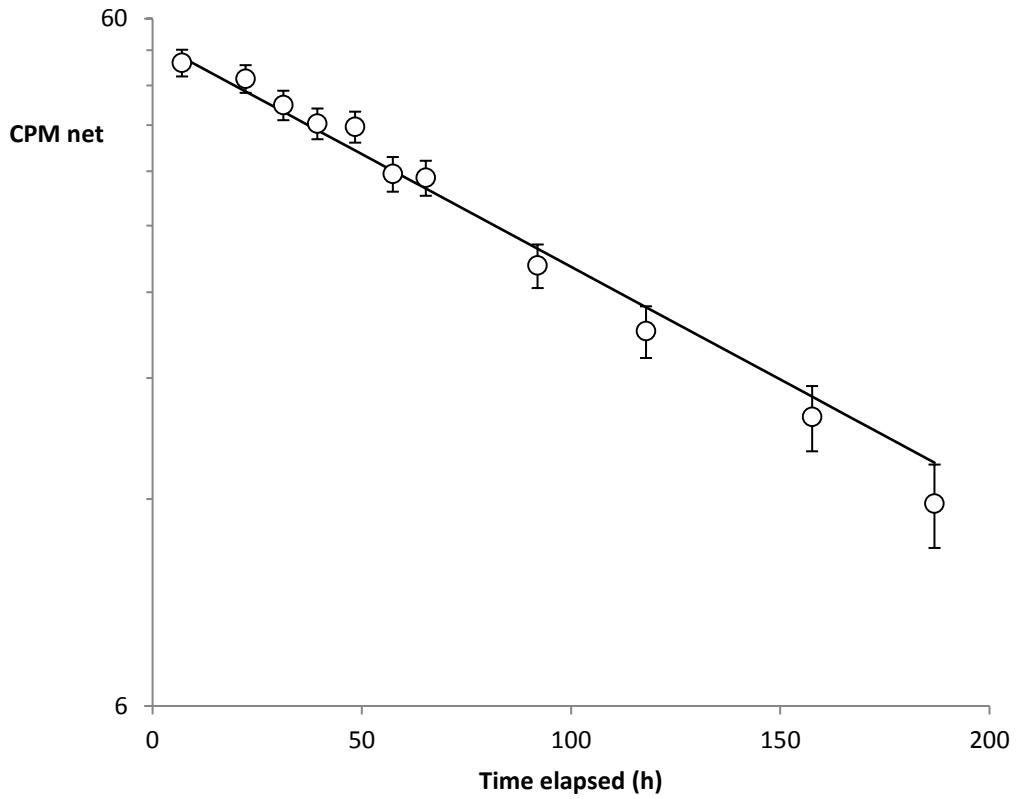
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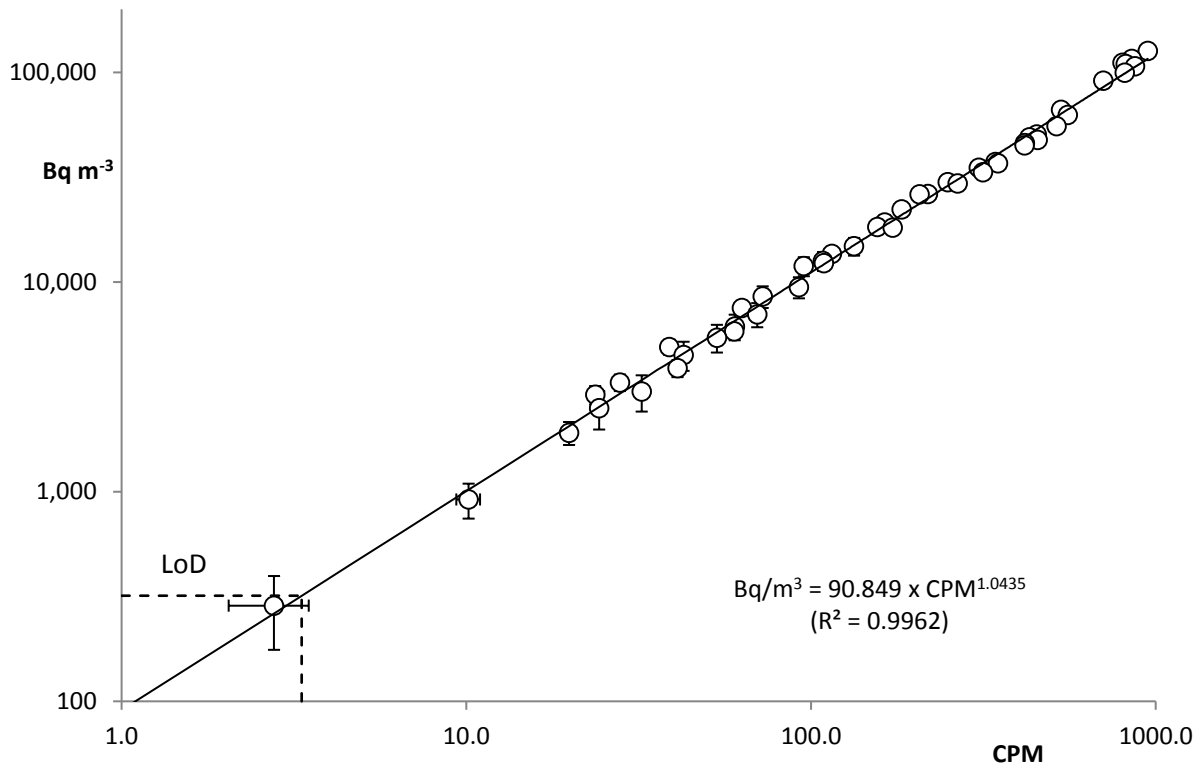
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486 **Figure 4.** Radon-222 activity (CPM net) in a liquid scintillation vial counted repeatedly after sampling
487 from soil gas and partitioning into ProScint Rn™ liquid scintillation cocktail. Vertical bars represent
488 2-sigma counting errors. The solid line shows the curve of declining activity expected if ²²²Rn and its
489 short-lived progeny are the sole contributors to radioactivity within the vial; the measured and
490 calculated activities were statistically indistinguishable ($\chi^2 = 1.001$, $p < 0.001$).

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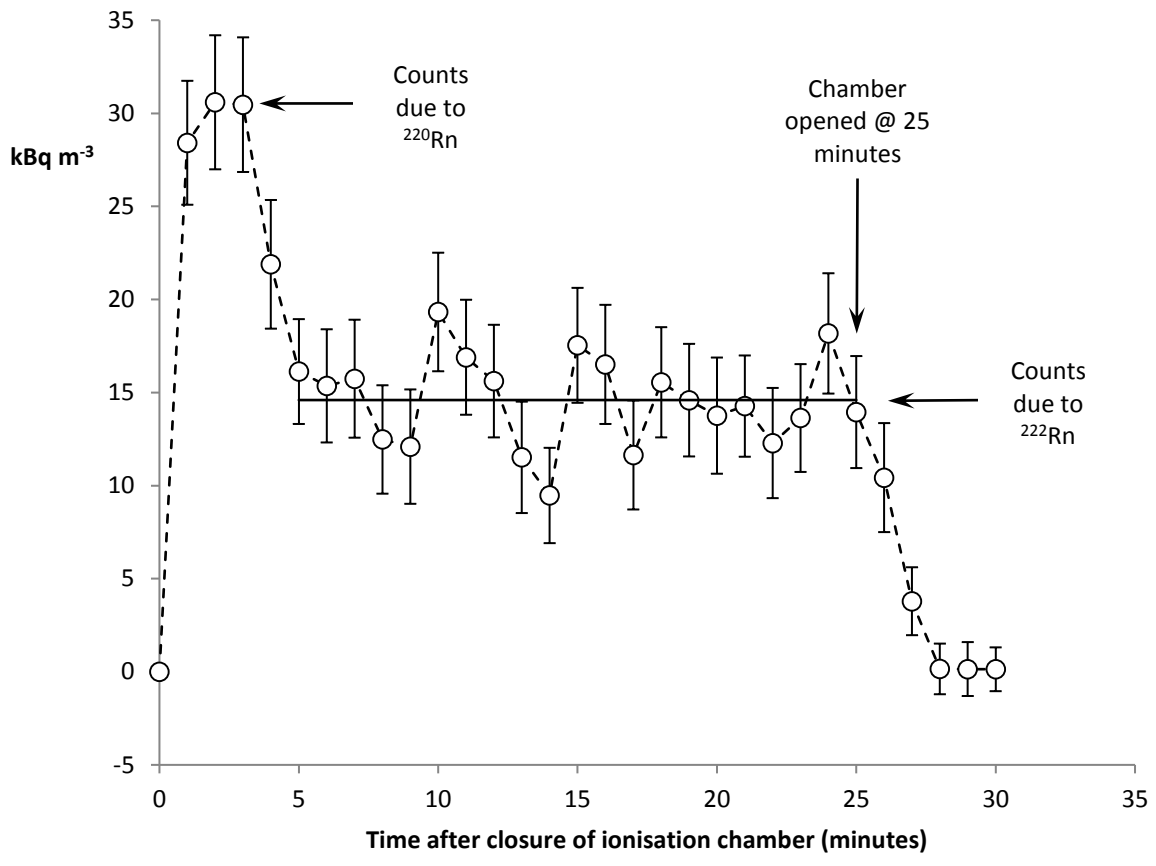
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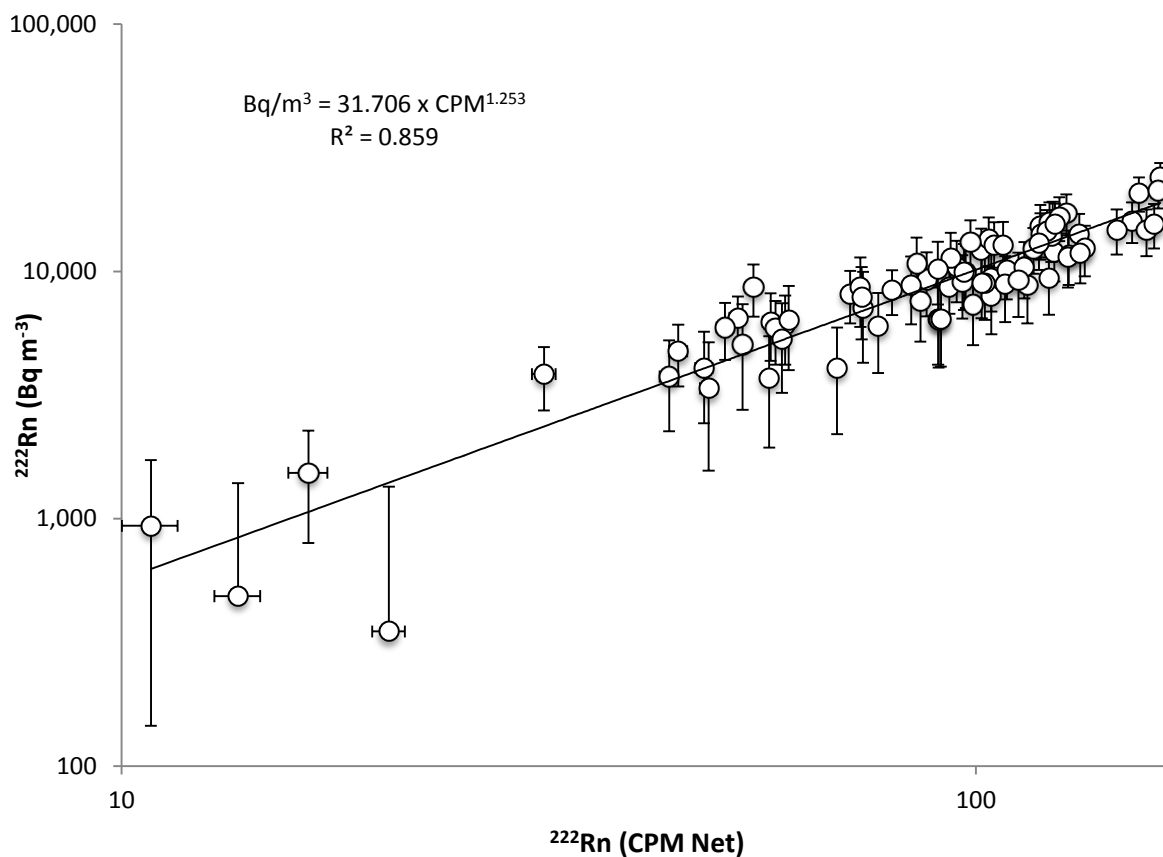
Figure 5. Radon-222 activities in gas samples obtained using two detection methods: liquid scintillation counting (CPM net) and an ionisation chamber (AlphaGUARD™, Bq m⁻³). The AlphaGUARD™ was used in ‘flow’ mode with a 10 minute count. Measurements were made using gas samples from a closed chamber system with barium-radium sulphate scale as the source of ²²²Rn; 45 cm³ (3 × 15 cm³) samples for liquid scintillation counting were taken directly from the ionization 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 minutes in ProScint Rn™.

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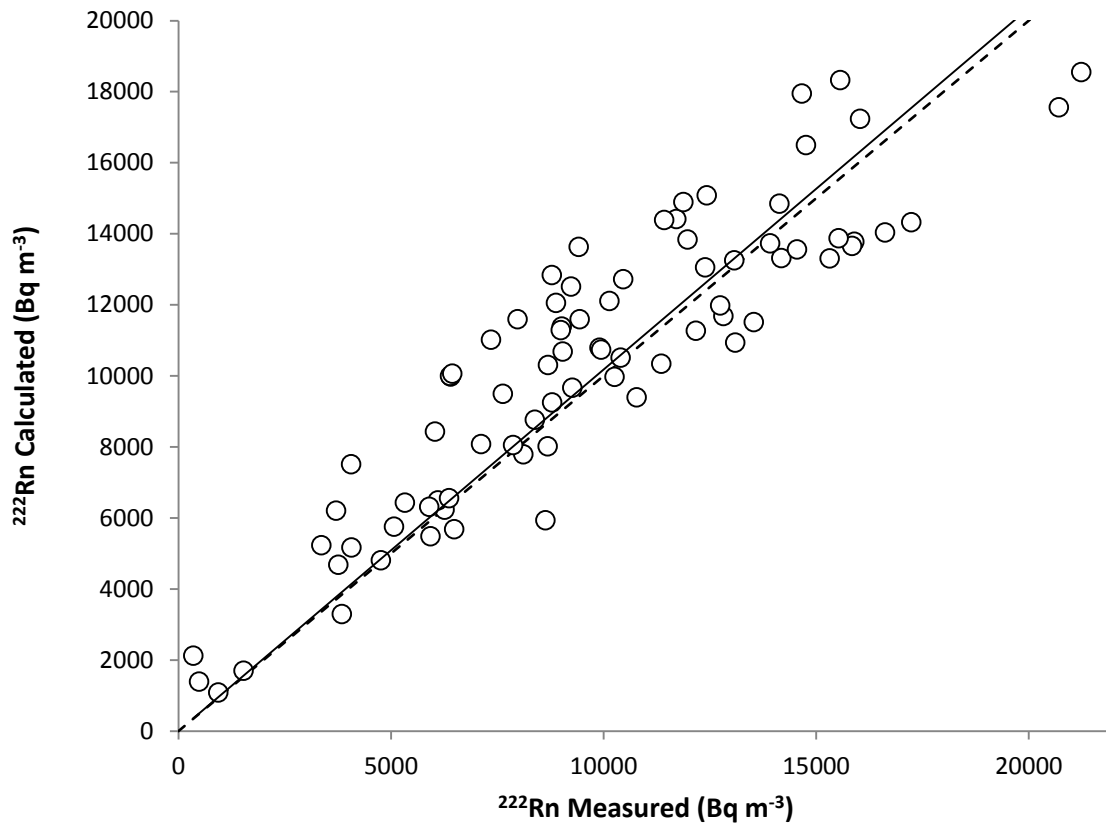
Figure 6. Typical activity concentration data from a 30 minute AlphaGUARD™ counting cycle in the field. The X axis shows time after a soil gas sample is sealed in the ionisation chamber. Vertical bars represent 1-sigma errors on 1 minute counts.



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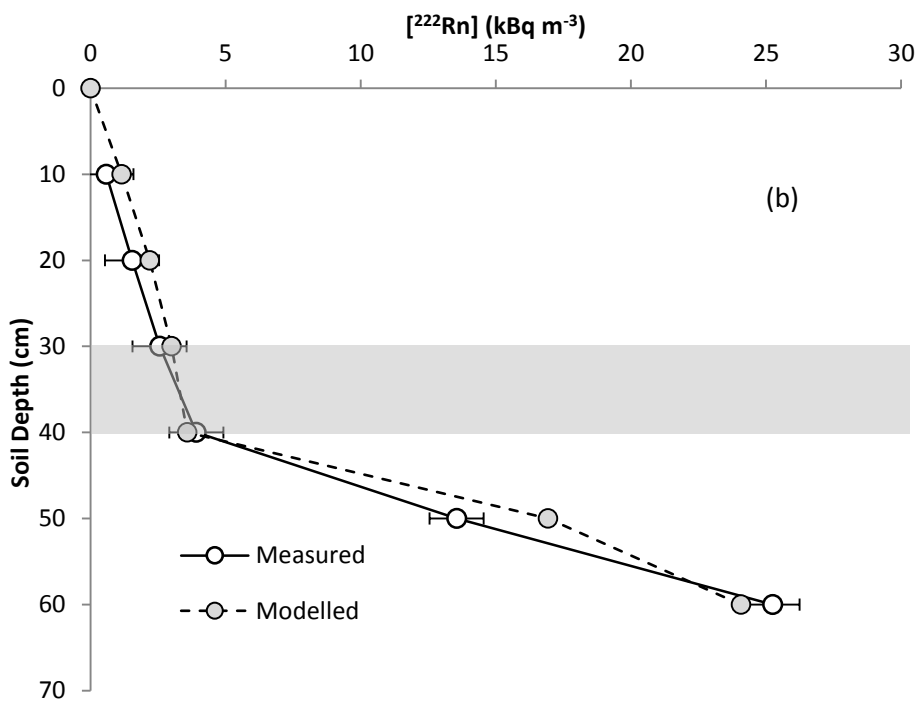
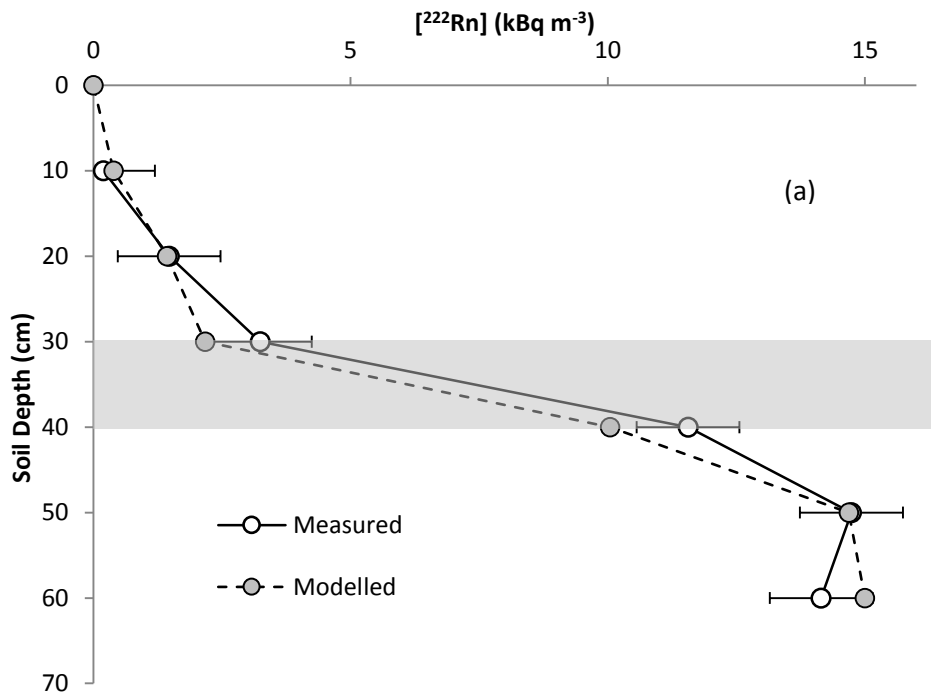
531 **Figure 7.** Radon-222 activity concentrations in field samples of soil gas (60 cm depth) measured on
 532 seven different days between September and December 2013 using two detection methods: liquid
 533 scintillation counting (CPM net) and an ionisation chamber (AlphaGUARD™, Bq m⁻³). The
 534 AlphaGUARD™ was used in ‘flow’ mode with a 1 minute count time following purging of the
 535 ionisation chamber with two chamber volumes (total volume sampled ~ 2 litres). 45 cm³ (3 × 15
 536 cm³) samples were removed directly from the ionisation chamber for analysis by LSC. Vertical and
 537 horizontal bars are 1-sigma errors.



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540 **Figure 8.** Comparison of ^{222}Rn activity concentrations in field samples of soil gas (60 cm depth)
 541 measured on seven different days between September and December 2013. Measurements were
 542 made in the field with AlphaGUARD™ (X axis) and in the laboratory by liquid scintillation counting,
 543 using the calibration curve in Figure 5 to convert CPM (net) to Bq m^{-3} . The dashed line is the line of
 544 unity while the solid line is a linear regression ($R^2 = 0.742$). The measured and calculated values
 545 were statistically indistinguishable ($\chi^2 = 0$, $p = 0$).



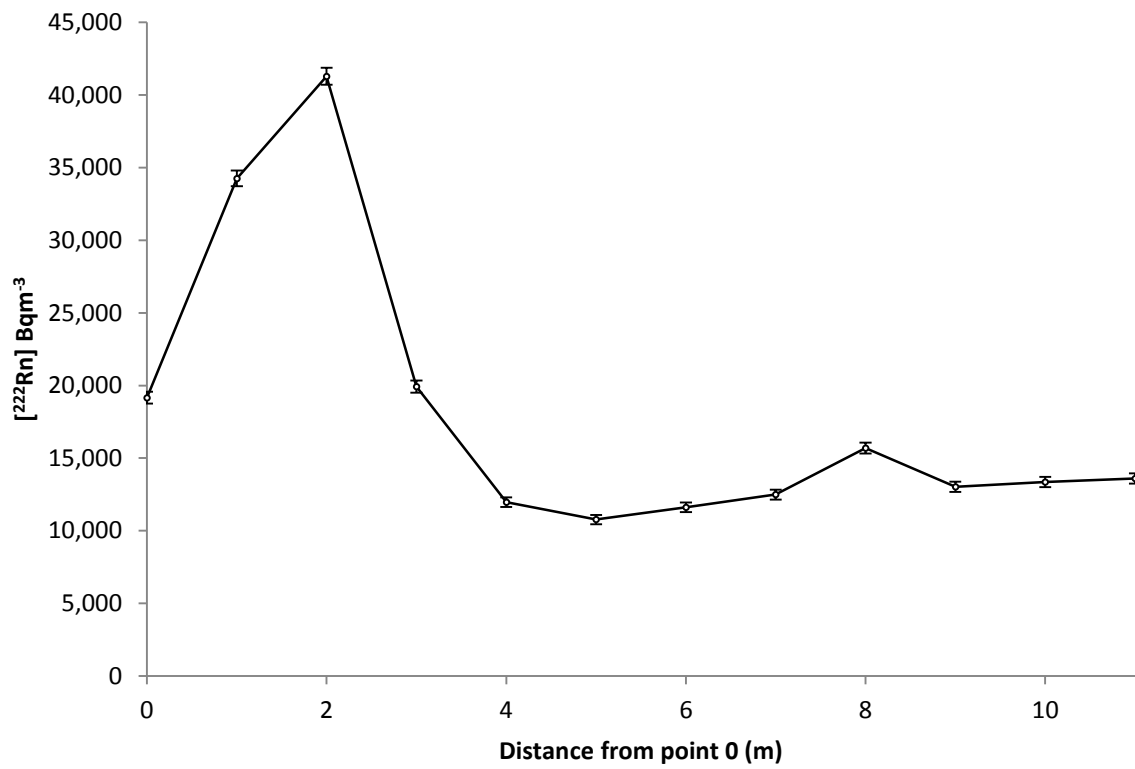
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549 **Figure 9.** Two depth profiles of ²²²Rn measured within a 15 m × 15 m plot in Sutton Bonington soil.
 550 Also shown are modelled curves using numerical solutions of the 1-D diffusion equation (see text for
 551 model parameters). The horizontal grey bar indicates the depth at which the soil texture changes
 552 from sandy loam to sandy clay, with a consequent change in effective diffusion coefficient for ²²²Rn
 553 and other gases. Error bars represent 2-sigma counting errors on measured ²²²Rn activity
 554 concentrations.

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