

Testing the Radon-in-Water Probe set-up for the measurement of radon in water bodies.

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ABSTRACT

Naturally occurring ²²²Rn is increasingly recognized as a powerful environmental tracer in hydrology. Radon-in-water concentrations can be measured in the field by stripping radon from a water sample into a gas volume and measuring the respective radon-in-gas concentration using a portable radon-in-gas monitor. Alternatively, radon is firstly extracted from the water body by diffusion through a radon exchanger such as polypropylene (PP) tubing and then is measured using a radon-in-gas monitor, connected in closed-loop to the PP membrane. The paper discusses results of field experiments in which the Radon-in-Water Probe (DurrIDGE co.), a 2.2 m long PP tubing, connected to a RAD7 monitor (method A), is used to determine dissolved radon concentration in four water bodies characterized by different water flow velocity and radon concentration. The efficiency of this method is validated by comparison with two established methods, gamma-ray spectrometer + charcoal canister (method B) and RAD7 monitor + Big Bottle RAD H2O accessory (method C). Relative efficiency of method A is directly proportional to water flow velocity, ranging from about 0.50 ± 0.05 at 0.01 m/s to about 0.92 ± 0.08 at 0.57 m/s. A minimum of 2-3 hours are needed to collect enough records to asymptotically fit radon-in-gas data and obtain equilibrium radon concentration, which is then converted into radon-in water concentration, considering the temperature-dependency of radon partition coefficient between water and air. Equilibrium condition is reached after about 6 - 8 hours. No correlation was found between relative efficiency and radon concentration. An equation is proposed to correct radon data as a function of water flow velocity, even for poorly moving water bodies. The DURRIDGE Water Probe is useful to monitor radon-in-water levels, without the potential risk of radon loss during water sampling and sample handling. However, it must be pointed out that duplicate or triplicate sampling using other methods similarly permit to evaluate whether radon loss is an issue.

Keywords: Radon-in-Water Probe; RAD7; water flow; equilibrium; Valle della Caffarella; Italy

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1. Introduction

During the last decades naturally occurring ^{222}Rn (hereafter referred to as “radon”) has become an established aqueous tracer in the field of environmental geosciences. Applications include the interactions between groundwater and surface water bodies such as rivers, lakes, or the open sea (Cable et al., 1996; Corbett et al., 1997; Burnett et al., 2001; Burnett et al., 2003; Dulaiova et al., 2005; Schubert et al., 2008; Su et al., 2014; Hatje et al., 2017), the time dependence of groundwater migration processes (Hoehn and von Gunten, 1989; Hamada, 2000) and residual aquifer contamination with Non-Aqueous Phase Liquids (NAPLs, Semprini et al., 2000; Schubert, 2015; De Simone et al., 2017; Castelluccio et al., 2018).

The examples given above demonstrate the broad applicability of radon as environmental aqueous tracer and confirm the need for methods that allow straightforward radon-in-water analysis. Determination of radon concentrations in water is usually made in the laboratory, but on-site methods have been developed (Jobbagy et al., 2017).

Analytical set-ups are generally based on radon stripping from the water into a closed circuit air stream where its concentration is measured by means of radon-in-air monitors. In most cases the stripping process is by bubbling the air through the water or by spraying the water into the air stream (Schubert et al., 2008). Alternatively, radon can be firstly accumulated onto specific materials which absorb radon, such as charcoal hosted in canister (Mancini and Giannelli, 1995; Procopio, 1996; Galli et al., 1999) or accumulators made of polydimethylsiloxane (PDMS) mixed with activated charcoal (AC, Voltaggio and Spadoni, 2013) and then counted. The main disadvantage of charcoal canisters and PDMS mixed with AC accumulators is the necessity of laboratories located nearby, where measurements should be carried out as soon as possible in order to maintain a good counting statistics, due to radon decay.

Additionally, other materials such as polypropylene placed underwater are able to absorb dissolved radon and exchange it with the air flowing through a closed-loop circuit, connected to a radon monitor (Kienzler and Naef, 2008; Schubert et al., 2008; Peano et al., 2011; Gilfedder et al., 2013). The Radon-in-Water Probe, marketed by Durrige Co., consists of about 2,2 m long Accurel tubing which has these properties.

The Radon-in-Water Probe is promoted for collecting and measuring radon from large water bodies, without the potential risk of radon loss during water sampling or water handling. The probe just needs to be submerged at the desired depth, left for a period of time and then connected to a RAD7 instrument which progressively monitor the increase of radon captured by the probe and simultaneously transferred to the air (Durrige, 2017). This process is controlled by the Ostwald coefficient and is temperature and salinity dependent (Schubert et al., 2012).

Here, we want to characterise the in-situ use of such device in small and shallow spring lakes and in small rivers both with high or low water flow, using surface water and groundwater with different radon concentration. We want to verify the efficiency of the technique, the time required to reach the equilibrium, considering the uncertainties associated to different radon levels. Equilibrium conditions will be verified and assessed using non-linear curve fitting calculation.

2. Study area

The area chosen for the experiments is Valle della Caffarella (Roma, Italy), already selected for calibration of devices and techniques regarding water sampling, water storage and measurements of radon dissolved in groundwater (De Simone et al., 2015; Tuccimei et al., 2015; Lucchetti et al., 2016). The site (Fig. 1) is very convenient for this kind of investigation because it is located very close to our laboratories, hosts several

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121 springs with high radon concentration and also three small streams. Rocks outcropping in the area are of
122 volcanic origin and belongs to the activity of Colli Albani volcano, located just 20 km south-east of Roma.
123 Springs emerge at the boundary between pyroclastic flow deposits and clayey alluvial sediments. The
124 hydrogeological complex is referred as “High Permeability Alban Volcanic deposit Complex”, Alban Hills
125 Hydrogeological Unit, in the recent Hydrogeological Map of Rome (La Vigna et al., 2016).
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128

129 3. Materials and methods 130

131 The location of investigated springs (labelled A, B and D) and that of Almone river (named C) is shown in
132 Fig. 1b. Springs and Almone river belong to the bicarbonate-alkaline earth facies, with a prevailing calcium-
133 bicarbonate (Ca^{2+} - HCO_3^-) chemistry, but a significant content of Na^+ and K^+ .
134

135 Water current velocity was measured using a common current meter with a rotor that revolves around a
136 vertical axis. An electronic signal is transmitted by the meter on each revolution allowing the revolutions to
137 be counted, timed and then converted into water velocity. Water velocity was measured every hour in
138 order to verify that it was constant during the working hours. No significant changes were recorded.
139

140 Three different methods for measuring radon dissolved in the water have been used: the first one, the
141 Radon-in-Water Probe + RAD7 (hereafter called method A) is the technique which we want to characterize
142 in this study. The other two, gamma-ray spectrometer + charcoal canister (hereafter called method B) and
143 RAD7 monitor + Big Bottle RAD H20 accessory (hereafter labelled method C) have been already validated
144 and cross-calibrated in De Simone et al. (2015), Tuccimei et al. (2015) and Lucchetti et al. (2016).
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148 3.1. Method A - RAD7 monitor + Radon-in-Water Probe accessory 149

150 The water probe (jokingly renamed “hanging bird cage”) is a 2.2 m long tube made from Accurel®, a
151 microporous polypropylene tubing, bended and mounted onto an open wire frame which can be immersed
152 in a body of water at the desired moderate depth (Fig. 2a). Since the behaviour of the probe at high depths
153 is not known, its performances in those conditions should be specifically checked.
154

155 The polypropylene has the property to be permeable to radon, but not to water. This way radon passes
156 through the membrane until its concentration in the air reaches an equilibrium value. The equilibrium ratio
157 of radon in the air to radon in the water is determined by temperature, which must be measured. The main
158 advantage of the probe is that it does not need a pump for water sampling, but conversely it takes at least
159 3 hours to reach the equilibrium, according to DurrIDGE specifications
160 (http://www.durrIDGE.com/featured_articles_radon_in_water_accessories.shtml). DurrIDGE recommends
161 that some flow has to be around and through the device since it removes radon from the water in its
162 vicinity as the gas passes into the membrane. Other advices are provided to optimise its use. The probe is
163 connected to a desiccant (drierite) and to a RAD7 radon monitor (DurrIDGE Co., Inc) in a closed loop circuit
164 (Fig. 2b).
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167 The RAD7 monitor is equipped with an electrostatic PIPS collector (passivated ion-implanted planar silicon
168 detector) of alpha emitters and a spectrum analyzer, to select counting of different radon daughters.
169 “Sniff” Mode allowed us to use only the short-lived ^{218}Po to detect ^{222}Rn , which has the advantage of
170 reaching radioactive equilibrium with the parent in just 15 min. Therefore, it was possible to set the cycle
171 time at 15 min, without fixing the number of cycles (the option recycle was set at 00). During the test, the
172 pump was on for the entire run. Radon data from each cycle were corrected, where necessary (significant
173 water content in RAD7), for the neutralization processes of radon daughters by water molecules which
174 reduce the collection of positively charged radon daughters on the silicon detector surface (De Simone et
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180 al., 2016). Corrected radon activity concentration were then plotted versus time and an exponential
181 function ("Asymptotic 1", $y = a - bc^x$, available in the program Origin Pro 9.0 (OriginLab Corporation, 2012)
182 was applied to fit data and evaluate the radon concentration in the air when equilibrium between radon in
183 the air and radon in the water was reached (C_a , Bq/m³). Another outcome is the time necessary to reach this
184 condition (within the fit error range). An example of data fitting is provided in Fig. 4.
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186 Radon in the water ($C_{w\ eq}$, Bq/L) is finally calculated using equation 1:
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$$189 \quad C_{w\ eq} = C_a \cdot \alpha / 1000 \quad (1)$$

190
191
192 where,

193 α is the radon partition coefficient between water and air at the experimental temperature and is equal to:
194 $0.105 + 0.405 e^{-0.0502 T}$ (Weigel, 1978); A temperature data logger (EL-USB-TC, EasyLog[®]) was used to
195 monitor water temperature during all measurements.
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201 Here we employed the probe in three springs and in a river, with different water flows (from 0.01 to 0.57
202 m/s) and radon concentration (from about 10 to 198 Bq/L) to test the device.
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205 3.2. Method B - Gamma-ray spectrometer and charcoal canister

206 This method developed by Mancini and Giannelli (1995) and modified by Procopio (1996) and Galli et al.
207 (1999) makes use of charcoal canisters and gamma-ray counting. (Fig. 3a). Gamma counting is performed at
208 least 20 h after sampling by γ rays emitted by ²¹⁴Pb and ²¹⁴Bi radon short-lived daughters, when the secular
209 equilibrium and uniform radon distribution in the charcoal is reached (Fig. 3b). The low-background
210 spectrometer available at INGV laboratories, Roma, consists of a shield made of lead, either casting or
211 pellets, surrounding a NaI(Tl) scintillator (3 x 3 in.), optically coupled to a photomultiplier. The pulse shaping
212 is performed by a preamplifier and an amplifier, and the counting of peaks at 295, 352, and 609 keV is done
213 by a 4-k multichannel analyzer. The spectrometer response is calibrated daily by counting an activated
214 charcoal canister containing a standard source of ²²⁶Ra (376 ± 10 Bq). Calibration is also periodically
215 repeated between measurements to account for climatic variations. Calibration accounts also for the
216 humidity absorbed by the charcoal (Procopio, 1996).
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222 Radon in the water (C_w , Bq/L) is calculated using equation 2:
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$$225 \quad C_w = cpm / (DF \times E) \quad (2)$$

226
227 where,

228 cpm = net counts per minute at 295, 352, and 609 keV peaks
229
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231 DF = decay factor ($\exp(-T/\tau)$), being T (min) the time elapsed from degassing to counting and τ (min) the
232 radon mean life (7938 min).
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239 E = Efficiency (cpm per Bq/L)
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243 3.3. Method C - RAD7 monitor with Big Bottle RAD H2O accessory

244 The RAD7 monitor (DurrIDGE Co., Inc.) was used, selecting the “Sniff” Mode, as mentioned before to
245 employ only the short-lived ^{218}Po to detect ^{222}Rn , which has the advantage of reaching equilibrium with the
246 parent in just 15 min. Therefore, it is possible to set the cycle time at 15 min and repeat it for eight times.
247 During the test, the pump was on for the entire run to ensure equilibrium between dissolved and extracted
248 radon. Air was extracted using a Teflon aerator, which consists of a single 23-cm-long vinyl tubing with an
249 air stone fixed at its lower end. Incoming air from RAD7 is delivered to the bottle via a check valve placed at
250 the upper end of the aerator and then it is retransmitted through a bubble trap to the desiccant (drierite).
251 Dried air is finally conveyed to RAD7 in a closed-loop circuit. A data logger records the temperature at the
252 bottle - elastic clinching strap interface during the measurement for calculating the radon solubility
253 coefficient. The experimental apparatus is shown in Fig. 3c (Lucchetti et al., 2016).
254

255
256 Radon in the water (C_w , Bq/L) is calculated using equation 3:
257
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$$259 C_w = C_{a\text{ FIT}30} ((V_a + \alpha V_w) - V_h/\alpha) / DF \cdot AF \quad (3)$$

260
261 where

262
263
264 $C_{a\text{ FIT}30}$ = radon concentration value at $t = 30$ min deriving from the application of an exponential fit of RAD7
265 data recorded during each 15-min cycle (from 30 to 120 min) (Bq/m³),
266

267 V_a = total volume of air in the system ($1.545 \cdot 10^{-3}$ m³),
268

269 V_w = volume of water in the bottle ($50 \cdot 10^{-2}$ m³),
270

271 V_h/α = radon loss in the head space occupied by air above the water in the plastic bottle, where V_h is the
272 head space volume
273

274 DF = Decay Factor ($= e^{-t/\tau_{\text{Rn}}}$, where t (min) is the time elapsed between water sampling and 30 min after the
275 beginning of the run and τ_{Rn} (min) is the radon average life, 7938 (min).
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277 AF = adjustment of instrument calibration factor
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280 Analyses were always carried out within 24 hours from sampling. Consequently, radon diffusion through
281 the 500 mL PET plastic bottles was negligible and not accounted for.
282
283

284 4. Results and discussion

285
286 Three springs and a river (Fig. 1b) were sampled several times from June 2017 to June 2018 to test the
287 performances of the Radon-in-Water Probe. Data on water sampling depth, water flow velocity, water
288 temperatures, radon partition coefficient between water and air (α) from Fritz von Weigel equation
289 (Weigel, 1978), time necessary to reach equilibrium and results of analyses using the three different
290 methods are reported in Table 1.
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298 Generally speaking, measurements were interrupted after about 3 hours because relative (and also
299 absolute humidity) in RAD7 increased too much after that time, even if equilibrium between radon in the
300 air and radon in the water was not reached yet. Radon concentration at equilibrium and time necessary to
301 approach this value were then calculated using an exponential fitting of measured radon data as described
302 in section 3.1 and shown in Fig. 4. The graph showing the behavior of the residual values is reported in the
303 Supplementary Material, as Fig. S1.
304

305
306 Spring A was sampled twice. The first time (June 13rd 2017) at 30 cm depth where water flow was negligible
307 (0.01 m/s) and the second time (June 26th 2017) at few centimetres depth where water velocity was higher
308 (0.07 m/s). First time, three more water aliquots were collected for comparison with methods B and C.
309 Second time only two samples were gathered for comparison with method B. The first measurement (Id. 1
310 in Table 1) provided an equilibrium activity concentration ($C_{w,eq}$ in equation 1) of 61 ± 5 Bq/L, which was
311 compared with results from the other methods: 123 ± 4 Bq/L and 121 ± 7 Bq/L, respectively for methods B
312 and C. These latter results agree within the error range, whereas the outcome of method A when referred
313 to the average results from methods B and C (hereafter called relative efficiency) reaches the value of 0.50
314 ± 0.05 . Second measurement (Id. 2) gave a radon in water concentration of 94 ± 4 Bq/L according to
315 method A and 124 ± 4 Bq/L by method B. Corresponding relative efficiency was 0.76 ± 0.04 (Table 1).
316

317
318 Spring B was sampled twice. The first time (June 19th 2017) the probe was immersed at 15 cm depth where
319 water was flowing at about 0.06 m/s; the second time (June 27th 2018) at few centimetres depth, with a
320 water flow velocity of 0.2 m/s. First and second time, two more samples were gathered for comparison
321 with methods B. Results of the first measurement (Id. 4) were 153 ± 11 Bq/L by method A and 198 ± 6 Bq/L
322 by method B. It must pointed out that radon value determined by method A for Id. 4 sample is moderately
323 underestimated because radon concentrations in the air (C_a in equation 1) used for fit overpassed 400 Bq/L,
324 which is quoted by Durrige Co. (Durrige, 2017) as the upper limit for radon measurement using RAD7.
325 Above such level, RAD7 readings are underestimated because the probability that two simultaneous decays
326 are detected as two distinct events progressively decreases. This means that also corresponding relative
327 efficiency datum is undervalued (Durrige, 2017). Consequently, radon activity concentration has been
328 increased by 6 % (Derek Lane-Smith, personal communication, see Acknowledgements). Corrected radon
329 groundwater concentration is now equal to 162 ± 12 Bq/L, giving corresponding relative efficiency of $0.82 \pm$
330 0.06 . Second determination by method A (Id. 3) provided a radon concentration of 151 ± 2 Bq/L, whereas
331 method B gave 174 ± 6 Bq/L, with a relative efficiency of 0.87 ± 0.03 (Table 1).
332

333
334 River C was monitored once (Id. 5, June 26th 2017) at about 10 cm depth, where flow velocity was 0.57
335 m/s. Water samples for analyses with methods B and C were collected too. Method A gave a radon activity
336 concentration of 10.3 ± 0.2 Bq/L, method B a value of 12 ± 1 and method C, 11 ± 1 Bq/L. The relative
337 efficiency was 0.92 ± 0.08 (Table 1)
338

339
340 Spring D was measured once (Id. 6, July 5th 2017) at about 15 cm depth, employing the three methods.
341 Water flow velocity was 0.1 m/s. Method A gave a radon concentration of 45 ± 2 Bq/L whereas methods B
342 and C provided 53 ± 1 Bq/L and 54 ± 3 Bq/L respectively. The correspondent relative efficiency was $0.84 \pm$
343 0.03 (Table 1)
344

345
346 In order to interpret the relative efficiencies of method A compared with methods B and C, we need to take
347 into account the value of water flow velocities and radon activity concentrations in the water bodies. Figure
348 5 reports the relative efficiency of method A compared with the average of methods B and C against water
349 flow velocity. A power fitting of relative efficiency against water flow velocity is applied. The graph showing
350 the behaviour of the residual values is reported in the Supplementary Material, as Fig. S2.

351
352 Relative efficiency of method A is directly proportional to water flow velocity, ranging from about $0.50 \pm$
353 0.05 at 0.01 m/s to about 0.92 ± 0.08 at 0.57 m/s. This result is due to the scarce gas availability around
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357 the device and thus to the low radon transfer from the water to the membrane, when water flow velocity is
358 low. On the basis of available data, a relative efficiency of 1 is reached only at 0.57 m/s flow rate,
359 considering the 95 % fitting confidence band. Unfortunately, the band is large in this section of the curve
360 because river C (sample Id. 5), the only characterised by a high velocity, has a low radon content and is then
361 affected by a large analytical uncertainty that strongly influences the 95 % fitting confidence band.
362 Moreover, as a consequence of the power fit, the uncertainty of the relative efficiency will be larger at low
363 water flow velocities.
364

365
366 No correlation between time necessary to reach equilibrium and radon concentration came out. Similarly,
367 no correlation is evident between equilibrium time and relative efficiency, the only significant relationships
368 being that between relative efficiency and water flow velocity (see Fig. 5).
369

370 Equilibrium time ranged between 345 and 495 minutes in this water-flow velocity interval (0.01 - 0.57
371 m/s). Lower time was indicated by Durrige (2 - 3 hours) because they probably tested the Radon-In-Water
372 Probe with low-radon concentration water, affected by relatively large uncertainties; consequently, it is
373 possible to assume that the equilibrium apparently appeared to have been achieved within the error range,
374 even if full equilibrium needed longer time.
375

376 It must be evidenced that such long time is compatible with a process of simple diffusion of radon from
377 water into the air circulating in the closed-loop circuit. Shorter time (30-40 minutes) is needed when radon
378 is firstly extracted by spraying the water into circling air and then exploiting air-air radon diffusion through
379 a similar Accurel® polypropylene tubing, prior to RAD7 determination (Burnett and Dulaiova; 2003;
380 Schubert et al., 2008).
381

382 Moreover, longer PP tubing (length > 2.2 m) and a higher flow rate in the system (> 0.8 L/min of RAD7
383 pump) would have reduced time to reach equilibrium radon concentration (Surbeck, 1996; Schubert et al.,
384 2008). As a matter of fact, the process is directly proportional to: i) the volume of air in contact with the
385 water (that is the air volume inside the membrane tube) compared to total air volume and, ii) the air
386 pumping rate which influences the radon exchange rate at the air-water interface (Surbeck, 1996).
387

388 A minimum flow of about 0.57 m/s is necessary to get full efficiency, within the error range of the
389 experimental procedure.
390

391 Using equation 4 (Fig. 5),
392

$$393 \text{Rel. Eff.} = 0.955 (\pm 0.034) \cdot \text{abs} [\text{Water flow vel.} - 0.010030 (\pm 0.000071)] ^{0.062 (\pm 0.016)}$$

394 (4)

395 it is possible to estimate the real dissolved radon concentration dividing the value obtained from method A
396 by the relative efficiency, even if the water body is characterised by scarcely moving water bodies.
397

398 In conclusion, although other techniques based on the RAD7 could easily measure radon concentration in
399 the range 10-198 Bq/L in much shorter times (about 30 minutes), such as the standard RAD-H2O with 250-
400 mL bottles and continuous measurements with RAD-AQUA (Burnett et al., 2001; Dulaiova et al., 2005),
401 performances of the Water Probe to monitor radon dissolved in rivers, lakes, or coastal ocean could be
402 further improved. Instead of relying on water movement (currents), one could install it on a moving boat
403 and easily generate water motion over the probe to shorten time necessary to reach equilibrium condition.
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405

406 407 **5. Conclusions**

408
409 The DURRIDGE Water Probe is useful to monitor radon levels in bodies of moving water, when other
410 sampling methods cannot be easily accomplished. The device is also useful to monitor radon-in-water,
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416 without the potential risk of radon loss during sampling. We applied this technique to springs and to a river
417 to evaluate its performances to measure radon in small and shallow spring lakes and in a river.
418

419 “RAD7 monitor + Radon-in-Water Probe” method (method A) was validated by comparison with two
420 established procedures. Relative efficiency of method A is directly proportional to water flow velocity,
421 ranging from about 0.50 ± 0.05 at 0.01 m/s to about 0.92 ± 0.08 at 0.57 m/s. A minimum of 2-3 hours are
422 needed to collect enough records to asymptotically fit radon-in-gas data and obtain equilibrium radon
423 concentration. Equilibrium condition is reached after about 6 - 8 hours. No correlation was found between
424 relative efficiency and radon concentration.
425

426 A minimum flow of about 0.57 m/s is necessary to get full efficiency, within the error range of the
427 experimental procedure. Using equation 4, it is possible to estimate dissolved radon concentration dividing
428 the value obtained from method A by the relative efficiency, even if the water body to monitor is
429 characterised by poorly moving water bodies.
430
431

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436 information to correct radon activity concentration detected by RAD7 at high levels (higher than the
437 instrumental dynamic range of 400,000 Bq/m³). Authors are also very grateful to Sister Mary Claire Alfonsa
438 Rubidora for making our time so good during field-work.
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440

441 442 **Appendix. Supplementary data**

443 Supplementary data to this article consist of two figures, Fig.S1 and Fig.S2, which show the residuals of
444 curve fittings reported in Figs. 4 and 5, respectively.
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563 564 565 **Figure Captions**

566
567 **Fig. 1.** Map of the Hydrogeological Units of Roma, Italy (a, [La Vigna et al., 2016](#)). The open square within the
568 G.R.A. (the Roma Ring Road) indicates the location of the of study area (b). Hydrogeological setting of the
569 study area (Valle della Caffarella, from [La Vigna et al., 2016](#)) with main springs sites. Yellow stars and red
570 capital letters stand for the springs (A, B and D) and the river (C) investigated in this work.
571

572 **Fig. 2.** Radon-in-Water Probe (a; [Durridge, 2017](#)). Radon-in-Water Probe experimental configuration (b):
573 the closed loop consists of the Water Probe, the RAD7 monitor and the desiccant.
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575 **Fig. 3.** Methods B (a and b) and C (c) . A portable degassing unit is attached to a 0.6 L bottle containing the
576 water samples; ²²²Rn is transferred to a charcoal canister connected to the bottle and to the pump in a
577 closed loop circuit (a). The charcoal canister is then placed into a gamma spectrometer with a lead shield.
578 Gamma counting is performed is performed at least 20 h after sampling using a NaI(Tl) detector through
579 the γ rays emitted by radon short-lived daughters (b). RAD7 monitor with Big Bottle RAD H2O accessory (c,
580 modified from [Lucchetti et al., 2016](#)). 1) Plastic soda bottle; 2) Screw-on Teflon aerator, with a single air
581 stone; 3) Elastic clinching strap; 4) Temperature data logger; 5) Bubble trap; 6) Laboratory dryer; 7) Clip; 8)
582 Check valve; 9) Vinyl tubing; 10) RAD7 radon detector; 11) Inlet filter.
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584 **Fig. 4.** Example of exponential fitting of radon activity concentration (C_a in equation 1, Bq/m³) in the Radon-
585 in-Water Probe setup (method A) plotted against time (minutes). This graph is referred to Spring B,
586 analyzed on June 19th 2017 (Id. 4 in Table 1). The function $Y = a - bc^X$, available in the program Origin Pro
587 9.0 ([OriginLab Corporation, 2012](#)) provides the equilibrium value (parameter a in the equation) between
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radon in the air and radon in the water and the time necessary to reach this condition. A graph showing the behaviour of residual values is reported in the Supplementary Material, as Fig. S1

Fig. 5. Relative efficiency of radon determination by method A versus water flow velocity. Data fitting is obtained by a power equation (model Power1) using the program Origin Pro 9.0 (OriginLab Corporation, 2012). A graph showing the behaviour of residual values is reported in the Supplementary Material, as Fig. S2.

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Table 1. Dataset of radon determination

Id.	Spring/River	Water sampling depth (m)	Water flow velocity (m / s)	Water temperature (°C)	α	$^{222}\text{Rn}_{\text{air}}$ (Bq / L)	Equilibrium ^a (minutes)	$^{222}\text{Rn}_A$ (Bq / L)	$^{222}\text{Rn}_B$ (Bq / L)	$^{222}\text{Rn}_C$ (Bq / L)	Relative efficiency ^b
1	Spring A	0.3	0.01	17.6	0.2724	223.7 ± 19.1	405	60.9 ± 5.2	123 ± 4	121.3 ± 7.2	0.498 ± 0.046
2	Spring A	0.05	0.071	17.6	0.2724	346.1 ± 13.2	480	94.3 ± 3.6	124 ± 4	-	0.763 ± 0.040
3	Spring B	0.05	0.2	17.7	0.2716	554.4 ± 8.6 ^c	495	150.5 ± 2.3	174 ± 6	-	0.867 ± 0.032
4	Spring B	0.15	0.06	17.7	0.2716	595.5 ± 42.5 ^d	345	159.5 ± 11.5	198 ± 6	-	0.815 ± 0.064
5	River C	0.1	0.571	23.4	0.2301	44.6 ± 1.0	360	10.3 ± 0.2	11.8 ± 0.9	10.5 ± 0.9	0.919 ± 0.081
6	Spring D	0.15	0.1	17.1	0.2766	161.7 ± 5.8	375	44.7 ± 1.6	53 ± 1	53.6 ± 3.1	0.843 ± 0.033

²²²Rn_A, ²²²Rn_B and ²²²Rn_C are the activity concentration obtained respectively with the Radon-in-Water Probe (A), Gamma-ray spectrometer (B) and BigBottle RAD H2O (C) methods.

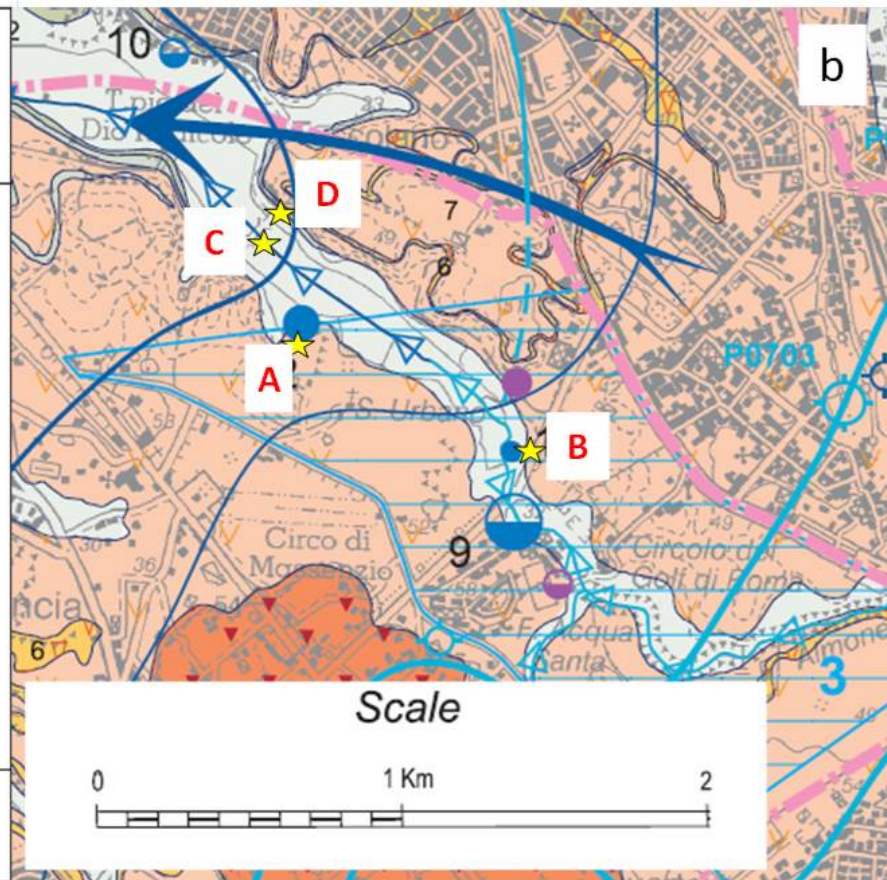
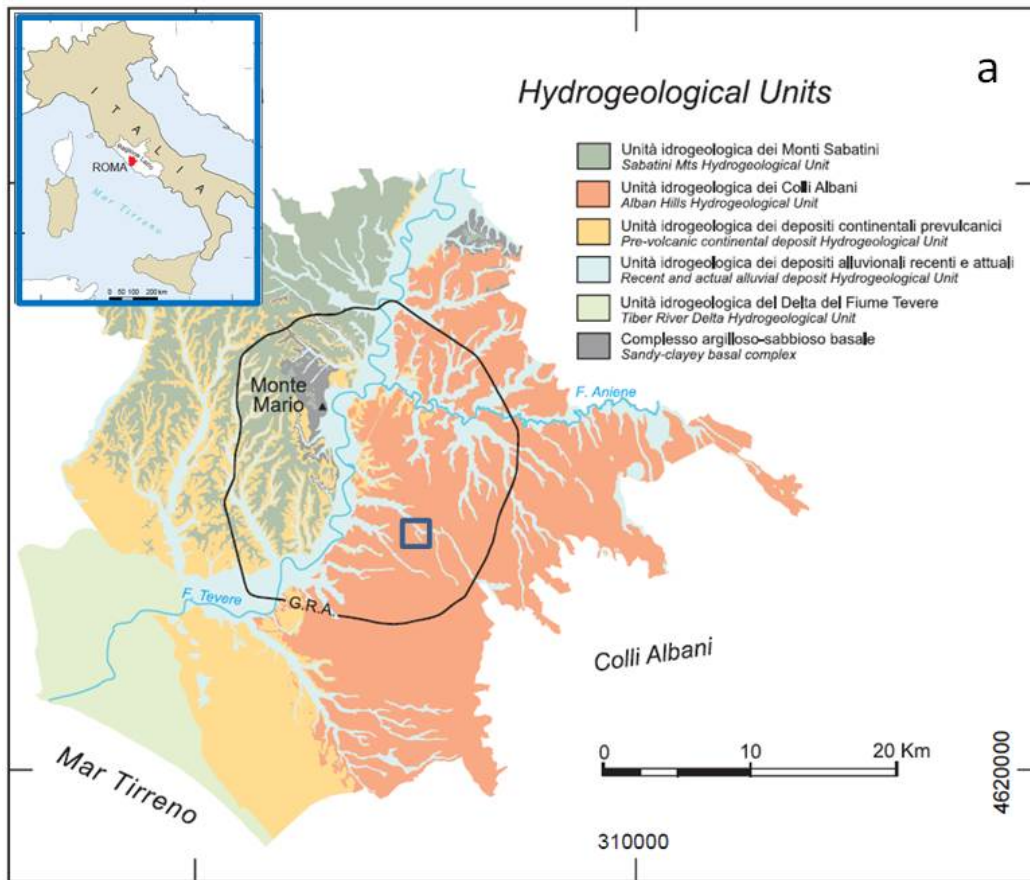
^a Time necessary to reach equilibrium (within the error range) between radon in the water and radon in the air contained in the Water Probe experimental configuration.

The equilibrium value was calculated with Origin Pro 9.0. (OriginLab Corporation).

^b Ratio between ²²²Rn obtained using method A and average ²²²Rn provided by methods B and C

^c This radon activity concentration has not been increased by 6%, because experimental data used for fit were below 400 Bq/L

^d This radon activity concentration has been increased by 6%, because experimental data used for fit were above 400 Bq/L, the upper dynamic range of RAD7 monitor (see text for explanation)

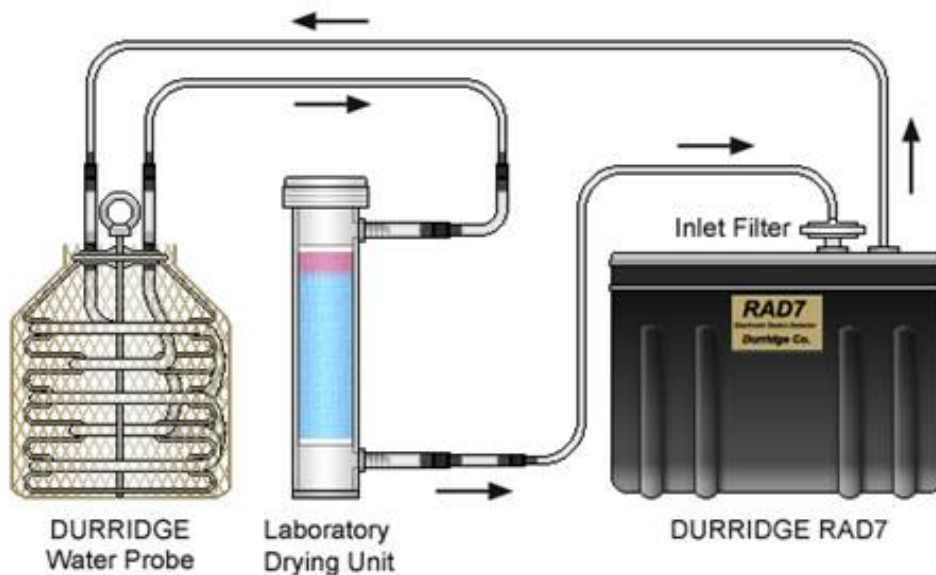




a

Water Probe Configuration

b



DURRIDGE
Water Probe

Laboratory
Drying Unit

DURRIDGE RAD7

