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Kinetics of the Water/Air Phase Transition of Radon and Its Implication on Detection of Radon-in-Water Concentrations: Practical Assessment of Different On-Site Radon Extraction Methods

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ABSTRACT: The on-site measurement of radon-in-water concentrations relies on extraction of radon from the water followed by its detection by means of a mobile radon-in-air monitor. Many applications of radon as a naturally occurring aquatic tracer require the collection of continuous radon concentration time series, thus necessitating the continuous extraction of radon either from a permanent water stream supplied by a water pump or directly from a water body or a groundwater monitoring well. Essentially, three different types of extraction units are available for this purpose: (i) a flow-through spray chamber, (ii) a flow-through membrane extraction module, and (iii) a submersible (usually coiled) membrane tube. In this paper we discuss the advantages and disadvantages of these three methodical approaches with particular focus on their individual response to instantaneously changing radon-in-water concentrations. After a concise introduction into theoretical aspects of water/air phase transition kinetics of radon, experimental results for the three types of extraction units are presented. Quantitative suggestions for optimizing the detection setup by increasing the water/air interface and by reducing the air volume circulating through the degassing unit and radon detector are made. It was shown that the flow-through spray chamber and flow-through membrane perform nearly similarly, whereas the submersible membrane tubing has a significantly larger delay in response to concentration changes. The flow-through spray chamber is most suitable in turbid waters and to applications where high flow rates of the water pump stream can be achieved (e.g., where the power supply is not constrained by field conditions). The flow-through membrane is most suited to radon extraction from clear water and in field conditions where the power supply to a water pump is limited, e.g., from batteries. Finally, the submersible membrane tube is most suitable if radon is to be extracted in situ without any water pumping, e.g., in groundwater wells with a low yield, or in long-term time series, in which short-term variations in the radon concentration are of no relevance.

INTRODUCTION

The application of radon as a naturally occurring aquatic tracer often necessitates the continuous detection of radon-in-water concentrations, i.e., radon time series. Related studies have been carried out in marine and terrestrial environments, as well as in industrial applications. Respective examples are the investigation of submarine groundwater discharge into the coastal sea (e.g., refs 1−3), the investigation of migration and interaction of groundwater and terrestrial surface waters (e.g., refs 4 and 5), and the determination of water residence times in water treatment facilities.[6]

Radon-in-water concentration time series are generally recorded by continuous extraction of radon either from a permanent water stream pumped through a flow-through extraction unit ("active extraction" applying a spray chamber or a membrane extraction unit; cf. Figure 1A) or by extracting radon directly from the investigated water body by means of a submersible extraction unit ("passive extraction"; cf. Figure 1B). In both cases radon is extracted from the water into a defined air volume, which is circulated in a closed loop through the respective extraction unit and a radon-in-air monitor.

Radon can be extracted from the water either by allowing direct contact between water and air or by liquid/gas membrane extraction keeping water and air physically separated. The most prominent example for a setup with direct water/air contact is the "RAD-Aqua" (Durridge Inc.). The device consists of a spray chamber where the radon concentration in the closed air loop is brought into equilibrium with the radon concentration in the water stream.[7] An exemplary membrane extraction unit is the "MiniModule degasifier" (Membrana GmbH), a parallel flow device where

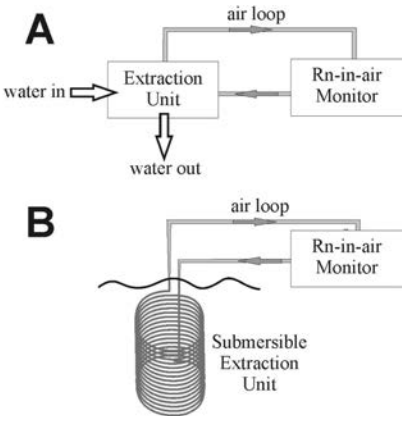

Figure 1. Principal options for the on-site detection of radon-in-water time series by (A) "active" radon extraction from a pumped water stream using a flow-through extraction unit or (B) "passive" extraction directly from the investigated water body by means of a submersible extraction unit.

the water is pumped through the inside of a bundle of hollow membrane fibers with the closed air loop passing on their outside.[8] Whereas RAD-Aqua and MiniModule are designed for radon extraction from a continuously pumped stream of water (cf. Figure 1A, active radon extraction), submersible coiled membrane tubes such as the "water probe" (Durridge Inc.) allow in situ radon extraction directly from the investigated water body and do not require pumping of water (cf. Figure 1B, passive radon extraction, e.g., refs 9 and 23). The designs and functionalities of the three different types of extraction units (RAD-Aqua, MiniModule, membrane coil) are not described here in further detail since they are comprehensively discussed in the cited literature.

For each of the three methodical approaches, the measured radon-in-air concentration (C_{air}) can be converted into the related radon-in-water concentration (C_{w}) if concentration equilibrium between air and water can be assumed (eq 1). At concentration equilibrium the radon concentration ratio between air and water is defined by the temperature- and salinity-dependent water/air partition coefficient ($K_{\mathrm{w/air}}$), which amounts, e.g., for seawater (S = 35) at a temperature of 20 °C (T = 293K) to 0.212 (eq 2, ref 10).

$$C_{\mathrm{air}} = C_{\mathrm{w}} {K_{\mathrm{w/air}}}^{-1} \tag{1}$$

$$\ln \beta = a_1 + a_2\left(\frac{100}{T}\right) + a_3 \ln\left(\frac{T}{100}\right) + S\left\{b_1 + b_2\left(\frac{T}{100}\right) + b_3\left(\frac{T}{100}\right)^2\right\}$$

$$K_{\mathrm{w/air}} = \beta T/273.15 \tag{2}$$

In eq 2 β is the Bunsen coefficient, S the salinity, and T the temperature (K). The variables a_1 to b_3 refer to six adjustable parameters that are specific for the diffusing gas phase. For radon they amount to $a_1 = -76.14$, $a_2 = 120.36$, $a_3 = 31.26$, $b_1 = -0.2631$, $b_2 = 0.1673$, and $b_3 = -0.0270$.[10]

Under steady-state conditions (i.e., constant radon concentration in the water) C_{air} represents C_{w} at any given point in time (cf. eq 1). However, in the case of a sudden change of the radon-in-water concentration, the air/water equilibrium is established only after a time delay, which depends on certain system parameters (e.g., refs 11 and 12). This equilibration time (Δt) can be defined as the time lag between a concentration change in the water and the time at which the recorded radon-in-air time series reaches the "plateau range", i.e., the equilibrium concentration plateau within statistical counting errors (Figure 2A).

The time lag is due to the kinetics of the water/air phase transition of radon and is observed for sudden increases as well as sudden decreases of the radon-in-water concentration as exemplarily shown in Figure 2A (see also ref 11). If a ^{218}Po detector is used for radon-in-air detection (e.g., the RAD7) instead of a direct ^{222}Rn counter (e.g., the AlphaGuard), an additional delay is introduced by the time required to establish radioactive equilibrium between the counted ^{218}Po and its parent nuclide ^{222}Rn. In this case, in practice about 6 min has to be added to the transition kinetics related response delay (Figure 2B).

An optimized instrumental setup (including a radon extraction unit and radon-in-air monitor) is to be designed in

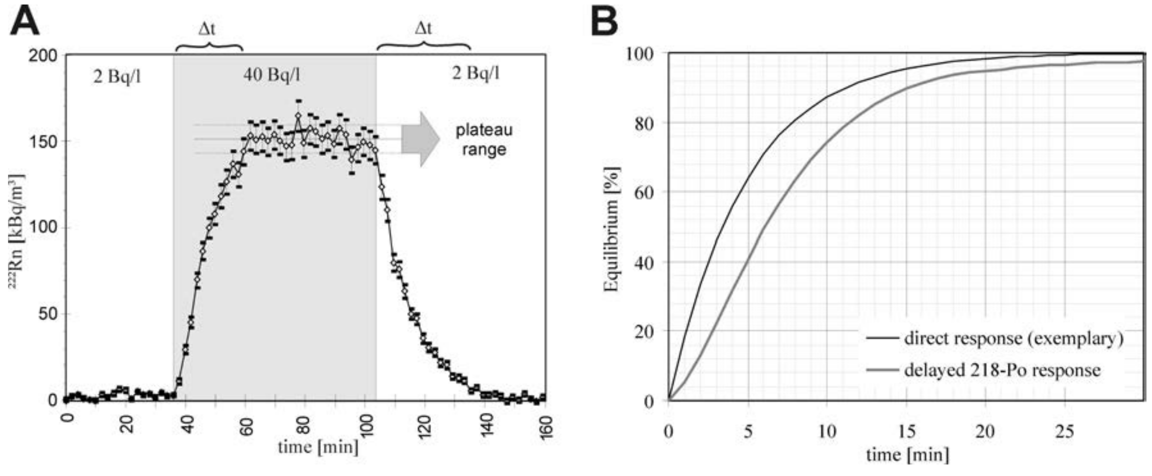

Figure 2. (A) Exemplary time series of the recorded radon-in-air concentration after sudden changes of the radon-in-water concentration (2 Bq/l → 40 Bq/l → 2 Bq/l) indicated by white and gray shaded sections (T = 18 °C, S = 0, $K_{\mathrm{w/air}}$ = 0.266). (B) Additional delay in equilibration time caused by delayed ^{218}Po decay (half-life 3.05 min) as relevant for the RAD7 monitor.

a way that keeps the equilibration time Δt as short as possible under instrumental constraints. Furthermore, to accurately interpret a recorded radon-in-air time series, Δt should be (at least approximately) quantitatively predictable for any given detection setup (cf. ref 11).

Previous studies that applied a setup as illustrated in Figure 1A have shown that Δt can be substantially shortened if water is pumped at a high rate through the flow-through extraction unit. Pump rates of up to 17.5 L/min through the RAD-Aqua spray chamber have been suggested.[12] However, whereas high water pump rates can easily be achieved in the laboratory employing high-capacity pumps, this requirement is constrained in many field conditions due to (i) the performance limitation of battery-operated pumps, (ii) the necessity of applying water filters with a considerable flow resistance, or (iii) the low yield of a sampled groundwater monitoring well. Hence, other "tuning options" aiming on (quantifiably) reducing the equilibration time of the setup are desirable.

The two major influential parameters besides the water pump rate are the size of the water/air interface in the extraction unit and the size of the circulating air volume. In the present paper we discuss experimental results, which allow evaluation of the impact of both parameters on the equilibration time of the detection equipment. As a result of the study an empirical correlation is introduced describing Δt as a function of the water/air interface and circulating air volume, $\Delta t = f(V,A)$. This correlation can be applied for quantitative prediction of the equilibration time to be expected for any suitable detection setup comparable to the one shown in Figure 1A. In this study a water flow rate of 2 L/min was used, which is without problems achievable under typical field conditions.

THEORETICAL BACKGROUND

The mass-transfer kinetics between two phases and the related time for establishing concentration distribution equilibrium between the phases (Δt) are directly proportional to the available interfacial area. Furthermore, the ratio of the phase volumes of the sampled phase and receiving phase has considerable influence on the equilibration time. This implies that a large interfacial area and a small circulating air volume should significantly reduce Δt of a specific setup for continuous radon-in-water detection.

The equilibration time of any radon-in-water detection setup is controlled by the physical mass-transfer resistance to the water ↔ air transfer of radon. The transfer resistance can be described by applying the "two-film model":[13,14] If a circulating air volume is in contact with a running water stream or a turbulent water body, both phases (water and air) can be described as turbulent fluids. However, thin stagnant layers ("films") have to be assumed on either side of the water/air interface (Figure 3). While convective radon transport in the turbulent bulk of a fluid is fast and gradients are equilibrated promptly, radon transport through the stagnant films of water and air solely occurs due to molecular diffusion, which is an orders-of-magnitude slower process.

If water and air are in direct contact and constantly kept in motion, as is the case for radon extraction by means of a spray chamber, the film thickness on the water side of the interface is on the order of 10 μm.[15] The film thickness on the air side can be assumed to be in the same range.[15] However, if air and water are separated by an air/radon-permeable but hydrophobic, i.e., water-repellent, membrane, as is the case for radon measurement after membrane extraction,[8,9] the film thickness on both sides of the interface is significantly different from the values valid for a fluid/fluid interface. In this case the film thickness on the air side equals the thickness of the applied membrane or is even larger if the membrane pores show a considerable tortuosity. The film thickness on the water side can be assumed to be in the range of about 10−100 μm, depending on the surface microstructure of the membrane and on potential water adhesion effects of the membrane material.[15]

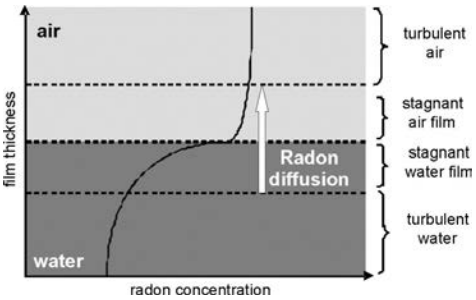

Figure 3. Two-film model for schematic illustration of the water/air phase transition of radon along a concentration gradient.

Generally, the total mass-transfer resistance to diffusion at a water/air interface (R_{tot}) equals the sum of the individual mass-transfer resistances of the water film (R_{w}) and the air film (R_{air}) as given in the following equation:

$$R_{\text{tot}} = R_{\text{w}} + R_{\text{air}} \tag{3}$$

This equation can alternatively be written with the mass-transfer coefficients for water-phase mass transfer (k_{w}), air-phase mass transfer (k_{air}), overall mass transfer (k_{tot}), and the water/air partition coefficient ($K_{\text{w/air}}$, cf. eq 1) as given in the following equation:

$$\frac{1}{k_{\text{tot}}} = \frac{1}{k_{\text{w}}} + \frac{1}{k_{\text{air}}} K_{\text{w/air}} \tag{4}$$

For the practical reason of parameter availability, the approximation of the mass-transfer resistance (R) can also be expressed as a ratio of the respective film thickness and diffusion coefficient. Thus, eq 4 can be transformed into eq 5,

$$R_{\text{tot}} = \frac{1}{k_{\text{tot}}} = \frac{\delta_{\text{w}}}{D_{\text{w}}} + \frac{\delta_{\text{air}}}{D_{\text{air}}} K_{\text{w/air}} \tag{5}$$

where δ_{w} and δ_{air} represent the film thicknesses on the water side and the air side of the interface, respectively. D_{w} and D_{air} represent the (radon) diffusion coefficient in water and air, respectively.

With the reported radon diffusion coefficients in air, 1.20×10^{-5} m^2 s^{-1},[16] and water, 1.16×10^{-9} m^2 s^{-1} [17] (valid for fresh water at a temperature of 15 °C), several air and water film thicknesses can exemplarily be assumed to evaluate the significance of the air film thickness on the overall mass-transfer resistance (i.e., the impact of the thickness of a membrane in the case of membrane extraction). Table 1 summarizes calculated results based on eq 5 for direct air/water contact ($\delta_{\text{w}} = \delta_{\text{air}} = 10$ μm) and for three different exemplary membrane thicknesses (δ_{air} = 100, 1000, and 10000 μm). The stagnant film thickness on the water side of the membrane-bound water/air interface is assumed to be 50 μm, which is a reasonable value for the scenario as it is representative of the possible range of values between 10 and 100 μm.[15] Shown are

Table 1. Relative Contributions of R_w and R_{air} to the Overall Radon Transfer Resistance at the Water/Air Interface R_{tot} for Direct Air/Water Contact and for Membrane Extraction with Four Different Air Film Thicknesses (i.e., Membranes) Valid for Fresh Water at 15°C ($K_{w/air}$ = 0.293)[a]

	δ_w [μm]	δ_{air} [μm]	R_w (% of R_{tot})	R_{air} (% of R_{tot})
direct contact	10	10	100.00	0.00
separated by membrane	50	10	100.00	0.00
	50	100	99.99	0.01
	50	1000	99.94	0.06
	50	10000	99.44	0.56

[a] Results are based on eq 5 with the radon diffusion coefficients as given in the text.

the relative contributions of R_w and R_{air} to the overall radon transfer resistance R_{tot} at the water/air interface.

The data summarized in Table 1 show that the kinetics of radon diffusion through the stagnant water film (i.e., on the water side) is practically entirely responsible for the resulting equilibration time Δt no matter what thickness is chosen for the air film, i.e., the air-filled hydrophobic membrane. Due to the high radon diffusion coefficient in air, which is about 4 orders of magnitude larger than the radon diffusion coefficient in water, the thickness of the air-filled membrane is practically insignificant for R_{tot} and hence for Δt in the case of radon membrane extraction.

A further theoretical remark shall be made with regard to the difference of Δt observed for decreasing and increasing concentrations, respectively (cf. Figure 2A). As discussed above, transfer kinetics of radon between gaseous and aqueous phases is governed by a process related to molecular solution thermodynamics. A widely accepted model assumption considers the process of introducing a solute molecule (radon) into a solvent (water) as a two-step process including (i) the creation of a "cavity" in the solvent that has to be of suitable size for accommodating the solute molecule and (ii) the introduction of the solute molecule into this cavity and its subsequent interaction with the surrounding solvent molecules.[18] The cavity formation step is substantial to the overall energy demand of the solution process. This is particularly the case for the solution of gases in water due to the continuous H-bond network of the water structure.[19,20] Little quantitative information is available on the kinetics of this process on the macroscopic scale. Nevertheless, the cavity formation model suggests different kinetics for water → air and air → water migration, respectively ("hysteresis"). Whereas radon degassing from the water into the air happens without significant molecular reorganization in the gaseous phase, radon migration from the air into the water is, due to the required molecular reorganization in the aqueous phase, more energy-demanding and hence slower.

EXPERIMENTAL SECTION

Several experimental designs were evaluated, applying either (a) extraction from a continuous water stream or (b) in situ extraction from a large water volume. In both cases, the surface area of the water/air interface and the circulating air volume were varied.

The setup for in situ radon extraction from a continuous water stream by means of a flow-through extraction unit (spray chamber or membrane unit) is shown schematically in Figure 1A. For simulation of instantaneously rising or falling radon concentrations in the water stream, water that was artificially enriched in radon was at a defined moment added to a constant tap water stream by means of a peristaltic pump and a three-way valve (at the "water in" position in Figure 4A). With this setup the radon concentration of the water stream could immediately be changed without significantly changing the water pump rate, for which a constant flow rate of 2 L/min was chosen for all experiments.

The setup for in situ radon extraction from a large water volume by means of a submersible extraction unit is shown schematically in Figure 1B. A water volume of 100 L was filled into a stainless steel tank that was kept tightly closed during the measurement (to avoid radon degassing). Since the efficiency of the submersible membrane coil depends on the concentration gradient at the water/air interface, which can only be maintained close to 100% if the water is in constant motion, the water in the completely filled tank was kept in motion by means of a battery-driven submersible circulating water pump (this issue is discussed in more detail in the Results and Discussion; cf. Figure 5). The lid of the tank was equipped with ports for air inlet and outlet to allow the closed air loop for radon-in-air detection. For an abrupt radon concentration change in the water, a second identical tank containing water with a different radon concentration was used. The membrane coil was changed between tanks in a rapid fashion, and gas loss during changing reservoirs is assumed to be minimal.

For all experimental setups, the closed air loop that circulated between the extraction module (or a cluster of extraction modules) and radon-in-air monitor (or a cluster of radon-in-air

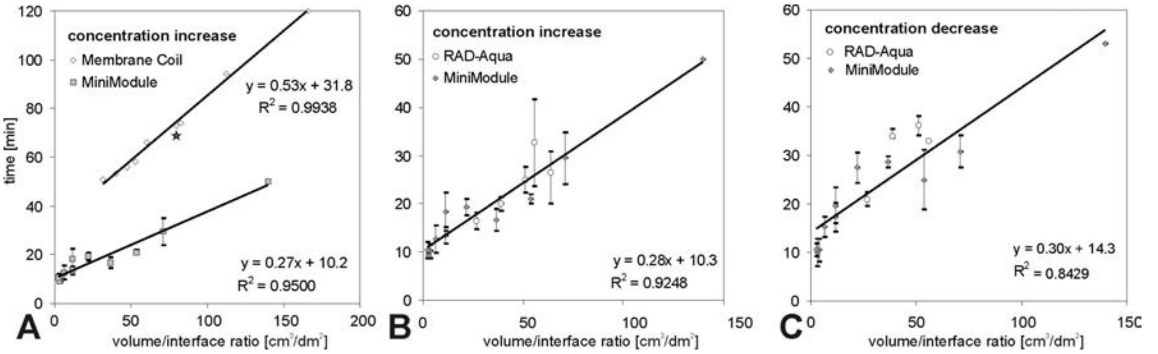

Figure 4. System equilibration time as a function of the volume/interface ratio for the two principally different experimental setups: (i) extraction from the water volume (submersible membrane coil) and (ii) extraction from the water pump stream (either MiniModule or RAD-Aqua).

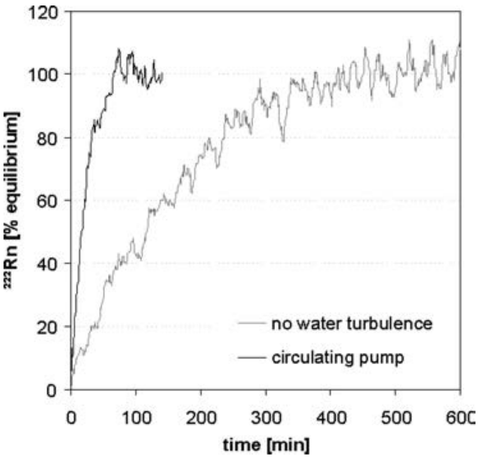

Figure 5. Comparison of system equilibration times of a submersed membrane coil with and without water turbulence in a 100 L water tank. In the first case the water inside the tank was kept in constant motion at a pump rate of 0.5 L/s.

monitors) was pumped at a rate of 1 L/min. At this air pump rate, the air circulates through the complete detection setup in a time span that is small with regard to the transition kinetics related response delay and thus does not play a significant role for the overall equilibration time.

MiniModule units of two different sizes were used, differing basically in the membrane interface area ("large" and "small" MiniModules). The MiniModule was applied either as a single unit or as a cluster of several units in series.

The applied "membrane coil" consists of a single, variable-length coil of membrane tubing that is submersed into the water body of interest (i.e., the 100 L tank described above) with the closed air volume pumped through its inside, without active water sampling needed[9] (cf. Figure 1B). For the experiments, tubing lengths between 2.7 and 17.1 m were chosen.

The interfacial areas of the applied membrane-based extraction units or clusters of extraction units reached from 6 dm^2 (2.7 m of membrane coil) to 480 dm^2 (four connected large MiniModules). The respective data are summarized in Table 2.

Table 2. Water/Air Interface Areas and Air Volumes of Relevant Equipment[a]

	air volume (cm^3)	interface area (dm^2)
Extraction Units		
MiniModule, small	35	18
MiniModule, large	132	120
1 m of membrane coil	38	2.3
RAD-Aqua	703	ca. 50[b]
Radon-in-Air Detectors		
RAD7 (including desiccant tube)	1466	na
AlphaGuard	620	na

[a] na = not applicable. [b] At a 2 L/min pump rate.

For the RAD-Aqua spray chamber, the effective surface area that is available for radon exchange between water and air cannot be determined as straightforwardly as for the membrane units. It is a function of the intensity of droplet formation during water injection through the spray nozzle in the chamber (BETE WL whirl nozzle). At constant chamber volume and spray characteristics, this area depends on the water flow rate only. An approximate estimate can be obtained from the spray characteristics of the chamber. At a flow rate of 2 L/min, the typical size of the (assumed spherical) droplets is 400 μm (http://www.bete.com/products/wl.html). At this flow rate the total surface area of the spherical droplets can be calculated at 3000 dm^2/min, which, at an assumed transit time of water through the chamber of 1 s, equates to a "stationary" surface area of 50 dm^2. This approximation is consistent with the result obtained by using the empirical relation given in eq 6 introduced below.

$$\Delta t\ (\text{min}) = 0.28\frac{V(\text{cm}^3)}{A\ (\text{dm}^2)} + 12 \pm 2\ \text{min} \tag{6}$$

The circulating air volume of the applied setups was varied by using multiple radon-in-air detectors of up to six AlphaGuard and/or RAD7 monitors with individual detection chamber volumes of 0.62 and 1 L, respectively. Thereby the air volumes of the individual experimental setups covered a range from 752 cm^3 (one large MiniModule + one AlphaGuard) to 5474 cm^3 (four large MiniModules + four AlphaGuards + two RAD7's). The air volumes and interface area of the individual pieces of equipment are summarized in Table 2.

All experiments were started with water containing a radon concentration of about 2 Bq/l (pure tap water). After reaching and establishing concentration equilibrium between water and the air loop, the radon concentration in the water was instantaneously increased to about 40 Bq/l either by using the three-way valve—cf. setup Figure 1A—or by submersing the extraction module into the tank containing radon-rich water—cf. setup Figure 1B. After the new, i.e., elevated, concentration equilibrium ("plateau range"; cf. Figure 2A) was reached, the radon-in-water concentration was suddenly reduced back to 2 Bq/l (cf. Figure 2). With each experimental setup (i.e., individual interface area and air volume), at least four independent experiments were carried out to allow statistically reliable results. Radon concentrations in the circulating air were recorded every 1 min and every 2 min by the AlphaGuard and RAD7, respectively. Radon-in-water concentrations were determined using eqs 1 and 2 assuming fresh water at a constant temperature of 20 °C in the laboratory.

RESULTS AND DISCUSSION

The determined specific equilibration times Δt of each applied experimental setup versus the respective ratios of circulating air volume and interface area ("volume/interface ratio") are shown in Figure 4. The displayed trend lines are based on all respective experimental results shown in the figures.

Figure 4A shows the results achieved using the MiniModule (active radon extraction from a continuous water pump stream with an abrupt concentration increase) and the submersible membrane coil (passive radon extraction from a 100 L water volume with an abrupt concentration increase). Figure 4B shows the results for suddenly increasing concentrations achieved using the MiniModule (as in Figure 4A) and RAD-Aqua.

The results show clearly that the equilibration time Δt of a detection setup can be controlled by adjusting its volume/interface ratio. The equilibration time is notably reduced with a decreasing circulating air volume and/or an increasing interfacial area (i.e., with a decreasing ratio of the two parameters) for all experimental designs.

Despite the theoretically less efficient gas transfer across the membrane when compared to direct water/air contact (see the Theoretical Background), the extraction efficiency of the MiniModule membrane is slightly higher if compared to the RAD-Aqua spray chamber operated at the same water supply. As displayed in Figure 4 B, the shortest equilibration time achieved with the MiniModule is about 11 min whereas the shortest equilibration time achieved with the RAD-Aqua is about 16 min. This is due to the fact that at the given 2 L/min pump rate the water/air interface in the RAD-Aqua (ca. 50 dm^2) is not as large as the water/air interface that can be reached with a cluster of MiniModules.

At similar volume/interface ratios, the equilibration time of the membrane coil setup is significantly longer than that of the setup using the MiniModule membrane where radon is extracted from a running water stream (Figure 4A). The prime reason for the slower response is the comparably slow movement of the water body past the submerged membrane coil (facilitated in this experiment by constantly but slowly circulating the water inside the 100 L tank), which was not sufficient for keeping the radon concentration gradient at the water/air interface constantly at 100%. The effect of the water circulation intensity past the submersed membrane coil is illustrated exemplarily in Figure 5. At a volume/interface ratio of 80 (4.2 m membrane coil and one AlphaGuard), the experiment was once carried out with a submersible pump circulating the water in the tank and once without any water movement. With water movement, an equilibration time of 73 min was recorded (in Figure 4A this data point is marked with an asterisk). Without the circulating water pump running, equilibrium was reached not until about 400 min (see also ref 21). (It should be noted that field experiments have shown that in sufficiently turbulent waters, e.g., fast running creeks, equilibration times of less than 30 min can be reached with, for example, a membrane coil of 2.0 m in length and one RAD7; Stieglitz & Aquilina, personal communication.)

Radon extraction from a running water stream generally yields consistent results for the RAD-Aqua spray chamber and the MiniModule membrane unit (Figure 4B). However, a sudden decrease in radon concentration results in slightly longer equilibration times than an increase in radon concentration (parts C and B, respectively, of Figure 4) (see also refs 11 and 12). This effect is due to the energy-consuming cavity formation step essential to the molecular solution thermodynamics discussed above.

However, for practical reasons the data points achieved with the MiniModule illustrated in Figure 4B,C were statistically analyzed as one data set yielding an equilibration time (Δt) vs volume/interface ratio (V/A) coefficient of determination of $R^2 = 0.90$. On the basis of these data, an empirical equation was determined that quantifies the dependence of Δt on V/A as given in eq 6 (achieved with a 2 L/min water flow rate). The used Δt values do not take into account the additional delay caused by ^{218}Po decay as relevant for the RAD7 monitor (approximately 6 min; cf. Figure 2B).

Since the interface area and the volume of the circulating air are generally known for an applied detection setup, eq 6 allows quantitative estimation of the related equilibration time, which in turn allows a user to choose an instrumental setup appropriate for the required study. In addition, eq 6 shows that the equilibration time cannot be less than about 12 ± 2 min (even though a noticeable change in concentration is registered earlier). This minimum equilibration time is in good agreement with theoretical considerations regarding the time needed for radon diffusion through a stagnant water film. If a radon-in-water diffusion coefficient of 1.16×10^{-9} m^2 s^{-1} is assumed,[22,17] an equilibration time of about 12 min for reaching 95% concentration equilibrium corresponds to radon diffusion through a ca. 80 μm stagnant water film (Figure 6), a result which is consistent with the previous postulation that in the case of membrane extraction a stagnant water film of about 10–100 μm can be assumed. The equation related to Figure 6 is given with eq 7, where x is the thickness of the stagnant water film, t is the time needed for diffusion, D_w is the radon diffusion coefficient in water, C_{max} and C_{min} are the radon concentrations on either side of the membrane prior to equilibration (i.e., 100% and 0%, respectively), and Ψ is the Gauss error function. The given equation results from the analytical solution of the partial differential equation according to Fick's second law on the assumption of a semi-infinite space and a constant radon source.

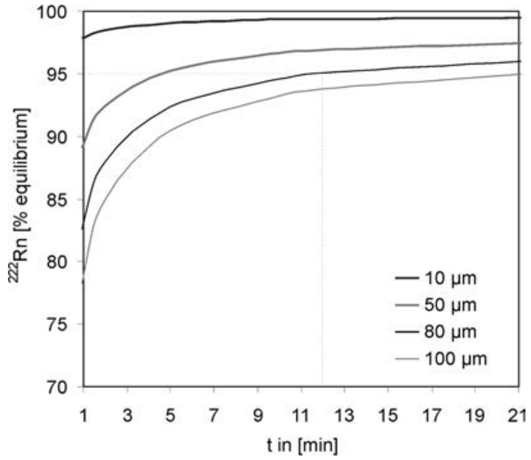

Figure 6. Time needed for radon diffusion through a stagnant water film with a thickness of 10, 50, 80, and 100 μm (cf. eq 7).

$$C^{Rn}_{x,t}(x, t) = C^{Rn}_{\min} + (C^{Rn}_{\max} - C^{Rn}_{\min})\left(1 - \Psi\left(\frac{x}{2\sqrt{D_{w}t}}\right)\right) \tag{7}$$

In summary, the results indicate that for continuous radon-in-water detection using one or multiple radon-in-gas monitors, equilibration times to sudden changes in radon-in-water concentrations and thus system performance can be controlled and optimized by selecting a large water/air interface and/or a small circulating air volume. As a guide for the determination of a suitable setup, an empirical equation was derived from which the equilibration time at a 2 L/min water flow rate can be calculated when radon is extracted by active extraction by means of the MiniModule membrane(s) (eq 6). Alternatively, where experimental conditions permit, an experimental setup may be considered that increases the extraction efficiency and equilibration time by increasing the water flow rate.[12] This is only possible in the RAD-Aqua spray chamber, since the MiniModule membrane does not permit flow rates greater than 2.5 L/min and cannot be operated in water with high suspended sediment concentrations. On the other hand, it may be desirable for safety reasons in long-term field deployments to employ the MiniModule approach because of the physical separation of the water and air phases, in which case the use of multiple membranes in series will significantly enhance the extraction efficiency (at an energetic cost; circulating water through multiple membranes will increase friction and thus the energy requirement).

In addition, the practical applicability of the used equipment has to be considered. The method of choice clearly depends on (a) energy requirements, (b) the environmental conditions on site, (c) protection of the equipment (e.g., to avoid vandalism), and (d) the time scale that is targeted. The membrane coil is most suitable if radon is to be extracted in situ without any water pumping, e.g., in groundwater wells that show a low yield or in long-term time series where the power supply to the pumps is restricted. The comparatively long equilibration time does not present a large problem in the case of long-term time series where high temporal resolution is usually not required. Since the efficiency of the submersible membrane coil depends on the concentration gradient at the water/air interface, which can only be maintained at close to 100% if the water is in constant and heavy motion, the water movement around the tube is a crucial factor. The MiniModule (or several of them in series) is ideally suited for radon detection in low-turbidity, clear groundwater. An alternative is the more robust RAD-Aqua. The experiments have shown that at a water pump rate comparable to that applied in this study (2 L/min) the RAD-Aqua yields minimum equilibration times of at least 16 min (cf. Figure 4B), i.e., significantly longer than that of the optimum MiniModule setup. However, if higher water pump rates (e.g., 6 L/min) are achievable on site (thereby increasing the water/air interface in the spray chamber), equilibration times with the RAD-Aqua can be reduced substantially. The RAD-Aqua is well suited to conditions where elevated suspended matter concentrations restrict the use of membrane-based extraction modules; the comparatively large opening of the spray nozzle is usually not affected by such conditions.

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Notes

The authors declare no competing financial interest.

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