Journal of Hazardous Materials 393 (2020) 122344

Contents lists available at ScienceDirect

Journal of Hazardous Materials

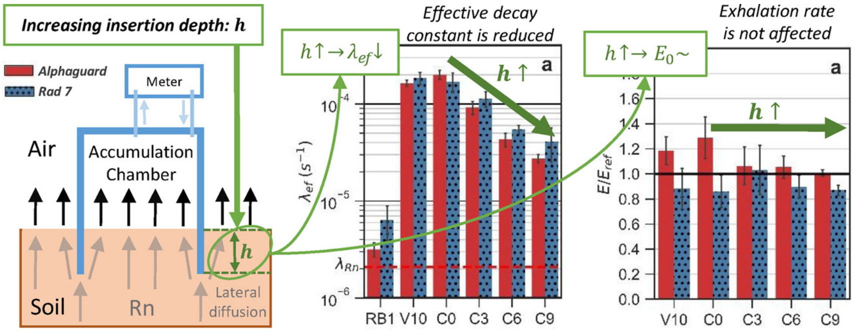
journal homepage: www.elsevier.com/locate/jhazmat

Influence of the accumulation chamber insertion depth to measure surface radon exhalation rates

I. Gutiérrez-Álvarez[a,*], J.L. Guerrero[a], J.E. Martín[a], J.A. Adame[b], J.P. Bolívar[a]

[a] *Integrated Sciences Department, Research Centre of Natural Resources, Health and the Environment (RENSMA), University of Huelva, Huelva, Spain*
[b] *Atmospheric Sounding Station – El Arenosillo, Atmospheric Research and Instrumentation Branch, National Institute for Aerospace Technology. INTA, Mazagón-Huelva, Spain*

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dr. R Teresa

Keywords:
Radon exhalation
Accumulation chamber
Insertion depth
Phosphogypsum

ABSTRACT

A common method to measure radon exhalation rates relies on the accumulation chamber technique. Usually, this approach only considers one-dimensional gas transport within the soil that neglects lateral diffusion. However, this lateral transport could reduce the reliability of the method. In this work, several cylindrical-shaped accumulation chambers were built with different heights to test if the insertion depth of the chamber into the soil improves the reliability of the method and, in that case, if it could limit the radon lateral diffusion effects. To check this hypothesis in laboratory, two reference exhalation boxes were manufactured using phosphogypsum from a repository located nearby the city of Huelva, in the southwest of Spain. Laboratory experiments showed that insertion depth had a deep impact in reducing the effective decay constant of the system, extending the interval where the linear fitting can be applied, and consistently obtaining reliable exhalation measurements once a minimum insertion depth is employed. Field experiments carried out in the phosphogypsum repository showed that increasing the insertion depth could reduce the influence of external effects, increasing the repeatability of the method. These experiments provided a method to obtain consistent radon exhalation measurements over the phosphogypsum repository.

1. Introduction

A relevant factor to take into consideration while studying radon gas is its exhalation from soils. Exhalation measurements have been used extensively to assess radon risk areas such as fault zones, uranium mines or some waste repositories (Chen et al., 2018; Jónás et al., 2017;

---

[*] Corresponding author.
E-mail address: isidoro.gutierrez@dfa.uhu.es (I. Gutiérrez-Álvarez).

https://doi.org/10.1016/j.jhazmat.2020.122344
Received 11 December 2019; Received in revised form 5 February 2020; Accepted 16 February 2020

Sun et al., 2004; Abril et al., 2009). Furthermore, it is a relevant topic in atmospheric sciences, as it is widely used as an atmospheric tracer (Levin et al., 2002; Cristofanelli et al., 2015; Ielsch et al., 2001). There exist several procedures to measure the exhalation rate, such as activated charcoal canisters (Alharbi and Akber, 2014; Tsapalov et al., 2016), electrets (Kotrappa, 2015; Grossi et al., 2008) or accumulation chambers (Jonassen, 1983; Dueñas et al., 1997), among others. In the last decades, there has been an extensive research using accumulation chambers, where several mathematical fits can be used to extract the exhalation rate from the radon accumulation curve inside the chamber. One of the key aspects of this method has to do with the leaks of the system, which restricts the applicability of the linear fit (Abo-Elmagd, 2014). In order to increase it, the leaks influence needs to be reduced as maximum as possible. On the other hand, some studies (Sahoo and Mayya, 2010) have pointed out that an important limitation of the accumulation method lies in the fact that is based on one-dimensional radon transport inside the soil. As a consequence, lateral diffusion produced under the chamber may increase the effective radon leaks of the system and alter the method's reliability.

A possible strategy to check and face these last issues, which is proposed and tested in this work, is to increase the insertion depth of the accumulation chamber into the soil. This procedure could help to reduce the effects of lateral radon diffusion by obstructing the lateral radon pathways near the chamber. Several cylindrical chambers with the same area and volume but with different insertion depths were designed and built to test the effect of the insertion depth into the soil on the leaks of the measurement system and on the reliability of the technique. These chambers were tested on laboratory and field measurements.

The material used to test these chambers was phosphogypsum (PG) collected in a repository generated by the fertilizer industry in the city of Huelva, to the southwest of the Iberian Peninsula. This industry produced phosphoric acid using phosphate rocks, with high levels of radioactive elements from the ^{238}U series, producing PG as a byproduct. This material has ^{226}Ra concentrations of $650 \pm 50\,\mathrm{Bq\ kg^{-1}}$ and is classified as a Naturally Occurring Radioactive Material (NORM). The PG was stacked in piles in the estuary of the Tinto river, less than 1 km from the urban area, covering an extension about 1000 ha. As a consequence, the repository was identified as a potential source of radon gas (Abril et al., 2009; Bolivar et al., 1996; Dueñas et al., 2007; López-Coto et al., 2014; Hernández-Ceballos et al., 2015).

To perform laboratory experiments, two reference exhalation soils were made with PG from those piles, simulating its surface, and allowing to study radon exhalation measurement systems based on the accumulation chamber method. To summarize, the main goals of this work are to evaluate the influence of the lateral diffusion on the system leaks and to reduce those undesired leaks, improving the reliability of gas accumulation methods for measuring radon exhalation while keeping the simpler one-dimensional mathematical approach.

2. Experimental and methods

2.1. Theoretical framework

As previously cited, one of the typical procedures to measure radon exhalation relies on the accumulation chamber method (Fig. 1). Radon exhaled from the ground is forced to stay inside the chamber and the exhalation can be obtained fitting the growth curve to a known equation.

This method supposes that the radon travels vertically through the soil and exhales to the ambient air once it reached the surface. The behaviour of radon accumulating inside the chamber can be approximated by the following equation (Jonassen, 1983; López-Coto et al., 2009; Seo et al., 2018):

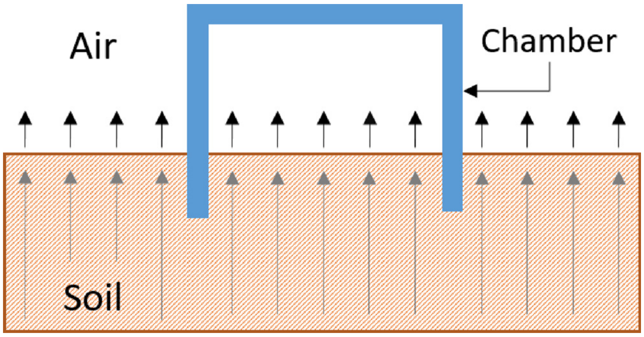


Fig. 1. Scheme of the accumulation chamber method.

$$\frac{dC(t)}{dt} = \frac{E_0\,S}{V} - (\lambda_{Rn} + \lambda_b + \lambda_l)C(t) \tag{1}$$

where:

- $C(t)$ Radon concentration inside the chamber ($Bq\,m^{-3}$)
- E_0 Free Exhalation rate ($Bq\,m^{-2}\,h^{-1}$)
- S Chamber-Soil Surface (m^{-2})
- V Accumulation volume (m^{-3})
- λ_{Rn} Radon decay constant (s^{-1})
- λ_b Bound exhalation constant (s^{-1})
- λ_l Leakage constant (s^{-1})

This equation describes a balance between radon generation, produced by exhalation from the soil, and several radon removal processes, such as radon decay, bound exhalation (López-Coto et al., 2009; Kernfysisch V.I. Aldenkamp et al., 1992) and possible leaks in the measurement system, considering these three processes linearly proportional to radon concentration. It is important to note that the 'leakage' constant term includes all effects aside radon decay and bound- exhalation, including but not limited to lateral radon diffusion and actual leaks in the measurement system. The solution for Eq. (1) is:

$$C(t) = C_{sat} + (C_0 - C_{sat})e^{-\lambda_{ef}t} \tag{2}$$

where λ_{ef} is the effective decay constant, the sum of the three radon removal constants, and, C_{sat}, the saturation concentration.

However, Eq. (1) can be simplified supposing that the initial concentration inside the chamber is negligible respect to the saturation concentration, (Jonassen, 1983; Seo et al., 2018; (Kernfysisch V.I. Aldenkamp et al., 1992; Onishchenko et al., 2015). Applying this condition, the radon accumulation inside the chamber is described by:

$$C(t) = C_{sat}(1 - e^{-\lambda_{ef}t}) \tag{3}$$

A fundamental parameter in Eq. (3) is λ_{ef}, which dictates how much time the system will need to reach saturation. With lower λ_{ef} radon grows linearly in the first moments of the accumulation. Thus, the exponential term of Eq. (3) can be approximated by $1 - \lambda_{ef}t$, obtaining a linear relation between radon concentration in the chamber and the time, given by the equation:

$$C(t)|_{\lambda_{ef}t \ll 1} \approx C_{sat}\lambda_{ef}t \tag{4}$$

In order to get the free exhalation rate, E_0, it is necessary to apply its relation with the saturation concentration and the effective decay constant:

$$E_0 = C_{Sat}\lambda_{ef}\frac{V}{S} \tag{5}$$

Eq. (5) provides a way to obtain the free radon exhalation rate after fitting the radon growth to the exponential fit (eq. (3)) or the linear fit (eq. (4)). Both of this equations considered the initial concentration to be exactly zero.

2.2. Linearity time

The linearity time can be used to decide whether to apply the exponential or linear fit (Gutiérrez-Álvarez et al., 2019). This parameter can be calculated from the ratio between the free exhalation rate predicted by the simplified linear model, E_{lin}, and the corresponding exponential one, E_{exp}. Combining Eq.s (3),(4) and (5):

$$\frac{E_{lin}}{E_{exp}} = \frac{(1 - e^{-\lambda_{ef} t})}{\lambda_{ef} t} \tag{6}$$

This ratio allows to stablish the maximum acceptable deviation between the two models. Taking into account the experimental uncertainties of the radon measurements, a 20 % variation could be an acceptable level ($E_{lin}/E_{\exp} = 0.8$). Eq. (6) can be numerically solved under this assumption, obtaining the following relation:

$$\lambda_{ef} t_{lin} = 0.46 \tag{7}$$

where t_{lin} is the linearity time, the maximum time the linear approximation can be used to calculate the free exhalation rate before it differs 20 % from the real value.

2.3. Reference exhalation soils

The radon accumulation experiments were carried out in laboratory over two reference exhalation boxes, RB1 and RB2, made with two polypropylene rectangular boxes containing a layer of PG from the NORM repository. These rectangular boxes had an empty volume of 172 L with an interior surface of 0.44 m^2. The polypropylene was chosen to minimize leakages while the dimensions allow measuring inside the boxes with accumulation chambers of different sizes (Fig. 2, a). Two covers were also built to hermetically close the reference boxes and force the radon to stay inside (Fig. 2, b). Different quantities of PG were deposited on each box to obtain distinct exhalation rates. More precisely, 35 kg were deposited on RB1 while 70 kg were used on RB2. The layer of PG reached 7 and 14 cm height whereas the volume left for radon accumulation was 148.1 L and 117.2 L, respectively.

The reference free exhalation rate for RB1 was $E_0|_{RB1} = 47.7 \pm 0.7\, Bq\, m^{-2}\, h^{-1}$, and $E_0|_{RB2} = 84.5 \pm 0.9\, Bq\, m^{-2}\, h^{-1}$ for RB2. From now on, the ratio between the measured free exhalation rate and the corresponding reference one will be used. The design and evaluation procedure of these reference exhalation soils was described in a previous work (Gutiérrez-Álvarez et al. (2019)).

To estimate the expected free exhalation rate, different parameters of the soils like its radium content, porosity and radon emanation factor, among others, need to be taken into consideration. Several approximations have been used to do this (Porstendörfer, 1994; Zhuo et al., 2006). The free radon exhalation rate is finally obtained as follows:

$$E_0 = \varepsilon \rho \lambda_{Rn} C_{Ra}\, tgh\left(\frac{z_0}{l_0}\right) \tag{8}$$

where ε is the emanation factor, ρ is the density, C_{Ra} is the soil's radium concentration, z_0 is the height of the soil layer and l_0 is the radon diffusion length.

The reference exhalation boxes designed in this work have a thin layer of PG which can be neglected in comparison with the radon diffusion length, which is around 1 m in this material (Keller et al. (2001)). In this case, (8) can be approximated by:

$$E_0 = \varepsilon \rho \lambda_{Rn} C_{Ra} z_0 \tag{9}$$

Once the characterization of the PG properties was made (López-Coto et al., 2009), the theoretical free exhalation rates obtained were $E_{th}|_{RB1} = 44 \pm 9\, Bq\, m^{-2}\, h^{-1}$ and $E_{th}|_{RB2} = 82 \pm 16\, Bq\, m^{-2}\, h^{-1}$. The higher uncertainty is associated to the uncertainty of the emanation factor. These results are in good agreement with the reference free exhalation rates measured.

2.4. Insertion chambers and measurement devices

To evaluate the influence of the insertion depth into the soil, six accumulation chambers, insertion chambers from now on, were built to be placed directly over the PG layer of the reference boxes (Fig. 2 a). These chambers were cylindrical-shaped, made of polypropylene to avoid radon leaks and had approximately the same accumulation volume and chamber-soil surface, but different height. If lateral diffusion plays a role, this should have an effect on the accumulation curve, either on C_{Sat} or λ_{ef}.

The accumulation volume of each chamber was measured pouring a known amount water inside. Each chamber-soil surface was estimated measuring the corresponding inner diameter several times across different axes, and computing the average. The mean accumulation volume was around $9.7\, L$ (uncertainty 0.3 %) and the mean chamber-soil surface was around $4.7{\cdot}10^{-2}\, m^2$ (uncertainty 0.9 %). These chambers will be referred as CX, were C refers to its cylindrical shape and X denotes the insertion depth in centimeters. Chamber C0 is merely placed over the measurement surface. Despite the fact that C9 chamber could not be fully buried on RB1, it was used to test the limit case of minimal lateral transport on RB1. In that case, the actual insertion depth was measured and the accumulation volume was recalculated to take this situation into account.

In addition to the insertion chambers, a rectangular-shaped chamber (referred to as V10, for its approximated volume) was used to compare with the accumulation chambers typically used in the literature. This chamber had a similar accumulation volume to CX chambers, around 9.9 L, with 0.1 m^2 of chamber-soil surface, and an insertion depth of 2.4 cm.

The radon concentration measurements were performed by an Alphaguard (AG) and a Rad 7 (R7). Both devices were configured to work in flow-through mode, performing measurements every 10 min.

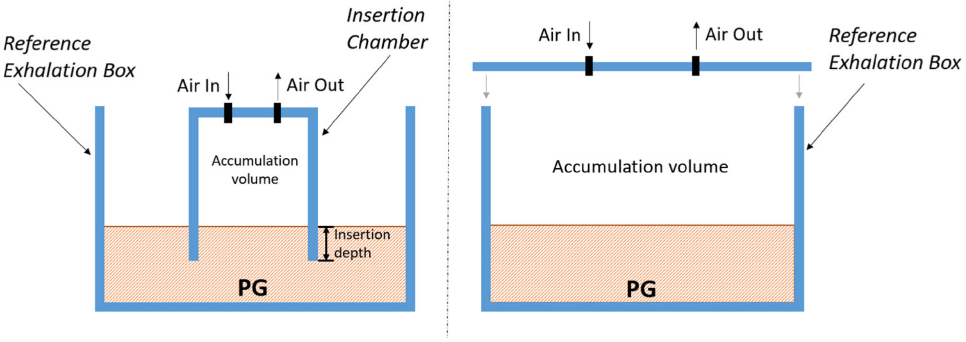


Fig. 2. Schemes of a closed reference exhalation box (a) and an insertion chamber placed inside an open reference exhalation box (b).

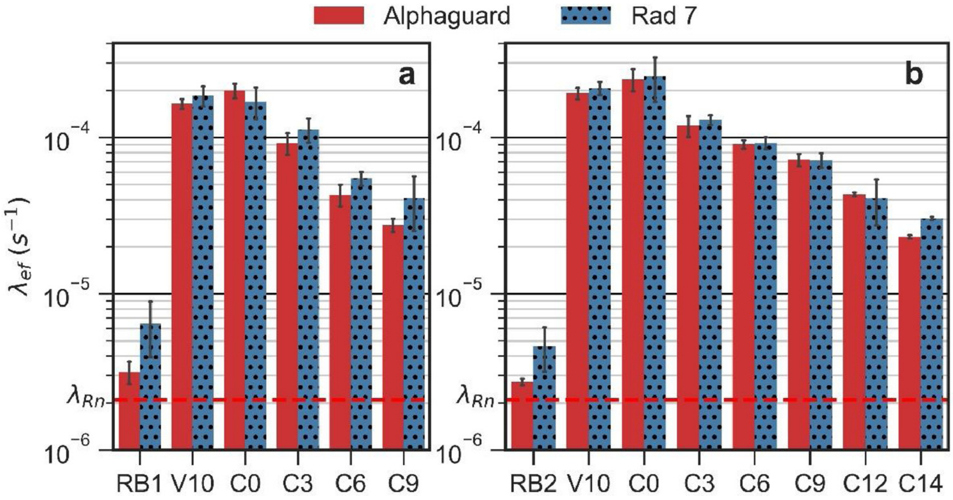


Fig. 3. Effective decay constant for the different accumulation chambers put on open RB1 (a) and RB2 (b) applying the exponential fit equation. Results for closed RB1 and RB2 are also included for comparison. The red dashed line represents the value for the radon decay constant ($\lambda_{Rn} = 2.1{\cdot}10^{-6}\,s^{-1}$) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3. Results and discussion

3.1. Insertion chamber effect on the effective decay constant

Each accumulation chamber was tested with every combination of reference exhalation box (RB1 and RB2) and measurement device (AG and R7). The duration of each of the experiments was around 18 h, enough time for the exponential behaviour of the accumulation curve to appear and maximize the number of available points for the fitting. At least 5 replicate experiments were made with each combination of reference exhalation box, accumulation chamber and measurement device.

The effective decay constant results, obtained with eq. (2), for the different chambers tested are shown in Fig. 3. Values are one or two orders of magnitude higher than those obtained for the reference boxes, RB1 and RB2, closed without any chamber inside, included for comparison. The higher the chamber is inserted into the soil, the lower is the effective decay constant of the system. It is noticeable that values for chamber V10 are more similar to those of C0 than to those of C3. This could be due to the higher perimeter of the former, 1.3 m, than the perimeter of the latter, 0.8 m.

Insertion chambers show a consistent decrease in the effective decay constant, starting around $2{\cdot}10^{-4}\,s^{-1}$, for chamber C0, an ending with values nearby $2-3{\cdot}10^{-5}\,s^{-1}$, which is the value for the chamber with the highest insertion depth in each case. This suggests the idea that there is a limit to the reduction of the effective decay constant; nevertheless, reaching the bottom does not guarantee the tightness of the accumulation chamber. This fact can explain the differences in the effective decay constant between C9 in RB1 and C14 in RB2 respect to their corresponding reference box, RB1 and RB2.

In addition, Fig. 3 also suggests the existence of a linear relationship between the depth of the insertion chambers and the logarithm of the effective decay constant. The results of the linear fit can be seen in Table 1. There is a good correlation between both magnitudes, proving the impact of the insertion depth in the reduction of the effective decay constant of the measurement system. It can be noticed that both linear regressions have the same intercept, represented by parameter b. This points out the maximum value for the effective decay constant, which is related to a situation with the highest radon interchange between inside and outside of the accumulation chamber.

Table 1
Linear regression fit parameters between the logarithm of the effective decay constant versus the insertion depth for the reference boxes. Slope is represented by parameter a and intercept by b. No distinction between device was made.

Reference Exhalation Box	a (cm^{-1})	b	R^2
RB1	−0.108 ± 0.006	−3.69 ± 0.03	0.993
RB2	−0.058 ± 0.005	−3.69 ± 0.04	0.97

3.2. Measuring the exhalation rate using the exponential fit

The corresponding results of exhalation rate for the insertion chambers can be seen in Fig. 4. In general, there is a good agreement with the reference, with the exception of C0 on both reference soils. The rest of the insertion chambers provide results within 20 % of the reference in all cases. Chamber V10 stays within 20 % as well, but further away from unity. There seems to be a reduction in the dispersion of the results as the insertion depth increases. Nevertheless, considering that accumulation chambers are normally inserted several centimetres, as happens for V10, results does not seem to indicate a reduction of the reliability of the method due to lateral diffusion.

It should be noted that there seems to be a difference between devices, as the Alphaguard tends to measure values above those of Rad 7. For the effective decay constant, Alphaguard had a lower values overall for all chambers tested (Fig. 3). This is linked to the higher saturation concentration reached by Alphaguard, as seen in Table 2, i.e. a lower effective decay constant allows more radon to accumulate inside the chamber. In any case, except for C0, these differences stay within 20 % of the reference value, supporting the idea that the insertion depth variations do not interfere with the radon exhalation measurement.

3.3. Exhalation rate obtained from short accumulation times

The reliability of the method must be also studied with shorter accumulation periods, as they are the typically used in field measurements. In this sense, accumulation times of 30, 60, 90, 120, 300 and 600 min were considered and both the exponential and linear simplified models were applied. The results of the corresponding experiments are shown in Fig. 5. In this set of experiments, no distinction between measurement devices was made to simplify the study.

The results for the exponential fit can be seen in Fig. 5 (a–b). This approach shows an overall inconsistent prediction of the reference exhalation rate for shorter durations. Chambers C3, C6 and C9 on RB1 and C3, C6, C9 and C14 on RB2 presents results within 20 % of the reference for accumulation periods longer than 120 min. C12 and C14 shows

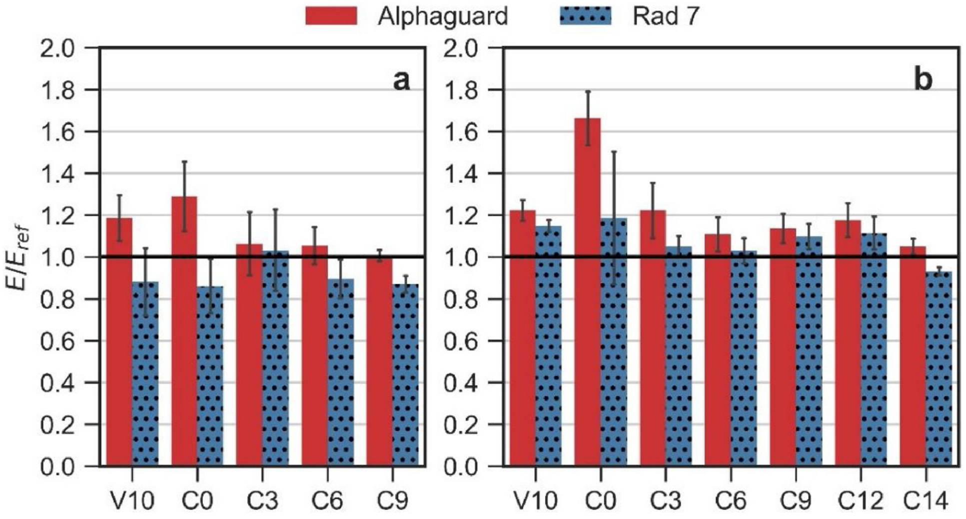


Fig. 4. Relative exhalation rate applying the exponential fit on RB1 (a) and RB2 (b), grouped by insertion chamber.

Table 2
Number of total experiments, N, and average saturation concentration, $\boldsymbol{C_{sat}}$, for each combination of measurement device, accumulation chamber and reference box. Uncertainties correspond to 1σ.

Chamber	Device	N	C_{sat} (Bq m^{-3}) *[RB1]*	N	C_{sat} (Bq m^{-3}) *[RB2]*
V10	**AG**	11	770 ± 70	5	1380 ± 40
	R7	10	630 ± 70	5	1350 ± 40
C0	**AG**	10	390 ± 40	5	670 ± 40
	R7	9	250 ± 21	8	600 ± 60
C3	**AG**	10	660 ± 50	5	1040 ± 30
	R7	12	500 ± 30	5	840 ± 24
C6	**AG**	10	1500 ± 200	5	1370 ± 40
	R7	9	900 ± 80	5	1140 ± 80
C9	**AG**	11	1900 ± 100	6	1710 ± 60
	R7	9	1100 ± 180	9	1600 ± 240
C12	**AG**	–	–	5	2390 ± 28
	R7	–	–	10	2600 ± 900
C14	**AG**	–	–	5	4690 ± 60
	R7	–	–	5	2900 ± 120
Reference	**AG**	12	12700 ± 1900	17	32500 ± 1500
Box	**R7**	15	6400 ± 1600	10	19000 ± 4000

really poor behaviour within the first 60 min, as its lower effective decay constant implies that it needs more time to start showing its exponential behaviour. V10 shows a more consistent behaviour than C0, presenting results within 20 % of the reference with only 60 min of accumulation. It is also noticeable how the average uncertainty can be reduced by increasing the fit duration. This is due to the higher number of points available to compute the parameters of the fit equation. Once again, insertion depth does not reflect any effect on the method's reliability.

The results for the linear fit appear in Fig. 5 (c–d). As expected, this fit provides better results for the shorter accumulation times, i.e. as long as the linear approximation holds. Attending to the results, this occurs for longer accumulation periods in the case of chambers with higher insertion depths. This points out the decrease in the effective decay constant due to the reduction of the effect of the lateral diffusion, which allows to apply the simplified linear fit for longer times. The dispersion of the results is higher for the shorter durations, reducing its dispersion as the accumulation time increases. As happened before, this is due to a higher number of points available to perform the fit of the parameters.

As explained in section 2.2, the linearity time can be used to study the applicability of the linear model to measure the exhalation rate. Assuming a 20 % variation of the linear model, i.e. $E_{lin}/E_{exp} = 0.8$, the linearity time ranges from 30 to 40 minutes, for C0 on both RB1 and RB2, 200–300 minutes for C9 on RB1 and 250–350 minutes for C14 on RB2. This means that, when the effective decay constant is unknown, a high insertion depth should be used (∼10 cm), as it would ensure the applicability of the linear fit during longer times, guaranteeing the reliability of the measurement.

3.4. *In-situ measurements*

On august 2018, a set of measurements were made on the phosphogypsum repository. Two experiments per week, eight in total, were made with the insertion chamber C6 and the rectangular-shaped chamber, V10, measuring the radon accumulation with an Alphaguard and a Rad 7 in a closed-circuit flow setup. Chambers were located at a distance of over 1 m and the experiments lasted two hours each.

In Fig. 6 the radon accumulation curves for the measurements at the phosphogypsum repository are shown. At first sight, the experiments using the insertion chamber C6 show a similar behaviour on all days, while the V10 chamber presents accumulation curves with different characteristics. On August 8th (Fig. 6 a) radon build up on C6 is almost a straight line while V10 reached saturation in one hour after the start of the accumulation. August 17th and 22nd (Fig. 6 b–c) show more similarity between chambers but V10 still appears to have higher leaks, especially on the latter. Finally, on August 29th (Fig. 6 d), the radon growth increases at a lower rate than in the previous experiments, reaching only 12 kBq m^{-3} for C6. On the other hand, V10 chamber accumulation was not successful and, after an initial increase in the first 30 min the radon levels dropped to near zero for the rest of the experiment.

On Table 3, exhalation results for all the days and experiments are shown. Linear fits were computed removing the first 20 min of measurements and using the next 30 min. This procedure allowed to avoid the variability of the first minutes of the accumulation while keeping enough points to perform a reliable linear regression (Gutiérrez-Álvarez et al., 2019). Due to its special behaviour, to obtain the exhalation rate of V10 on august 29th only the first 20 min, after removing the first 10, were used. Finally, for the exponential fit, the first 20 min were discarded using the rest of the accumulation curve for the fitting.

Experiments using C6 shows a strict linear behaviour that makes the exponential fit difficult to use, as it is reflected by the uncertainty of the first day. This implies a lower effective decay constant respect to the laboratory experiments. In the case of V10 chamber, the effective decay constants are similar to those obtained in the laboratory for the second and third days, being higher than in laboratory on the first day. The linear fit on C6 gave exhalation values around 2100 Bq m^{-3} h^{-1} for the

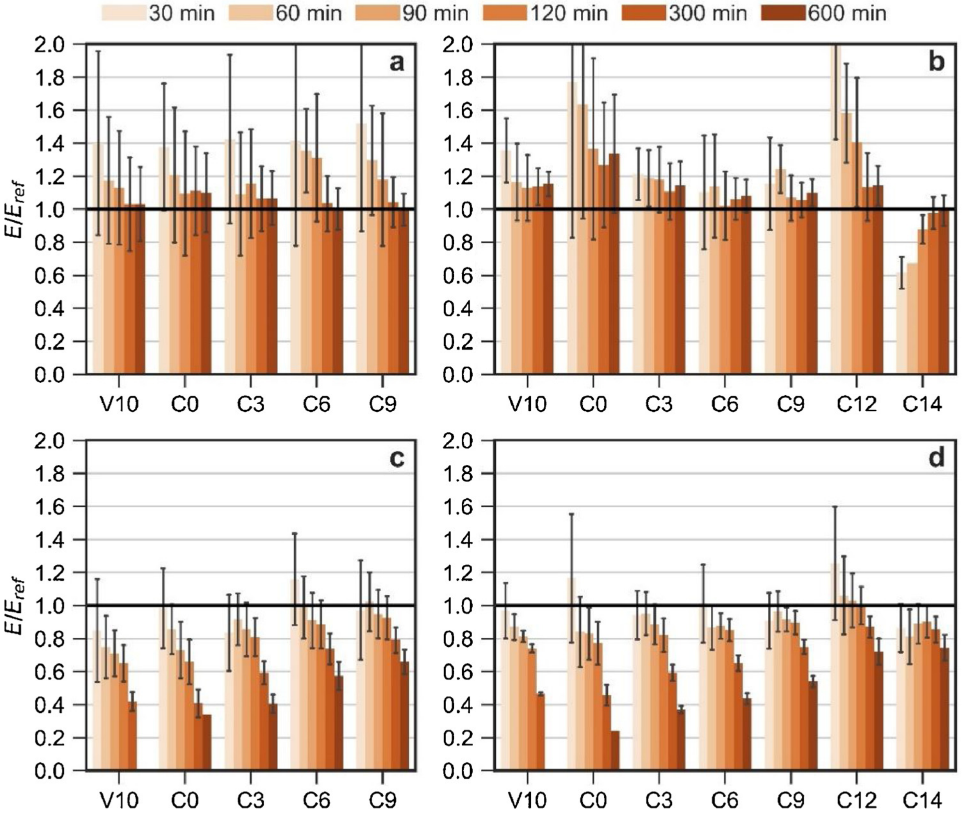


Fig. 5. Relative exhalation rate applying the simplified exponential fit for RB1 (a) and RB2 (b) and applying the simplified linear fit for RB1 (c) and RB2 (d), grouped by insertion chamber.

first three days, which are consistent with the exponential fit results obtained for V10 in the second and third days (2000 and 2100 Bq m^{-3} h^{-1}). This situation is in agreement with the different effective decay constant of the chambers since the higher value of this parameter for V10 makes possible to apply the exponential fit, but, reduces the linearity time of the system to around 30 − 40 min, producing lower and less reliable results for the linear fit.

The experiments in the first and last days show that the accumulation curve measured in C6 was not as altered by ambient circumstances as the completely modified accumulation curve in V10. In this sense, considering the exhalation results, the higher difference for V10 than for C6 between the results in the first and last days, in comparison to those in the middle days, points to a higher exposure of the former to ambient conditions that might influence the accumulation process.

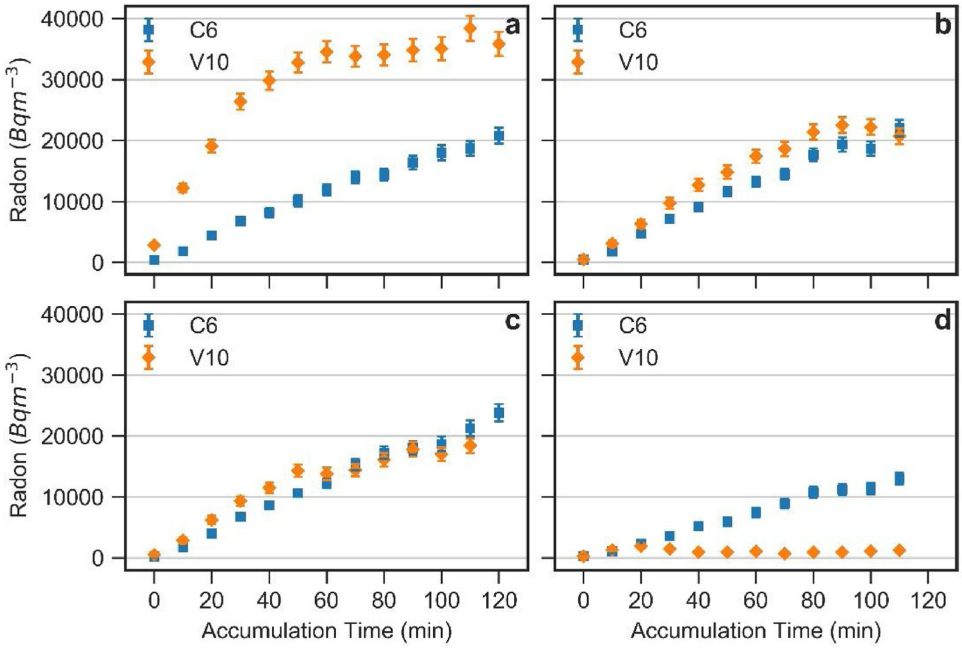


Fig. 6. Radon accumulation experiments performed on the phosphogypsum repository on August 8th (a), 17th (b), 22nd (c) and 29th (d).

Table 3

Exhalation rate and effective decay constant results for the experiments performed on the phosphogypsum piles, sorted by accumulation chamber, device and type of fit. NF (Not Found) refers to experiments where the algorithm could not find appropriate parameters for the curve. The bounds for λ_{ef} are computed considering the maximum concentration reached in the chamber as the minimum limit for the saturation concentration.

Experiment Date	Chamber	Device	Fit Type	Exhalation (Bq m^{-2} h^{-1})	λ_{ef} (10^{-4} s^{-1})
2018/08/08	C6	Rad 7	Linear	2300 ± 200	< 1.3
			Exp.	2500 ± 6700	0.1 ± 0.3
	V10	Alphaguard	Linear	4200 ± 200	< 3.0
			Exp.	6600 ± 600	4.4 ± 0.4
2018/08/17	C6	Alphaguard	Linear	2200 ± 100	< 1.3
			Exp.	*NF*	*NF*
	V10	Rad 7	Linear	1600 ± 120	< 1.8
			Exp.	2000 ± 700	1.2 ± 0.3
2018/08/22	C6	Alphaguard	Linear	1920 ± 90	< 1.0
			Exp.	*NF*	*NF*
	V10	Rad 7	Linear	1600 ± 100	< 2.0
			Exp.	2100 ± 500	2.0 ± 0.4
2018/08/29	C6	Rad 7	Linear	1200 ± 140	< 1.1
			Exp.	*NF*	*NF*
	V10	Alphaguard	Linear	420 ± 50	< 6.0
			Exp.	*NF*	*NF*

Unlike V10, experiments using C6 chamber appear to be more consistent in all days, suggesting that increasing the insertion depth strengthen the reliability of the accumulation method. This effect is to be confirmed in future stages of the research.

4. Conclusions

In order to check the influence of lateral diffusion in the radon accumulation method, several accumulation chambers with different insertion depths were built and tested on laboratory and field measurements.

Laboratory tests showed that insertion depth had a deep impact on the effective decay constant of the system, showing a linear relationship between the logarithm of the effective decay constant and the insertion depth. Due to the significant reduction of the effective decay constant, these chambers allowed to apply the linear fit for longer periods of time. Laboratory experiments suggest that chambers should be inserted some centimeters (At least 3 or more) into the soil to provide reliable radon exhalation measurements. The optimal insertion depth for each case will probably depend on parameters like soil porosity, humidity or radon emanation factor and should be studied for each case. Once this condition is fulfilled, experiments do not seem to reflect a lack of reliability related to lateral diffusion.

Field measurements showed that the reduction of the effective decay constant due to insertion depth was even higher than in laboratory. This effect did not allow the exponential fit to provide results within the first 2 h of accumulation due to the low effective decay constant of the system. Experiments over the PG repository using accumulation chambers were more consistent overall with a higher insertion depth, being less influenced by external conditions. This result indicates a certain lack of reliability for shallower insertions depths.

This study confirms that lateral diffusion plays a significant role in the effective decay constant of radon exhalation measurement systems. This effect could be used to modify the effective decay constant and increase the precision of the fit applied to the accumulation curve. More in situ measurements on the PG stacks and other soils will be carried out in the future to better quantify the effect of lateral diffusion on radon exhalation measurements.

CRediT authorship contribution statement

I. Gutiérrez-Álvarez: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization. **J.L. Guerrero:** Methodology, Investigation, Resources, Data curation, Writing - review & editing, Visualization. **J.E. Martín:** Conceptualization, Methodology, Supervision, Project administration, Writing - review & editing. **J.A. Adame:** Conceptualization, Methodology, Supervision, Project administration, Writing - review & editing. **J.P. Bolívar:** Conceptualization, Methodology, Supervision, Project administration, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

None.

Acknowledgements

This research was supported by the Spanish Ministry of Science, Innovation and Universities, by the project 'Fluxes of radionuclides emitted by the PG piles located at Huelva; assessment of the dispersion, radiological risks and remediation proposals' (Ref.: CTM2015-68628-R) and the Junta de Andalucía Regional Government by the project "Basic processes regulating the fractionation and enrichment of natural radionuclides under Acid Mine Drainage" (Ref.: UHU-1255876). Special thanks are given to Antonio Padilla for his invaluable technical support and know-how.

References

(Kernfysisch V.I. Aldenkamp, F.J., (Kernfysisch V.I. de Meijer, R.K., (Kernfysisch V.I. Put, L.W., (Kernfysisch V.I. Stoop, P., 1992. An assesment of in situ radon exhalation measurements and the relation between free and bound exhalation rates. Radiat. Prot. Dosim. 45, 449–453.

Abo-Elmagd, M., 2014. Radon exhalation rates corrected for leakage and back diffusion – evaluation of radon chambers and radon sources with application to ceramic tile. J. Radiat. Res. Appl. Sci. 7, 390–398. https://doi.org/10.1016/j.jrras.2014.07.001.

Abril, J.M., García-Tenorio, R., Manjón, G., 2009. Extensive radioactive characterization of a phosphogypsum stack in SW Spain: 226Ra, 238U, 210Po concentrations and 222Rn exhalation rate. J. Hazard. Mater. 164, 790–797. https://doi.org/10.1016/J.JHAZMAT.2008.08.078.

Alharbi, S.H., Akber, R.A., 2014. Radon-222 activity flux measurement using activated charcoal canisters: revisiting the methodology. J. Environ. Radioact. 129, 94–99. https://doi.org/10.1016/j.jenvrad.2013.12.021.

Bolivar, J.P., García-Tenorio, R., García-León, M., 1996. On the fractionation of natural radioactivity in the production of phosphoric acid by the wet acid method. J. Radioanal. Nucl. Chem. Lett. 214, 77–88. https://doi.org/10.1007/BF02164808.

Chen, Z., Li, Y., Liu, Z., Wang, J., Zhou, X., Du, J., 2018. Radon emission from soil gases in the active fault zones in the Capital of China and its environmental effects. Sci. Rep. 8, 1–12. https://doi.org/10.1038/s41598-018-35262-1.

Cristofanelli, P., Scheel, H.-E., Steinbacher, M., Saliba, M., Azzopardi, F., Ellul, R., Fröhlich, M., Tositti, L., Brattich, E., Maione, M., Calzolari, F., Duchi, R., Landi, T.C., Marinoni, A., Bonasoni, P., 2015. Long-term surface ozone variability at Mt. Cimone WMO/GAW global station (2165 m a.s.l., Italy). Atmos. Environ. 101, 23–33. https://doi.org/10.1016/J.ATMOSENV.2014.11.012.

Dueñas, C., Fernández, M.C., Carretero, J., Liger, E., Pérez, M., 1997. Release of 222Rn from some soils. Ann. Geophys. Discuss. 15, 124–133. https://doi.org/10.1007/s00585-997-0124-0.

Dueñas, C., Liger, E., Cañete, S., Pérez, M., Bolívar, J.P., 2007. Rn from phosphogypsum piles located at the Southwest of Spain. J. Environ. Radioact. 95, 63–74. https://doi.org/10.1016/j.jenvrad.2007.01.012.

Grossi, C., Vargas, A., Arnold, D., Grossi, C., et al., 2008. Quality Study of Electret Radon Flux Monitors by an in Situ Intercomparison Campaign in Spain, in: Sources Meas. Radon Radon Progeny Appl. to Clim. Air Qual. Stud., International Atomic Energy Agency, Vienna, pp. 39–48.

Gutiérrez-Álvarez, I., Martín, J.E., Adame, J.A., Grossc, C., Vargas, A., Bolívar, J.P., 2019. Applicability of the Closed-circuit Accumulation Chamber Technique to Measure Radon Surface Exhalation Rate (In Publishing Process).

Hernández-Ceballos, M.A., Vargas, A., Arnold, D., Bolívar, J.P., 2015. The role of mesoscale meteorology in modulating the ^{222}Rn concentrations in Huelva (Spain) - impact of phosphogypsum piles. J. Environ. Radioact. 145, 1–9. https://doi.org/10.1016/j.jenvrad.2015.03.023.

Ielsch, G., Thiéblemont, D., Labed, V., Richon, P., Tymen, G., Ferry, C., Robé, M.C., Baubron, J.C., Béchennec, F., 2001. Radon (222Rn) level variations on a regional scale: influence of the basement trace element (U, Th) geochemistry on radon exhalation rates. J. Environ. Radioact. 53, 75–90. https://doi.org/10.1016/S0265-931X(00)00106-5.

Jónás, J., Somlai, J., Tóth-Bodrogi, E., Hegedűs, M., Kovács, T., 2017. Study of a remediated coal ash depository from a radiological perspective. J. Environ. Radioact. 173, 75–84. https://doi.org/10.1016/j.jenvrad.2016.11.010.

Jonassen, N., 1983. The determination of radon exhalation rates. Health Phys. 45, 369–376. https://doi.org/10.1097/00004032-198308000-00009.

Keller, G., Hoffmann, B., Feigenspan, T., 2001. Radon permeability and radon exhalation of building materials. Sci. Total Environ. 272, 85–89. (accessed January 23, 2019). http://www.ncbi.nlm.nih.gov/pubmed/11379942.

Kotrappa, P., 2015. Electretion Chambers for Characterizing Indoor, Outdoor, Geologic and Other Sourced of Radon. in: Nova Sciencie Publishers.

Levin, I., Born, M., Cuntz, M., Langendörfer, U., Mantsch, S., Naegler, T., Schmidt, M., Varlagin, A., Verclas, S., Wagenbach, D., 2002. Observations of atmospheric variability and soil exhalation rate of radon-222 at a Russian forest site: technical approach and deployment for boundary layer studies, Tellus. Ser. B Chem. Phys. Meteorol. 54, 462–475. https://doi.org/10.1034/j.1600-0889.2002.01346.x.

López-Coto, I., Mas, J.L., Bolívar, J.P., García-Tenorio, R., 2009. A short-time method to measure the radon potential of porous materials. Appl. Radiat. Isot. 67, 133–138.

López-Coto, I., Mas, J.L., Vargas, A., Bolívar, J.P., 2014. Studying radon exhalation rates variability from phosphogypsum piles in the SW of Spain. J. Hazard. Mater. 280, 464–471. https://doi.org/10.1016/j.jhazmat.2014.07.025.

Onishchenko, A., Zhukovsky, M., Bastrikov, V., 2015. Calibration system for measuring the radon flux density. Radiat. Prot. Dosimetry 164, 582–586. https://doi.org/10.1093/rpd/ncv315.

Porstendörfer, J., 1994. Properties and behaviour of radon and thoron and their decay products in the air. J. Aerosol Sci. 25, 219–263. https://doi.org/10.1016/0021-8502(94)90077-9.

Sahoo, B.K., Mayya, Y.S., 2010. Two dimensional diffusion theory of trace gas emission into soil chambers for flux measurements. Agric. For. Meteorol. 150, 1211–1224. https://doi.org/10.1016/j.agrformet.2010.05.009.

Seo, J., Nirwono, M.M., Park, S.J., Lee, S.H., 2018. Standard measurement procedure for soil radon exhalation rate and its uncertainty. J. Radiat. Prot. Res. 43, 29–38. https://doi.org/10.14407/jrpr.2018.43.1.29.

Sun, K., Guo, Q., Zhuo, W., 2004. Feasibility for mapping radon exhalation rate from soil in China. J. Nucl. Sci. Technol. 41, 86–90. https://doi.org/10.1080/18811248.2004.9715462.

Tsapalov, A., Kovler, K., Miklyaev, P., 2016. Open charcoal chamber method for mass measurements of radon exhalation rate from soil surface. J. Environ. Radioact. 160, 28–35. https://doi.org/10.1016/j.jenvrad.2016.04.016.

Zhuo, W., Iida, T., Furukawa, M., 2006. Modeling radon flux density from the Earth's surface. J. Nucl. Sci. Technol. 43, 479–482. https://doi.org/10.1080/18811248.2006.9711127.