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# Measuring effective radium concentration with large numbers of samples. Part I – experimental method and uncertainties

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ABSTRACT

Effective radium concentration $EC_{Ra}$, product of radium concentration and radon emanation, is the source term for radon release into the pore space of rocks and the environment. To measure $EC_{Ra}$, we have conducted, over a period of three years, more than 5500 radon-222 accumulation experiments in the laboratory with scintillation flasks, and about 700 with integrating solid state nuclear track detectors, leading to experimental values of $EC_{Ra}$ for more than 1570 rock and soil samples. Through detailed systematic checks and intercomparison between various repeated experiments, the experimental uncertainty has been assessed, and ranges from 30% (1 $\sigma$) for $EC_{Ra}$ values smaller than 0.2 Bq kg$^{-1}$ to about 8–10% for $EC_{Ra}$ values larger than 50 Bq kg$^{-1}$. The detection limit, defined as the 90% probability for obtaining a non-zero experimental $EC_{Ra}$ value at 68% confidence level, depends on the mass of the sample with respect to the volume of the accumulation volume, and typically varies between 0.04 and 0.09 Bq kg$^{-1}$. To measure $EC_{Ra}$ from large numbers of samples with sufficient accuracy and uncertainty for our purpose, i.e. for the most natural objects encountered in the environment, the accumulation method with scintillation flask emerged as particularly useful and robust. Properties of $EC_{Ra}$ and interpretations inferred from this large data set are presented in the companion paper.



## 1. Introduction

Effective radium concentration is the product of radium activity concentration $C_{Ra}$ (expressed in Bq kg$^{-1}$) and the dimensionless emanation coefficient $E$, which is the probability that, after radioactive decay, the daughter radon atom is released in the pore space of the medium, from where it can be subsequently transported to the environment (Tanner, 1964; Nazaroff, 1992; Stoulos et al., 2004). Thus, in the case of radium-226, in the uranium-238 decay chain, $EC_{Ra}$ is the natural source term of radon-222, a radioactive noble gas with a half-life of 3.8 days which, after inhalation, accounts for half of the radiation dose to the general population (Porstendörfer, 1994) and is a major cause of lung cancer (Al-Zoughool and Krewski, 2009). Thus, values of $EC_{Ra}$ from soils, rocks, and construction materials are needed to evaluate and mitigate health hazard in practical situations (Nazaroff et al., 1985). Furthermore, once the source term $EC_{Ra}$ is known, measuring the radon-222 flux at the earth surface provides important insights on geophysical processes occurring in volcanic systems (Morelli et al., 2006; Cigolini et al., 2007; Laiolo et al., 2012) or active fault zones (Steinitz et al., 2003; Perrier et al., 2009; Barbosa et al., 2010).

Radon-222 exhalation and its distribution in rocks and soils reflect the radon source term $EC_{Ra}$, but also the transport properties of the subsurface such as porosity, fluid content and velocities. However, relationships between radon-222 distributions and geological formations, which could provide the basis for risk assessment methods (Reimer, 1992; Varley and Flowers, 1992; Ielsch et al., 2001; Minda et al., 2009), are not straightforward and, long ago, while not ruled out, were deemed difficult to interpret (Botset and Weaver, 1932). The relationship between $EC_{Ra}$ and local geology must be complicated. The parameter $EC_{Ra}$, indeed, is the product of two spatially varying quantities. Radium concentration results from uranium distribution and subsequent dissolution, transport and precipitation by geological fluids (Voltaggio et al., 2004; Przylibski, 2004). As for the emanation coefficient $E$ (Sakoda et al., 2011), it depends on the spatial distribution of radium (Morawska and Phillips, 1993; Sakoda et al., 2010), the properties of the porous network (Semkow, 1991; Greeman and Rose, 1996), moisture (Fleischer, 1987; Barillon et al., 2005; Adler and Perrier, 2009; Meslin et al., 2011) and temperature (Iskandar et al., 2004; Lee et al., 2010; Girault and Perrier, 2011); it can vary from values smaller than 1% to values larger than 50% (Przylibski,

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2000; Righi and Bruzzi, 2006). $EC_{Ra}$ has been found to depend on other important processes, such as deformation (Holub and Brady, 1981; Tuccimei et al., 2010; Mollo et al., 2011), and in a recent study (Breitner et al., 2010), both $E$ and $C_{Ra}$ were found to be enhanced for fine grains fractions, which substantiates some clues that $EC_{Ra}$ is also sensitive to physical and chemical alteration processes (Przylibski, 2000, 2011). Thus, $EC_{Ra}$ captures an intermingled set of geochemical and geophysical properties, which, conversely, might contain very important and subtle messages about the processes taking place in the subsurface, messages which could be extremely precious provided they can be deciphered. To clarify this matter, first of all, it would be essential, so that structures can emerge, to gather comprehensive experimental values of $EC_{Ra}$ in various contexts.

While $EC_{Ra}$ can be estimated indirectly, for example from the radon content of groundwater (Przylibski, 2000), $EC_{Ra}$ is usually measured in the laboratory by letting radon-222 concentration build up in sufficiently air-tight containers (accumulation method). Precise accumulation experiments can be carried out with high precision continuous radon monitors (Chao et al., 1997; Ferry et al., 2002; Stoulos et al., 2003; Tuccimei et al., 2006; Sakoda et al., 2008; Hassan et al., 2011a). However, such methods using expensive equipment, while they are extremely useful to study the details of the radon emission and the physics of the accumulation process, in general have not been able to provide experimental values of $EC_{Ra}$ beyond about two dozens of samples and, thus, are not appropriate for large numbers of samples. Accumulation experiments can also be performed with more cost-effective techniques (Stoulos et al., 2003) such as scintillation flasks and Solid State Nuclear Track Detectors (SSNTDs). Nevertheless, the number of samples measured so far, mostly construction materials, in general remains low: 17 (Tuccimei et al., 2006), 24 (Kitto et al., 2009), 42 (Righi and Bruzzi, 2006), about 50 (Stoulos et al., 2003), with larger numbers of about 150 in the case of constructions materials in the U.S. (Ingersoll, 1983) and 205 from several locations (Al-Jarallah et al., 2005). Concerning rock samples not used as building materials, the reported number of samples, most of the time, does not exceed a dozen (Kumar et al., 2003; Singh et al., 2008; López-Coto et al., 2009) and even less (Richon et al., 2005; Ferry et al., 2002). The relationship between $EC_{Ra}$ of soils and geology was often studied with less than 100 samples, for example 36 (Prasad et al., 2008) or 72 (Ramola and Choubey, 2003). In one study (Markkanen and Arvela, 1992), more than 400 Finnish soil samples were studied with accumulation experiments using scintillation flasks, but this work focussed on the sensitivity of $EC_{Ra}$ to grain size and its variations with moisture content or temperature, and few comparisons with geology were attempted. To conclude, the number of available measurements so far is largely insufficient yet to fully appreciate the potential properties of $EC_{Ra}$.

In this paper, we revisit the experimental methodology of radon accumulation experiments and we present the lessons gained from more than 6000 radon accumulation experiments performed in the laboratory over a period of three years with scintillation flasks and SSNTDs. In this endeavour, the goal was to design and test an optimal experiment method able to measure large numbers of rock, soil and possible plant samples while keeping experimental uncertainties smaller than 10% for $EC_{Ra} > 5$ Bq kg$^{-1}$, and smaller than about 20% for $0.1 < EC_{Ra} < 5$ Bq kg$^{-1}$, allowing to explore with the same methodology the whole range of values relevant in geological systems. Thus, in this work, we focus on the practicability with large numbers of samples and on reducing the detection limit, but not on reducing the experimental uncertainties below 5%. In this manuscript, we first describe the experimental method, its assumptions and its limitations and, second, we analyse its efficiency, its reliability and we examine in details the assessment of the experimental uncertainties. Results obtained with this dataset are presented in the companion paper (Girault and Perrier, 2012, JER, companion paper).

## 2. Basics of radon accumulation experiments and assumptions

In this section, we present some theoretical background and describe the assumptions behind the experimental measurements. Unless stated otherwise, we deal with radium-226 and radon-222.

We consider a sample of mass $m$ and porosity $\varepsilon$ with a possible volumetric water content $S_w$, thus having an air porosity $\varepsilon_a = \varepsilon(1 - S_w)$ and a water-filled porosity $\varepsilon_w = \varepsilon S_w$. After the sample is installed in a sealed container of volume $V_0$, at radioactive equilibrium, the radon concentration $C$ in the free air volume is homogeneous. Radon concentration gradients in the air volume of the container usually cannot be maintained because of convective mixing and in most cases the container dimensions are small compared with the diffusion length of radon-222 in air (2 m). In the absence of leakage and when diffusion effects of radon-222 in the sample itself can be ignored, then, at radioactive equilibrium, the radon concentration $\overline{C}$ is given by (Ferry et al., 2002; Stoulos et al., 2003):

$$\overline{C} = \frac{m}{V_a} EC_{Ra}. \tag{1}$$

In Eq. (1), $V_a$ is the total air volume available in the container, which can be written in general $V_a = V_0 - (m - m_w)/\rho_m - m_w/\rho_w$, where $m_w$ is the mass of water, $\rho_w$ the density of water and $\rho_m$ the mean matrix density of the sample.

Let us now allow for the possibility of some leakage in the container with some volumetric relative rate given by $\lambda_V$. Instead of $\lambda_V$, it appears more convenient to use the normalised leakage rate $a_V$ defined by $a_V = \lambda_V/\lambda$, where $\lambda$ is the decay constant of radon-222 ($2.1 \times 10^{-6}$ s$^{-1}$). Thus, this parameter is employed throughout the whole manuscript when discussing quantification of leakage. In a first approximation, the temporal evolution of radon concentration $C(t)$ in the container is then given by:

$$\frac{dC}{dt} = \lambda\left[\overline{C} - C - a_V(C - C_e)\right], \tag{2}$$

where $C_e$ is the mean concentration of radon in the laboratory, which is considered negligible in our case. We then have:

$$C(t) = C_\infty\left(1 - e^{-\lambda(1+a_V)t}\right), \tag{3}$$

where $C_\infty$ is the radon concentration at steady state equilibrium:

$$C_\infty = \frac{1}{1 + a_V}\overline{C}. \tag{4}$$

Examples of accumulation curves are shown in Fig. 1 without (continuous line) or with leakage (dotted line). The slope at origin is not affected by the presence of leakage.

The situation is modified slightly when diffusion effects in the sample cannot be neglected. Then, radon concentration in the pore air of the sample can show spatial variations, essentially when the diffusion length of radon-222 is small compared with the sample dimensions. As we consider only samples with dimensions of a few cm at most, this rarely occurs in our experiments. Indeed, the effective diffusion coefficient $D_e$ of radon-222 in rocks varies between $10^{-6}$ and $10^{-7}$ m$^2$ s$^{-1}$, in which case the radon diffusion length $L_d = \sqrt{D_e/\lambda}$ varies between 60 and 20 cm. Smaller values of $D_e$, reaching a few $10^{-10}$ m$^2$ s$^{-1}$, leading to diffusion length of the