Effective radium-226 concentration in rocks, soils, plants and bones

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Abstract: Effective radium-226 concentration, $EC_{Ra}$, is the product of radium activity concentration, $C_{Ra}$, multiplied by the emanation coefficient, $E$, which is probability of producing a radon-222 atom in the pore spaces. It is measured by accumulation experiments in the laboratory, achieved routinely for a sample mass >50 g using scintillation flasks to measure the radon concentration. We report on 3370 $EC_{Ra}$ values obtained from more than 11 800 such experiments. Rocks ($n = 1351$) have a mean $EC_{Ra}$ value of $1.9 \pm 0.1$ Bq kg$^{-1}$ (90% of data in the range 0.11–35 Bq kg$^{-1}$), while soils ($n = 1524$) have a mean $EC_{Ra}$ value of $7.5 \pm 0.2$ Bq kg$^{-1}$ (90% of data between 1.4 and 28 Bq kg$^{-1}$). Using this large dataset, we establish that the spatial structure of $EC_{Ra}$ is meaningful in geology or sedimentology. For plants ($n = 85$), $EC_{Ra}$ is generally <1 Bq kg$^{-1}$, but values of larger than 10 Bq kg$^{-1}$ are also observed. Dedicated experiments were performed to measure emanation, $E$, in plants, and we obtained values of $0.86 \pm 0.04$ compared with $0.24 \pm 0.04$ for sands, which leads to estimates of the radium-226 soil-to-plant transfer ratio. For most measured animal bones ($n = 26$), $EC_{Ra}$ is >1 Bq kg$^{-1}$. Therefore, $EC_{Ra}$ appears essential for radon modelling, health hazard assessment and also in evaluating the transfer of radium-226 to the biosphere.

Radon-222, a radioactive noble gas with a half-life of 3.8 days and a decay product of radium-226 in the uranium-238 chain, is ubiquitous in the environment (Tanner 1964). Migrating from the ground into living spaces, it constitutes half the radiation dose to the general population (Porstendorfer 1994) and is a major cause of lung cancer (Darby et al. 2005). Radon-222 is a health hazard, especially in underground and poorly ventilated spaces (Gillmore et al. 2011) or above uranium mine tailings (Ferry et al. 2001; Pereira et al. 2010; Barbosa et al. 2015). It receives also a lot of attention because it is a powerful tracer of the transport of shallow groundwater (Przylibski 2011) or deep geological fluids: for example, around geothermal systems (Weinlich et al. 2013; Girault et al. 2014a), volcanoes (Cigolini et al. 2009) and active faults (Walia et al. 2005, 2008; Cigolini et al. 2015). Further progress in radon health hazard assessment and the use of radon to quantify environmental and geological processes requires better modelling of the radon signatures in groundwater and ground gases, which, first of all, needs a better understanding of the radon source.

The radon-222 exhalation from any porous medium is proportional to the activity concentration of radium-226, $C_{Ra}$, and to the probability of a radium atom emitting its radioactive product radon into the pore space, this is called the emanation coefficient, $E$ (Tanner 1964; Adler & Perrier 2009; Sakoda et al. 2011). Thus, to quantify the radon source, the relevant quantity to consider is the product $EC_{Ra}$, referred to as the effective radium concentration (Stoullos et al. 2004; Girault & Perrier 2012a). This quantity can be measured by accumulation experiments in the laboratory, placing varying masses of sample material (usually 100 g, but can be >1 kg) in a closed container, with the radon concentration being measured by continuous radon monitors (Ferry et al. 2002; Sakoda et al. 2008; Nicolas et al. 2014; Menon et al. 2015), integrating devices (Stoullos et al. 2004; Girault & Perrier 2012a; Menon et al. 2015) or scintillation flasks (Stoullos et al. 2003; Meslin et al. 2011; Girault & Perrier 2012a).

To process large numbers of samples, the most efficient and reliable method was found to be the use of scintillation flasks (Girault & Perrier 2012a), a method that could also be extended to sample masses smaller than 5 g (Perrier & Girault 2012). In the present paper, we review and update the major results for $EC_{Ra}$ obtained using this standardized method with rocks and soils, and present new results, in particular using natural materials rarely investigated before. Some perspectives for the use of $EC_{Ra}$ in heuristic geological and environmental problems are then presented.

Experimental method and uncertainties

The experimental method has been presented before (Girault & Perrier 2012a) and is only briefly summarized here. A sample of mass $m$ was installed in

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a sealed container of volume $V_0$ that is initially free of radon. After an accumulation time $t$, the radon concentration in the container had grown to $C_{Ra(t)}$. In a perfectly sealed container with impermeable walls and when diffusion effects of radon-222 in the sample can be ignored, we have (Girault & Perrier 2012a):

$$EC_{Ra} = \frac{V_a}{m} \frac{C_{Ra(t)}}{1 - e^{-\lambda t}}$$

(1)

where $\lambda$ is the decay constant of radon-222 ($2.1 \times 10^{-6}$ s$^{-1}$), $EC_{Ra}$ is expressed in Bq kg$^{-1}$ and $V_a$ is the total air volume available in the container, including the sample-connected pore space. To estimate $V_a$, the total volume of the container was reduced by the volume of the solid matrix of the sample. A rough estimate of the average mineral density was sufficient to obtain a sufficiently accurate estimate of $V_a$. In our case (Fig. 1a), we measured $C_{Ra(t)}$ by sampling the container air using previously evacuated 125 ml scintillation flasks (Algade, France), using a valve equipped with a filter and syringe needles (Fig. 1a), and we corrected for dilution during sampling (Girault & Perrier 2012a). The radon concentration in the container was then inferred after the scintillating flasks had been inserted (Fig. 1b) and counted twice in CAL-EN™ photomultiplier counters (Algade, France). The background counts of the flasks is determined before sampling, and subtracted to obtain the net signal. For the levels of $EC_{Ra}$ reported in the present paper, the initial radon concentration due to the laboratory room was negligible compared with the radon concentration produced by the samples in the accumulation containers. In the standard procedure reported here, we used a sample mass, $m$, larger than 50 g, and counting times of 5 and 10 min. We repeated each accumulation experiment three or four times, using different accumulation times, $t$, that varied between 5 days and 3 weeks, and the final value of $EC_{Ra}$ was obtained by averaging the results.

To achieve optimal detection, the accumulation container was chosen so that the radon concentration was maximized in the container and in the scintillation flask. The radon concentration in the container was larger for a smaller air volume, $V_a$. However, $V_a$ could not be too small as: first, it could not be smaller than the scintillation flask volume, otherwise the benefit of an increased concentration in the container was lost by dilution during sampling in the flask; and, second, $V_a$ should not be smaller than about half of the container volume.

Fig. 1. (a) View of the various instruments used for the sampling of the air in an accumulation bottle using a scintillation flask. The scintillation flasks are evacuated using a hand pump and sampling is performed using a syringe and needle assembly equipped with a valve and a filter. (b) View of a typical counting session using photomultipliers after sampling 24 accumulation containers.
in order to avoid back-diffusion complications (Sakoda et al. 2008). As the method was developed further after its initial testing phase (Girault & Perrier 2012a), different containers were considered (Fig. 2) and less practical containers that resulted in occasional leakage were eliminated. It was sometimes difficult to find air-tight containers for small or large samples, and, for sampling with syringe needles (as shown in Fig. 1a), we preferred to use large pre-perforated natural rubber stoppers rather than lids equipped with stoppers. The bottles shown in Figure 2 (No. 7 with $V_0 = 262$ ml, No. 4 with $V_0 = 518$ ml and No. 3 with $V_0 = 1022$ ml) turned out to be the best containers for routine use, with no case of leakage detected, but these could only be used for crushed samples or samples that occurred naturally in small pieces. Large samples or precious samples that had to be returned intact needed to be installed in containers with larger openings, for which variants are being constantly investigated.

Each new type of container was systematically tested with a set of known materials, which were mostly crushed granite samples. For example, the large glass container labelled No. 1 in Figure 2, with a volume of $V_0 = 1574$ ml, gave an $EC_{Ra}$ value of $30.1 \pm 0.9$ Bq kg$^{-1}$ for a granite powder that had a value of $30.5 \pm 0.5$ Bq kg$^{-1}$ in bottle No. 7 (see Fig. 2) with a volume of $V_0 = 262$ ml. Reference samples have been measured repeatedly since 2008 to ensure the continuity of the results and to test the consistency of the method. For example, one reference container (No. 4 type in Fig. 2) with a Permian schist sample (Salagou Ruffe, France) gave an $EC_{Ra}$ value of $12.42 \pm 0.27$ Bq kg$^{-1}$ in June 2013 and $11.29 \pm 0.25$ Bq kg$^{-1}$ in April 2015. Another reference soil sample gave $40.6 \pm 1.3$ Bq kg$^{-1}$ in March 2011, in one Erlenmeyer flask, and $38.12 \pm 0.58$ Bq kg$^{-1}$ in April 2015, in a 262 ml bottle. The efficiency of the detection chain has been monitored since 2009 using radium-doped scintillation flasks. No systematic aging of the scintillation flask detection level or of the photomultipliers efficiencies, possible in principle, have been noticed so far.

Experimental uncertainties were dominated by the photomultiplier counting statistics, which decreased for larger radon concentration, and the uncertainty of the dilution correction, which increased for smaller air volumes. The resulting relative uncertainty, shown in Figure 3 v. $EC_{Ra}$ values, varied, on average, from about 10% for $EC_{Ra} = 1$ Bq kg$^{-1}$ to 3% for $EC_{Ra} = 30$ Bq kg$^{-1}$. When a sample mass larger than 200 g was used, then the uncertainty was reduced to 7% for $EC_{Ra} = 1$ Bq kg$^{-1}$ and to 20% for $EC_{Ra} = 0.1$ Bq kg$^{-1}$. Sample masses, $m$, of the order of 50 g gave sufficiently accurate values (uncertainty <5%) for $EC_{Ra} > 10$ Bq kg$^{-1}$, which was also the case for most granites and soil samples with a high radium concentration. To this uncertainty, which is statistically independent for the two independent measurements, an overall systematic uncertainty of 5%, due to the absolute calibration of the method, must be added quadratically when relevant.

Detection limit depends on $m$, $V_a$ and on the counting time used. Routine counting time was 5 min, but 10 min was used for lower $EC_{Ra}$ values.

![Fig. 2. A view of various containers used in recent accumulation experiments.](http://sp.lyellcollection.org/)
For a counting time of 10 min, the detection limit for the radon concentration in the accumulation container was $C_{\text{RnDL}} = 13 \text{ Bq m}^{-2}$ (Girault & Perrier 2012a). The corresponding detection limit in terms of $EC_{\text{Ra}}$ was then: $EC_{\text{RaDL}} = C_{\text{RnDL}} V_a/m$. For 50 g in a 262 ml bottle, we had $EC_{\text{RaDL}} = 0.068 \text{ Bq kg}^{-1}$, which covered almost all of the samples of interest in most applications. For 800 g in a 1 l container, we could reduce the detection limit to $EC_{\text{RaDL}} = 0.016 \text{ Bq kg}^{-1}$, sufficient for all applications considered here.

The quantity $EC_{\text{Ra}}$ depends on the temperature and water content. The slight increase in $EC_{\text{Ra}}$ with temperature (Girault & Perrier 2011, 2012b) is interesting to consider in the case of hydrothermal and volcanic systems, but still remains insufficiently known for volcanic rocks. The dependence on water content (Sakoda et al. 2010; Meslin et al. 2011; Girault & Perrier 2012b) is moderate as long as residual water remains in the pore space, in agreement with numerical models (Adler & Perrier 2009). Consequently, samples for $EC_{\text{Ra}}$ measurement are not oven-dried, but left in their original condition. When necessary (e.g. in the case of soaked soil samples), they were only gently dried on the laboratory bench without heating.

**General results in rocks and soils**

A total of 3370 measurements of $EC_{\text{Ra}}$ have been carried out so far with this method, corresponding to more than 11 800 accumulation experiments. The majority of samples were collected during our fieldwork in Nepal, France and other European countries. We also borrowed a few samples from colleagues and reference rock archives. Identification was performed according to the available geological maps, and discussed with local geologists when confirmation was needed. Detailed results for specific sites have been presented (Girault et al. 2011, 2012, 2014b) and will be presented in further dedicated papers. In the following, we concentrate on general results. All average values mentioned are geometric means.

**Effective radium concentration in rocks**

A total of 1351 rock samples have been studied, from numerous different contexts, and provide a reasonable coverage of rock types. The $EC_{\text{Ra}}$ values for rocks vary over more than six orders of magnitude (Fig. 4a), with a mean value of $1.9 \pm 0.1 \text{ Bq kg}^{-1}$, and with 90% of the values falling between 0.11 and 35 Bq kg$^{-1}$. The largest $EC_{\text{Ra}}$ values observed so far, in excess of $10^6 \text{ Bq kg}^{-1}$, were measured for pitchblende uranium ore from the French La Crouzille mine (Limousin), while uraniferous granites usually had $EC_{\text{Ra}} > 1000 \text{ Bq kg}^{-1}$. These anomalously high values were not considered when giving the above estimate of the average value.

The $EC_{\text{Ra}}$ values, on average, are according to expectations for various types of rocks: granitic rocks give larger values than other rocks; but the distributions are wider than might be expected for the same type of rock (Fig. 5). The average value for
Granites was about 17 Bq kg\(^{-1}\), but the distribution (Fig. 5a) was wide. Various Variscan granites from France (South Cévennes and Limousin), Germany and Poland had similar and relatively large EC\(_{\text{Ra}}\) values (Table 1), of around 22 Bq kg\(^{-1}\), while a smaller value was measured in Mont Lozère (16.0 ± 5.1 Bq kg\(^{-1}\)) in the Northern Cévennes range, and an even smaller value (6.9 ± 0.2 Bq kg\(^{-1}\)) in Ballon d’Alsace granite. The value for Mont Lozère, however, was similar to that of the Ullerig gneiss (15.7 ± 1.5 Bq kg\(^{-1}\)) in Nepal (Girault et al. 2012). This suggests that, more than local variability, the value of EC\(_{\text{Ra}}\) is more dependent on anatexis (partial melting) or other mechanisms occurring during metamorphism.

Volcanic rocks, with a mean of the order of 1 Bq kg\(^{-1}\), covered a large range of EC\(_{\text{Ra}}\) values, from <0.1 Bq kg\(^{-1}\), for Stromboli lavas, to >5 Bq kg\(^{-1}\), for some Azores lavas. Other rocks with small EC\(_{\text{Ra}}\) values were calcareous rocks, which thus far have given an average value of about 0.34 Bq kg\(^{-1}\). Some limestone samples, however, had EC\(_{\text{Ra}}\) values of >2 Bq kg\(^{-1}\), which are larger than most volcanic rocks, and even larger than some rocks labelled as granites. For example, one Jurassic massive black limestone from the Cévennes front and one Lutetian limestone sample from a quarry in Paris gave values of EC\(_{\text{Ra}}\) = 3.26 ± 0.21 and 3.20 ± 0.29 Bq kg\(^{-1}\), respectively. By contrast, one so-called granite from Cotentin (France) has EC\(_{\text{Ra}}\) = 1.50 ± 0.13 Bq kg\(^{-1}\), and one from Haute-Vienne (France) has a value of EC\(_{\text{Ra}}\) = 0.63 ± 0.04 Bq kg\(^{-1}\). In both cases, one may raise some doubts on the accuracy of the sampling or of the available geological mapping, but this may also just reflect the ambiguity of some geological terms to account for local geological complexity. In this instance, low values suggest gneisses rather than granites, since they are characterized by low values, as was established in the case of the Greater Himalaya gneisses (Girault et al. 2012). These data reflect the complex history of uranium and radium over geological time, and suggest that caution should definitely remain mandatory when assuming potential radon exhalation levels without having performed any measurement of EC\(_{\text{Ra}}\).

The current dataset indicates that EC\(_{\text{Ra}}\), when actually measured or not just estimated from indirect arguments, is a useful geological index for rock classification and geological interpretation.

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**Fig. 4.** Distribution, with logarithmic scales, of EC\(_{\text{Ra}}\) for rocks and soils. The entire available dataset using our experimental method, measured between 2007 and 2015, is shown. Vertical dashed lines represent the geometric means.
One important question to be addressed in each case, however, is whether the experimental value obtained from a given rock sample is representative of the geological formation, and whether some dispersion must be expected and at which spatial scale. This question has been discussed previously in general terms (Girault & Perrier 2012b), and has been also investigated in detail for selected outcrops in Nepal (Girault et al. 2012; Girault & Perrier 2014). Dispersion should be investigated at sample level (decimetre scale), scarp level (metre scale) and formation level (decametre scale). The cases investigated so far showed that dispersion increased from the decimetre scale to the decametre scale, but that $EC_{Ra}$ values remained specific at the level of the geological formation (lithostratigraphic unit). In fact, not only is the average value of interest for a given outcrop or geological formation, but also the shape of the distribution of values. The shape of geological distributions, indeed, contains important

Table 1. Comparison of $EC_{Ra}$ results from some granitic rocks. Average refers to the geometric mean

<table>
<thead>
<tr>
<th>Pluton</th>
<th>Average (Bq kg$^{-1}$)</th>
<th>$n$</th>
<th>Range (minimum/maximum) (Bq kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Cévennes granite, France</td>
<td>26.2 ± 2.3</td>
<td>32</td>
<td>4.6/56.4</td>
</tr>
<tr>
<td>Mont Lozère, France</td>
<td>16.0 ± 5.1</td>
<td>6</td>
<td>6.5/27.3</td>
</tr>
<tr>
<td>Limousin granite, France</td>
<td>21.2 ± 3.7</td>
<td>21</td>
<td>5.6/65.0</td>
</tr>
<tr>
<td>Ballon d’Alsace, France</td>
<td>6.9 ± 0.2</td>
<td>6</td>
<td>4.9/8.2</td>
</tr>
<tr>
<td>Erzgebirge granite, Germany</td>
<td>22.2 ± 0.44</td>
<td>1</td>
<td>14.6/48.9</td>
</tr>
<tr>
<td>Sudetes granite, Poland</td>
<td>24.1 ± 7.8</td>
<td>4</td>
<td>4.1/30.1</td>
</tr>
<tr>
<td>Ulleri gneiss, Nepal</td>
<td>15.7 ± 1.5</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>
information on the nature of grain mixing (Fieller et al. 1990) or on the underlying processes (Allègre & Lewin 1995; Buccianti 2015). While the log-normal distribution seems a reasonable approximation in numerous cases, in particular for radon concentration distributions (Bossew 2010), it does not account for the large tails often observed in practice, which are not representation artefacts, but real geological fluctuations, and is unable to account for the rich multimodal distribution observed in Figure 4a. In this respect, it is also interesting that $EC_{Ra}$ values of the Variscan granites in Table 1 have similar average values and similar ranges. In addition to dispersion, smooth coherent variations in $EC_{Ra}$ within a formation are possible, but cases still remain insufficiently studied in this regard.

The large potential variations in $EC_{Ra}$ from formation to formation, even, for example, among granites of similar mineral composition but different geological histories, combined with usually relatively small dispersion, are particularly useful in the context of geological contacts or fault zones. Profiles of $EC_{Ra}$ across such geological discontinuities are then particularly useful. One interesting case has been reported across the Penninic Front in the French Alps (Girault & Perrier 2012b). The most extensive and exemplary study, however, and the first systematic study of $EC_{Ra}$ in relation to geological formation remains, to date, the study across the Main Central Thrust (MCT) in the Nepal Himalayas (Girault et al. 2012). This work showed clear evidence of a large reduction in $EC_{Ra}$ among rocks of similar fabric (gneisses and schists) across the MCT, a fault whose position remains controversial and which could be refined accurately using $EC_{Ra}$ data. These pioneering and promising results suggest that large-scale mapping of $EC_{Ra}$ could be an essential and cost-effective tool in geologically complex areas, beyond the interest in the radon source term, complementing other tools such as neodymium isotope ratios.

**Effective radium concentration in soils**

A total of 1524 soil samples have been studied, collected during our work in different geographical contexts, mostly Nepal and France, providing a reasonable coverage of numerous soil types, as well as the underlying rock types. In this study, all types of unconsolidated surface deposits were referred to as soils. The $EC_{Ra}$ values for soils varied over only about three orders of magnitude (Fig. 4b), with a mean value of $7.5 \pm 0.2$ Bq kg$^{-1}$, with 90% of the values of soils between 1.4 and 28 Bq kg$^{-1}$. The largest $EC_{Ra}$ value observed so far for soils (8770 ± 200 Bq kg$^{-1}$) was measured for iron-rich soil deposits around a cold spring in the High Himalayas of Nepal (Girault & Perrier 2014). Two other exceptional values ($1249 \pm 14$ and $1181 \pm 59$ Bq kg$^{-1}$) were reported at a CO$_2$ release zone around the Chilime hot spring in central Nepal (Girault et al. 2014a). Other large and rather rare values above 100 Bq kg$^{-1}$ were observed for soils in former uranium mining zones in Limousin, France. By contrast, values of <2 Bq kg$^{-1}$ were observed for sands (Fig. 4b), which were characterized by a mean value of $0.42 \pm 0.06$ Bq kg$^{-1}$, but varied from 0.109 ± 0.078 to 2.03 ± 0.18 Bq kg$^{-1}$.

Measuring $EC_{Ra}$ could also be an interesting method of revealing separation processes of radioelements during pedogenesis. Now that we have a significant database of experimental values, we can study the relationship between the effective radium concentration of a soil ($EC_{Ra}$) and the effective radium concentration ($EC_{Ra}$) of the closest available rock (Fig. 6), where the closest measured rock must be at a distance of less than 250 m. This distance is arbitrary, and must be reasonable given the local conditions. From the 226 soils that satisfied this condition, interesting structures emerged (Fig. 6). For $EC_{Ra}$ values of <3 Bq kg$^{-1}$, $EC_{Ra}$ is always larger than $EC_{Ra}$, but the range spanned by $EC_{Ra}$ increases for smaller $EC_{Ra}$ values. This suggests that rocks with smaller $EC_{Ra}$ values are more prone to alteration, with mechanisms producing soils that can be either radium-enriched or radium-depleted, and probably both types being separated by the erosion process. Soils with more organic matter and finer fractions, characterized by larger $EC_{Ra}$ values, are deposited further away than the quartz-rich and heavy fractions. This process is probably very different for aerial and water erosion processes. For $EC_{Ra}$ values of >3 Bq kg$^{-1}$, $EC_{Ra}$ can be either larger or smaller than $EC_{Ra}$. Data points with $EC_{Ra}$ smaller than $EC_{Ra}$ in Figure 6 corresponded to soils over Variscan granites, which can also produce $EC_{Ra}$ values slightly larger than $EC_{Ra}$, when $EC_{Ra}$ is >10 Bq kg$^{-1}$. Some points in Figure 6 also showed $EC_{Ra}$ values of >100 Bq kg$^{-1}$, when $EC_{Ra}$ was close to 10 Bq kg$^{-1}$. These points systematically corresponded to soils developed in the vicinity of a particular mica-schist outcrop near MCT in the upper Trisuli Valley in central Nepal (Girault et al. 2012). The relationship between $EC_{Ra}$ and $EC_{Ra}$ appears to be a promising tool that should be studied systematically in natural sites where the current and past alteration processes are well constrained.

As in the case of rocks, the question as to whether the $EC_{Ra}$ value of a given soil sample is representative of a given context must be raised. Sample-scale dispersion of $EC_{Ra}$ of soils tends to be very small, with soils separated by less than 10 cm giving similar $EC_{Ra}$ values within the experimental uncertainties. Thus, $EC_{Ra}$ appears as a particularly stable index to correlate sedimentary
profiles (Girault et al. 2011a). In the case of river terrace deposits, we also observed a remarkable stability of values on a given level, with different terraces characterized by specific EC\textsubscript{Ra} values (Girault \textit{et al.} 2011b), allowing the possibility of long-distance correlation, possibly due to large-scale consistency of soil particle size and composition. The variations in soil EC\textsubscript{Ra} over distances larger than 1 km have not yet been studied, but this offers a nice possibility of soil characterization or site mapping.

Vertical variations in soil EC\textsubscript{Ra} were studied at small scale using terrace scarps in the Kathmandu Valley (Girault \textit{et al.} 2011a). Smooth variations in EC\textsubscript{Ra} were observed within sediment layers, with large variations over a few centimetres across layers. Vertical variations over larger distances were studied at the site of the French National Magnetic

![Fig. 6. Soil EC\textsubscript{Ra} v. EC\textsubscript{Ra} of the closest rock sample in place, when one rock sample is available at a distance of less than 250 m.](image)

![Fig. 7. Location of the trenches and boreholes investigated at the French Magnetic Observatory site at Chambon-la-Forêt (CLF).](image)
Observatory, located in the Orléans Forest at the southern edge of the Parisian Basin (Fig. 7). The local geology is dominated by more than 50 m of Quaternary sediments above Burdigalian Miocene marls and Aquitanian limestone. In the compound of the observatory, three 1 m-deep trenches (1 × 1 × 1 m holes) were excavated at points O, E and M, separated by about 132–187 m (Fig. 7), each complemented with a 10 m-deep borehole. Small-scale horizontal variations in $EC_{Ra}$ were studied in trench O (Fig. 8) at 20 cm (sandy soil) and 65 cm depth (clay-rich dark soil). Significant horizontal variations were observed, probably organized as smooth structures; we observed 25% RMS (standard deviation) at 20 cm depth and 8.5% RMS at 65 cm depth. However, the $EC_{Ra}$ values, at the two different depths, were statistically different, with an average $EC_{Ra}$ value of $3.31 \pm 0.25$ Bq kg$^{-1}$ at 20 cm depth and $14.0 \pm 0.36$ Bq kg$^{-1}$ at 65 cm depth, two typical low and high values of soils in the reference distribution shown in Figure 4b.

Results from the vertical profiles in the trenches and boreholes (Fig. 9) spanned the whole range of $EC_{Ra}$ values from soils (Fig. 4b), ranging in this case from $2.32 \pm 0.15$ to $39.79 \pm 0.89$ Bq kg$^{-1}$, with an overall average of $10.05 \pm 0.74$ Bq kg$^{-1}$. Significant smooth and, sometimes, large variations in $EC_{Ra}$ were observed with depth. At the surface, significant variations were observed between the sites O, E and M, but large variations (47% RMS) were observed locally from sample to sample collected in the forest (grey points in Fig. 9). For all three sites, the value at 1 m depth in the trench coincided well with the value at 1 m depth in the borehole, located 1 m away laterally from the trench. Two sites (O and M) showed remarkably similar $EC_{Ra}$ values over the whole available depth range. Site E, however, was different. This result is interesting because it illustrates the case of possible large horizontal discrepancies in a context of homogeneity. Thus, over distances of the order of 100 m and at a depth of 10 m, spatial scales relevant for most subsurface environmental problems and soil contamination studies, a tabular background can coexist with extended lateral anomalies. While a 1D approximation must be rejected, selected 3D pockets scattered within a 1D background probably provide a good conceptual model for a tabular sedimentary domain. The measurement of $EC_{Ra}$ provides a straightforward and effective method to support or reject such conceptual schemes for a given natural site.

**General results in biosphere matter**

While measurements in living matter are more limited, we report here on the initial results obtained with 111 selected materials from the biosphere (Fig. 10). Various plant materials ($n = 50$) such as dried vegetables and fruits ($n = 21$), seeds ($n = 6$), mushrooms ($n = 4$), and grass and moss ($n = 12$) have been considered. While $EC_{Ra}$ values in plant samples tended to be low, with an average of $0.72 \pm 0.17$ Bq kg$^{-1}$, the covered range of values extended from $0.020 \pm 0.0014$ to
Fig. 9. Vertical profiles of $EC_{Ra}$ in trenches and boreholes at the E, O and M locations at CLF (see Fig. 7). Grey points refer to soil samples collected at various locations in the compound or in its vicinity.

Fig. 10. Distributions of $EC_{Ra}$ for (a) plants, (b) tree samples (bark, branches and leaves) and (c) bones. Vertical dashed lines represent the geometric means.
16.6 ± 1.1 Bq kg⁻¹ (Fig. 10a), the latter being obtained with moss growing on Variscan granite, and the former with chestnuts collected on the ground. Printer paper, characterized by EC₉ value of 0.42 ± 0.03 Bq kg⁻¹ (n = 7), was included in this vegetal sample set.

Compared with the plant samples considered before, samples from trees, including bark, branches and leaves (n = 35), gave significantly larger EC₉ values, with an average of 3.8 ± 1.4 Bq kg⁻¹, and a range of values extending from 0.147 ± 0.063 to 34.0 ± 1.9 Bq kg⁻¹ (Fig. 10b). The largest value was observed on branches of a common oak tree (Quercus pedunculata) growing on the same granite as the moss mentioned previously. Leaves from various oak trees, collected at the same location, gave a value of 25.3 ± 1.0 Bq kg⁻¹. At the same location, a branch from a European ash tree (Fraxinus excelsior L.) gave a value of 31.8 ± 1.2 Bq kg⁻¹, while bark from a stone pine tree (Pinus pinea L.) gave 1.0 ± 0.1 Bq kg⁻¹. These results suggest different radium sequestration from a given local subsurface for different tree species.

To study further the radium concentration of plants under various conditions, the EC₉ value for plant and tree materials (EC₉P) was compared with the EC₉ value of the closest available soil (EC₉S), provided that it was at a distance of less than 100 m (Fig. 11). The value of this threshold distance is arbitrary, but has to be reasonable given the site conditions. Despite the still limited statistics (n = 38), an interesting structure emerged. One group was characterized by rather low EC₉P (<1 Bq kg⁻¹) values, while EC₉S remained in the typical range (3 < EC₉S < 28 Bq kg⁻¹). Another group displayed larger values of EC₉P, up to EC₉S and even larger. This was also the case for the tree samples with EC₉P > 25 Bq kg⁻¹ mentioned in the previous paragraph, for which EC₉S = 25.9 ± 1.4 Bq kg⁻¹. The largest EC₉P value in Figure 11 (32.0 ± 1.4 Bq kg⁻¹) was obtained for an oak tree branch collected in the Sudetes Mountains near Świeradów Zdroj, Poland (Przylibski & Gorecka 2014), for which EC₉S = 11.2 ± 0.8 Bq kg⁻¹. It is interesting to note that a value for the ratio EC₉P/EC₉S that is >1 coincides in this instance, with the presence of anomalous groundwater circulation, here it is a spring characterized by an extremely large radon concentration. From Figure 11, different regimes of radium intake from soils emerged. This suggests that systematic measurement of EC₉ for biological samples could be of great help in heavy metal contamination studies and remediation (Vandenhove et al. 2009; Willey 2014), a revival of an issue raised in the 1960s (Pearson & Jones 1966).

Another material of interest for radon emanation studies is bone. Indeed, calcium is exchanged in bones during the whole life of a mammal, and radium, like strontium, can be sequestrated in place of calcium. Radium studies in bones so far have remained scarce (Wrenn et al. 1985; Mirka

![Fig. 11. Plant and tree EC₉ v. EC₉ of the closest soil sample, when one soil sample is available at a distance of less than 100 m.](http://sp.lyellcollection.org/Downloaded from by guest on November 22, 2016)
et al. 1996), but a renewed interest has recently been noticed (Solecki et al. 2015). Here, we report on 26 animal bone samples, obtained from local shops, and, surprisingly, all samples were easy to measure using the standard method. The average \( E_{Ra} \) value for our bone samples was significant, at 2.7 \( \pm \) 0.7 Bq kg\(^{-1}\), and the range of values extended from 0.21 \( \pm \) 0.17 to 19.4 \( \pm \) 1.2 Bq kg\(^{-1}\) (Fig. 10c). The smaller \( E_{Ra} \) value was obtained for pork rib bones, and the larger value for beef tibia pieces sold for bone marrow. These beef bones were obtained from a commercial food distributor, which did not enable individual animals to be tracked, and so, consequently, were of an unknown origin. One given batch of samples was characterized by similar \( E_{Ra} \) values, suggesting that one animal may have been characterized by a specific \( E_{Ra} \) value. All pieces of beef bones definitely gave \( E_{Ra} \) values of \( > 1 \) Bq kg\(^{-1}\), while human teeth were characterized by \( E_{Ra} = 0.255 \pm 0.067 \) Bq kg\(^{-1}\). Why some beef bones showed such high radium concentration remains unclear at this stage, except the fact that these animals must have consumed either grass or meat-and-bone meal or groundwater with a high radium content, or all of the above. Bone composition can be rather diverse, but one major component is hydroxyapatite, which may offer an interesting analogue, at least with respect to radium chemistry, for carbonate precipitation.

**Direct measurement of radon emanation coefficient**

When concerned only with the radon source term, then \( E_{Ra} \) is the relevant quantity. However, when investigating the geological or biological meaning of \( E_{Ra} \) results, it can be helpful to separate the radium concentration, \( C_{Ra} \), which is a purely chemical component, from the emanation coefficient, \( E \), a quantity (defined between 0 and 1) that reflects the texture and microstructure of the porous medium (Tanner 1964; Adler & Perrier 2009). Radium concentration, \( C_{Ra} \), can be separately measured by gamma spectroscopy (Pereira et al. 2012), the value of \( E \) can then be inferred once \( E_{Ra} \) is measured (Ferry et al. 2002). This is actually the standard method to measure \( E \) (Sakoda et al. 2011). However, measuring with gamma spectroscopy requires destruction of the original rock sample, to produce fine powders, which obviously has to be avoided in the case of precious samples. In such cases, conversely, \( C_{Ra} \) can be inferred from \( E_{Ra} \) using some knowledge of \( E \). In the following, we present such an alternative method that can be used in some cases, when a sufficiently reliable knowledge of \( E \) can be obtained from a similar sample. Thus, once \( E_{Ra} \) of a given precious sample is measured, \( C_{Ra} \) is derived using the \( E \) value estimated for this sample type.

To estimate \( E \), the following method is proposed. First, the effective activity \( E_{Ra} \) of some sample of a given material of mass \( m \) is measured, and then this porous sample is soaked with a known quantity of a radium-rich solution of known concentration, corresponding to some injected radium activity, \( A_{Ra} \). The water is then evaporated, and the measurement of the effective activity \( E_{Ra} \) is repeated. To preserve the sample, the water is evaporated passively at ambient room temperature. The inferred value, \( E_{meas} \), of the emanation coefficient in the presence of the injected radium is then:

\[
E_{meas} = m \frac{E_{RaF} - E_{RaI}}{A_{Ra}}
\]

Two types of such measurements have been performed. In the first type of experiments, we selected crystals that are soluble in water. First, their \( E_{Ra} \) was measured, and then we dissolved the crystals in the reference radium solution. The crystals, now incorporating radium, were then re-created when crystallization occurred during evaporation. In this case, the radium was distributed over the whole solid material, more or less homogeneously. One experiment was performed using common salt (NaCl) and one with baking sugar (saccharose). The results (Table 2) were similar, giving an emanation coefficient, \( E \), of about 0.1, illustrating the loss of radon when radium gets incorporated within a crystal lattice. This is compatible with measurements with mineral crystals, which, however, tend to be rather diverse, but one major component is hydroxyapatite, which may offer an interesting analogue, at least with respect to radium chemistry, for carbonate precipitation.

**Table 2. Determination of the radon-222 emanation coefficient by doping experiments with radium-226 solution and subsequent measurements of \( E_{Ra} \)**

<table>
<thead>
<tr>
<th>Material</th>
<th>( E )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallization experiments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugar (saccharose)</td>
<td>0.145 ( \pm ) 0.011</td>
<td>1</td>
</tr>
<tr>
<td>Salt (NaCl)</td>
<td>0.081 ( \pm ) 0.009</td>
<td>1</td>
</tr>
<tr>
<td>Sands</td>
<td>0.242 ( \pm ) 0.035</td>
<td>6</td>
</tr>
<tr>
<td>Measurements with plants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oak tree leaves</td>
<td>0.95 ( \pm ) 0.08</td>
<td>2</td>
</tr>
<tr>
<td>Broccoli</td>
<td>0.828 ( \pm ) 0.082</td>
<td>1</td>
</tr>
<tr>
<td>Oak tree core wood</td>
<td>0.82 ( \pm ) 0.07</td>
<td>2</td>
</tr>
<tr>
<td>Average all plant samples</td>
<td>0.862 ( \pm ) 0.044</td>
<td>5</td>
</tr>
<tr>
<td>Artificial fibre materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter paper</td>
<td>0.74 ( \pm ) 0.05</td>
<td>2</td>
</tr>
<tr>
<td>Vegetal sponges</td>
<td>0.69 ( \pm ) 0.04</td>
<td>9</td>
</tr>
<tr>
<td>Printer paper</td>
<td>0.63 ( \pm ) 0.03</td>
<td>6</td>
</tr>
<tr>
<td>Soaking tissue</td>
<td>0.52 ( \pm ) 0.03</td>
<td>6</td>
</tr>
<tr>
<td>Blotting paper</td>
<td>0.72 ( \pm ) 0.06</td>
<td>4</td>
</tr>
<tr>
<td>Average of all fibre materials</td>
<td>0.626 ( \pm ) 0.017</td>
<td>27</td>
</tr>
</tbody>
</table>
to give values that can sometimes be as small as 1 or 0.1% (Sakoda et al. 2011).

In the second type of experiments, the porous material was soaked by the reference radium solution without disturbing the structure of the initial solid material. A total of 32 such experiments were performed (Table 2). For sands, we obtained a mean value of $E_S = 0.242 \pm 0.035$, in agreement with the commonly accepted value of 0.25 for soils (Sakoda et al. 2011). This comparatively large value suggests that, in most soils, radium is accumulated on the surface of mineral grains, with a negligible fraction incorporated inside them (Adler & Perrier 2009). Thus, radon emanation from soils would mainly result from secondary radium deposition.

With dry plant materials, we have obtained (Table 2) rather large values of $E$, with an average of $E_P = 0.862 \pm 0.044$. Large values were, in fact, expected because, in a cellular biological material, it is unlikely that a radon atom, emitted after radium decay, can be trapped within a closed mineral network. The obtained value of $E$, which is slightly less than 1, suggests, instead, the presence of radon adsorption, which is enhanced in the absence of water (Meslin et al. 2011). Values are significantly smaller for artificial fibre materials than for plants (Table 2), with an average value of $0.626 \pm 0.017$. Such values can probably also be interpreted as representing a more significant contribution of radon adsorption.

Taking the mean values of $E$ determined from plants ($E_P$) and sands ($E_S$), we derived experimental values of the soil-to-plant transfer ratio, $R_{SP}$, from the previously determined ratio $EC_{RaP}/EC_{RaS}$:

$$R_{SP} = \frac{E_S \ EC_{RaP}}{E_P \ EC_{RaS}}$$

The values varied from 0.002, and even smaller, to 1 (Fig. 12). The statistics remain limited ($n = 39$), but some values clustered around 0.02 and around 0.3. It is too early to draw conclusions on the differences between tree and plant species in a given soil context, but the method appears definitely to be a powerful and cost-effective means of studying radium accumulation in plants, which could be of importance for the remediation of polluted sites (Soudek et al. 2007, 2010).

### Conclusion and perspectives

In this paper, we have presented general results of the radon emanation potential of various natural materials, such as rocks, soils, plants and bones. While the measurement methods have been known for decades, the efforts have been concentrated on methodological issues with a limited numbers of samples, such as granites and rocks considered for geological waste storage (Ferry et al. 2002). Recently, a reliable and efficient method using scintillation flasks (Girault & Perrier 2012) has been developed, and more than 11 000 accumulation experiments have been carried out and more than

![Fig. 12. Distribution of the soil-to-plant radium-226 transfer ratio, inferred from the measurements of $EC_{Ra}$ and the emanation coefficients obtained from doping experiments.](http://sp.lyellcollection.org/)
3300 samples have been studied systematically. The measurement of $EC_{Ra}$ interesting in itself for radon transport modelling (Girault & Perrier 2014) or health hazard assessment (Girault & Perrier 2012c; Perrier & Girault 2013), also appears as an interesting parameter, considerably easier to measure than radium concentration, with the additional, sometimes crucial, advantage of keeping the sample in its original condition.

In the case of rocks, a significant number of results allowing statistical analysis is already available, with 1351 measured rock samples and $EC_{Ra}$ values that cover several orders of magnitude from the detection level, on average 0.03 Bq kg$^{-1}$ with our standard technique, to more than 10$^7$ Bq kg$^{-1}$, excluding uranium ore minerals characterized by values larger than 10$^6$ Bq kg$^{-1}$. Smaller variations within rock group are also of great significance. Indeed, the geological potential of $EC_{Ra}$ has now been clearly demonstrated to distinguish rock types or to reveal geological processes. It might be important, for future applications, to study in detail the differences that are sometimes observed between $EC_{Ra}$ values of intact and crushed samples.

Geological applications can now be considered broadly in a systematic fashion. The available results suggest that promising contributions may be made to a number of geological questions. In the case of granites, which are particularly easy to measure, a promising systematic study of Variscan granites is suggested. The tentatively impressive correlation at large distances ($>3000$ km) need to be confirmed. Furthermore, in a given region, it might be possible to distinguish different granite bodies using specific $EC_{Ra}$ properties. The fact that $EC_{Ra}$ contains one purely chemical part ($C_{Ra}$) and one textural part ($E$) resulting from the porous medium, thus, appears as an asset rather than a limitation.

While more difficult to study because of their lower radium content, the measurement of $EC_{Ra}$ in mantelic components might have powerful applications: for example, in the case of lavas. Different lava flows are, indeed, characterized by specific radionuclides (Allègre & Condomines 1982). A systematic investigation of known and dated lava flows might indicate that $EC_{Ra}$ measurements would have a wider application in volcanology.

Applications of $EC_{Ra}$ to calcareous rocks have also barely started. Potential applications, however, are of great interest and should be given sufficient attention in the future. Limestones, indeed, are hosts of important sites, such as painted caves and precious underground ecosystems. In such sites, the radon concentration has been measured extensively to study the microclimatic conditions, which are essential to understand when considering preservation (Bourges et al. 2014). Radon transport, however, needs a better understanding of the source term from the encasing rocks, which, especially in such sites, competes with radon released from groundwater.

In the case of soils, more than 1500 samples have now been measured and, in this case too, the dispersion of values is a major question to address when attempting detailed interpretations. However, the $EC_{Ra}$ values of common soils tend to be less variable than the $EC_{Ra}$ of rocks, with most values falling between 4 and 20 Bq kg$^{-1}$. Dark soils rich in iron oxides or organic matter were characterized by values ranging commonly up to 20 Bq kg$^{-1}$ (Girault et al. 2011a). The relevance of $EC_{Ra}$ for sedimentary studies, demonstrated in the Kathmandu Valley (Girault et al. 2011a), can now be applied in a more extensive manner in Quaternary geology. With large numbers of samples processed routinely, 2D mapping can now be attempted in dedicated cases.

Further interesting applications can be considered using samples from the biosphere. Measurements of $EC_{Ra}$ of plants are for the moment less numerous than for rocks and soils, with a total of 85 $EC_{Ra}$ values available. Contrary to expectations, such samples were actually easy to measure and the range of values extended from the detection limit to more than 30 Bq kg$^{-1}$. Large values were observed for moss and tree samples growing on a granitic domain, suggesting that significant radium transport and, consequently, $EC_{Ra}$ could be a proxy for heavy metal transfer from soil to the biosphere – essential knowledge in contamination and remediation studies. Our initial results raised new questions. For example, is there a characteristic value for a given tree, and for its fruits, seeds, roots, sap wood, bark, branches and leaves? Are there significant and systematic differences between tree species in a given soil condition?

The value of the emanation coefficient for soils remains a difficult problem (Tanner 1964). While there is consensus for a typical average value of around 0.25 (Sakoda et al. 2011), values can vary from a few per cent up to 50%. By contrast, we measured that emanation coefficient values for plant samples clustered around 0.86. Tentatively, we determined values of the radium-226 soil-to-plant transfer ratio from our $EC_{Ra}$ measurements, but the answer to the question concerning different tree species in a given soil condition needs to be determined from dedicated investigations.

The fact that $EC_{Ra}$ was found to be relatively large for all tree branch samples suggests another domain of application. Indeed, radon emanation from wood artefacts could be investigated using accumulation experiments, as already successfully applied in the case of dial watches (Gillmore et al. 2012). The advantage of radon emanation is that it does not affect the sample in any manner: pieces
of furniture, statues, weapons or other precious samples of historical or archaeological interest can be investigated without any risk of damage.

Similarly, our initial measurements with bones open up numerous unexpected perspectives. The statistics remains limited (n = 26), but all samples were measured without difficulty and values of >2 Bq kg\(^{-1}\) were observed for most beef bone samples. These initial results suggest that there is tremendous interest in studying in detail the radon emanation from animal samples. Human bones have not yet been studied, except for teeth.

Further improvements of the \(EC_{Ra}\) measurement technique could lead to significant improvements in the detection limit (e.g. using longer counting sessions). Such improvements could open up novel perspectives such as high-sensitivity measurements of samples with low radium content (e.g. some gneiss, limestone, lava or extraterrestrial samples). Effective radium concentration, beyond the recently renewed interest, could then become one of the most significant indices to characterize porous materials. This could then open up a new age for radon emanation studies for geological applications or for the investigation of the biosphere as part of a new generation of methods to be developed for the preservation of the environment and for understanding the critical zone.

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