Radon decay products and 10–1100 nm aerosol particles in Postojna Cave

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Abstract. At the lowest point along the tourist route in Postojna Cave, the activity concentration of radon (222Rn) decay products and the number concentration and size distribution of aerosol particles in the size range of 10–1100 nm were monitored, with the focus on the unattached fraction (f_{un}) of radon decay products (RnDPs), a key parameter in radon dosimetry. The total number concentration of aerosols during visits in summer was lower (700 cm^-3) than in winter (2800 cm^-3), and was dominated by < 50 nm particles (related to unattached RnDPs) in summer and by > 50 nm particles (related to the attached RnDPs) in winter. This explains the higher f_{un} values in summer (0.75) and the lower winter measurement (0.04) and, consequently, DCF values of 43.6 and 13.1 mSv WLM^{-1} respectively for the calculated dose conversion factors. The difference is caused by an enhanced inflow of fresh outside air, driven in winter by the higher air temperature in the cave compared to outside, resulting in the introduction of outside aerosol particles into the cave.

1 Introduction

In a great number of karst caves worldwide, elevated radon (222Rn) levels in the air have been observed (Cigna, 2005; Field, 2007; Vaupotič, 2010). Radon α-transformation (half-life t_{1/2} = 3.82 days) is followed by a radioactive chain of its short-lived radon decay products (RnDPs) (Nero, 1988): 218Po (α, 3.05 min) → 214Pb (β/γ, 26.8 min) → 214Bi (β/γ, 19.7 min) → 214Po (α, 164 μs). Initially, they appear mostly as positive ions (Chu and Hopke, 1988; Pagelkopf and Porstendörfer, 2003; Porstendörfer and Reineking, 1992), which react with molecules of trace gases and vapours (mostly water) in the air and form small clusters, which are then neutralised (Chu and Hopke, 1988; Pagelkopf and Porstendörfer, 2003) and attach to the background aerosol particles (Dankelmann et al., 2001; Hopke, 1996; Pagelkopf and Porstendörfer, 2003; Papastefanou, 2008). Eventually, RnDP aerosols mostly show a bimodal size distribution one in the 1–10 nm size range (referred to as unattached RnDPs) and the other between 100 and 500 nm (attached RnDPs) (Gründel and Porstendörfer, 2004; Porstendörfer and Reineking, 1992; Porstendörfer et al., 2000). Total concentration of RnDP in the air is reported as equilibrium-equivalent activity concentration (C_{RnDP}, Bq m^{-3}) expressed by the following (Nero, 1988):

\[
C_{RnDP}^A = 0.1065 \times (A_{216Pb})^A + 0.515 \times (A_{214Pb})^A + 0.379 \times (A_{214Bi})^A \tag{1}
\]

where A (Bq m^{-3}) stands for the individual activity concentrations of 218Po, 214Pb and 214Bi. Because of its short half-life, 214Po activity is equal to the activity of 218Bi and is therefore already included in the last term of Eq. (1). Due to air movement and deposition of RnDP to surfaces, individual activity concentrations of 218Po, 214Pb and 214Bi are always lower than that of radon (C_{Rn}), and secular equilibrium between radon and RnDP is never reached in the ambient air, its degree being expressed by the equilibrium factor (F):

\[
F = \frac{C_{RnDP}^A}{C_{Rn}^A} \tag{2}
\]

On the world average, RnDPs contribute more than half to the effective dose (the radon contribution is minor) received by members of the general public from all natural radioactivity (UNSCEAR, 2000) and are a significant cause of lung cancer, second only to cigarette smoking (Darby et al., 2005). For this reason their levels in the living and working environment, including karst caves, are of great concern to us and are

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a research challenge. While the exposure of tourists is negligible during their visit to a cave, it may easily reach high levels for cave employees who spend the majority of their working time underground (Field, 2007; Káváši et al., 2003; Somlai et al., 2009; Vaupotic et al., 2001).

For the general purposes of radiation protection, the International Commission on Radiological Protection (ICRP), in its Publication 65, recommends for radon dosimetry a dose conversion factor (DCF) of 4 mSv/WLM in the workplace (ICRP, 1993), as the values deduced from epidemiological studies. Nevertheless, dose conversion factors are subject to constant investigation and upgrading, and an increase of their recommended values is foreseen in the near future (Harrison and Marsh, 2012; ICRP, 2010). A value of 1 WLM (working-level month) corresponds to the exposure from 170 h of breathing air in which the potential $\alpha$-energy concentration of RnDP ($E_{\alpha\text{RDP}}$) is $1.3 \times 10^8$ MeV m$^{-3}$. $E_{\alpha\text{RDP}}$ (MeV m$^{-3}$) is expressed through the activity concentrations ($C^{A}$, Bq m$^{-3}$) of $^{218}$Po, $^{214}$Pb and $^{214}$Bi (Nero, 1988):

$$E_{\alpha\text{RDP}} = 3690C^{A}_{\text{Pb}} + 178230C^{A}_{\text{Pb}} + 13120C^{A}_{\text{Bi}}. \quad (3)$$

On the other hand, Birchall and James (1994) and Marsh et al. (2002) elaborated on a dosimetric approach to calculating the dose conversion factor (DCF$_D$), which is used mainly for research purposes. They also showed that the parameter most affecting DCF$_D$ is the fraction ($f^{\text{un}}$) of unattached RnDPs, defined as follows (Nero, 1988):

$$f^{\text{un}} = \frac{C^{A}_{\text{un}\text{RDP}}}{C^{A}_{\text{RDP}}} \quad (4)$$

where $C^{A}_{\text{un}\text{RDP}}$ is the equilibrium-equivalent concentration of unattached RnDPs, obtained if activity concentrations of only the unattached $^{218}$Po, $^{214}$Pb and $^{214}$Bi are taken into Eq. (1). Furthermore, they expressed DCF$_D$ based on $f^{\text{un}}$ with an empirical formula:

$$\text{DCF}_D = 11.35 + 43f^{\text{un}}. \quad (5)$$

In order to reveal how levels of unattached and attached RnDPs (a crucial parameter in radon dosimetry) (Hofmann and Koblinger, 1990; Nikezić et al., 2006) are controlled by the presence of background aerosol particles with which RnDPs are associated, measurement of number concentration and size distribution of aerosol particles in the 10–1100 nm size range has recently been introduced (Iskra et al., 2010).

Background aerosols are formed in the atmosphere by various natural processes (e.g. rock grinding and crushing, volcanic eruptions, wildfires) and anthropogenic influences (e.g. biomass and fossil fuel burning, traffic emissions). The concentration of background aerosols in outdoor air depends strongly on emission factors and meteorological conditions (Colbeck, 1998). In general, the highest number concentrations are observed in urban areas during winter, caused by biomass and fossil fuel burning, while in summer the levels are usually lower. In the indoor (living) environment the main sources are human beings and their activities.

Background aerosols were measured in urban and rural outdoor air during our previous work (Smerajec and Vaupotic, 2012). The average total number particle concentration ($C^N_{\text{b}}$(tot)) and geometric mean particle diameter ($d_{GM}$) obtained in the urban environment was 14 750 ± 7220 cm$^{-3}$ and 46 ± 10 nm, respectively. In the rural environment $C^N_{\text{b}}$(tot) of 7800 ± 5250 cm$^{-3}$ and $d_{GM}$ of 63 ± 19 nm were measured (Smerajec and Vaupotic, 2012).

In the present paper, simultaneous measurements of the activity concentration of radon decay products and the number concentration and size distribution of aerosol particles at the lowest point along the guided route in summer and winter are described, and the results presented with a commentary.

## 2 Materials and methods

### 2.1 Site description

Postojna Cave is a part of a larger cave system in Slovenia, which also includes the Pivka, Magdalene, Black and Island caves (Fig. 1) and has a total length of about 20 km. It is one of the biggest show caves in the world. Postojna Cave is a horizontal cave with passages developed on two levels. The Pivka river sinks at the lower entrance to the cave at 511 m a.s.l (above sea level). The entrance to the main, currently dry passage is situated at 529.5 m a.s.l. (Šebela, 1998). This entrance is used as a tourist entrance. As in the majority of karst caves, the only ventilation is natural air circulation. Air temperature is practically constant at around 10–11°C all year round, and relative air humidity is in the range 94–100%. Air flow differs considerably in summer and winter. In winter, when the cave temperature is higher than outside, cave air is released from the cave into the outdoor atmosphere due to the air draught caused by the “chimney effect”, thus allowing fresh and cold outside air to enter the cave through...
low-lying openings (Gregorič et al., 2011). This effect is not produced in summer, when the outside temperature is higher than in the cave and the air draught is minimal or reversed. In any case, the air speed is low, never exceeding 1.5 m s$^{-1}$ along the main entrance corridor, and is much less or zero in other parts of the cave. As a result of the different natural ventilation regime, the cave interior, at least along the main air paths, is less wet in winter than in summer.

The cave is open to visitors every day from 10:00 a.m. to 04:00 p.m. LT (local time) in winter and from 09:00 a.m. to 06:00 p.m. LT in other seasons. The daily number of visitors is around 3500 in summer and from 50 to several hundred in winter, totalling around half a million a year. Visitors ride an electric train for the first 2 km from the entrance to the train stop, walk 1.8 km on a figure-of-eight route and return back to the train in about an hour and a half. Our study site is located at the lowest point of the path (508 m a.s.l., Fig. 1), approximately 500 m on from the train stop along the guided route. This is also the point of regular radon monitoring for the purpose of radon dosimetry of the cave employees. The path is paved with a special concrete containing silica sand to prevent it from becoming slippery when wet.

The major source of particulate matter in the cave air is the inflow of fresh outside air in winter. Deposition of dust is observed on surfaces in the main corridor all the way from the entrance to the train stop, but no further. Another source is the railway. Particles originate from the rusting of iron parts, grinding of sand, and rotting and damage to wooden sleepers. They are lifted and resuspended by the air draught caused by the train running at a speed of 1.6 m s$^{-1}$ through the narrow corridors and galleries. Human activity, both visits and maintenance work on the cave infrastructure, is also a potential source of particulate matter.

### 2.2 Radon decay products

Individual activity concentrations ($C^A$, Bq m$^{-3}$) of $^{222}$Rn, $^{218}$Po, $^{214}$Pb, $^{214}$Bi and $^{214}$Po have been measured using the EQF3020-2 device (Equilibrium Factor Monitor System, Sarad, Germany). Air is pumped for 6 min at a flow rate of 2.4 dm$^3$ min$^{-1}$ over a metal mesh grid on which aerosol particles smaller than 5 nm (considered as unattached RnDPs) are separated from those above this size (considered as attached RnDPs), and the two fractions are deposited electrostatically on two separate 150 mm$^2$ semiconductor detectors. Gross $\alpha$ activity is measured over three consecutive intervals within 110 min of the end of pumping, and, applying the Markov method (Markov et al., 1962; Streil et al., 1996), individual activity concentrations of $^{218}$Po, $^{214}$Pb and $^{214}$Bi in the unattached and attached fractions are obtained. The device also gives the equilibrium-equivalent activity concentration of RnDPs ($C_{RnDP}$), the equilibrium factor between Rn and RnDPs ($F$), the fraction of unattached RnDPs ($f^{un}$) and potential $\alpha$-energy concentration of RnDPs ($E_{\alpha RnDP}$), as well as air temperature and relative humidity.

In order to facilitate comparison of the number concentration of background aerosols and concentrations of $^{218}$Po, $^{214}$Pb and $^{214}$Bi aerosols, the activity concentrations ($C^A$) of radionuclides are converted into their number concentrations ($C^N$), by applying the radioactivity law equation:

$$C^A = \lambda \times C^N,$$

with

$$\lambda = \ln 2 / t_{1/2}. \quad (7)$$

The obtained number concentrations of $^{218}$Po, $^{214}$Pb and $^{214}$Bi atoms (cm$^{-3}$) are denoted by, respectively, $C_{218Po}^{Num}$, $C_{214Pb}^{Num}$ and $C_{214Bi}^{Num}$ for unattached RnDPs and $C_{218Po}^{Natt}$, $C_{214Pb}^{Natt}$ and $C_{214Bi}^{Natt}$ for attached RnDPs.

### 2.3 Background aerosols

The term “background” is used here to comprise all particles in the cave air, both with and without associated RnDPs (although the contribution of the latter in the number concentration is negligible, as will be seen later).

The number concentration and size distribution of background aerosol particles were measured with a SMPS+C
instrument (scanning mobility particle sizer + counter), Series 5,400 (Grimm, Germany). For this purpose, the long DMA (differential mobility analyzer) unit, designed for the 10–1100 nm size range, was used. The DMA unit separates charged particles based on their electrical mobility, which depends on the particle size and electrical charge: the smaller the particle and the higher its electrical charge, the higher its mobility. Particles enter the CPC (condensation particle counter) unit containing a heater saturator in which alcohol vapour molecules condense onto the entering particles, thus causing them to grow into droplets. The droplets are then detected with a laser beam (dynamic light scattering detection) and counted. The frequency of measurement is once in 7 min. The instrument gives the total number concentration \( C_b^{N} \text{(tot)} \) and size distribution \( \frac{d C_b^{N}(d)}{d \ln d} \) (with \( d \) the electrical mobility equivalent particle diameter). Because the DMA unit is not designed for sizes below 10 nm, and bearing in mind that RnDPs in Postojna Cave are attached to aerosol particles bigger than 100 nm (Butterweck et al., 1992), we selected 50 nm as the boundary between unattached and attached RnDPs. Thus, we are interested in concentrations of particles smaller than 50 nm \( (C_b^{N} (< 50)) \), those bigger than 50 nm \( (C_b^{N} (> 50)) \) and the fraction of the smaller particles, defined as

\[
x_b = \frac{C_b^{N} (< 50)}{C_b^{N} \text{(tot)}}.
\]  

Several 5–10 day measurements were carried out with EQF devices in summer 2009 and winter 2010 at the lowest point along the guided walking route in the cave. Within these periods, the SMPS+C instrument was also used, but only for a few hours during morning visits, because the instrument is not designed for such high air humidity and its operation was therefore minimised.

3 Results and discussion

3.1 Previous results

Previous measurements (Vaupotić, 2008a; Vaupotić et al., 2001) indicated that the difference in air temperature outside and inside the cave played a dominant role in governing both diurnal and seasonal variations of the environmental conditions in the cave. Radon levels were lowest in winter, when the cave temperature is higher than outdoors, because radon-rich air is released from the cave into the outdoor atmosphere and fresh outdoor air with low radon concentration is driven into the cave. This effect is not produced in summer, when the outdoor air temperature is higher than in the cave, and the resulting radon levels in the cave air are higher.

As an example, at the lowest point the following average values were obtained in 1999 (Vaupotić, 2008a; Vaupotić et al., 2001) in summer: \( C_{\text{Rn}}^A \) of 4540±600 Bq m\(^{-3}\), \( C_{\text{RnDP}}^A \) of 1580±280 Bq m\(^{-3}\), \( F \) of 0.35±0.09 and \( f_{\text{un}} \) of 0.60±0.16, and in winter: \( C_{\text{Rn}}^A \) of 2070±1160 Bq m\(^{-3}\),

\[
C_{\text{RnDP}}^A \text{ of } 1130 \pm 530 \text{ Bq m}^{-3}, \ F \text{ of } 0.58 \pm 0.11 \text{ and } f_{\text{un}} \text{ of } 0.14 \pm 0.08.
\]

3.2 Present summer results

For one of the measurements carried out in summer, Fig. 2a shows size distribution of background aerosols before visits started and during regular visits. A low-size peak of bimodal distribution (Butterweck et al., 1992) was not observed, because our instrument is designed for the 10–1100 nm range. Their geometric mean values of 26 and 31 nm do not differ significantly. The decrease in concentration from 2700 to 700 cm\(^{-3}\) is mainly due to the smaller particles as seen in Fig. 3a, showing a constant concentration of >50 nm particles and a steady decrease of <50 nm particles during visits. This is presumably because the smaller particles are preferentially deposited on the cave surfaces (Papastefanou, 2008; Porstendörfer, 1984), caught by clothing (Balcazar et al., 1999; Rovenská et al., 2008) and taken up by the lungs (Hofmann and Koblinger, 1990) of tourists walking through the corridor at the lowest point, with a cross section of about 25 m\(^2\).

Figure 4a shows radon activity concentration \( C_{\text{Rn}}^A \), the equilibrium factor \( F \), the equilibrium-equivalent activity concentration of RnDPs \( C_{\text{RnDP}}^A \) and the fraction of
Fig. 3. Time run of number concentrations ($C^N_{b}(d)$) of background aerosol particles smaller than 50 nm ($C^N_{b}(<50)$) and bigger than 50 nm ($C^N_{b}(>50)$), and the fraction of smaller ones ($x_b(<50)$) at the lowest point in Postojna Cave (a) in summer 2009 and (b) in winter 2010.

unattached RnDPs ($f^{un}$). As expected from previous monitoring in summer (Vaučić, 2008a), $C^A_{Rn}$ and $f^{un}$ are high and $F$ is low. During the period when background aerosols were also monitored, $f^{un}$ values were around 0.75 (Fig. 4a), resulting in a DCFD value (Eq. 5) of 43.6 mSv WLM$^{-1}$. For this time interval, Fig. 5a shows the individual activity concentrations of the unattached and attached RnDPs, and the related number concentrations of the unattached and attached RnDPs, $^{218}$Po, $^{214}$Pb and $^{214}$Bi, respectively. The measurement frequency of the EQF device is much lower (once in 2 h) than that of the Grimm device (once in 7 min), and therefore the time variations of the parameters measured with the two cannot be adequately compared. The number concentration of the unattached $^{218}$Po atoms is lowest, because it has the shortest half-life (cf. Eq. 6) in comparison to $^{214}$Pb and $^{214}$Bi. On the other hand, the ratio of the numbers of the unattached and attached $^{218}$Po atoms was initially 26, far higher than those of $^{214}$Pb and $^{214}$Bi, which were 5.3 and 0.65 respectively. There are several reasons for this high ratio for $^{218}$Po. Because of its short half-life in comparison to $^{214}$Pb and $^{214}$Bi, it has less time available to become attached to atmospheric particles. The second reason is based on the values of diffusion coefficients. These are in the range of 0.024–0.039 cm$^2$ s$^{-1}$ for the charged RnDP species and 0.068–0.085 cm$^2$ s$^{-1}$ for the neutral species (Porstendörfer and Mercer, 1979). At a radon activity concentration of about 5500 Bq m$^{-3}$, as in our case (Fig. 4a), 13 % of $^{218}$Po species are estimated to be charged (Chu and Hopke, 1988). As a result of lower mobility, the attachment of these charged species is hindered. This effect cannot be estimated for $^{214}$Pb and $^{214}$Bi, because the data are not available. At the end of our measurement, the ratios of numbers of unattached versus attached $^{218}$Po, $^{214}$Pb and $^{214}$Bi atoms were 6.6, 5.0 and 0.86, respectively. The value for $^{218}$Po decreased drastically, concomitantly with the falling concentration of the $<50$ nm particles (Fig. 3a), while the other two did not change significantly.

Concentrations of $^{218}$Po, $^{214}$Pb and $^{214}$Bi atoms are lower by several orders of magnitude than the total concentration of background aerosols. We therefore assume that the reason for high $f^{un}$ values in the cave air is not simply the
Fig. 5. Activity concentrations and number concentrations of $^{218}\text{Po}$, $^{214}\text{Pb}$ and $^{214}\text{Bi}$ in the time interval of Fig. 4, when background aerosols were also monitored, from top to bottom: activity concentrations in the unattached form ($C_{\text{Aun}}^{218}\text{Po}$, $C_{\text{Aun}}^{214}\text{Pb}$ and $C_{\text{Aun}}^{214}\text{Bi}$), activity concentrations in the attached form ($C_{\text{Aatt}}^{218}\text{Po}$, $C_{\text{Aatt}}^{214}\text{Pb}$ and $C_{\text{Aatt}}^{214}\text{Bi}$), number concentrations in the unattached form ($C_{\text{Nun}}^{218}\text{Po}$, $C_{\text{Nun}}^{214}\text{Pb}$ and $C_{\text{Nun}}^{214}\text{Bi}$) and number concentrations in the attached form ($C_{\text{Natt}}^{218}\text{Po}$, $C_{\text{Natt}}^{214}\text{Pb}$ and $C_{\text{Natt}}^{214}\text{Bi}$) (a) in summer 2009 and (b) in winter 2010.

The substantial decrease in $x_b$ (<50) during morning hours (Fig. 3a) could result in an increase in $f_{\text{un}}$, but it did not, and in fact the opposite was observed (Fig. 4a). Actually, such rapid changes (lasting a matter of minutes) in size distribution are not expected to cause immediate change in $f_{\text{un}}$, i.e. redistribution between unattached and attached Po, Pb and Bi atoms. Rather, they will only influence newly formed Po, Pb and Bi atoms and clusters. Creation of these atoms by radioactive transformations takes time; also, their neutralisation, clustering, and attachment to (Tokonami, 2000) and detachment from background aerosol particles by recoil are processes with definite values of rate constants. Taking this into account, calculations would show (Nikolopoulos and Vogiannis, 2007) that a time delay of some hours (Wang et al., 2011) necessarily occurs between a change in particle size distribution of background aerosols and a change in $f_{\text{un}}$. Therefore, a true dependence of $f_{\text{un}}$ on rapid changes in background aerosols in our case was masked or even totally obscured. A similar situation has been observed in an indoor environment (Smerajec and Vaupotič, 2012).

3.3 Present winter results

For a measurement carried out in winter, Fig. 2b shows the size distribution of background aerosols before visits started and during regular visits. The related geometric mean diameters are similar ~113 and 110 nm respectively – and are substantially higher than in summer (Fig. 2a). Because our measurements of the number size distribution in outdoor air show a geometric mean of $63\pm19$ nm (Smerajec and Vaupotič, 2012), we may assume that in winter the inflow of fresh air brings outside aerosol particles into the cave. In contrast to the situation in summer, the total concentration...
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References


Sebela, S.: Tectonic structure of Postojnska jama cave system, ZRC Publishing (Scientific Research Centre), Ljubljana, 112 pp., 1998.


