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ORIGINAL PAPER

Radon in potable waters in Luxembourg

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Abstract. The presence of elevated concentrations of radon in water is a potential health risk when the water is used in public water supply, mainly because of the increase of radon concentration in the indoor air due to degassing [16]. Samples were taken from a large number of Luxembourg's drinking water springs in 2007 to determine the major ion chemistry and potential contaminants, mainly from agriculture. The natural radioactive isotopes were analysed as part of this program. Two sampling campaigns were performed, one in summer, one in winter, to consider seasonal variations. This paper presents the radon activities, which were sampled during the two field campaigns and measured using liquid scintillation counting (LSC). For quality assurance of our results we made three replicates from each collected water sample. This methodology was used because it is more accurate than other possible methods of radon measurement, and its limit of detection is sufficiently low, i.e., 700 $Bq \cdot m^{-3}$. The correlation between radon and radium levels was estimated, as well as the dependence of radon levels on geology. The results from the year 2007 were compared to previous measurements from the year 2003. Five springs in the program were sampled monthly throughout a year to account for possible seasonal variations, additionally to the large spatial extend of the program.

Key words: radon concentration • geological dependence • seasonal radon variation • waters in Luxembourg

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Introduction

Public drinking water supplies account for about 145 000 m^3 of water per day in Luxembourg. Two-third are drawn from groundwater resources, mainly from the Liassic sandstone aquifer, called Luxembourg Sandstone, which itself supplies 90% of the drinking water originating from groundwater resources [1, 6]. The unconfined part of the sandstone is located in the centre of the country and covers about 300 km^2 with a surface to water table depths ranging from 0 to 100 m. Most of the groundwater captures are natural springs or shallow wells (80% of the volume) and the majority of the springs are distributed along the main river valleys, where contacts of the Luxembourg Sandstones and Lower Jurassic (Lias) marls crop out [4]. This formation encompasses local carbonate-bound sandstone as part of the Paris Basin. Only a few springs do not derive from this aquifer, but they were sampled as well for comparison reasons. The adjacent aquifers, which hosts these springs are a fractured rock shist aquifer in the North, Devonian in age and a carbonate bound sandstone unit from the Upper Dogger in the South of Luxembourg.

In 2007, 316 springs in Luxembourg were sampled within the framework of a SPATIAL MONITOR project. Major ion chemistry data and physical parameters were measured in Luxembourg's drinking water supplies. In

addition, radioisotopes, such as ^{222}Rn and U/Th-series isotopes were determined for the same samples at the radio-physics laboratory of the University of Luxembourg. These results are important for the use of radioisotope data as groundwater and surface water tracers.

Most of the sampled springs are used as a drinking water resource [4] and the knowledge of radionuclide content and their variability with different lithologies is crucial.

Due to observation of elevated levels of ^{222}Rn in the indoor environment in many countries, it has been realized that residential ^{222}Rn is a possible public health issue, especially in the western world where buildings are often well insulated and ventilation is not given. It was assumed that the contribution from ^{220}Rn and its progeny is about 10% of that of ^{222}Rn and its progeny [11]. Hence, there is a need to generate a comprehensive database on radon levels in water and indoor air. With this in mind, the determination of natural radioactivity in groundwaters was included in the SPATIAL MONITOR program.

The aim of this part of the project is to deliver a high resolved spatial radon distribution and an analysis for

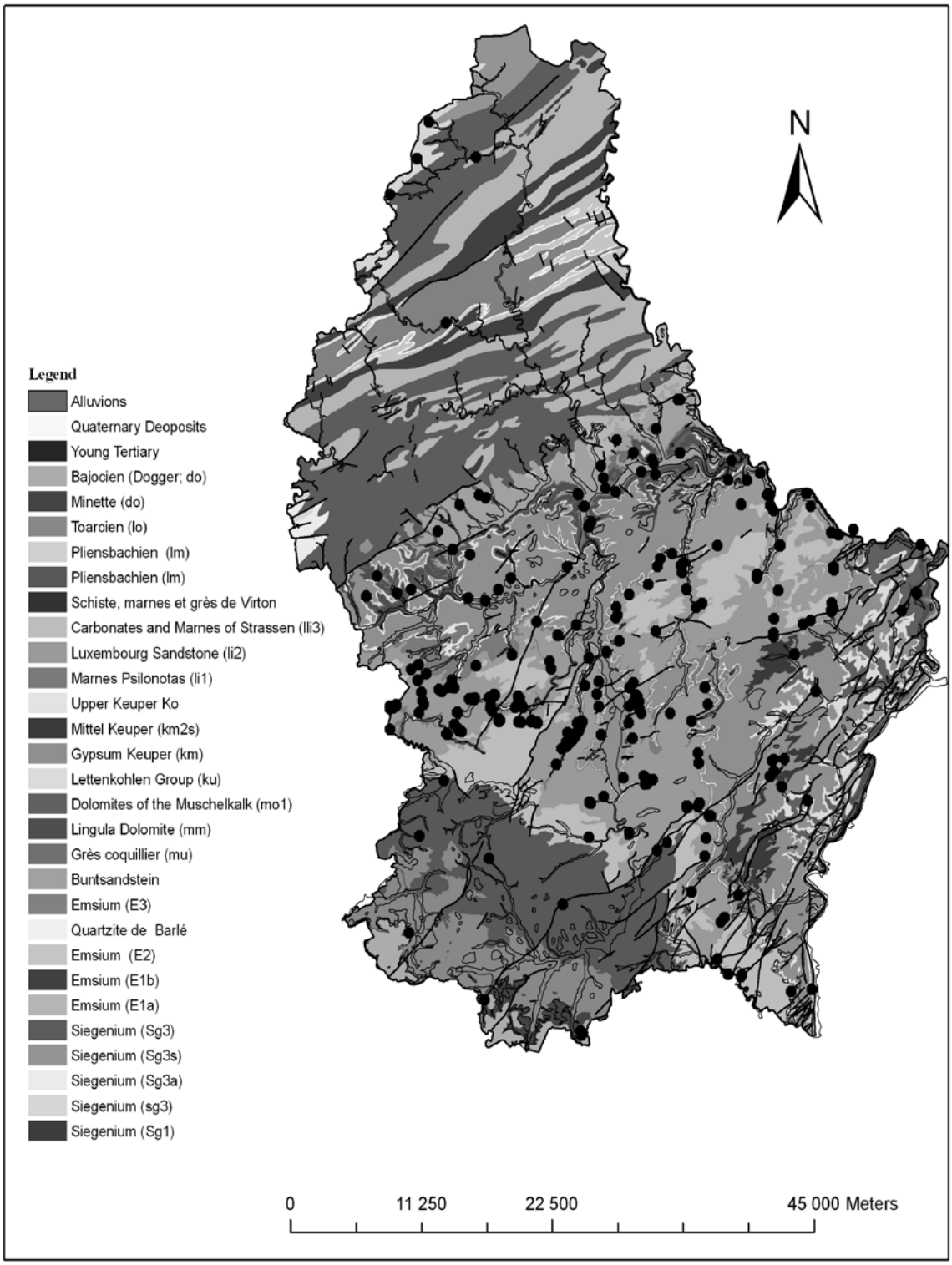

Fig. 1. Map of sampling points in the geology map of Luxembourg.

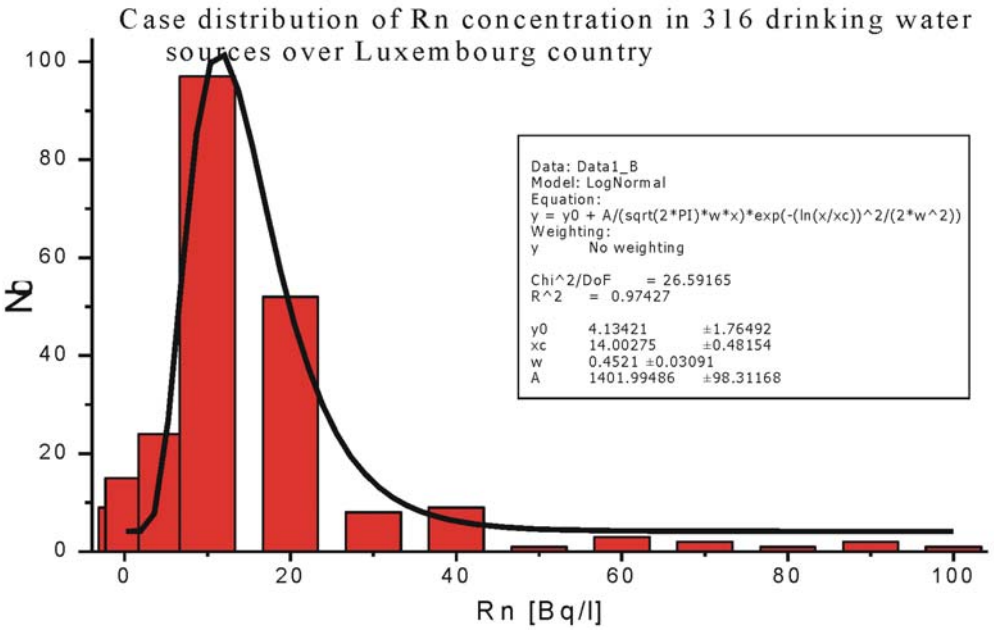

Fig. 2. Statistical distribution of radon in water over Luxembourg.

the causes of activity variations. Besides, a dense spatial resolution, temporal variations were analyzed as well. The 316 springs were sampled twice, once during the winter month, and once during the summer month, and therefore during base flow conditions. Furthermore, five of the selected springs have been equipped with continuous flow and electrical conductivity (EC) devices and have been sampled for radon on monthly bases for a whole year. Data from a previous campaign in 2003 are used for comparison as well.

Known geology and hydro-geological conditions are used to interpret the radon variations.

Material and methods

The samples were collected in 250 mL glass bottles with polytetrafluoroethylene (PTFE) cap. The bottles were filled to the top to prevent losses of radon due to degassing and exchange with air.

The water samples were measured in laboratory conditions a few hours after the sampling. Three replicates were measured from each sample to obtain a better statistics. Every tenth sample was measured twice. Radon measurements were done by LSC on a Guardian PerkinElmer liquid scintillation counter, using 10 ml of Ultima Gold F scintillator mixed with 12 mL of water sample [10].

For quality assurance purposes, 10% of all this laboratory samples were additionally measured on portable LSC device or in flushing chamber RAD 7-Drexel method [13]. Supplementary the results from several sources were compared to the results of continuous *in-situ* measurements to test their validity. The *in-situ* measurements were performed at intervals of 30 min with diffusion membranes Acurell coupled to different measurement equipment like AlphaGuard (Genitronik Inc.), Rad 7 (Durridge Inc.) etc.

The standard procedures for control of equipment and for calibration were applied, too.

Result and discussions

The predominant interest was the correlations between radon and physical and chemical parameters of these waters as well as the influences of the radium as a precursor for radon. The used method is quite sensitive (700 Bq/m^3) for the purposes of our screening.

Figure 1 shows a map of the sampling points and the different geological units they are in. As above-mentioned, the majority of the natural springs occurs in the outcropping region of the Luxembourg Sandstone in the central part of the country. The normal background radon concentrations in water vary in the range of 2–60 Bq/L with an average value of 17 Bq/L. The histogram in Fig. 2 shows distribution of the obtained data. It follows a positively skewed log-normal dependence with the maximum at 15 Bq/L that is characteristic for deeper groundwater in this area. Only 3% of the obtained results are close to 100 Bq/L and are well explained with the high mineralization of these sources.

From the point of view of a radiological hazard, the concentrations do not exceed UNSCEAR [12] standards and, therefore, do not pose any health risks. The comparison between indoor radon concentrations over the country and water radon concentrations show no direct relation. The maximum concentrations of indoor radon occur mainly in Devonian formation (shits and quartzite sandstones) in the northern part of the country. The reasons for this lack of relationship are not clear because soil air radon and, therefore, indoor radon concentrations are dependent on the geological substrates and their U-bearing minerals in general. A small number of samples from the North is not representative and further research should be done in this part of Luxembourg.

The geographical distribution of the radon shows two axes of elevated concentrations. One is located in the north-western region, followed by the second one in the central East of the country. They both are mainly

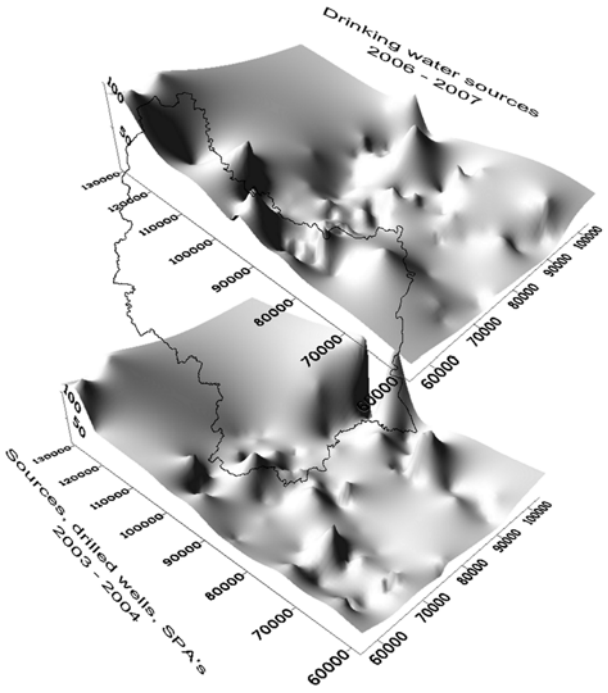

Fig. 3. Comparison of two investigation campaigns for spatial distribution of radon in water.

situated on Lower Jurassic and Triassic formations. Radiation profile map of Luxembourg, prepared with aero-gamma measurements in 1995 [3], also reveals that these parts of the country have high radiation levels as a consequence of high geochemical distribution of ^{238}U in the rocks of these formations.

Figure 3 shows the results from the sampling in 2007 and the ones from 2003. Both show a similar distribution. The results from central eastern region can be positively correlated for the same sources for both campaigns with a factor of 0.74. They show that concentrations are stable, on average, in a long-term perspective.

The test of radon dependency on main physical parameters, such as EC, temperature and pH, did not show any correlation for all sampled springs. The pH is around neutral (6–8) and, therefore, does not influence the radon accumulation. The temperature of the waters varied in between 8–16°C with average values in the range of 10–12°C. An anti-correlation of the radon and temperature in 65% of the cases is known from the literature, but this could not be observed in this case due to the small temperature fluctuations of the groundwater [2, 5]. The same situation was found for the EC. The small variation in EC could not be correlated to the radon activities. This fact is explained with a previous knowledge from continuous measurements in several sources as some sources have a strong correlation with conductivity and another just opposite strong anti-correlations.

Special attention was paid to a number of springs close to Luxembourg City, as half of the population of the country is concentrated in this area and uses this water. These springs did not show large variations in radon concentration over the year 2007 and, therefore, it can be concluded that seasonal influences in this area can be excluded.

Nevertheless, radon concentrations in the northern-central part show some differences in the 2003 and the 2007 campaigns. The latter campaign coincides with the recent construction of the northern highway in the time of this investigation. A hydro-geological and hydro-geochemical study of the Geological Survey of Luxembourg showed that the construction works influenced the flow regime and the hydro-geochemistry. A decreasing radon concentration could be observed in the same period. It is assumed that drilling and blasting works changed the flow path within the aquifer and, therefore, also changed the water chemistry. This was correlated with degreasing discharges in most of the monitored springs.

The spatial variations can be led back to the different geological materials and structural/tectonic features. Figure 6 shows that the radon activity changes with different geological units where the springs are located. Most aquifers in the region are double porosity aquifers, with proportion of matrix storage and fracture flow. Radon concentrations are influenced by the contact time between the water and the aquifer rock. Water from fast fracture flow is usually in contact with the rock matrix only for a short period of time and, therefore, cannot accumulate so much radon. On the other hand, radon with its short half-life reaches secular equilibrium after approximately 30 days. Hence, the groundwater flow should not influence its concentrations because groundwater flow is usually by magnitudes slower. Nevertheless, hydraulic conductivities of up to 100 m/d have been found along open fracture zones through tracer tests [7], which support the results of this study.

It was assumed spatial heterogeneity in the rocks with different correlation lengths. Long-scale effects were dominant for more of the groups both of sources.

Long-scale effects are much more important than small-scale effects, as shown by the differences in the variations of radon concentrations from Figs. 4 and 5. The seasonal variations of radon were masked by the globalization of monthly data. The processes that influence the long-term changes are not understood in detail so far, but besides the anthropogenic factors of construction works on northern highway, surely climatological factors play an important role. This still needs to be investigated. Nevertheless for northern part

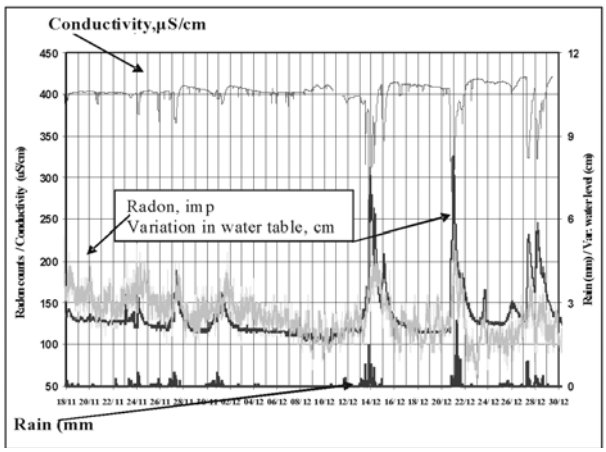

Fig. 4. Correlation between radon data from central-eastern region of Luxembourg sources.

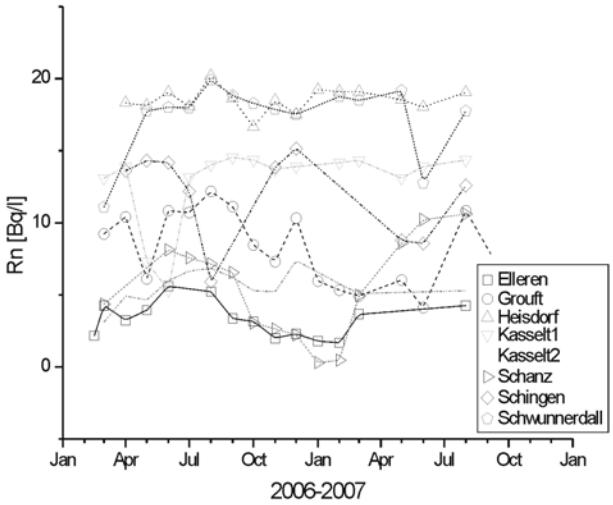

Fig. 5. Short-time variation of radon content in some water sources.

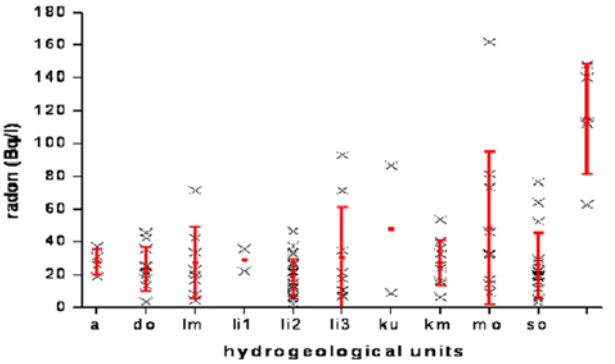

Fig. 6. Radon distribution vs. geological formations.

decrease of the radon activity concentration in winter period and increasing in July–August were observed as was supposed logically.

The relation between radon and radium is of particular interest. Radon is a tracer, which can be used in a variety of groundwater studies, such as hydrograph separation, or any other type of groundwater/surface water interaction [8, 15]. It is a daughter isotope of radium. Reasonable amounts of radium get into the hydrological cycle mainly through the dissolution of silicates and carbonates. It is not very mobile and can precipitate with other bivalent cations, such as Ba^{2+} or Ca^{2+}, as sulfates or carbonates. Nevertheless, considerable amounts of radium were measured in the 316 sampled springs.

It is interesting to notice that the air-gamma measurements have shown a strong anti-correlation of radon and radium over Luxembourg, especially in the central-eastern part of the country. The radium concentrations in water are negatively correlated with radon. High levels of radium are associated with low levels of radon and *vice versa*. Radon activity in groundwater is controlled by the concentration of radium in the aquifer matrix [9, 14]. However, the amount of radon that can enter the groundwater depends on the emanating coefficient of the radium bearing material in the aquifer. This means that the radon emanation potential of the rocks is in some cases very low, especially for low permeable rocks. Then again, low radium content rock can nevertheless emit higher concentrations of radon, when their porosity and interconnected pore space is large. Both interpretations do not explain the negatively correlated behavior in Luxembourg. The waters from the Devonian rocks, low porosity, show high concentrations in radon (Fig. 6), but low concentrations in radium, whereas the waters from the Lias and Buntsandstein, higher porosity, formations are low in radon (Fig. 6), but high in radium. Hence, a possible interpretation is that in the first case the radon derives directly from emanating form the rock. The Devonian shits and sandstones are rich in uranium and radium, whereas the radon comes form dissolved radium in the water in the second case. The relation between radium and oxygen content shows higher radium concentrations associated with lower oxygen content. The initially anoxic water, poor in oxygen, mobilizes only a little amount of radium. If this water is deposited on the surface layer, it will produce elevated concentrations of radon in the springs.

Conclusions

Tackling the spatial and temporal radon distribution is an ambitious problem. A lot of factors influence the concentrations in space and time and it is hard to predict which physical, such as temperature, discharge, or flow paths, and chemical, such as pH, redox potential, or mineral content, have the strongest influences. Radon has been measured in a vast number of springs over a longer period and evolutions could be observed. In some areas, like the central-northern part, concentrations have chanced to anthropogenic activities, in others, such as the central-east, concentrations were stable in short-term perspectives but changed on a larger time scale. Nevertheless, spatial differences in radon concentration could be explained by the different aquifer host rocks and their mineralogy. However, it is not as simple as such, because porosity and, therefore, emanation potential are an important factor as well.

The measurements showed detectable concentrations. We did not measure exceeding values of radon in the drinking water that may cause problems from radiological point of view.

The correlations between radon and the different components were qualitative and quantitative estimated with geology and some radiological and physical parameters. The two main axes of radon concentration over the country in north-middle part and middle-east part were explained with the specific geology, radium behavior and partially with physical parameters.

Seasonal variations in northern axis are reasonable and follow water table charge.

It was not observed surface distribution influence of water radon on the indoor radon concentration over the country.

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