

# METHODOLOGICAL APPROACHES TO RADON IN WATER MEASUREMENTS: COMPARATIVE EXPERIENCES BETWEEN ROMANIA AND SPAIN

S. CELAYA<sup>1,2\*</sup>, I. ENCIAN<sup>3</sup>, I. FUENTE<sup>1</sup>, D. RABAGO<sup>1</sup>, M. MOLDOVAN<sup>4</sup>, T. DICU<sup>4</sup>,  
A. CUCOŞ<sup>4</sup>, A. FERNÁNDEZ<sup>1</sup>, L. QUINDOS<sup>1,2</sup>, C. SAINZ<sup>1,2,4</sup>

<sup>1</sup> Radon Group (LaRUC), University of Cantabria, Avda Cardenal Herrera Oria s/n,  
39001, Santander, Spain

\*E-mail: santiago.celaya@unican.es

<sup>2</sup> The Cantabrian International Institute for Prehistoric Research (IIIPC), University of Cantabria,  
Avda de Los Castros nº52, 39005, Santander, Spain

<sup>3</sup> CNCAN, National Commission for Nuclear Activities Control, Bucureşti, Romania

<sup>4</sup> Babeş-Bolyai University, Faculty of Environmental Science and Engineering,  
“Constantin Cosma” Radon Laboratory (LiRaCC), Cluj-Napoca, Romania

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*Abstract.* The EC Directive 2013/51/EURATOM of 22 October 2013 represents the first time that a radon limit for drinking water has been proposed. Transposition of this Directive into Spanish legislation was by means of the recent RD 314/2016 which sets a limit value of 500 Bq l<sup>-1</sup> for radon (<sup>222</sup>Rn) in water for human consumption while that in Romanian legislation the Law 301/2015 provides a limit value of 100 Bq l<sup>-1</sup> for <sup>222</sup>Rn concentration in water for human consumption as well as a total effective dose of 0.1 mSv y<sup>-1</sup> from all radionuclides present in water (same dose value established by Spanish law).

For several years, both in Romania and in Spain, there have been campaigns to measure the concentration of <sup>222</sup>Rn in waters of different origins in order to determine the possible exposure of the population through this irradiation path, and also to use the presence of radon dissolved in water as a source of indoor radon in thermal spa facilities, and also as a tracer of dynamic processes (C. Sainz et al., Sci. Tot. Envir. 543, 460 (2016); 1).

In this article, an assessment of the results from measurement campaigns in both countries will be presented and compared. In addition, the different measurement techniques used will be described, and the description of an intercomparison exercise on radon measurement in water organized by the Environmental Radioactivity Laboratory of the University of Cantabria (LaRUC) will be presented, in order to evaluate the quality of the performance of the techniques used.

*Key words:* radon in water, intercomparison exercise, gamma spectrometry, liquid scintillation counting.

## 1. INTRODUCTION

The <sup>222</sup>Rn, like radon isotope [2], presents its same chemical characteristics, which make it an inert, odorless, colorless and tasteless gas. Despite this pleasant description, the World Health Organization attributes to radon between 3 and 14% of cases of lung cancer, being the second cause after tobacco [3]. Its danger lies in

its two short-lived progeny,  $^{218}\text{Po}$  and  $^{214}\text{Po}$  with alpha emission energies (6002.55 keV, 7686.90 keV) and half-life periods (3.11 min; 163.39  $\mu\text{s}$ ) [4]. They are two solid alpha emitters that can be linked to the particles of 0.1 microns suspended in the air accessing the respiratory tract by inhalation [5].

The presence of  $^{222}\text{Rn}$  dissolved in water is mainly due to two possible mechanisms, either by the presence of  $^{226}\text{Ra}$  in the water itself or by the recoil of  $^{222}\text{Rn}$  from the disintegration of  $^{226}\text{Ra}$  when it is at the boundary of the solid-liquid interface. Their concentrations can be very variable depending on the origin of the water, finding values normally lower than  $2\text{ Bq l}^{-1}$  when it comes to surface water (the aeration generated by the movement of the water causes its desorption and consequently such low concentrations) compared to quite high concentrations in groundwater that even reach values of  $50\text{ KBq l}^{-1}$  when water moves through cracks with high contents in  $^{226}\text{Ra}$  [6].

The appearance of the EC Directive 2013/51/EURATOM of 22 October 2013 [7] and its subsequent transposition into the legislation of the different countries has led to the setting of different limit values for the concentration of  $^{222}\text{Rn}$  in water for human consumption. In this study, two  $^{222}\text{Rn}$  in water measurement campaigns are carried out, ones of them by the Radioactivity Laboratory of the University of Cantabria (LaRUC) under its national regulations [8] and another by the “Constantin Cosma” Radon Laboratory (LiRaCC) of Babeş-Bolyai University under its national legislation [9].

The techniques used by LaRUC for the measurement of  $^{222}\text{Rn}$  in water in this study were Gamma Spectrometry and *Liquid Scintillation Counting* (LSC) while LiRaCC used LUK-VR system that is based on radon gas measurement with Lucas cell. In order to guarantee the quality of the results, both laboratories participated in the third edition of the  $^{222}\text{Rn}$  in water intercomparison exercise carried out by the University of Cantabria together with the company Iproma S.L, in which 24 European laboratories participated [10].

The aim of the study is to present the results obtained by both laboratories (LaRUC and LiRaCC) in their respective  $^{222}\text{Rn}$  measurement campaigns in public water network and groundwater, comparing both the results under their respective national regulations and the different measurement techniques used.

## 2. MATERIAL AND METHODS

### 2.1. SAMPLE COLLECTION

#### **LaRUC**

The 123 samples analyzed were taken in two different campaigns. The first was based on the collection of water samples in 92 springs distributed throughout the Spanish territory, as can be seen in Fig. 1, while in the second, 31 samples were taken from the public water network in the Region of the Saja-Pas-Besaya (Cantabria, Spain).

These 31 samples were taken from public sources in an environment of 40 km around the Zinc mine located in the village of Reocín, in operation between 1856 and 2003, whose reopening is currently being valued.

For the collection of samples 1 l glass bottles were used, which were filled totality to avoid air spaces that could favor the desorption of the  $^{222}\text{Rn}$ . Once in the laboratory, the samples were transferred to the corresponding containers according to the measurement technique used. In the case of gamma spectrometry, the container used was a 270 ml PVC bottle with double lid to avoid water leaks (LDPE inner lid and PP external lid), while for LSC were used 20 ml glass vials. In each vial, 6 ml of sample were added below the 14 ml of the scintillation liquid previously introduced.

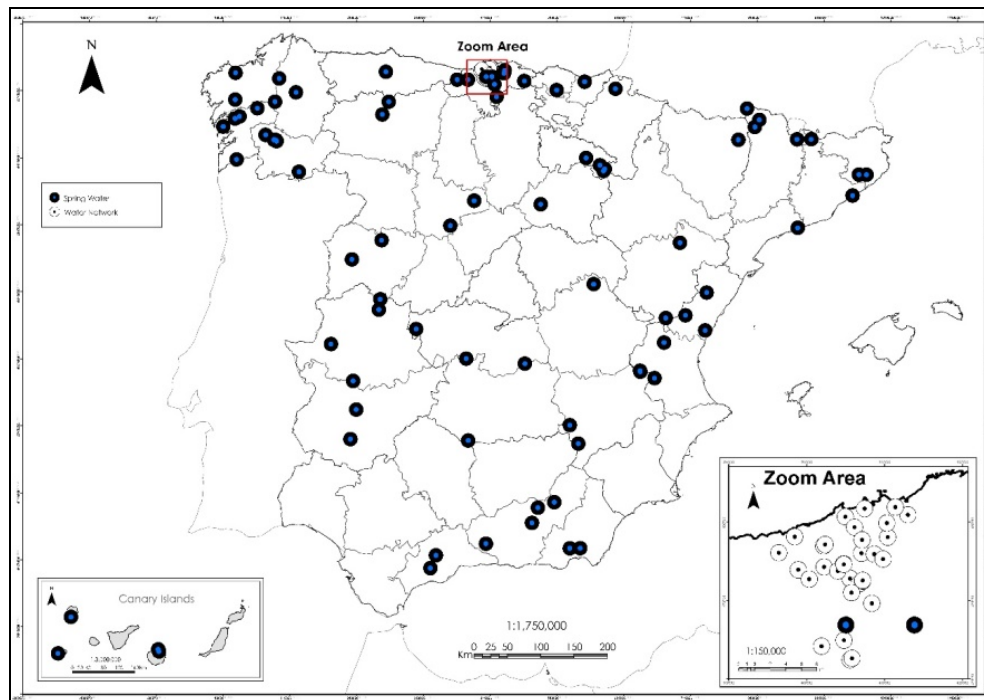


Fig. 1 – Localization of samples taken in Spain.

### LiRaCC

The water samples were collected in different campaigns, so they have different origins, but very similar to the samples collected by LaRUC, such as springs, wells and public network. The location of these 200 samples can be seen in Fig. 2.

For its collection and transport, polyethylene bottles were used that were completely filled (without bubbles) and hermetically sealed in order to avoid possible leaks of  $^{222}\text{Rn}$ . The 200 samples were measured in the laboratory in a maximum time of 24 hours after collection.

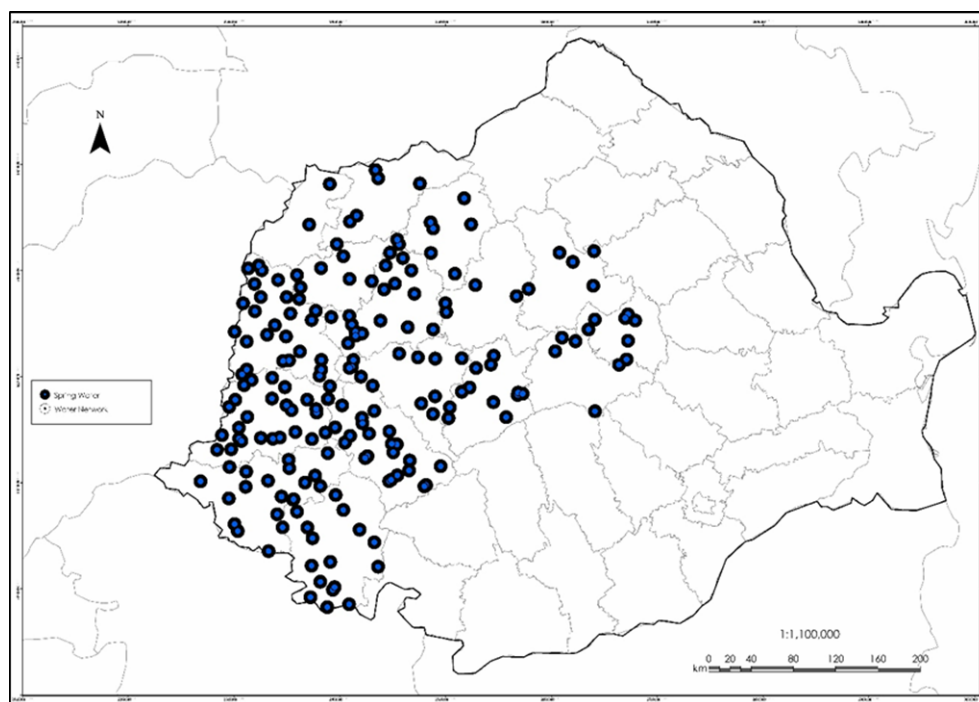


Fig. 2 – Localization of samples taken in Romania.

## 2.2. MEASUREMENT TECHNIQUES

### 2.2.1. LaRUC

The measurement techniques used were Gamma Spectrometry and *Liquid Scintillation Counting* (LSC).

#### **Gamma Spectrometry**

Gamma spectrometry equipment used has been an HPGe coaxial detector (model GL-2015-7500, Canberra, USA). This equipment allows the detection of gamma emissions between 30 and 3000 keV regardless of the type of sample (soil, mud, ash, environmental filters, water, etc.).

The concentration of  $^{222}\text{Rn}$  in water was determined from the peak corresponding to  $^{214}\text{Pb}$  (emission energy: 351.932 keV) as can be seen in Fig. 3 after 3 h from the preparation of the sample in the measuring container. This elapse time (3 h) is the time necessary to achieve secular equilibrium between  $^{222}\text{Rn}$  and its progeny ( $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$  and  $^{214}\text{Po}$ ).

The determination of the concentration of  $^{222}\text{Rn}$  in water is made from the Eq. 1:

$$C(\text{gamma}) = \frac{N - f \cdot t}{m \cdot t \cdot PE \cdot Ef} \quad (1)$$

Where:

$C(\text{gamma})$  is the concentration of  $^{222}\text{Rn}$  in water in  $\text{Bq l}^{-1}$  determined by gamma spectrometry.

$N$  is the total counts in the peak ( $^{214}\text{Pb}$ ).

$f$  is the background in counts per second in a sample of distilled water (cps).

$t$  is the measuring time (s).

$m$  is the weight of the sample (kg).

$PE$  is the emission intensity (%).

$Ef$  is the efficiency of the equipment (cps/Bq).

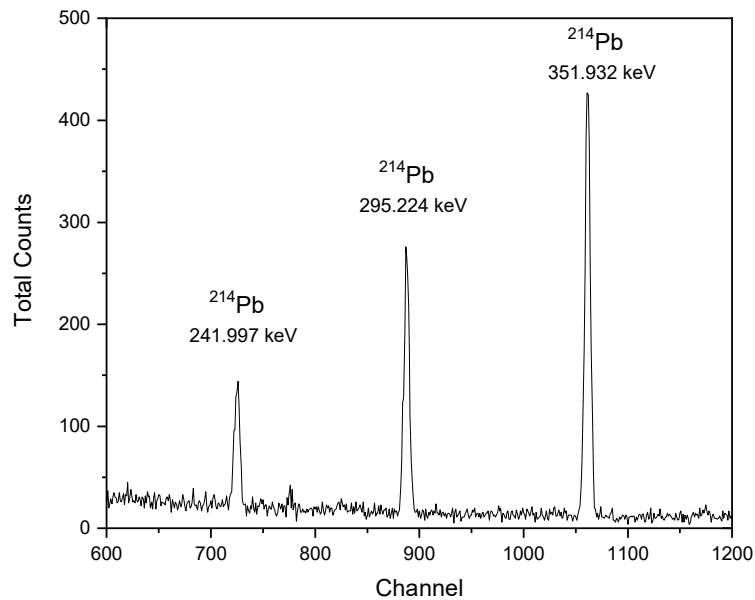


Fig. 3 – Gamma spectrum of a water sample with  $^{222}\text{Rn}$ .

### **Liquid Scintillation Counting (LSC)**

The equipment used was a Triathler (model 425–034, Hidex, Finland). It is an equipment that allows to discriminate between alpha and beta particles by the difference in the duration of the pulse generated when coming into contact the particles emitted with the liquid of scintillation. This discrimination is carried out through the setting of the *Pulse Length Index* (PLI) parameter during the calibration of the equipment [11].

The scintillation liquid used has been Aqualight (Hidex), an organic liquid used in the one-phase method, so called because the result of the process of mixing

the sample with the liquid scintillation is a one-phase solution. The advantage of this method compared to the two-phase method is that all counts issued by all the alphas emitters in the water appear in the spectrum, which makes it possible to determine the presence of  $^{226}\text{Ra}$ . In the case of using scintillation liquids that generate two phases, this is not possible, since in the spectrum only appear the counts due to the presence of  $^{222}\text{Rn}$  and alpha emitting descendants ( $^{218}\text{Po}$  and  $^{214}\text{Po}$ ). The  $^{226}\text{Ra}$  or any other alpha emitter dissolved in the other phase will not generate pulses.

The concentration of  $^{222}\text{Rn}$  in the water samples was determined from the counts located in the spectrum (Fig. 4) after 3 h from the preparation of the sample in the measuring container.

In this technique the concentration of  $^{222}\text{Rn}$  in water is determined from:

$$C(LSC) = \frac{G - B}{V \cdot 60 \cdot Ef} \quad (2)$$

Where:

$C(LSC)$  is the concentration of  $^{222}\text{Rn}$  in water in  $\text{Bq l}^{-1}$  determinate by LSC.

$G$  are the counts per minute (cpm) of the sample.

$B$  is the background in counts per minute (cpm) in a sample of distilled water.

$V$  is the volume of the sample (l).

$Ef$  is the efficiency of the equipment (cps/Bq).

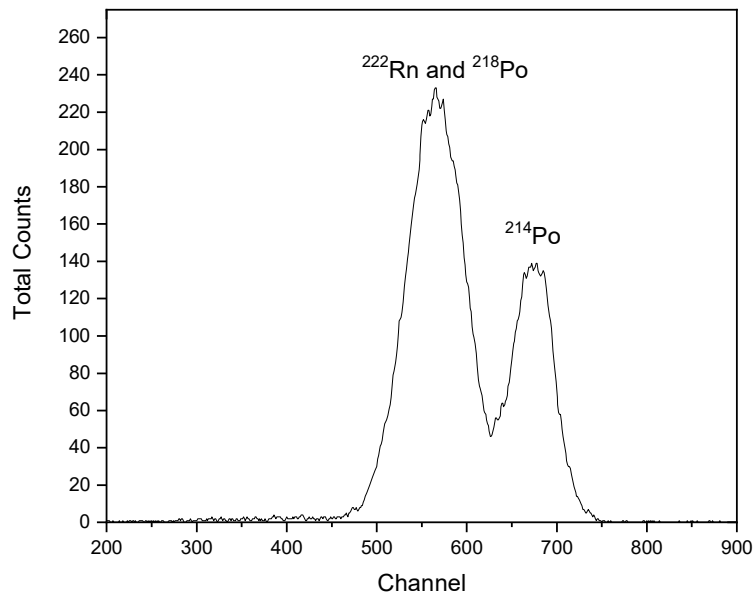


Fig. 4 – LSC spectrum of a water sample with  $^{222}\text{Rn}$  (one phase method).

## 2.2.1. LiRaCC

The measurement of radon concentration in water used by this lab is based on the method of extracting radon from water and measuring it by scintillation with Lucas cells like you can see in Fig. 5 (LUK-VR system).

The Lucas cell has on its inner surface a thin layer of zinc sulphide (ZnS), which transforms the kinetic energy of the alpha particles to the impact with it in bright radiation. These radiation pass through a window at the top of the Lucas cell in a photomultiplier tube, closely linked to it. The signal generated by the photomultiplier is then measured using a single-channel analyzer [12].

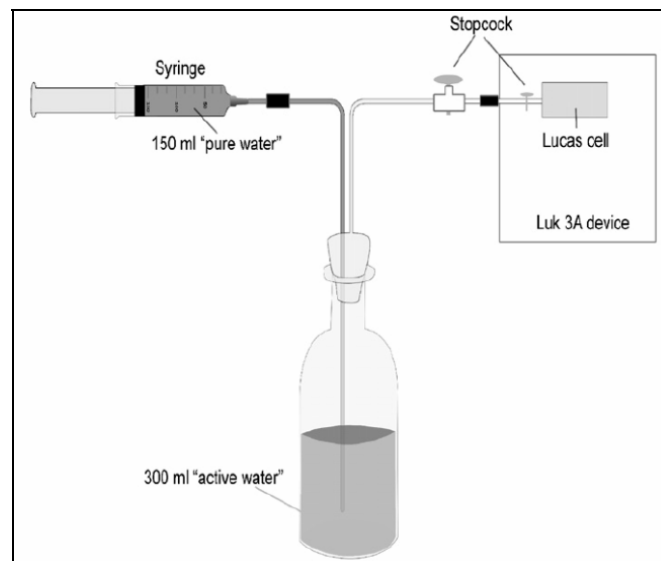


Fig. 5 – Method of measuring radon in water using Lucas cells (LUK-VR system) [12].

Determining the concentration of  $^{222}\text{Rn}$  in water using this method is done by the relationship:

$$C_{Rn} = C_{LUC} \cdot \left( k + \frac{V_A}{V_W} \right) \quad (3)$$

$$C_{LUC} = \frac{N_S - N_B}{s \cdot t \cdot e^{-\lambda} Rn^t} \quad (4)$$

Where:

$C_{Rn}$  radon concentration in water ( $\text{Bq l}^{-1}$ ).

$C_{LUC}$  is the concentration of radon in the Lucas cell.

$k$  is the solubility coefficient of radon in water (coefficient Ostwald).  
 $V_A$  is the air volume in the measurement system (connection, tubes and Lucas cell).  
 $V_W$  is the volume of water sample (0.5 l).  
 $N_S$  is the number of pulses in sample measurement.  
 $N_B$  is the number of impulses in the measurement of the background.  
 $\varepsilon$  is the Lucas cell efficiency.  
 $t$  is the measuring time (100 s).  
 $\lambda_{Rn}$  is the radon disintegration constant.

### 2.3. INTERNATIONAL INTERCOMPARISON OF RADON IN WATER

In order to guarantee the quality of the measurements made in this study, both laboratories participated with their respective measurement techniques in the International Intercomparison of  $^{222}\text{Rn}$  in water organized by LaRUC in April 2019. In this third edition, a total of 24 laboratories participated (21 Spanish laboratories, 1 Portuguese laboratory, 1 Italian laboratory and 1 Romanian laboratory).

The organization sent each participant two glass bottles (sample A and sample B). Sample A was a continental water collected in a thermal spa located in the village of Las Caldas de Besaya (Cantabria, Spain), while sample B was prepared in the laboratory from a certified source of  $^{226}\text{Ra}$ .

The aim of the intercomparison was to measure  $^{222}\text{Rn}$  in sample A with respect to a reference date (01/04/2019 12:00 h) while with sample B they had to wait a month to measure the  $^{222}\text{Rn}$  in secular equilibrium with  $^{226}\text{Ra}$ .

## 3. RESULTS AND DISCUSSION

### *Results of the LaRUC*

In Table 1, you can see the results obtained by LaRUC in the two water campaigns carried out. In the first part of Table 1, the results of samples taken from public water network located in the region Saja-Pas-Besaya are presented. In the second part are the results obtained in waters taken in springs throughout the Spanish territory.

Table 1

Results of LaRUC

		Region Saja-Pas-Besaya						
$^{222}\text{Rn}$ (Bq l <sup>-1</sup> )	< MDA	5–10	10–35	35–40	40–45	45–50	50–55	≥ 60
n° Samples	25	3	0	1	0	1	1	0
		Spring waters of Spain						
$^{222}\text{Rn}$ (Bq l <sup>-1</sup> )	MDA-50	50–100	100–150	150–200	200–250	250–500	500–1000	≥1000
n° Samples	59	15	7	3	1	3	2	2

MDA: Minimum Detectable Activity. MDA is 2 Bq l<sup>-1</sup>.



Most of the waters taken in public sources in this study have low concentrations of  $^{222}\text{Rn}$ , between Minimum Detectable Activity (MDA  $< 2 \text{ Bq l}^{-1}$ ) and  $10 \text{ Bq l}^{-1}$ , values that are expected due to the physical and chemical treatments done to guarantee their potability and that favor its desorption. In the same way, it is remarkable the existence of three samples with values between 35 and  $55 \text{ Bq l}^{-1}$ . These values suggest that samples are underground waters with a high quality for consumption and that they are subjected to simple treatments of potabilization with low desorption.

As you can see in Fig. 6, most of the sampling points close to the Zinc mine taken from public water network are mostly located on Lower Cretaceous areas constituted by Marl, Clay Marl, Limestone, Sandstone, Turbidite, Sand and Conglomerates, and on Pleistocene areas constituted by Conglomerates, Gravel, Sand, Clays and River terraces. Samples with higher values appear in the lithostratigraphies associated with Marl, Clay, Turbidite, Calcareous Marl and Marly Limestone.

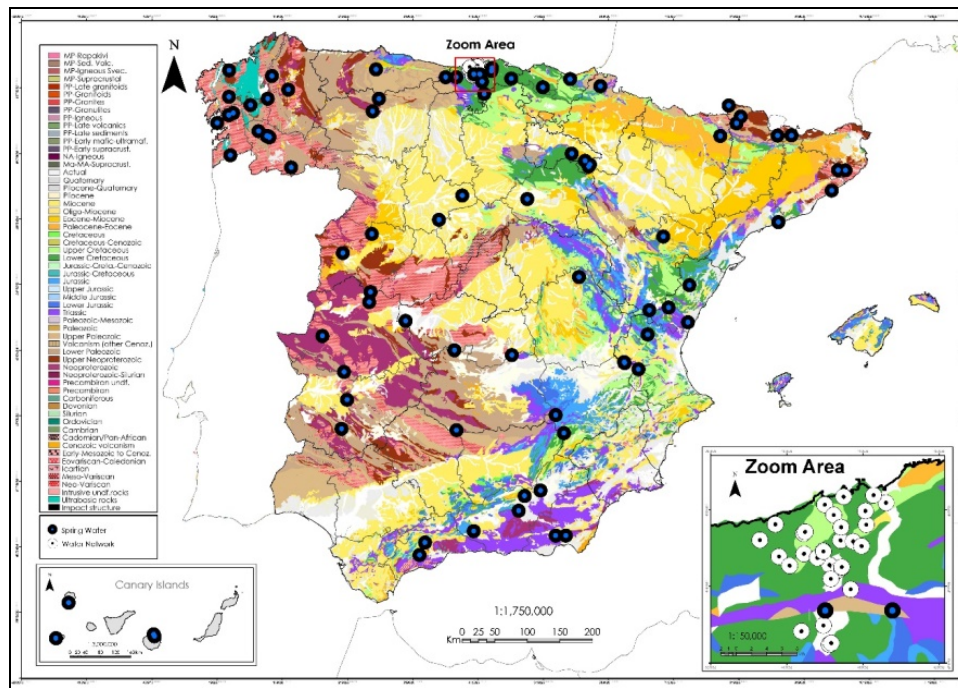


Fig. 6 – Geological Information on the localization of samples taken in Spain [13].

The values obtained in the measurements of the spring waters range mostly between values lower than MDA and  $100 \text{ Bq l}^{-1}$ , although there are 18 samples that exceed  $100 \text{ Bq l}^{-1}$ , among which 4 exceed the  $500 \text{ Bq l}^{-1}$  established by the RD 314/2016. In this case, seeing Fig. 6 it is verified that the spring water samples were taken on different geologies. It is significant because high values were found in lithostratigraphies with hypothetical low levels of  $^{226}\text{Ra}$ , but in some cases are

close to geological structures such as the active fault of the Escudo de Cabuérniga in Cantabria. These type of geological structures favor movements of  $^{222}\text{Rn}$  from deep zones rich in uranium to waters of upper levels.

**Results of LiRaCC**

Table 2 shows the results obtained for the 200 samples measured by LiRaCC. Although most of these samples were taken in wells, the values of  $^{222}\text{Rn}$  in water obtained are low, with 90% of the samples lower than  $20 \text{ Bq l}^{-1}$  and only 3 values above  $100 \text{ Bq l}^{-1}$  (value fixed by Law 301/2015).

Table 2  
Results of LiRaCC

$^{222}\text{Rn}$ ( $\text{Bq l}^{-1}$ )	Samples of Romania							
	MDA-20	20-40	40-60	60-80	80-100	100-120	120-220	$\geq 200$
n° Samples	180	14	1	2	0	2	0	1

MDA: Minimum Detectable Activity. MDA is  $0.5 \text{ Bq l}^{-1}$ .

In Fig. 7, geological information shows that sampling areas are mainly Miocene, Cretaceous and Precambrian while the lithostratigraphic information for the 3 points with the highest concentration of  $^{222}\text{Rn}$  in water are constituted by granitoid, leucogranite and metamorphic zones. The rest of sampling points are mainly located in zones of undifferentiated sediment, loess, soil, conglomerate, alluvium and eluvium, which are materials with low / no presence of  $^{226}\text{Ra}$ .

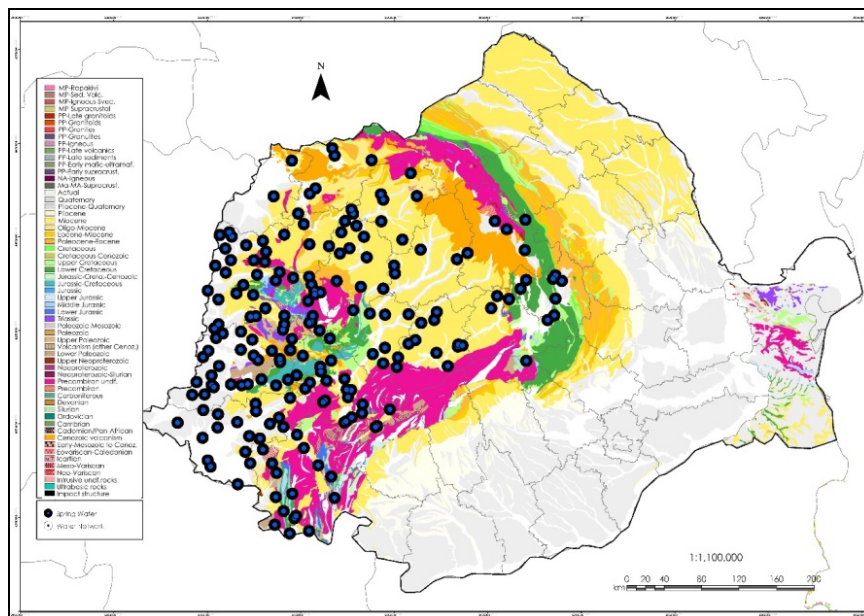


Fig. 7 – Geological Information on the localization of samples taken in Romania [13].

### Intercomparison Results

In Fig. 8 and Fig. 9, are shown the results obtained by LaRUC, identified as laboratory R5 (LSC technique) and R5.1 (gamma spectrometry technique), and by LiRaCC, with code R3 (technique of Lucas cells). These results are highly satisfactory because they are graphically within the ranges marked as acceptable for the two intercomparison samples (sample A and sample B). These good graphical results are also numerical results according to Z-SCORE values obtained by both laboratories, which are between 0 and 0.4.

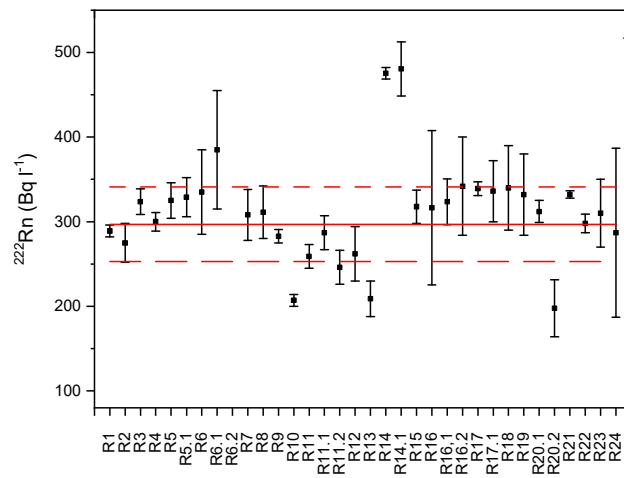


Fig. 8 – Results measured by each Laboratory for sample A, showing the consensus value (red line) and the target standard deviation  $\pm 20\%$  (red discontinue line) (Color online).

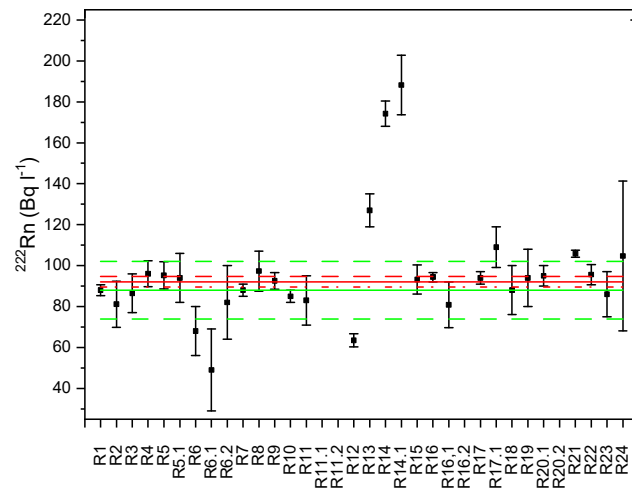


Fig. 9 – Results measured by each Laboratory for sample B, showing the consensus value (green line) and the target standard deviation  $\pm 20\%$  (green discontinue line), the reference value (red line) and its uncertainty (red discontinue line) (Color online).

#### 4. CONCLUSION

The results obtained by LaRUC and by LiRaCC in the intercomparison of  $^{222}\text{Rn}$  in water, where 24 specialized laboratories participated, guarantee the quality of the results presented in this study.

In the results of the water campaign carried out by LaRUC in springs, it is observed as expected, that the majority groundwaters presented concentrations of  $^{222}\text{Rn}$  higher than those measured in the water campaign of public network. These last are normally superficial waters that are treated physically and chemically to purify them causing the desorption of the  $^{222}\text{Rn}$  dissolved in the water.

Only 4 waters of 123 samples analyzed by LaRUC between the two campaigns exceeded the limit value of  $500 \text{ Bq l}^{-1}$  established by Spanish law for human consumption [8].

Although the samples were taken mainly in wells, only 3 samples of the 200 studied by LiRaCC exceed  $100 \text{ Bq l}^{-1}$  established Romanian law 301/2015, but far from  $500 \text{ Bq l}^{-1}$  fixed by Spanish regulations as parametric value.

Seeing the results of the campaigns carried out in Spain and Romania, by LaRUC and by LiRaCC, it can be indicated that the Spanish groundwaters present contents in higher  $^{222}\text{Rn}$ , mainly because of the presence of granitic zones or because of geological structures such as Fallas.

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