A SIMPLE NATIONAL INTERCOMPARISON OF RADON IN WATER

Santiago Celaya González[(1)]*, Daniel Rábago Gómez(1), Ismael Fuente Merino[(1)], Luis Quindós López[(1)], Núria Bon Carreras[(2)], María Trinidad Valero Castell[(2)], José Luis Gutierrez Villanueva[(1)], Carlos Sainz Fernández[(1)].

[(1)] LARUC. University of Cantabria. C/Cardenal Herrera Oria s/n. 39011, Santander, Spain

[(2)] IPROMA S.L. Department of Quality, Environment and Prevention. Road de la Raya nº46. 12006, Castellón, Spain

*Corresponding author: celayas@unican.es, phone: +34942202207

Abstract

Radon-222, a naturally occurring radioactive gas, responsible together with its progeny of around 50% of the average effective dose received by the population, has not been regulated by law until the recent Directive 2013/51 /Euratom. Its transposition into Spanish legislation was made in the recent RD 314/2016, which sets at limit value of 500 $Bq·l^{-1}$ for radon-222 in water for human consumption. Intercomparison exercises, such as those carried out by IPROMA SL and the Laboratory of Environmental Radioactivity of the Cantabria University (LARUC) in November 2015 and December 2016, represent the most useful tool available for detecting problems and taking corrective actions necessary for an efficient measurement by part of the laboratories. The participants in these exercises used three techniques: liquid ccintillation counting, gamma spectrometry and desorption followed by ionisation chamber detection.

Keywords: radon, water, intercomparison, liquid scintillation counting, gamma spectrometry, ionisation chamber.

INTRODUCTION

Radon gas has essentially three isotopes: ^{222}Rn ($T_{1/2}$=3.82 d), ^{220}Rn ($T_{1/2}$=55.6 s) and ^{219}Rn ($T_{1/2}$ = 3.96 s) (Chu et al., 1999). ^{222}Rn (hereinafter referred as radon in this manuscript) is a natural radioisotope belonging to the series of ^{238}U (an alpha particle emitter, 5590.3 keV, with a half-life of 3.82 days). Its two short-lived alpha emitting progeny are ^{218}Po (6002.55 keV, 3.11 min) and ^{214}Po (7686.90 keV, 163.69 μs) (2). Exposure to radon and its progeny has an estimated average effective dose of around 50% (1.3 mSv) of the total effective dose received by the general population (3), based on results of the numerous studies conducted in dwellings (4-6). However, little attention has been paid to the radon that is ingested in drinking water, and to the additional risk that arises due to the low transferability of radon from water to air, with an estimated transfer coefficient for dwellings of 10^{-4} (7).

Although the dose received by ingestion of water with radon is significantly less than by inhalation of its progeny (8), the measurement of radon concentration in water has additional interest in other respects. The radon coming from water contributes very little to the concentration of radon inside dwellings, but it can be significant in certain workplaces such as some thermal spas. In addition, radon gas dissolved in water has proved to be a useful tracer of hydrodynamic processes in aquifers and underground currents (9). Being a noble gas, it is not assimilated by any chemical compounds in the environment, but due to its moderate solubility, (0.225 $cm^3 \cdot g^{-1}$ at 20 °C), it can be detected in water, especially groundwater (2). Its concentration in groundwater will depend mainly on the radium content of the substrate, the specific surface area of the aquifer, the permeability of the soil and the characteristics of the water itself. When these groundwaters discharge at the surface, the concentration of dissolved radon decreases abruptly due to water movement and purification processes. However, where these waters are consumed directly at the point of upwelling, the risk of ingesting radon and its progeny may be significant.

There was no limit for radon in the recently repealed RD 140/2003 [10], which concerned drinking water quality. Thus, the range 100-1000 $Bq \cdot l^{-1}$ in the EC Directive 2013/51/Euratom of 22 October 2013 represents the first time that a radon limit for drinking water has been set [11]. Transposition of this Directive into Spanish legislation was by means of the recent RD 314/2016 [12] which sets a limit value of 500 $Bq \cdot l^{-1}$ for radon in water for human consumption.

The intercomparison exercise reported in this paper, organized by the Radon Group of Cantabria University in collaboration with IPROMA S.L., arose from the need for a quality control for all the national laboratories that measure radon in water. Eleven laboratories participated in November 2015, and 17 in December 2016 (Table 1):

MATERIALS AND METHODS.

Sample collection

The chosen sampling location was the spa of Las Caldas de Besaya, which has been studied by the Radon Group Cantabria University since the 1980s [9,13]. The geographical location of the site can be seen in Figure 1.

The spa is located on the banks of the river Besaya in the town of Corrales de Buelna, ~30 km from Santander. These hot springs are characterised by temperatures of 34-37 °C, and are rich in sodium chloride, bicarbonates and nitrates [9]. A single homogenous water sample was collected from the spa on 23 November, 2016 in a 25-litre container, and taken to the LARUC laboratory where, on the same day, aliquots were transferred to 1-litre low density plastic bottles for shipment to the participating laboratories. These bottle have double stoppers, in order to minimise leaks and the formation of bubbles, which could introduce uncertainty into the participants' measurements. A “protocol” was drawn up by the organisers of the exercise, and sent to each participant. This protocol explained everything necessary for the proper development of the exercise, including implementation a data protection policy that assigned a code to each laboratory to maintain anonymity of results.

Participants received the samples 24-36 hours after sampling, except for the University of Palmas, where customs clearance took six days, though no incident occurred during shipment that would have delayed the exercise.

Measurement techniques

The measurement techniques used by the participating laboratories in the intercomparison exercise can be seen in Table 2, which also shows the number of participants using each. Three participants sent results using two different techniques, which is why there were twenty results from only 17 laboratories.

Desorption technique ^{222}Rn in water with ionisation chamber

The equipment used is an AlphaGuard PQ2000-PRO which uses a specific attachment for measuring ^{222}Rn in water. By means of a pump, the water is bubbled continuously, which causes desorption of radon from the water and directs it to the detector via a desiccator column. Once inside the detector, the radon enters an ionisation chamber (where a potential of 750V is maintained) flowing over a large-surface fiberglass filter that prevents entry of radon progeny and aerosols. Alpha particles emitted by the radon ionise the air, the cathode attracts the positively charged particles, while the anode attracts the negatively charged ones [(14)].

To calculate the concentration of ^{222}Rn in water, the following equation is used:

$$C_{water} = \frac{C_{air} \cdot \left(\frac{V_{system} - V_{sample}}{V_{sample}} + k \right) - C_0}{1000} \quad (1)$$

where C_{water} is the concentration of ^{222}Rn in the water sample ($Bq \cdot l^{-1}$), C_{air} is the concentration of ^{222}Rn in air ($Bq \cdot m^{-3}$) on the AlphaGuard screen, C_0 is the background ($Bq \cdot m^{-3}$) that can be considered 0, V_{system} is the inside volume of the equipment (1117.58 ml), V_{sample} is the volume of the sample (100 ml) and "k" is a factor for the transfer of radon from water to the air, which is a function of temperature [15] .

Gamma spectrometry

This technique is for detecting gamma emissions from soil, sludge, ash, environmental filters and, ultimately, from any sample whose gamma emission falls between 30 and 3000 keV. The equipment used is a HPGe detector. The photons resulting from gamma emissions from the sample enter the active volume of the detector and interact with its atoms. These interactions are converted to electrical pulses that are proportional to the energy of the photons emitted, and which are stored in finite energy increments equivalent over the range of the spectrum [16].

^{222}Rn activity is determined three hours after preparing the bottle with the water sample with the count made in the area of the spectrum for ^{214}Pb (351.93 keV). This elapsed time that is necessary to achieve secular equilibrium between radon and its short-lived progeny (^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po).

To calculate the activity due to ^{222}Rn in the water, the following equation is used for peak ^{214}Pb:

$$A = \frac{(N-f\cdot t)}{v\cdot t\cdot PE\cdot E_f} \quad (2)$$

where:

- A is the radon concentration ($Bq\cdot l^{-1}$).
- N are the counts.
- f is the background in counts per second (cps).
- t is the count time (sec).
- v is the volume of the sample (litres).
- PE is the emission intensity (%).
- E_f is the efficiency (cps/Bq).

Liquid scintillation counting with alpha/beta separation

The water sample containing ^{222}Rn is mixed with a liquid scintillation solution in a transparent vial. The alpha/beta emissions of ^{222}Rn and its progeny transfer energy to the scintillator, which releases this energy as photons (measured as light pulses). A distinction between alpha and beta emissions is possible since alpha particles lead to slightly longer light pulses than beta particles.

The electrical pulses derived from the photon release is proportional to the radioactive energy emitted. The continuous emission of alpha/beta particles from the radioactive material causes a continuous generation of pulses, so that the counts accumulates progressively [(17)].

Equation 3 is used to calculate activity from the ^{222}Rn in water (alpha particles) after three hours elapsed time explained above.

$$A = \frac{G-B}{Ef\cdot 60\cdot V} \quad (3)$$

where A is the activity in Bq·l^{-1}; G are the counts per minute (cpm); B is the background in cpm what the equipment counts for a sample prepared with distilled water; Ef is the equipment's efficiency for ^{222}Rn, ^{218}Po and ^{214}Po; V is the sample volume in litres; the inclusion of 60 in the denominator is to transform counts per minutes to counts per second.

RESULTS AND DISCUSSION

Measurements were returned to the organiser by 14 December. By 22 December, each participant received the report of the exercise showing the results and techniques used by each one (Table 2).

Statistical treatment of the measurements by the participants began by discarding data outside of the range median ± 50% as being incorrect data. By this means, the result from laboratory R04 was eliminated. The most relevant statistics were then calculated, as seen in Table 3.

A quantile-quantile plot (q-q plot) was applied to test whether results fit a normal distribution, whereby any deviation from linearity as in Figure 2 implies a non-normal distribution.

To establish the consensus statistic for the exercise, an iterative algorithm was applied, according to ISO 13528: 2015, whereby extreme values are given less weight than in a classical treatment of statistical data. This algorithm considers the measurements, of all participants and repositions the extreme values within the interval of acceptable deviation, thus obtaining robust estimators of the consensus value X and the standard deviation $\sigma_{exercise}$. As for the objective sigma, σ_p, was established as 20%, while for uncertainty μ_x, the following equation is applied:

$$\mu_x = 1.25 \cdot \frac{\sigma_{exercise}}{\sqrt{N}} \quad (4)$$

where:

- $\sigma_{exercise}$ is the standard deviation.
- N is the number of results sent by laboratories

The statistics of the exercise are presented in Table 4:

For the determination of the Z_{score} of each participant, the following equation is applied:

$$Z_{score} = \frac{x - X}{\sigma_p} \quad (5)$$

where:

- x is the measurement provided by each participant.
- X is the consensus value calculated according to ISO 13528:2015.
- σ_p is the target standard deviation, set at 20%.

The Z score values are interpreted as follows:

$|Z_{score}| \leq 2$ indicates satisfactory performance.

$2 < |Z_{score}| \leq 3$ indicates dubious performance and generates an alert.

$|Z_{score}| > 3$ indicates unsatisfactory performance and generates a signal for action.

A graphical presentation of the Z scores obtained by each laboratory is given in Figure 3, where the Z scores are ranked low to high.

Figure 4 shows the concentrations reported by each laboratory with their respective uncertainties. The red horizontal lines represent the consensus value (112.1 $Bq \cdot l^{-1}$) and the target standard deviation of ± 20 % (134.5 and 89.7 $Bq \cdot l^{-1}$).

As a result of the six-day delay in the delivery of the sample to one of the participants, the organisers decided to do a radon-leak test of the containers used to send samples to the participants. The bottles used in both exercises were made of low density polyethylene (LDPE). The importance of the bottle-material is not significant, other than to know its permeability to radon for future exercises with a reference value (in these exercises were used consensus value).

In order to quantify the leakage λ_{leaks} of the material, a sample of water containing ^{222}Rn was divided and stored in two bottles made of different materials, one LDPE plastic and another glass. Samples were taken every 3-4 days and analysed in a liquid scintillation α spectrometer (Triathler 425-034); the results were plotted to observe the decay in the sample over several days. Each graph was fitted to a function of the type:

$$A = A_o \cdot e^{-(\lambda radon + \lambda leaks) \cdot t} \qquad (6)$$

where:

- A is the final activity of the sample ($Bq \cdot l^{-1}$).
- A_o is the initial activity of the sample ($Bq \cdot l^{-1}$).
- $\lambda radon$ is the decay constant for radon (h^{-1}).
- $\lambda leaks$ is the constant of the permeability of the material to radon (h^{-1}).

This graph (Figure 5) indicates a value of λ_{leaks} of $3.3 \cdot 10^{-3}$ h^{-1} for LDPE, compared to $3.5 \cdot 10^{-4}$ h^{-1} for glass.

CONCLUSIONS

More laboratories participated in the performance testing in 2016 than 2015, demonstrating a growing interest in measuring ^{222}Rn in drinking water. The reason is probably the recent transposition of Directive 2013/51 / EURATOM into Spanish law (as RD 314/2016 of 29 July), establishing for the first time the legally permissible levels of ^{222}Rn in drinking water.

This intercomparison exercise by IPROMA and LaRUC, included 17 national laboratories in 14 provinces, representing 8 of the 17 Autonomous Communities in Spain.

The Liquid Scintillation Counting (LSC) technique, is the most widely used technique by Spanish laboratories specialising in the measurement of ^{222}Rn in water (Figure 6). One of the great advantages of this technique is the small amount of sample required for measurements, with the majority of participants using between 6 and 10 ml.

In terms of Z_{score}, the results of the intercomparison exercise (Figure 3), indicate that all the participants produced a satisfactory measurement of ^{222}Rn in water, even though (Figure 4), laboratories R04 and R17 presented out of range results with respect to the consensus value ± σ_p. In general, the results of both the 2015 and 2016 exercises, demonstrate the good preparedness of national laboratories for measuring ^{222}Rn in water.

As for the suitability of bottle material used in terms of radon leaks, the results clearly show that the most suitable material is glass, which gives a λ_{leaks} ten times less than plastic.

REFERENCES

1. (Chu et al.,1999) S.Y.F. Chu, L.P. Ekström and R.B. Firestone. (1999, February). *Table of Radioactive Isotopes. August* 10 2015, from http://nucleardata.nuclear.lu.se/toi/
2. Galán López, M., Martín Sánchez, A. and Gómez Escobar, V. *Application of ultra-low level liquid scintillation to the determination of 222Rn in groundwater*. J.Radioanal. Nucl. Chem. 261(3), 631–636 (2004).
3. Belloni, P., Cavaioli, M., Ingrao, G. and Mancini, C. *Optimization and comparison of three different methods for the determination of Rn-222 in water.* Sci. Tot.Environ. 173/174, 61–67 (1995).
4. Quindós, L. S., Fernández, P. L. and Soto, J. *National Survey on indoor radon in Spain*. Environ. Int. 17, 449–453 (1991).
5. Quindós, L. S. *Un Gas Radiactivo de Origen Natural en su Casa* (Santander, Cantabria: Consejo de Seguridad Nuclear y Universidad de Cantabria) (1995) ISBN: 84-87275-59-1.
6. Vázquez, B. F., Consuegra Ávila, F. M., Olaya, M. A. and Fernández, C. S. *Técnica de ventilación como medida de rehabilitación frente a la inmisión de gas radón en edificios y su repercusión en la eficiencia energética*. Comunicación Congreso Latinoamericano REHABEND 2014 del 1 al 4 abril del 2014. Santander, España (2014).

7. Hess, C. T., Vietti, M. A., Lachapelle, E. B. and Guillemette, J. F. Chapter 5—Radon transferred from drinking water into house air. In: Radon, Radium and Uranium in Drinking Water. Richard Cothern, C. and Rebers, P. A. Eds (Chelsea, MI: Lewis Publishers, Inc) (1990) ISBN 0-87371-207-2.

8. National Research Council. *National Research Council (US) Committee on Risk Assessment of Exposure to Radon in Drinking Water* (Washington, DC: National Academies Press (US)) (1999) 1999. Risk Assessment of Radon in Drinking Water.

9. Sainz, C., Rábago, D., Fuente, I., Celaya, S. and Quindós, L. S. *Description of the behavior of an aquifer by using continuous radon monitoring in a thermal spa*. Sci. Tot. Environ. 543, 460–466 (2016).

10. de España, G. REAL DECRETO 140/2003 del 7 de Febrero por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano. Madrid: BOE 45. 7228–7245 (2003).

11. Council Directive 2013/51/EURATOM. Council of the European Union. *Council Directive 2013/51/EURATOM of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption.* Brussels: O.J. EU (2013).

12. de España, G., REAL DECRETO 314/2016 del 29 de Julio por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano. Madrid: BOE 183. 53106–53126 (2016).

13. Soto, J., Delgado, M. T., Fernández, P. L., Gómez y, J. and Quindós, L. S. *Niveles de 222Rn en el Balneario Las Caldas de Besaya*. Rev. Sanidad Higiene Públ. 65 (1), 71–75 (1991).

14. Aquakit. *Accessory for radon in water measurement in combination with the radon monitor*. Alphaguard, User Manual, Genitron Instruments Germany (1997).

15. Clever, H. L., u.a. *Temperature dependency of the diffusion coefficient 'k'*. In: Solubility Data Series, Krypton, Xenon, Radon Gas Solubilities 2. Pergamon Press, Oxford, pp. 463–468 (1985).

16. Fuente Merino, I. Puesta a punto de un equipo de fluorescencia de rayos x portátil con fuentes radiactivas: aplicaciones medioambientales. Tesis Doctoral, University of Cantabria (2015).

17. Neame, K. D. and Homewood, C. A. Introduction to Liquid Scintillation Counting London, England: (Butterworth & Co) (1974) ISBN: 0-408-70637-6.

FIGURES

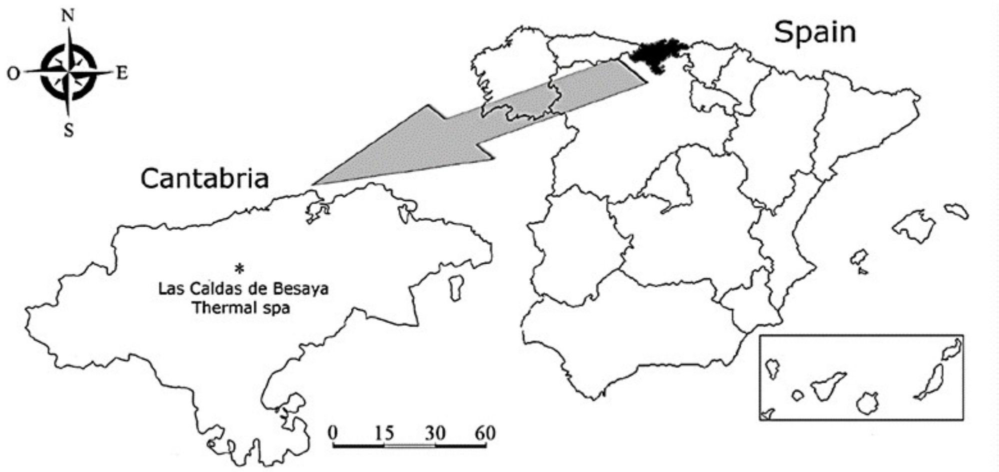

Figure 1: Location of Caldas Besaya Spa

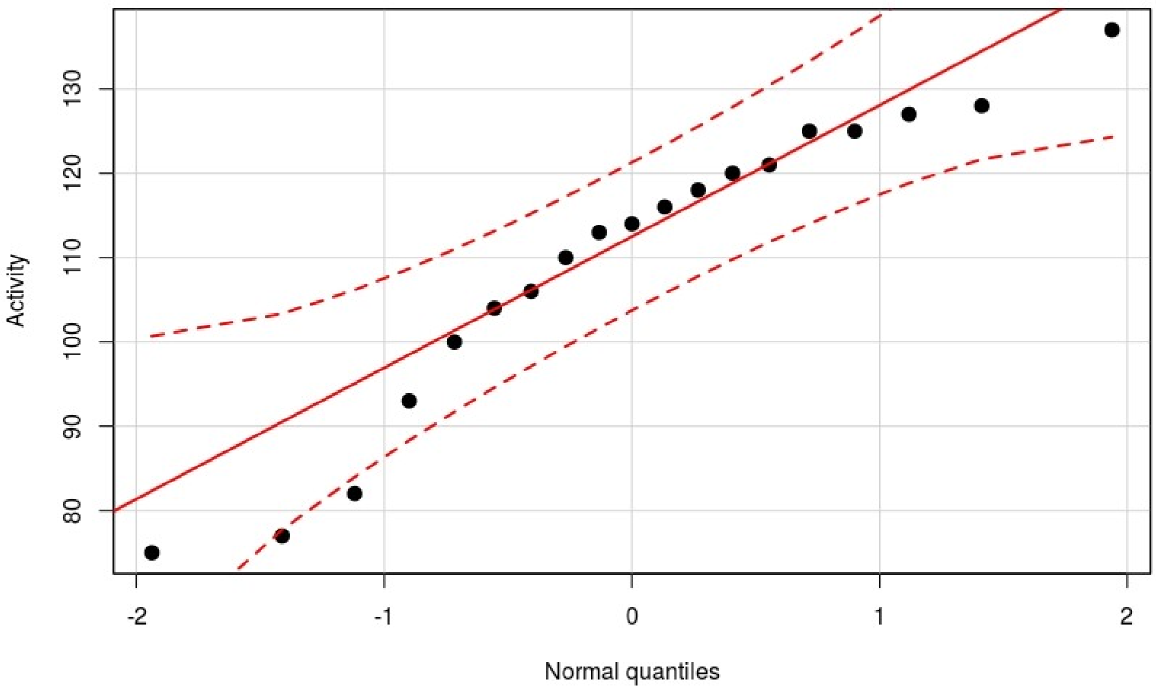

Figure 2: Graph q-q plot of the results of the exercise. Dashed line represents the 95% confidence interval

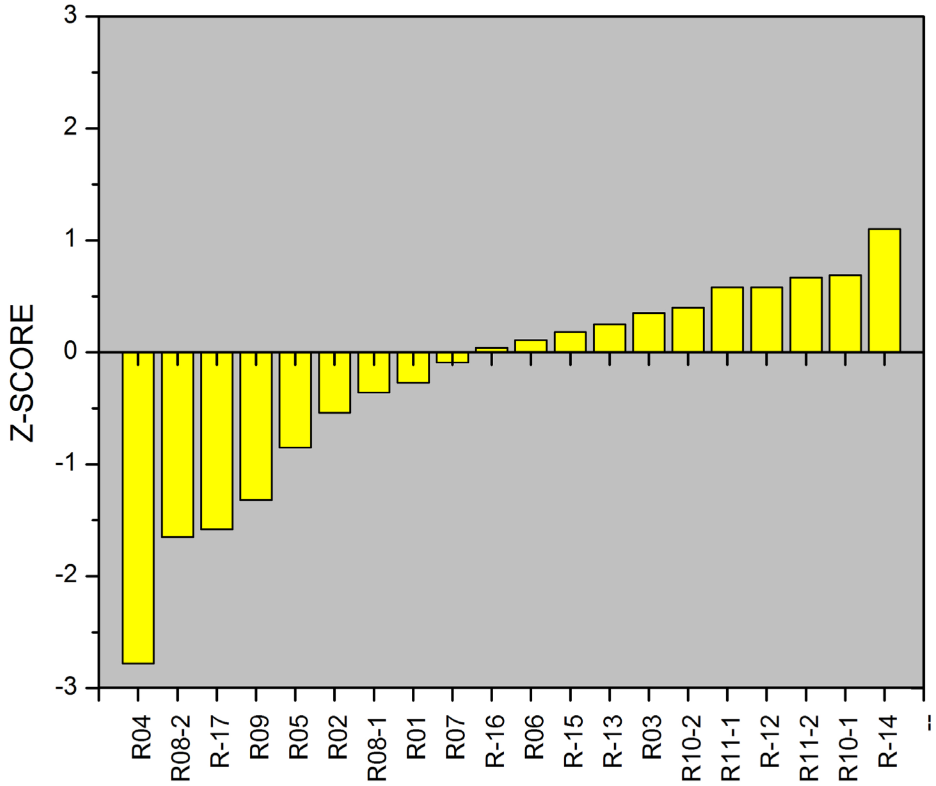

Figure 3: Z score of laboratories participating in the exercise

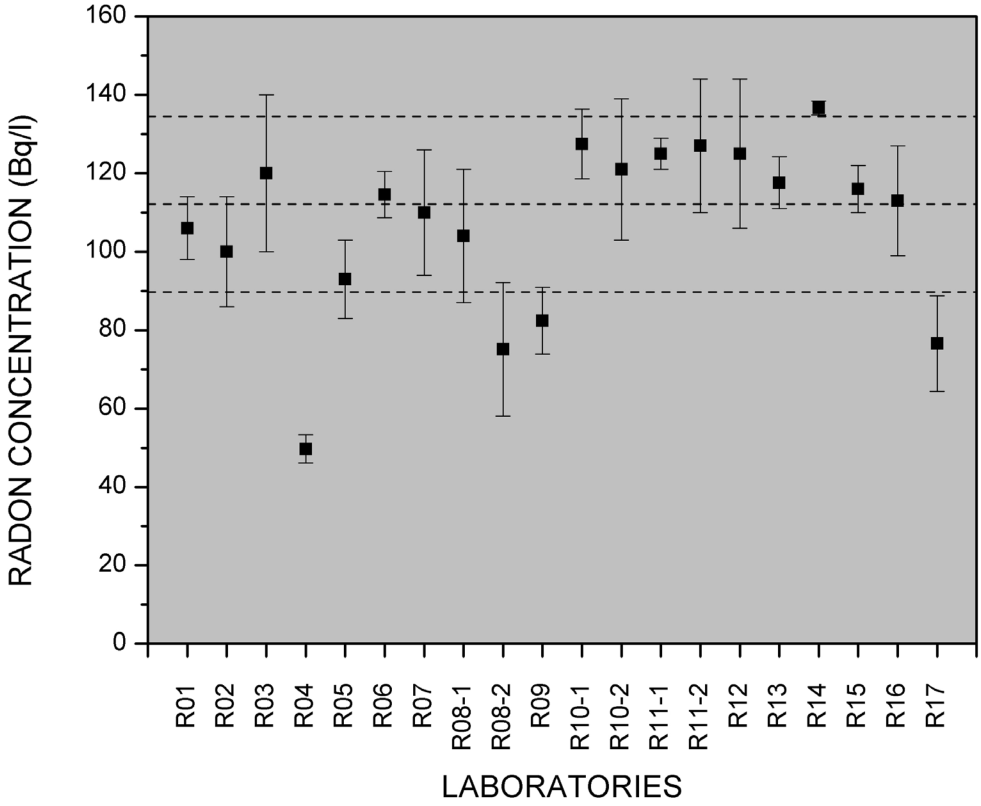

Figure 4: Activities measured by each laboratory, showing the consensus value and the target standard deviation of ±20%.

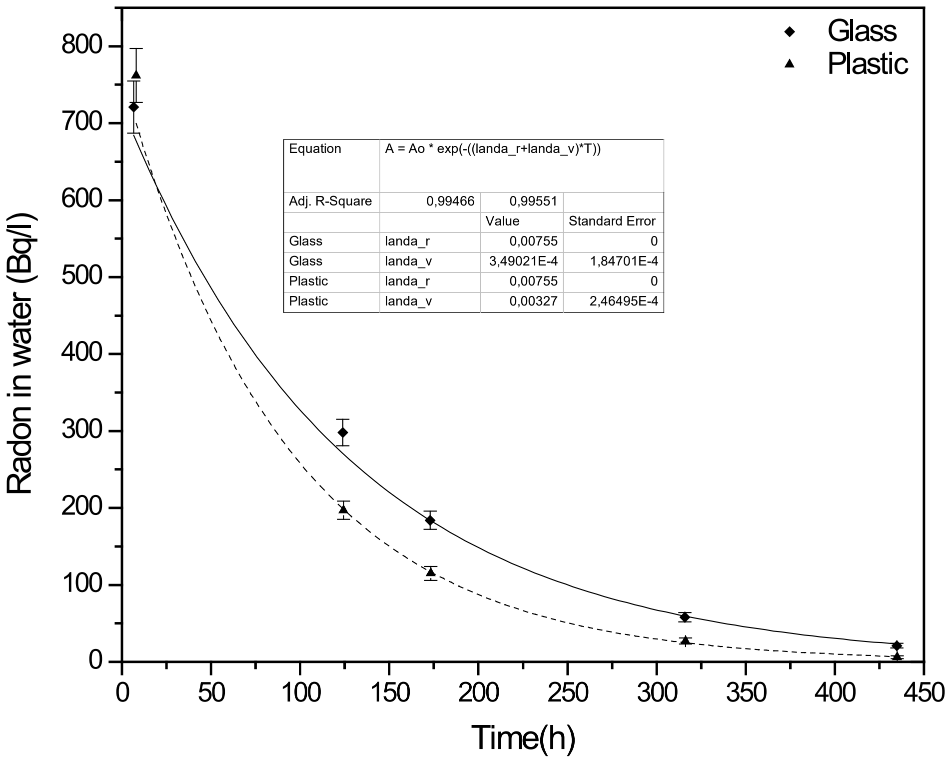

Figure 5: Exponential adjustment of the radon decay of a water sample in LDPE plastic and glass containers

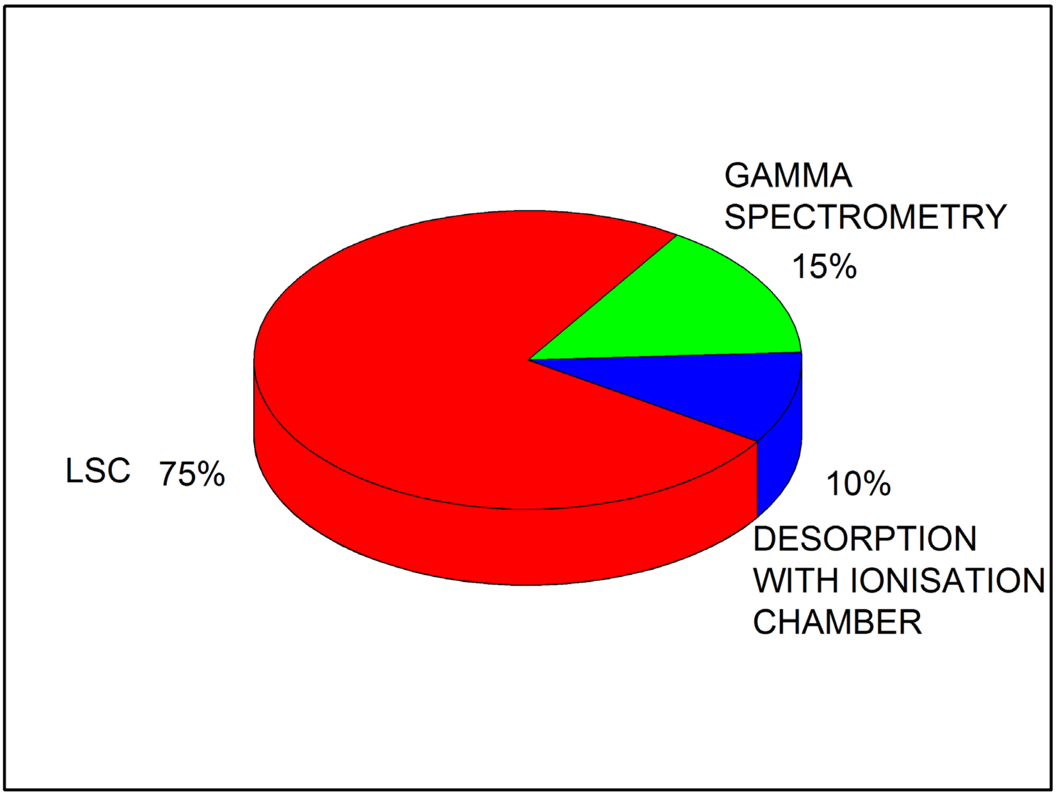

Figure 6: Distribution of results by measurements techniques employed

TABLES

Table 1: Name and location of the 17 participating laboratories in the intercomparison of December 2016

1	Iproma	Physic-Chemical Laboratory, Castellón
2	University of Extremadura	Dept. of Atomic Physics, Badajoz
3	University of Las Palmas de Gran Canaria	Dept. of Physics, Las Palmas
4	Laboratory Labaqua	Alicante
5	University Politécnica de Valencia	Lab. of Environmental Radioactivity, Valencia
6	University Politécnica de Cataluña	Lab. of Radioactivity analysis, Barcelona
7	University of Barcelona	Environmental Radiology Lab, Barcelona
8	University of Valencia	Institute of Corpuscular Physics, Burjassot
9	Environmental and Sanitary Radiochemistry Unit	Emergency laboratory and water quality, Tarragona
10	University of Cáceres	Lab. of Environmental Radioactivity, Cáceres
11	University of Cantabria	Radon Group, Santander
12	University of Bilbao	Dept. of Nuclear Engineering and Fluid Mechanics, Bilbao
13	University of Málaga	Radioactive Installation, University of Málaga
14	Canal de Isabel II Management	Area of Instrumental Analysis, Madrid
15	University of Granada	Dept. of Inorganic Chemistry. Radiochemical Laboratory and Environmental Radiology. Granada.
16	AGQ Labs & Technological Services	Lab. of Environmental Radioactivity, Sevilla
17	Health Institute Carlos III	Radioprotection Service, Madrid

Table 2: Results sent by participants ("GS"=gamma spectrometry HPGe detector, "LSC"=liquid scintillation counting and "D"=desorption with ionisation chamber).

Laboratory	Result ($Bq \cdot l^{-1}$)	Uncertainty ($Bq \cdot l^{-1}$)	Technique	Volume (ml)	Time (min)
R01	106	8	LSC	10	60
R02	100	14	LSC	10	100
R03	120	20	LSC	10	400
R04	49.7	3.6	LSC	10	200
R05	93	10	LSC	10	30
R06	114.6	5.9	LSC	10	30
R07	110	16	LSC	10	30
R08-1	104	17	GS	1000	3583
R08-2	75.1	17	D	490	30
R09	82.4	8.5	LSC	10	10
R10-1	127.5	8.9	GS	270	120
R10-2	121	18	LSC	6	10
R11-1	125	4	LSC	10	30
R11-2	127	17	GS	100	16.6
R12	125	19	LSC	6	10
R13	117.6	6.6	LSC	5	30
R14	136.63	1.75	LSC	200	100
R15	115.98	5.97	LSC	10	10
R16	113	14	LSC	10	200
R17	76.6	12.2	D	100	100

Table 3: Statistics of the results, with values expressed in $Bq \cdot l^{-1}$

Parameter	Value
Number of participants (dimensionless)	16
Number of measurements (dimensionless)	19
Average	110
Median	115
Geometric average	109
Minimum	75
Maximum	137
Standard Deviation	18
Standard Deviation Geometric	1.2

Table 4: Parameters of the exercise

Parameter	**Consensus Value, X**	**Rob. standard deviation, $\sigma_{exercise}$**	**Objective sigma, σ_p**	**Uncertainty, μ_x**	**No. of results**
Radon ($Bq \cdot l^{-1}$)	112.1	15.2	22.4	4.4	19