Comparison of several methods for measuring ^{222}Rn in drinking water

LSC 2017

Advances in Liquid Scintillation Spectrometry

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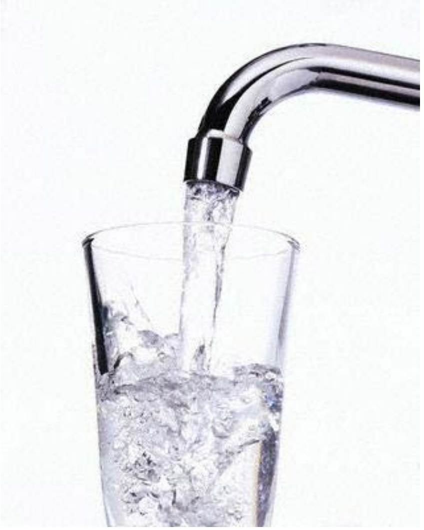
Summary

- Introduction.
  - ✓ Radiological control in drinking water.
  - ✓ Radiological control in radon.
- Study area.
  - ✓ Predictive map of radon in Spain.
  - ✓ Duoro River Basin.
- General sampling techniques for radon.
- Measurement methods of radon.
- Results and discussion.
- Comments and recommendations.


Introduction

Protection of radioactive substances in water for human consumption

Water quality is one of the most important concerns in environmental studies because of its use for human consumption and its ability to transport pollutants in the environment.



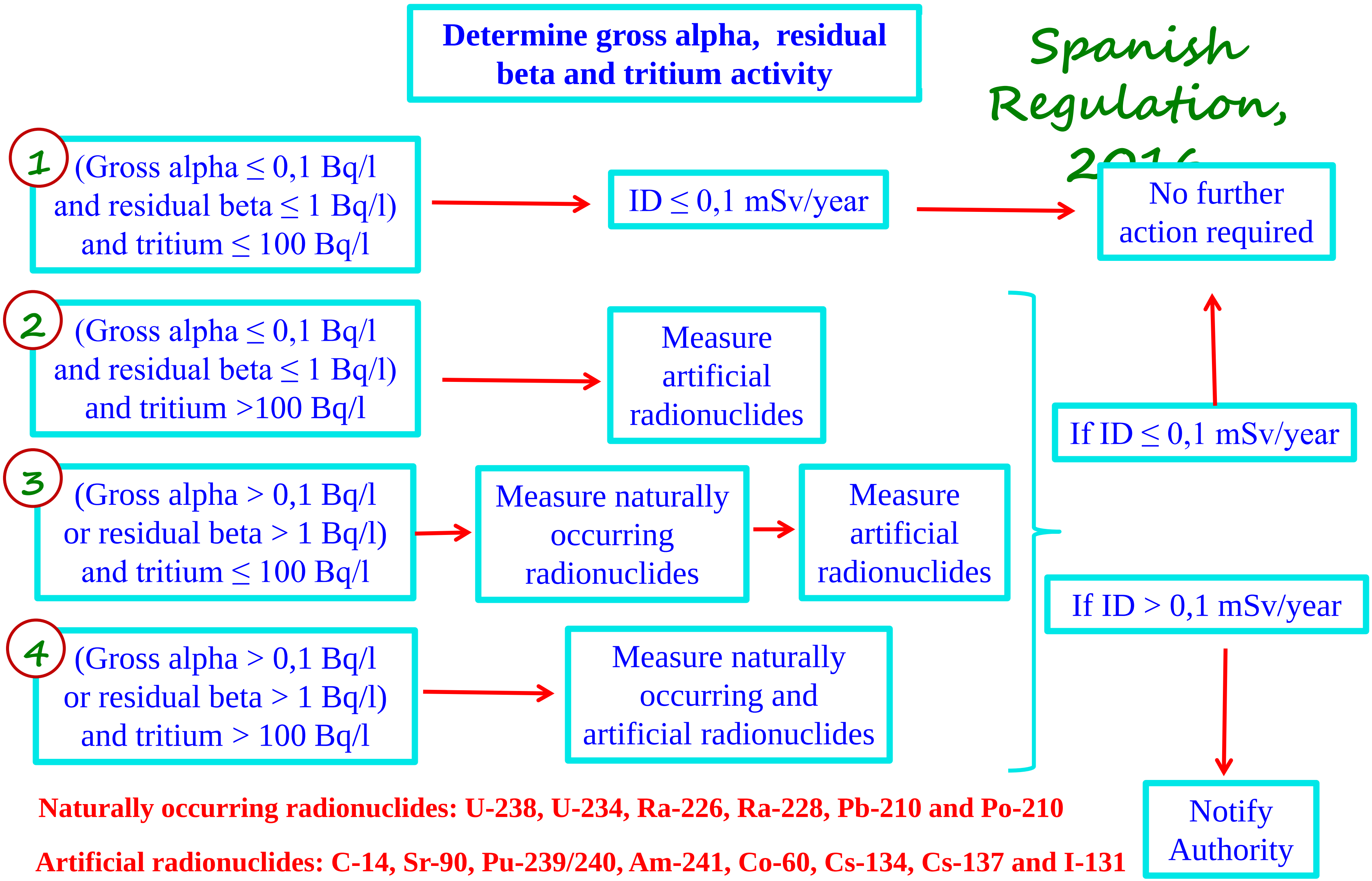
Radiological control in drinking water

The approach taken in national and international radiological control in drinking water has two stages (WHO, 2008):

- ✓ initial screening for gross alpha and/or beta activity to determine whether the activity concentrations are below levels at which no further action is required (Indicative Dose ≤ 0.1 mSv/year); and.
- ✓ if these screening levels are exceeded, investigation of the concentrations of individual radionuclides and comparison with specific guidance levels.

In 2013, the European Commission published the EURATOM Drinking Water Directive (E-DWD).
The Spanish legislation transposed the E-DWD in 2016.

Flow chart of Indicative Dose Procedure



Naturally occurring radionuclides: U-238, U-234, Ra-226, Ra-228, Pb-210 and Po-210

Artificial radionuclides: C-14, Sr-90, Pu-239/240, Am-241, Co-60, Cs-134, Cs-137 and I-131

International radon guidance and parametric value in drinking water

Directive/recommendation	Parametric value (Bq/l)	Reference
2001/928/Euratom Recommendation	100 - 1000	EURATOM, 2001
WHO guidance level	100	WHO, 2008
2013/51/Euratom Directive	100 – 1000*	EURATOM, 2013
Spain National legislation (RD 314/2016)	500*	BOE, 2016

*Remedial action is deemed to be justified on radiological protection grounds, without further consideration, where radon concentrations exceed 1000 Bq/l.

Monitoring of Radon

(Annex II, 2013/51/Euratom Directive)

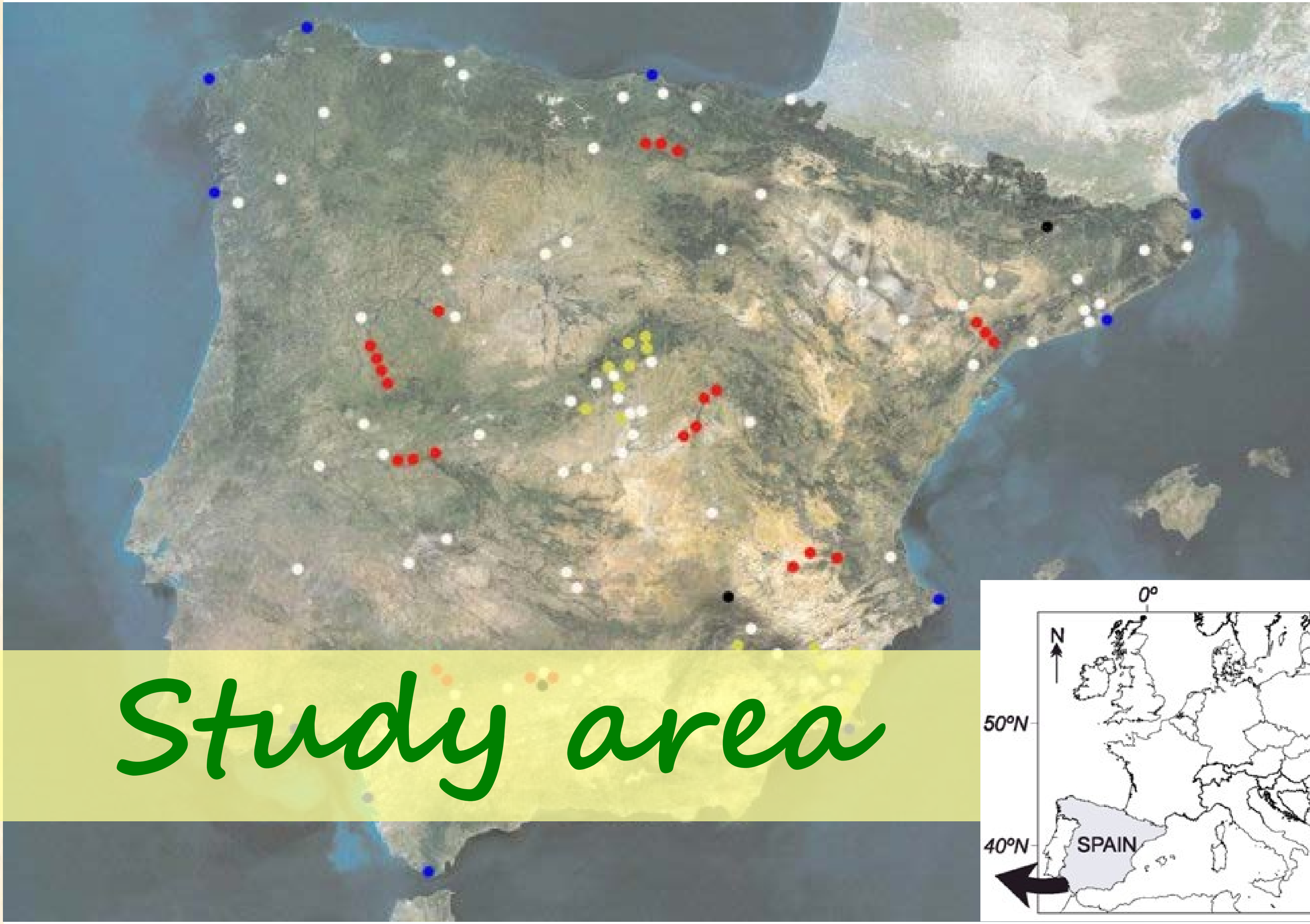
Member States shall ensure that representative surveys are undertaken to determine the scale and nature of likely exposures to radon in water intended for human consumption originating from different types of ground water sources and wells in different geological areas.

The surveys shall be designed in such a way that underlying parameters, and especially the geology and hydrology of the area, radioactivity of rock or soil, and well type, can be identified and used to direct further action to areas of likely high exposure .

Standard water radon measurement methods

Standard	Title
ISO 13164-1:2013 Water quality – Radon-222	Part 1: General principles
ISO 13164-2:2013 Water quality – Radon-222	Part 2: Test method using gamma-ray spectrometry
ISO 13164-3:2013 Water quality – Radon-222	Part 3: Test method using emanometry
ISO 13164-4:2015 Water quality – Radon-222	Part 4: Test method using two-phase liquid scintillation counting
ASTM D5072-09 (2016)	Standard Test Method for Radon in Drinking Water based on LSC

Study area



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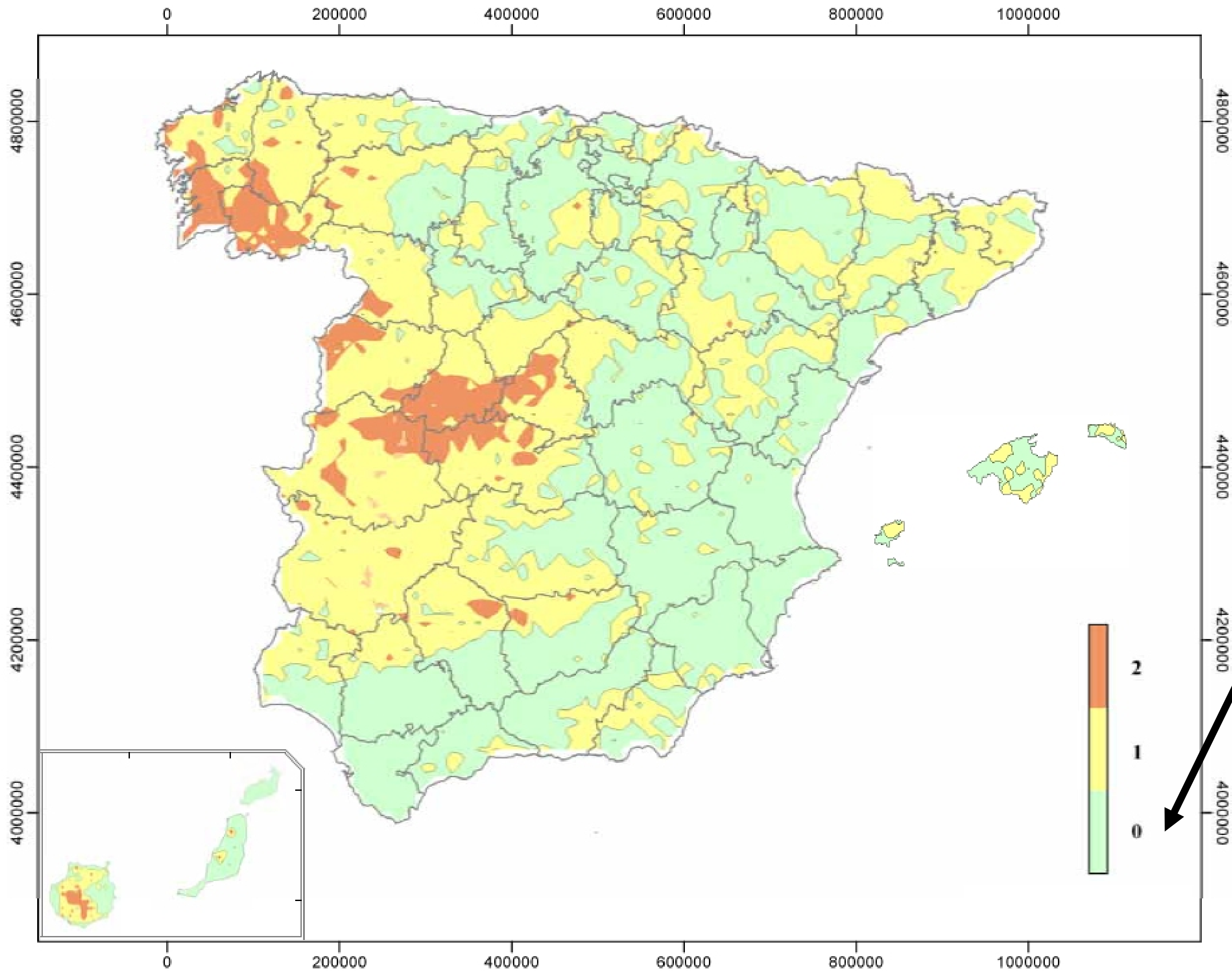
Predictive map of the radon exposure in Spain



Geological Area (0)
Lime soil: alpine areas, Mediterranean coastal region and northern part of the peninsula
.

Source: Spanish Nuclear Safety Council (CSN, 2013)

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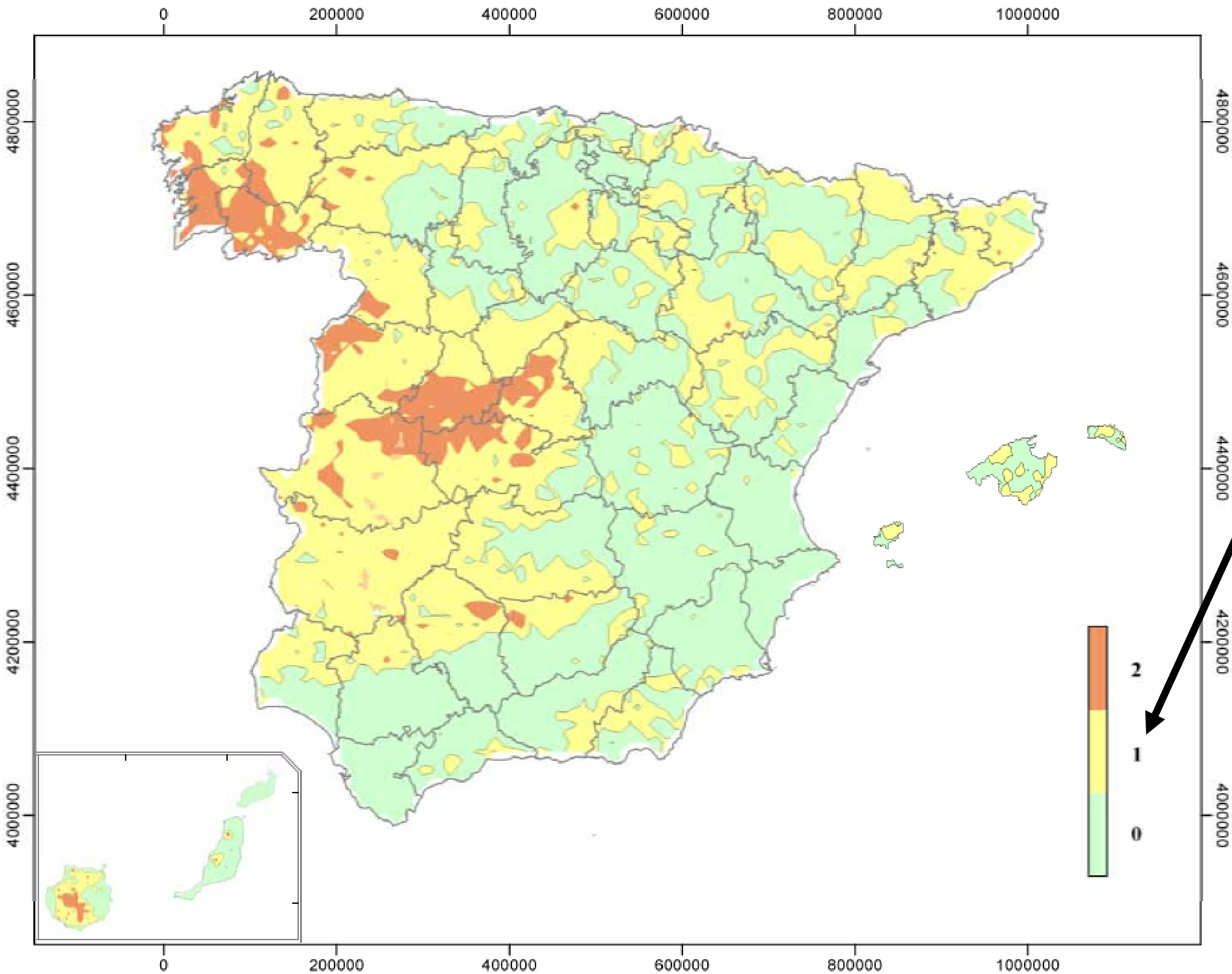
Predictive map of the radon exposure in Spain



Geological Area (1)
Clay soil, sendimentary rocks. It covers most regions of Aragón, Castilla-León, Castilla-La Mancha and La Rioja.

Source: Spanish Nuclear Safety Council (CSN, 2013)

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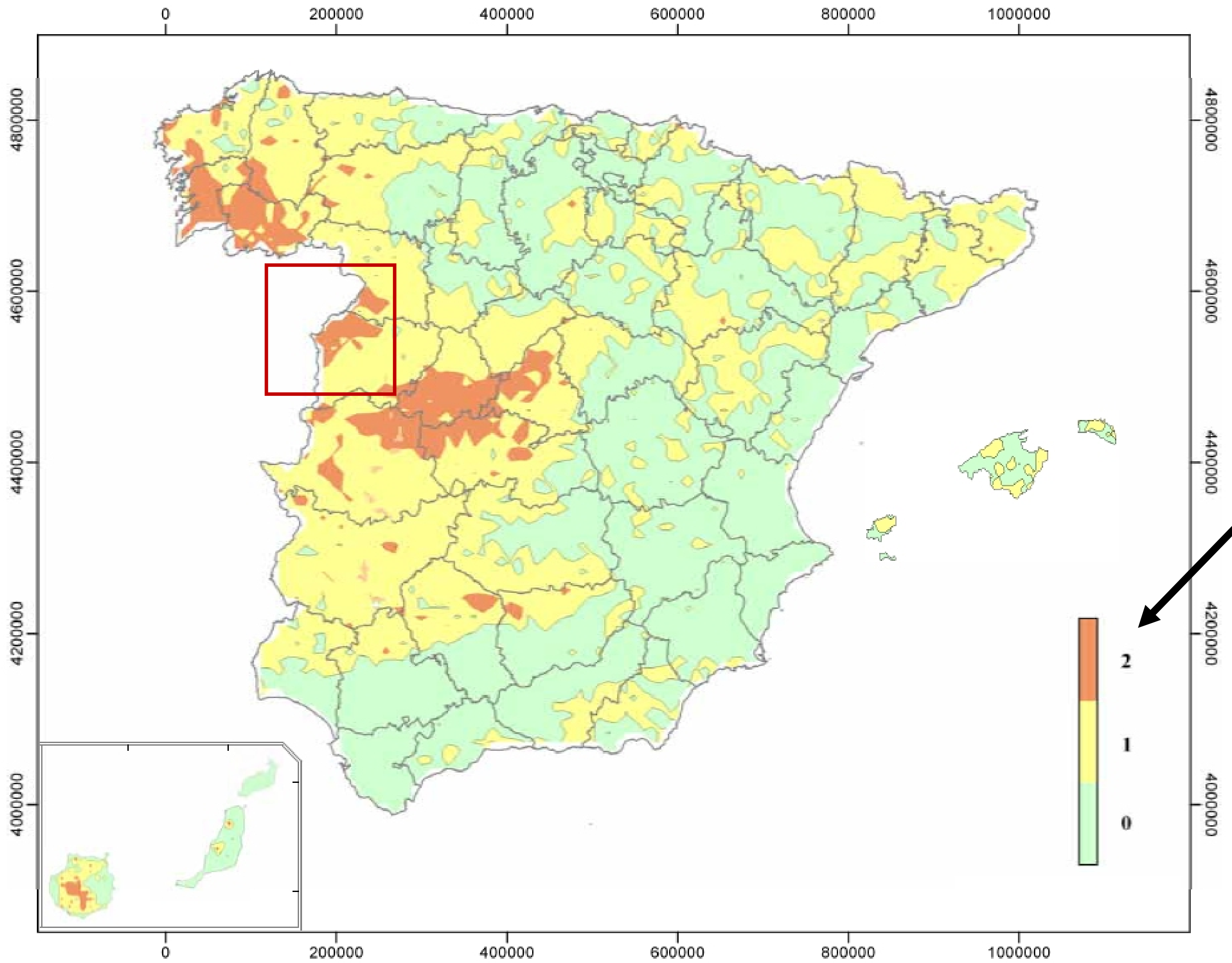
Predictive map of the radon exposure in Spain



Geological Area (2)
Silicious soil: composed of igneous rocks, such granites. This area occupies the western part of the peninsula; its includes Galicia, Extremadura and Madrid.

Source: Spanish Nuclear Safety Council (CSN, 2013)

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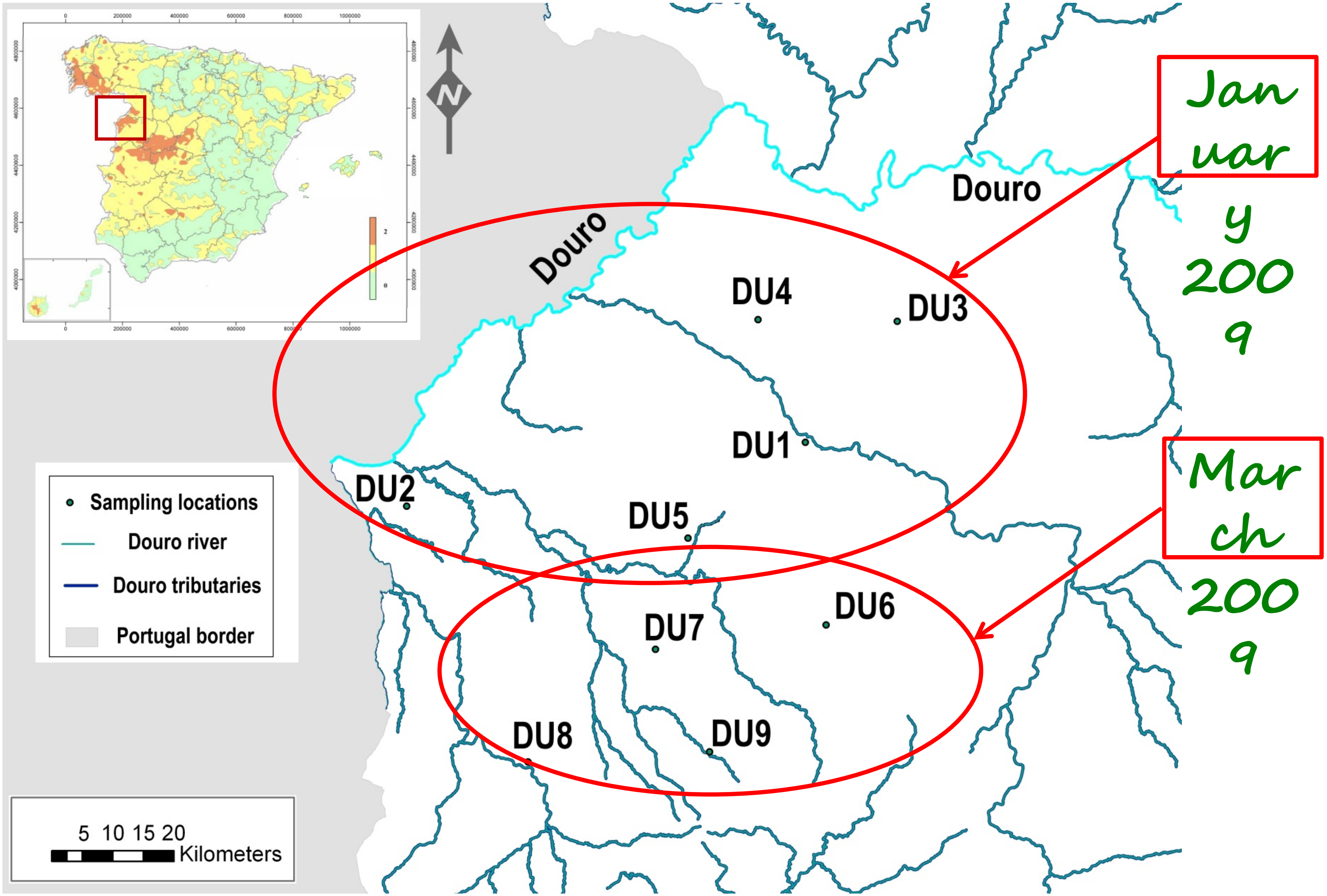
Sampling area in left-side of Douro basin



Types of water sources

Water samples were collected from groundwater supplies:

7 different drilled wells

1 borehole

1 public spring

Public spring next to a spa

DU 4

Drilled well

DU1, DU2, DU3, DU5, DU6, DU7,

Borehole

DU 9

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Sampling techniques

General radon sampling conditions

- ✓ Purge the supply system.
- ✓ Limit the contact between air and water to reduce gas escape during the sampling procedure.
- ✓ Take the sample carefully, minimizing any turbulence.
- ✓ Fill the container completely in order to avoid the presence of air.

Sampling for AlphaGuard

A sample of 500 ml was injected into the degassing vessel by suction from the container. A 100 ml syringe was used.

Because of the fast degassing of radon from water, contact between the water sample and the outside air was strictly minimized.

After sample injection, the gas cycle is closed and the gas pump is switched on.

Sampling for gamma spectrometry

Samples were collected from the bottom of a container with two types of Marinelli beakers: 1.75 litres and 0.25 litres.

The Marinelli beakers were completely filled and hermetically sealed.

Sampling for liquid scintillation counting

Before sampling, 12 ml of a scintillation cocktail was transferred into a 20 ml vial. During the sampling, 8 ml of water was carefully taken by suction from the bottom of the container with a syringe avoiding air bubble formation.

Immediately, the sample was injected into the bottom of the vial. The vial was then thightly capped, vigorously shaken, and transported to the laboratory for measurement. **Samples were collected in duplicate.**

Sampling for liquid scintillation counting: Vials/cocktails combinations

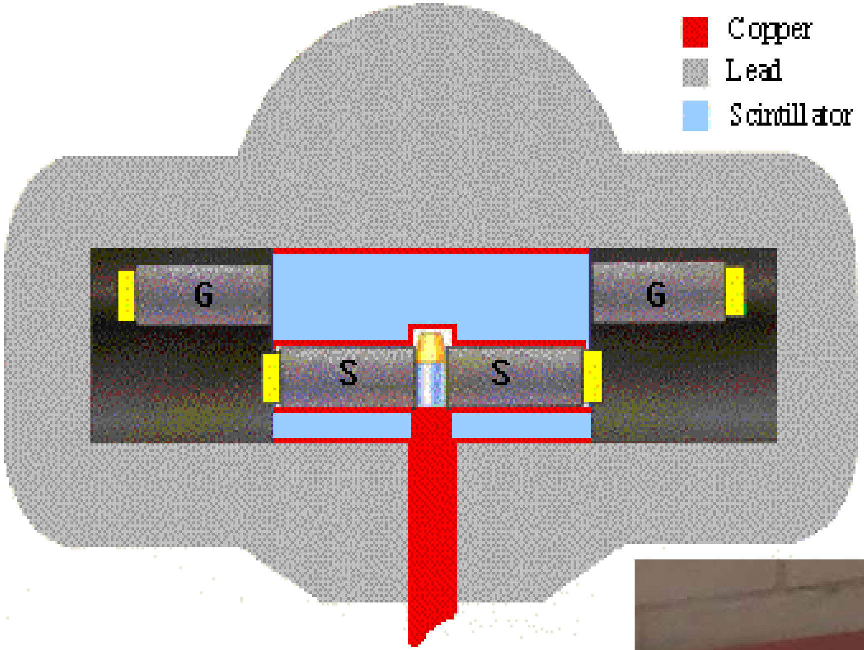
Sampling campaign (January 2009): 5 locations

- ✓ Three vial types were used: 20 ml polyethylene vials (PE), polyethylene low diffusion vials (PET), and glass vials from PerkinElmer.
- ✓ Cocktail: Ultima Gold LLT from PerkinElmer

In duplicate

Sampling campaign (March 2009): 4 locations

- ✓ Three types of commercially available high capacity cocktails were used: Optiphase Hisafe 3 (OPH3), Ultima Gold LLT (UGLLT), and Ultima Gold AB (UGAB) from PerkinElmer.
- ✓ Vials: polyethylene low diffusion vials (PET) from PerkinElmer.

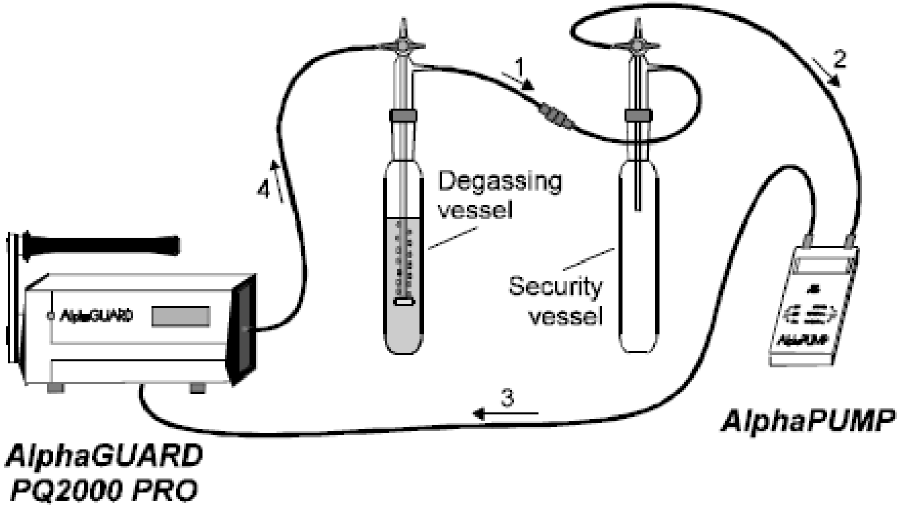


Measurement methods

Degassing Method: AlphaGuard PQ2000 PRO

This is an ionisation chamber, designed for measuring radon in air, soil and water. For water measurements the additional equipment AquaKIT was used.

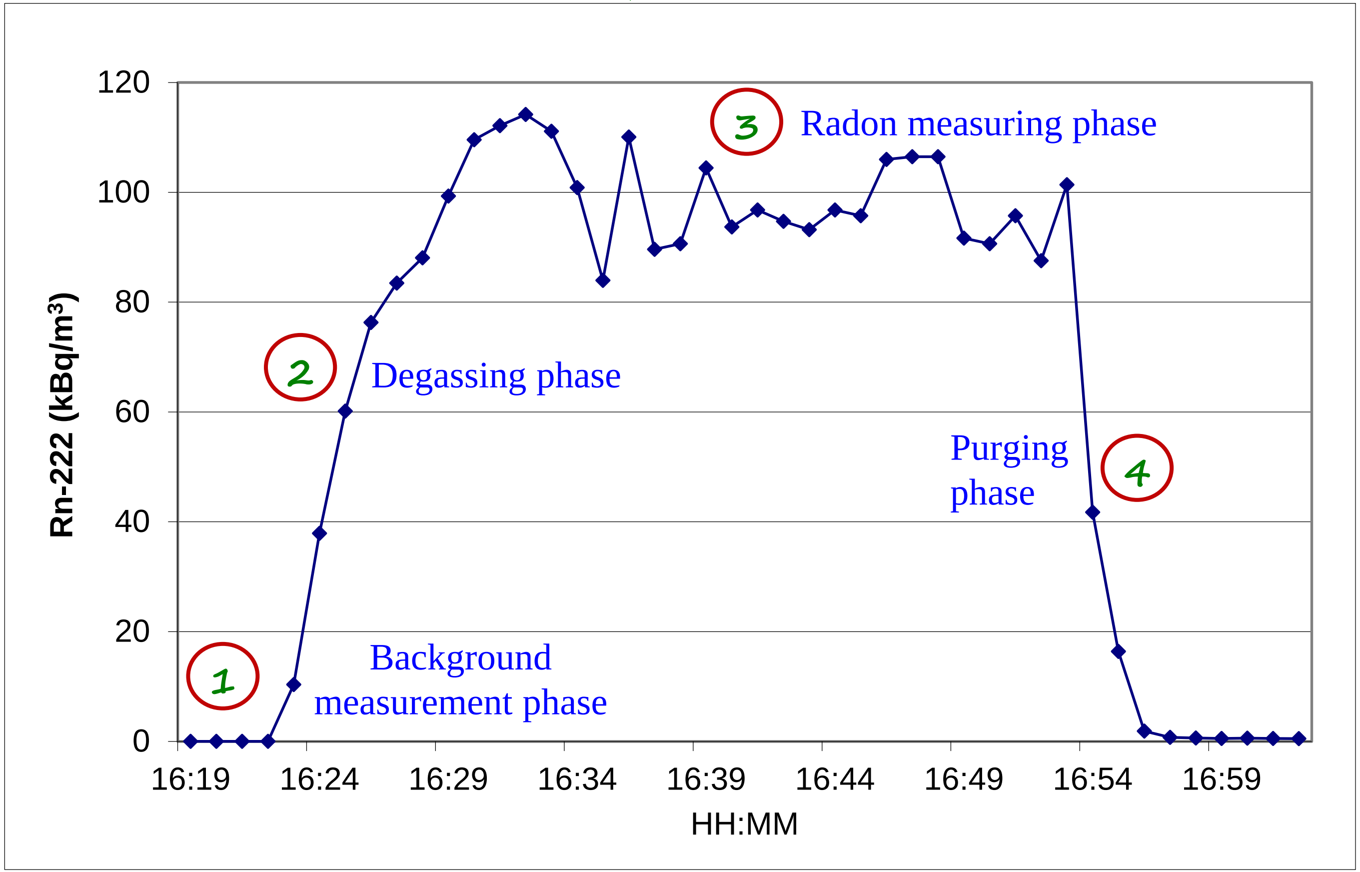
This equipment consists in a closed circuit where a known volume (100-500 ml) of the water to be analysed is introduced in the degassing cell. A pump is used to circulate the air in the system bubbling it through the degassing cell to degas the radon dissolved in the water.



$$C_{water} = C_{air}\left(\frac{V_{air}}{V_{water}} + K_{water/air}\right) - C_b \left[Bq/l\right]$$

(Schubert, 2006)

Change in the activity concentration of radon in the air within the system (code sample: DU7)



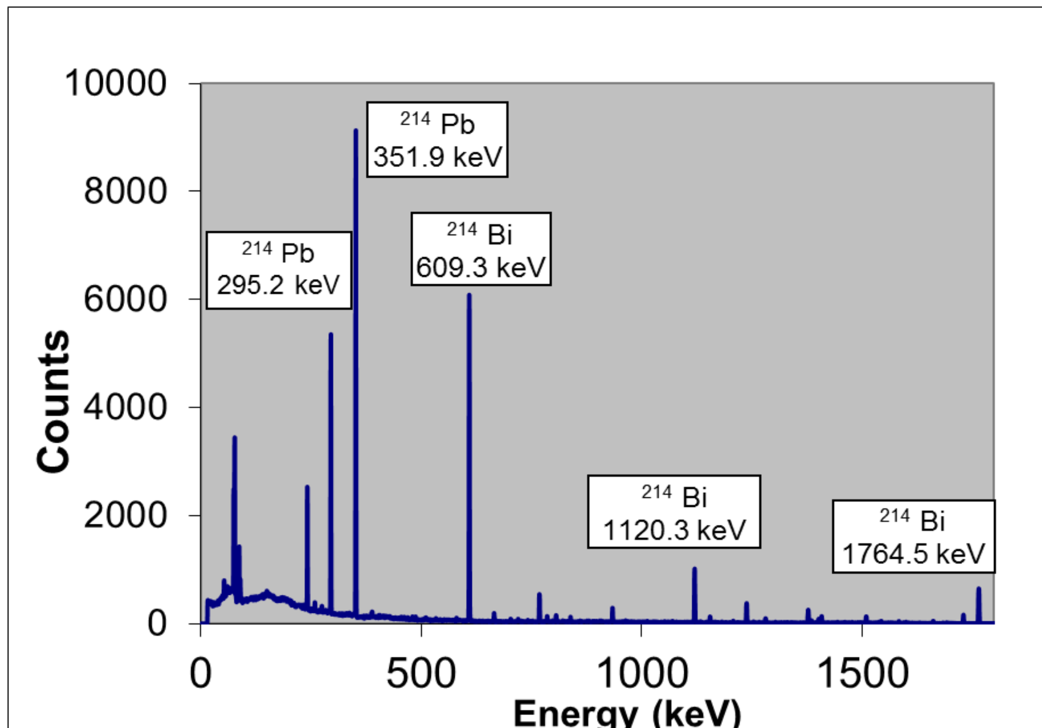
After less 10 minutes, equilibrium concentration is reached, then at least 10 more minutes the air circulate in the measuring system. After this time the pump is stopped and the system purged.

Gamma spectrometry

Gamma spectrometry was carried out by three HPGe detectors (GR2522, GR2520 and GX4020, Canberra) with relative efficiency 25%, 25%, and 40%, respectively.

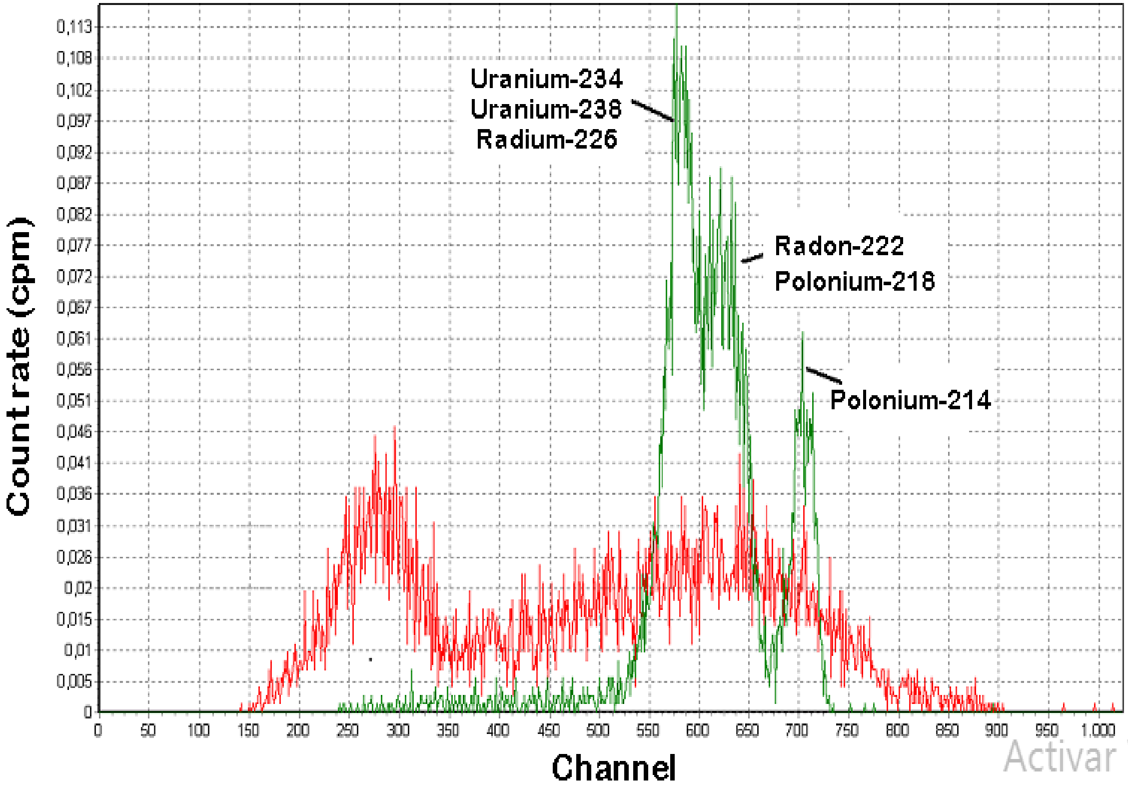
Gamma spectrometry

The samples were measured once the equilibrium between ^{222}Rn and its daughters was reached. Dominant peaks are from ^{214}Pb and ^{214}Bi. Radon concentration was determined using the ^{214}Pb emission at 351.9 keV because this peak does not require summing correction.



Liquid scintillation Counting

Counting was carried out using the liquid scintillation system Quantulus 1220™ from PerkinElmer. It is provided with a pulse-shape analyser (PSA) which separates pulsed caused by alpha or beta decays into different spectra, respectively.



$$f_d = e^{-\lambda \cdot \Delta \cdot t}$$

Results and discussion

Degassing Method: AlphaGuard

$$C_{water} = C_{air}\left(\frac{V_{air}}{V_{water}} + K_{water/air}\right) - C_b \left[Bq/l\right]$$

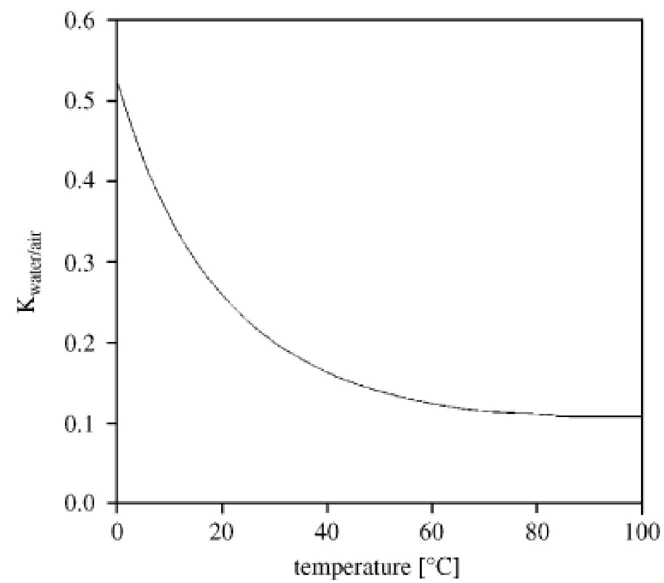
(Schubert, 2006)

V_{water} is the water sample volume (circa 500 ml).

V_{air} is the total volume air in the system (inner volume of all the system components: 1536 ml – V_{water}).

$K_{water/air}$ is the radon distribution coefficient at the given temperature.

C_b is the radon background concentration.



Dependency of the partitioning coefficient $K_{water/air}$ on temperature (Clever, 1979)

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Degassing Method: AlphaGuard

Mean value of **at least ten single** equilibrium concentration readings, recorded minute by minute was used.

Code sample	Number meas.	C_{air} (kBq/m^3)	V_{water} (ml)	T (ºC)	k	C_b (Bq·m^3)	C_{water} (Bq/l)
DU1	6	21.5	514	13	0.33	0.05	49.9 ± 2.5
DU2	6	160	464	14	0.32	4	420 ± 11
DU3	9	30.2	505	12	0.34	9	71.9 ± 1.5
DU4	8	539	480	10	0.36	58	1379 ± 19
DU5	6	105	480	12	0.34	182	290 ± 2
DU6	22	10.8	480	13	0.33	39	27.3 ± 0.7
DU7	22	99.9	486	15	0.30	10	246 ± 4
DU8	26	5.2	492	10.5	0.35	19	12.8 ± 0.3
DU9	22	0.014	500	12	0.34	20	N.D.*

Quoted uncertainties correspond to *k* =2.
*** N.D.: No detectable.**

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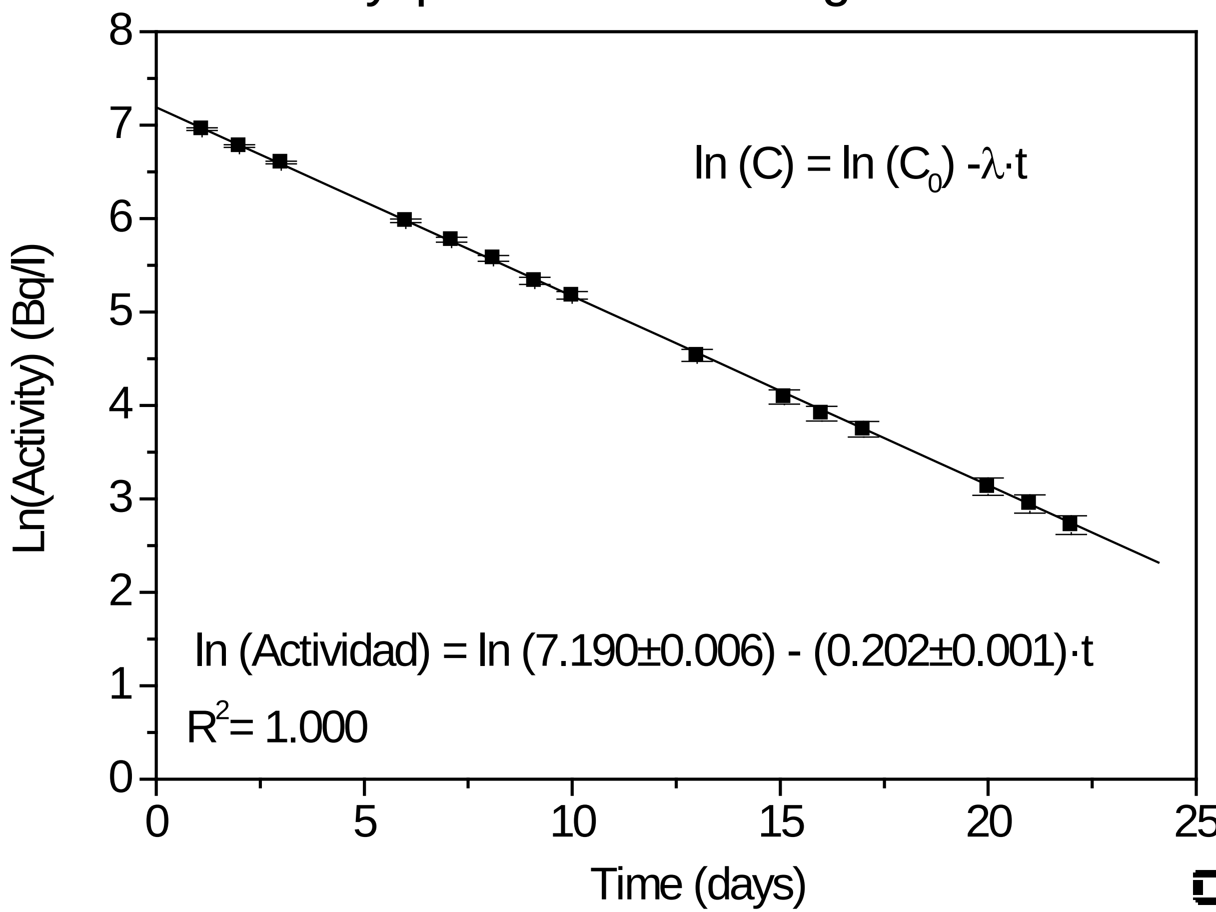
Gamma spectrometry

A set of measurements was made over several days. A straight fit line for each sample was used to calculate the initial radon concentration at the time of sampling (C_0) and the constant decay parameter using:



Sample:

DU4

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Gamma spectrometry

Fitted straight line parameters with Marinellis of 1.75 litres:

Code sample	$\lambda \cdot 10^{-6}$ (s^{-1})	ln (C_0)	C_0 ($Bq \cdot l^{-1}$)	R^2
DU1	2.3189 ± 0.0378	3.7651 ± 0.0271	43.2 ± 1.2	0.998
DU2	2.3449 ± 0.0084	6.2229 ± 0.0080	504 ± 4	1.000
DU3	2.3567 ± 0.0345	4.2562 ± 0.0195	70.5 ± 1.4	0.999
DU4	2.3553 ± 0.0094	7.1987 ± 0.0093	1338 ± 12	1.000
DU5	2.3675 ± 0.0156	5.7374 ± 0.0178	310 ± 5	0.999
DU6	2.3625 ± 0.0594	3.3354 ± 0.0319	28.1 ± 0.9	0.997
DU7	2.3785 ± 0.0067	5.4403 ± 0.0045	230 ± 1	1.000
DU8	2.4194 ± 0.0772	3.1351 ± 0.0481	23.0 ± 1.1	0.995
DU9	2.4958 ± 0.3893	1.2146 ± 0.1885	3.4 ± 0.6	0.911

Quoted uncertainties correspond to *k* =1.

Gamma spectrometry

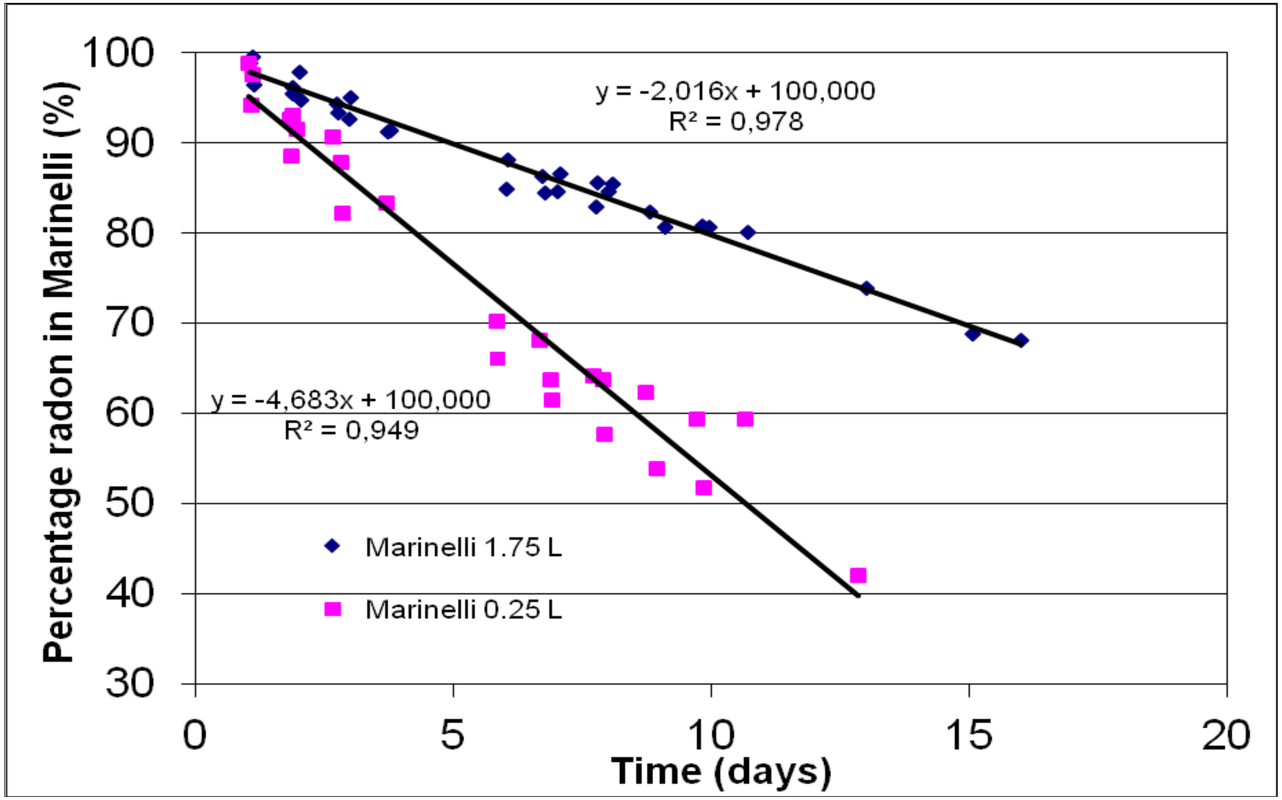
Fitted straight line parameters with Marinellis of 0.25 litres:

Code sample	$\lambda \cdot 10^{-6}$ (s^{-1})	ln (C_0)	C_0 ($Bq \cdot l^{-1}$)	R^2
DU1	2.1420 ± 0.1049	3.8741 ± 0.0751	48.1 ± 3.6	0.983
DU2	2.6876 ± 0.0418	6.3886 ± 0.0295	595 ± 18	0.998
DU3	2.6333 ± 0.0659	4.4907 ± 0.0427	89.2 ± 3.8	0.996
DU4	2.8871 ± 0.0129	7.4080 ± 0.0083	1649 ± 14	1.000
DU5	2.7394 ± 0.0737	5.9282 ± 0.0473	375 ± 18	0.995

Quoted uncertainties correspond to *k* =1.

Results shows that **constant decay parameter** of the fitted straight lines are higher than the theoretical one, λ_0 (^{222}Rn) = **$2.0984 \cdot 10^{-6}$ s^{-1}**. In general, it is higher for 0.25 litres Marinelli geometry beaker than for 1.75 litres Marinelli geometry beaker. The explanation of this result may be in the higher leakage of the first one.

Gamma spectrometry: radon losses during measurements with Marinelli beakers



^{222}Rn determination for both Marinellis have been corrected for decay.

Figure shows that about 2.0% and 4.7% of the ^{222}Rn is lost from samples measured using Marinelli beakers geometry of 1.75 litres and 0.25 litres, respectively, after 1 day (86400 s) between the sampling and the measuring.

Liquid scintillation counting

Also a set of measurements was made over several days for LSC for samples from DU1 to DU5. Fitted straight line parameters for code sample DU1 are shown **by each vial combination** and in duplicate.

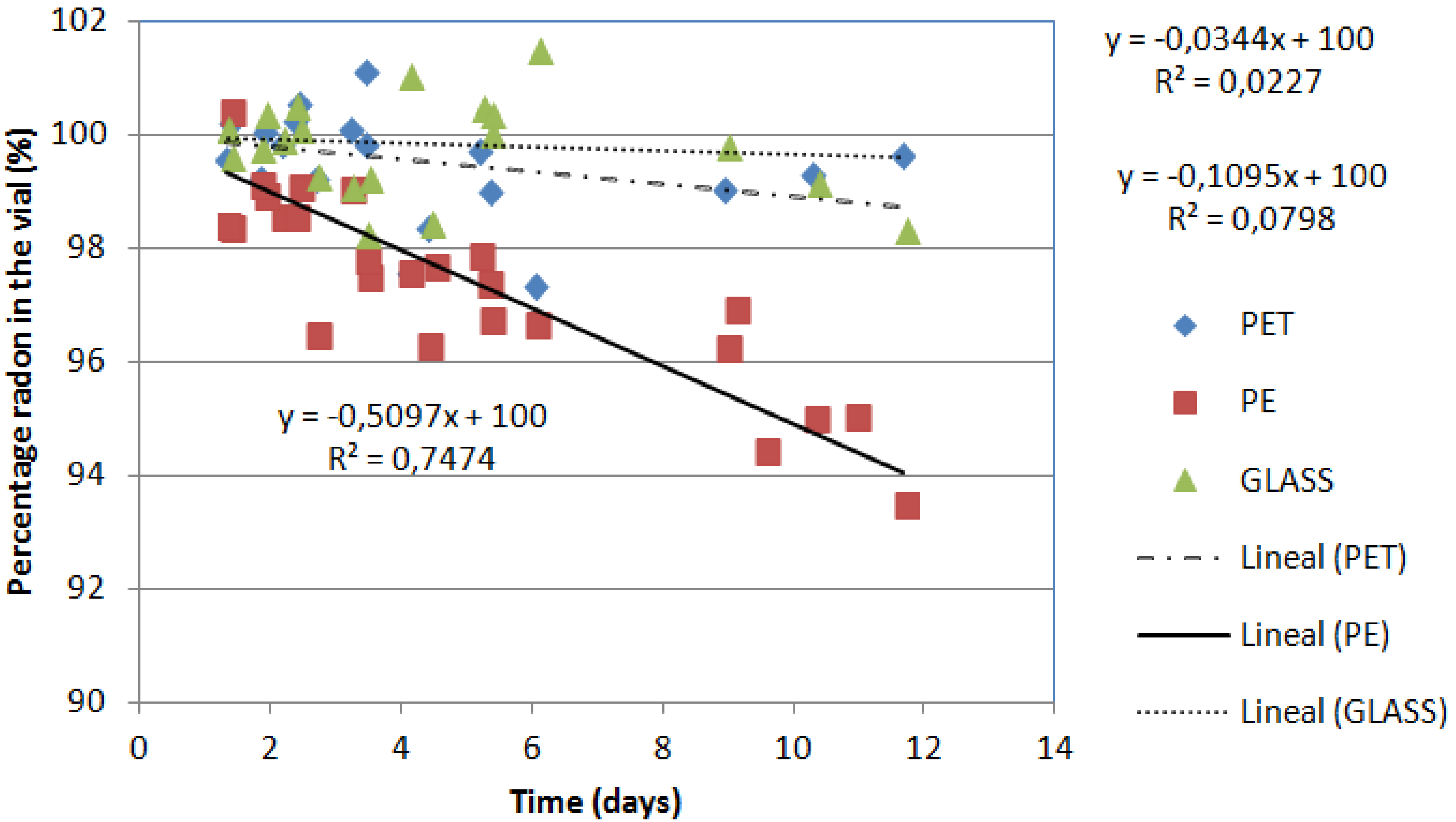
Code Sample	Vial	$\lambda \cdot 10^{-6}$ (s^{-1})	ln (C_0)	R^2
DU1	PET A	2.2240 ± 0.0538	3.8157 ± 0.0333	0.995
	PET B	2.0830 ± 0.0490	3.6734 ± 0.0304	0.996
	PE A	2.2573 ± 0.0612	3.7990 ± 0.0380	0.994
	PE B	2.1988 ± 0.0634	3.7535 ± 0.0394	0.993
	GLASS A	2.1158 ± 0.0430	3.6547 ± 0.0268	0.997
	GLASS B	2.1207 ± 0.0514	3.7180 ± 0.0321	0.995

Quoted uncertainties correspond to *k* =1.
Ultima Gold LLT cocktail was used for all vials.

Fitted straight line parameters for code sample DU2, DU3, DU4 and DU5 also were determined (not shown).

Liquid scintillation counting: radon diffusion

Radon leaks slightly from PET (low diffusion) and GLASS vials.



^{222}Rn determination for vials have been corrected for decay.

Liquid scintillation counting

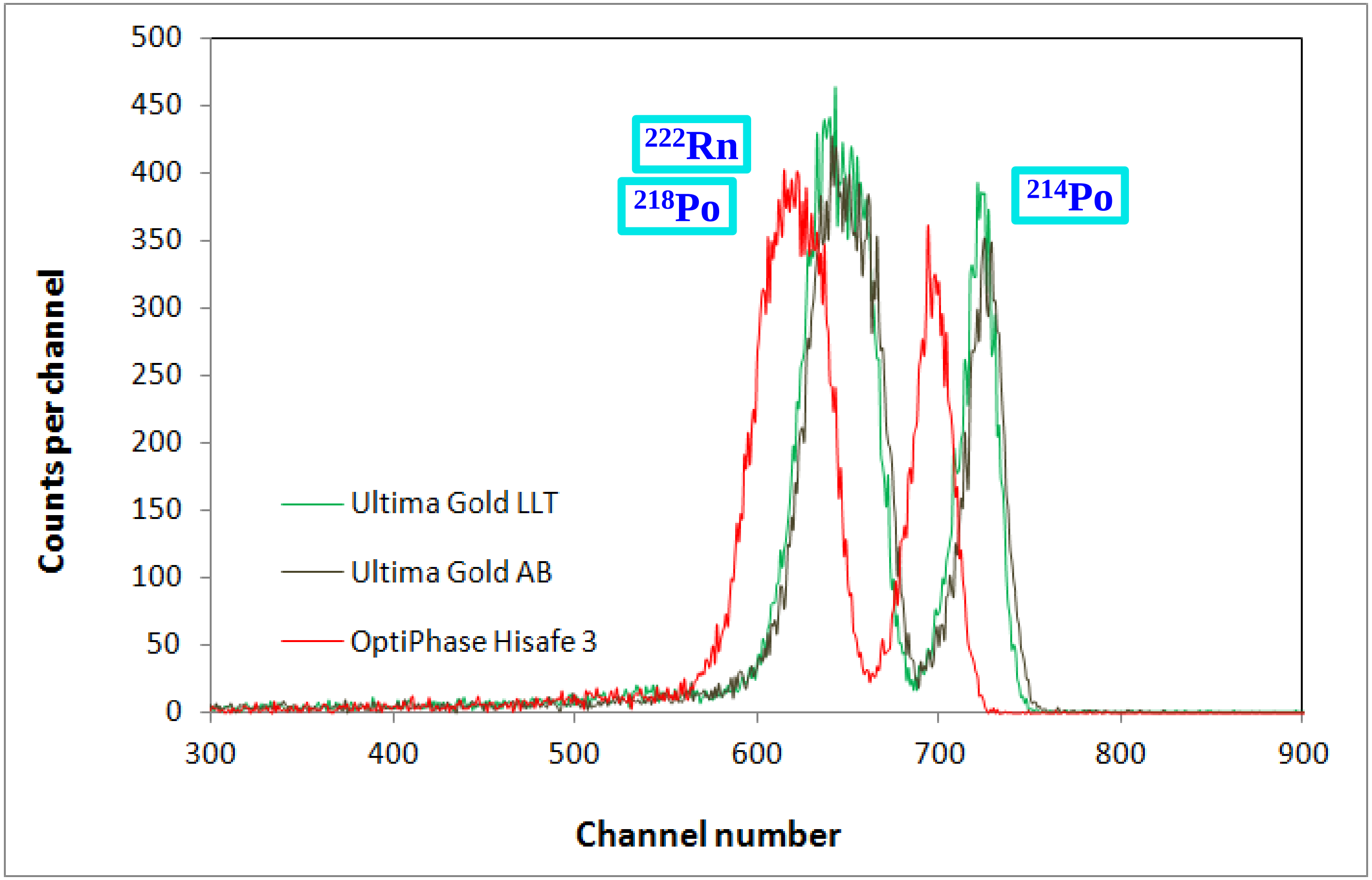
Also a set of measurements was made over several days for LSC for samples from DU6 to DU9. Radon was not detected in sample DU9. Fitted straight line parameters for code sample DU6 are shown **by each cocktail combination** and in duplicate.

Code Sample	Cocktail	$\lambda \cdot 10^{-6}$ (s^{-1})	ln (C_0)	R^2
DU6	UG LLT-1	2,2703 ± 0.1085	3.3714 ± 0.0624	0.989
	UG LLT-2	2.1969 ± 0.1273	3.2938 ± 0.0735	0.983
	UG AB-1	2.1841 ± 0.0823	3.3127 ± 0.0485	0.993
	UG AB-2	2.1722 ± 0.1149	3.2822 ± 0.0679	0.986
	OPH3-1	1.9115 ± 0.0956	3.1308 ± 0.0580	0.987
	OPH3-2	2.1781 ± 0.0901	3.3116 ± 0.0540	0.991

Quoted uncertainties correspond to *k* =1.
PET vials were used for all cocktails.

Liquid scintillation counting

Alpha Spectra for the different cocktails (sample code DU7):



Any cocktail may be used for ^{222}Rn measurements, although UG LLT and UG AB are more quench resistant than OptiPhase Hifase 3.

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Liquid scintillation counting

The mean concentration ^{222}Rn activity for several vials (PET, PE and GLASS) and the same cocktail (UGLLT) were determined:

Code Sample	Vial	PET & UGLLT	PE & UGLLT	GLASS & UGLLT	C_0 (Bq/l)
DU1	A	45.4 ± 3.0	44.7 ± 3.4	38.7 ± 2.1	42.0 ± 2.7
	B	39.4 ± 2.4	42.7 ± 3.4	41.2 ± 2.6	
DU2	A	423 ± 9	490 ± 12	465 ± 10	467 ± 26
	B	467 ± 10	495 ± 9	464 ±13	
DU3	A	75.9 ± 3.6	72.2 ± 2.8	73.5 ± 2.2	74.3 ± 1.5
	B	74.9 ± 3.0	76.0 ± 3.5	73.4 ± 3.8	
DU4	A	1402 ± 15	1348 ± 13	1343 ± 12	1348 ± 31
	B	1333 ± 15	1306 ± 19	1353 ± 24	
DU5	A	282 ± 6	304 ± 7	305 ± 6	296 ± 9
	B	287 ± 7	294 ± 7	301 ± 6	

Quoted uncertainties correspond to *k* =2.

Liquid scintillation counting

The mean concentration ^{222}Rn activity for several cocktails (UG LLT, UG AB and OptiPhase Hisafe 3) and the same vial (PET) were determined:

Code Sample	Vial	PET & UGLLT	PET & UGAB	PET & OPH3	C_0 (Bq/l)
DU6	A	29.1 ± 3.6	27.5 ± 2.7	22.9 ± 2.7	26.7 ± 2.1
	B	26.9 ± 4.0	26.6 ± 3.6	27.4 ± 3.0	
DU7	A	234 ± 7	231 ± 7	238 ± 9	233.4 ± 3.4
	B	232 ± 10	236 ± 9	229 ± 8	
DU8	A	21.3 ± 3.2	17.5 ± 1.9	21.3 ± 3.9	20.1 ± 1.9
	B	20.4 ± 2.1	22.0 ± 1.7	18.1 ± 1.5	
DU9	A	< MDA	< MDA	< MDA	< MDA
	B	< MDA	< MDA	< MDA	

Quoted uncertainties correspond to *k* =2.
MDA: Minimum Detectable Activity.

Sample volume, efficiency, counting time and MDA for several ^{222}Rn determination techniques in this work

	Method	Detector Type	In–situ measur.	Sample volume (l)	Effic (%)	Count. time (s)	MDA (Bq/l)
	Degassing method	Alpha Guard	Yes	0.5	100	600	**0.5**
	Gamma spectrometry	HPGe detector	No	1.75	2	7200	**3**
	Liquid scintillation counting	Quantulus 1220	No	0.008	300	600	**0.5**

The limit of detection recommended by the E-DWD for Radon measurements is 10 Bq/l

^{222}Rn activity concentration (Bq/l) with different methods

Sample code	Degassing method	Gamma spectrometry	Liquid Scintillation counting
DU1	49.9 ± 2.5	43.2 ± 2.4	42.0 ± 2.7
DU2	420 ± 11	504 ± 8	467 ± 26
DU3	71.9 ± 1.5	70.5 ± 2.8	74.3 ± 1.5
DU4	1379 ± 19	1338 ± 24	1348 ± 31
DU5	290 ± 2	310 ± 5	296 ± 9
DU6	27.3 ± 0.7	28.1 ± 1.8	26.7 ± 2.1
DU7	246 ± 4	230 ± 2	233.4 ± 3.4
DU8	12.8 ± 0.3	23.0 ± 2.2	20.1 ± 1.9
DU9	N.D.*	3.4 ± 1.2	< MDA

Quoted uncertainties correspond to *k* =2.

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Hints and Tips

General comments

- ✓ The performance of the three methods used in this work is adequate for radon activity measurements in drinking water. All the methods of analysis used are capable of measuring activity concentrations of radon with a limit of detection above 10 Bq/l, as recommended by the E-DWD.
- ✓ All of these techniques present advantages and drawbacks. Therefore, whichever of these techniques may be chosen for radon measuring: either on-site systems for radon-in-water analysis, or laboratory measurement techniques such as LSC or gamma spectrometry.
- ✓ The chosen technique will depend on the laboratory capabilities or customer demands.

Advantages and drawbacks of each technique

- ✓ Field-based measurements of radon in water allow modifying the sampling strategy in almost real-time instead of having to wait for laboratory results.
- ✓ The advantage of LSC technique for radon in water measurements is that it allows processing a large number of samples with simple sampling procedure and low water volumes. Furthermore, the use of automatic sample changers permits the counting of numerous samples in a short time.
- ✓ Gamma spectrometry presents a reduced counting efficiency and consequently, the water volumes to be counted are large. The advantage of gamma counting is in the common instrumentation employed by environmental radioactivity laboratories.

Recommendations

- ✓ In any case, sampling technique is very important for all the methods as it is necessary to limit contact between air and water to reduce the radon escapes from the sample.
- ✓ Beakers used in Gamma spectrometry in this work present an important radon leakage (2% per day for 1.75 litres Marinelli). Therefore, it is recommended radon leakage correction in radon determination equation. Marinellis of 0.25 litres are discarded for its high radon leakage.
- ✓ Radon leakage from PET and glass vials is very slight, but is significative from PE vials. Therefore, we recommend the use of PET or glass vials for radon determination. In our study, any cocktail may be used: UGLLT, UGAB or OPH3, although UGLLT and UGAB are more quench resistant.

Thank you very much for your attention

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