Radon measurement in karstic waters with Lucas cell technique (*)(**)

J.-P. Morin (1), C. Baixeras (1), L. Gourcy (2), J. Ramoneda (2), A. Freixes (2)
M. Manolopoulou (3), P. Meus (4), J.-L. Seidel (5), J. C. Corbin (6)

(1) *Grup de Física de les Radiacions, UAB - Bellaterra, Spain*
(2) *Junta d'Aigües - Barcelona, Spain*
(3) *Physics Department - Thessaloniki, Greece*
(4) *CNRS, Laboratoire Souterrain - Moulis, France*
(5) *CNRS, Géofluides-Bassins-Eau - Montpellier, France*
(6) *CNR, Istituto di Geocronologia e Geochimica Isotopica - Pisa, Italy*

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Summary. — Based on Lucas cell technique, the portable device named "PRASSI" (SILENA mod. 5S) was used to realise discrete radon measurements in water samples. The calibration factor is (64.7 ± 6.9) cpm$\cdot$Bq^{-1} and, with the present set-up for measuring radon in water, the detection and the determination limits are, respectively, 0.007 and 0.020 Bq. Thus, the device is well adapted for determining low radon content in karstic waters. Several discrete radon samplings were performed nearly every week in the three main springs of the Bastareny karstic system (Catalonian Pyrenees, N-E Spain). Thus, it was possible to estimate the reproducibility of the methodology as well as to characterise every spring of the aquifer in relation to their hydrogeological features. With the portable radon monitor, some useful measurements were achieved to estimate radon loss due to degassing process over short distances, with important consequences for radon studies in karstic waters. Lastly, it was possible to perform intensive sampling during a flood and the results point out the great variability of radon levels, closely related to the flow rate trend. That permitted also an intercomparison with other radon probes installed previously in every spring, for continuous radon measurements.

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1. – Introduction

Among the numerous applications of radon in earth sciences [1], one is being developed especially in the field of hydrogeology. A part of this research is dedicated to

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radioprotection or earthquake predictions, that implies an intensive measurement campaign of groundwater radon contents. Some authors use hydrogeological conceptual models for explaining possible high radon levels in dwellings or in caves [2, 3]. Another research direction is the study of radon as a potential tracer for hydrogeological purposes [4-6]. Recent studies favour continuous radon measurement in the aquifer outlets, that permits a reliable comparison of the radon trend with physical parameters as flow rate, temperature or conductivity [7, 8]. Accurate measurements of radon concentration can be performed thanks to techniques known since long but more available after recent technological progress; they are principally liquid scintillation, ionisation chamber and Lucas cell techniques [9]. This paper presents an application of this last technique to the study of radon levels in the whole of the springs of a Pyrenean karstic system (Catalonia-NE Spain).

2. – The methodology

Water samples were collected in the degassing units directly from the outlet of the springs and whenever it was possible in water without any important turbulence. The degassing units consisted from 250 ml borosillicate bottles supplied with a two-outlet head with two stopcocks and a sintered distributor with porosity 1 (100–160 μm). Just prior to the sampling the unit was evacuated with a hand pump down to about 17–20″ Hg. The vacuum was enough to pull the water in the degassing unit through a tube, even if the sampling point was somewhat lower than the unit itself. A three-way valve inserted between the stopcock and the tube permitted to exhaust the air of the tube and to pull the water up to the connection with the stopcock using the hand pump.

The samples were generally analyzed in the laboratory with the portable radon monitor PRASSI, which is a commercially available monitor manufactured by the Italian Company SILENA ([1]). This monitor is suitable for radon gas continuous or grab sampling measurements with the scintillation cell technique. It consists basically of a 1.83 l cell coated with zinc sulfide activated with silver [ZnS(Ag)] coupled to a low–gain-drift photomultiplier. The sampled air is pre-filtered before reaching the measurement chamber and the sampling flow rate is electronically regulated to compensate for filter clog-up. A computation algorithm allows compensating the counts coming from radon daughters plate-out.

The measurement is performed in a closed loop circuit (fig. 1), which includes the scintillation cell, the pump, the degassing unit and a dehumidification column of drierite ($CaSO_4$). Just prior to the measurement the circuit is washed out from the air with pure nitrogen. The flow rate during the degassing process was $3\,\text{l}\cdot\text{min}^{-1}$, electronically regulated, with duration of 15 min to ensure the total mixing in the circuit. The measurements were carried out after 3 h, to allow equilibrium between radon and its daughters.

Calibration of the above procedure was performed with a calibrated radium-226 solution provided by Amersham. For this purpose, numerous samples were prepared with known radium concentrations in the range (0.5–50) $\text{Bq}\cdot\text{m}^{-3}$. These values reflect the usual radon concentrations found in karstic waters. The calibration factor obtained

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([1]) SILENA, Società per l'Elettronica Avanzata SpA, Via Firenze, 3, I-20063 s/N., Italy.

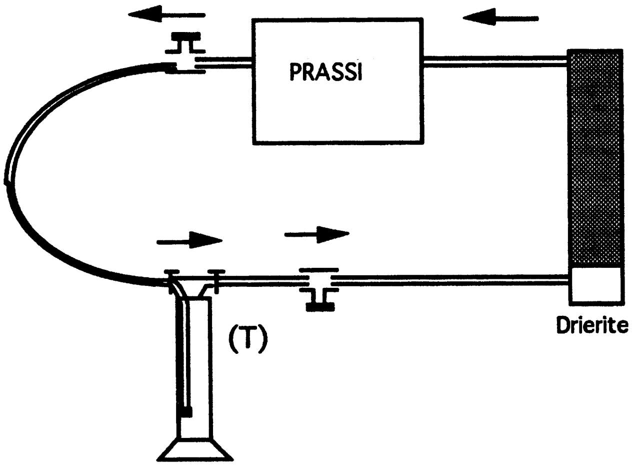

Fig. 1. – Water measurement set-up.

for radon concentration measurements is (64.7 ± 6.9) cpm$\cdot$Bq^{-1}. With the present set-up for measuring radon in water, the detection and the determination limits are, respectively, 0.007 and 0.020 Bq with a mean background count rate equal to (1.17 ± 0.08) cpm [10]. The value of the calibration factor and its associated uncertainty point out that reliable measurements can be achieved in the case of waters with radon levels as low as 0.5 kBq$\cdot$m^{-3}.

The samples were generally carried to the laboratory for analysis. In order to test the radon loss during the transportation procedure duplicate samples were collected and analyzed in the field and in the laboratory, several times. No statistically significant loss of radon could be found during these measurements. Generally, all the samples (4 to 6) are analyzed in less than three days.

3. – Field measurements

The Bastareny karstic system is located in the Cadí-Moixeró Natural Park, in the Southern Catalonian Pyrenean unit, N-E Spain. Three permanent springs drain this aquifer: Adou del Bastareny, Bullidor de Sant Esteve and Violí springs. A permanent small spring, Tortera, is located in the upper part of the catchment area and is related to the epikarst.

The three main springs were equipped with devices for recording, in continuous flow rates, temperature and conductivity. Automatic radon probes based on semi-conductor technique (Clipperton II probes) were also installed for continuous measurement of the gas in every spring.

3˙1. *Normal sampling at Bastareny springs.* – Radon measurements with PRASSI were performed nearly every week in the three main springs of the Bastareny system. Some measurements were also realised in Tortera spring.

Nine complete samplings were performed at each spring. When it was possible, in two of the springs, one pair of samples was collected at the same time to check the

TABLE I. – *Radon concentrations measured with PRASSI at Adou system springs and reproducibility test.*

Spring	Mean Rn (kBq/m^3)	Standard deviation (kBq/m^3)	Reproducibility					
			mean difference %	standars deviation %	maximum difference %	minimum difference %	no. pairs samples	no. pairs < 15%
Violí	7.22	0.85	10.1	8.8	25.8	0.1	8	6
Bullidor	6.02	0.45	6.4	9.0	23.6	1.0	6	5
Adou	4.26	0.51	11.5	—	—	—	1	1
Tortera	21.94	8.52	8.6	5.7	14.0	2.7	3	3

reproducibility of the measurement. The mean radon concentration and the standard deviation as well as the mean difference, its standard deviation, the maximum and minimum difference and the number of sampling pairs are presented in table I. The difference between the results for a given pair of samples ranges between 1.0% and 14.0%, except for three pairs, two in Violí and one in Bullidor springs, due probably to water turbulence effects. In this case, differences between 20% and 26% have been observed.

All the samples were collected during rather stable hydrological conditions (winter-spring 1997). The radon concentration in every spring appeared to be rather constant and it was possible to detect a significant difference of radon content between the three springs (see table I). The Adou spring, the main one of the karstic system, differs clearly from the two others by lower radon contents. Recent studies confirm that this spring is connected to the upper part of the saturated zone of the aquifer, probably rather karstified and is influenced by water supplies from the infiltration zone [11]. So, there must be important exchanges between the water phase and the air phase, at least at the vicinity of the outlet, that favours radon degassing. The higher radon content found in the two other springs can reflect longer residence time of the water in the aquifer, associated with lower flow rates than in Adou spring. Moreover, Bullidor spring has a clear relation with the saturated zone of the aquifer [11], that limits a lot radon loss by degassing process.

The whole of these data is in the range of the radon concentrations given in the literature for karstic waters [3, 12, 13]. Tortera spring was sampled three times and showed clearly much higher radon content. That is probably due not only to the relatively high Ra-226 content (about 50 $\mathrm{Bq \cdot kg^{-1}}$) in the soils at the immediate vicinity of the spring, but also to the diffusive characteristics of the water flows supplying the spring.

Because of technical problems of installation, a Clipperton probe was settled in the stream flowing from Adou spring, 100 m downstream from it. Thus, it was necessary to estimate the difference in radon concentration between the two points. With PRASSI device, it was possible to detect an important radon loss due to degassing process over this short distance. During stable hydrological conditions, this loss remains rather constant; after 9 samplings, it equals $(54 \pm 3)\%$.

At Violi spring, all the electronic devices are set in a deposit located at about 12 m from the real spring. The two points are connected by a small gallery through which the water can flow with more or less turbulence, leading to radon losses. These losses have been estimated with PRASSI protable monitor and are the range (8–28)%.

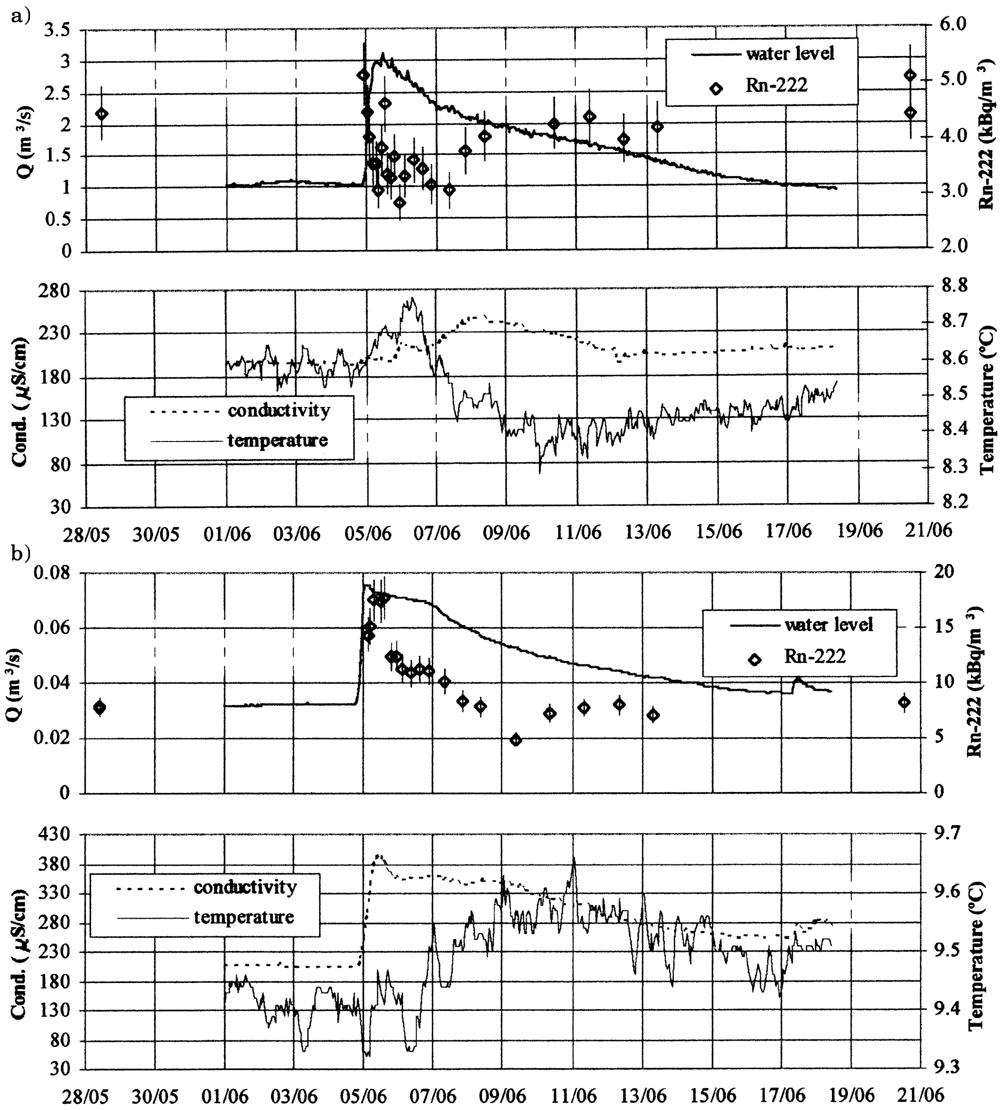

Fig. 2. – a) Comparison between radon concentration and hydrological parameters during the flood at Adou spring (June 1997). b) Comparison between radon concentration and hydrological parameters during the flood at Violi spring (June 1997).

As mentioned in the case of Adou spring, the consequences of these observations on the interpretation of radon measurement in karstic waters could be very important since in the final part of the karstic network, the flow can be also very turbulent, with an important contact between the air phase and the liquid phase.

3·2. *The flood at Bastareny system.* – At the beginning of June 1997 a flood was studied at the springs of Bastareny system. Radon samples were taken every two hours

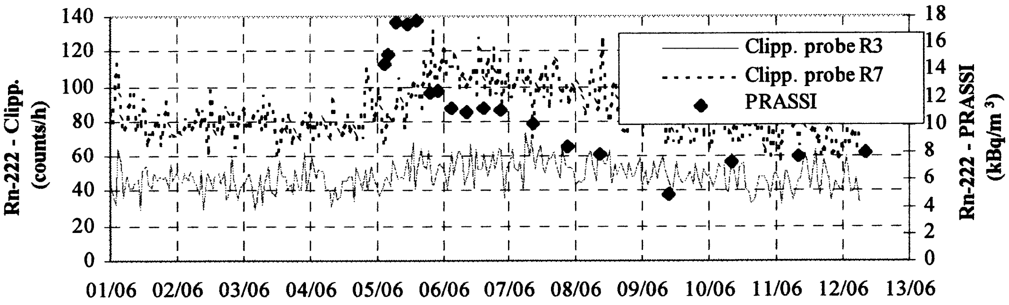

Fig. 3. – Comparison between the radon concentration measured with PRASSI and with Clipperton probes during the flood at Violí spring (June 1997).

the first day and less frequently when the flow rates began to decrease. The PRASSI and the associated equipment could be easily carried to the field, thus, it was possible to start immediately the sample analysis. Figure 2 shows the comparison between the radon trend and the hydrological parameters. The radon concentration is mainly related to the flow rate. In both springs, it increases nearly simultaneously with the discharge. Then, the radon concentration falls off faster than the flow in agreement with other observations [8].

In Violí spring, the radon level rises immediately with the flow rate, by a factor 2 according to the basic level. Afterwards, the concentration decreases very quickly in comparison with the flow discharge, then more slowly until the basic level over about four days. Waters coming from the infiltration zone must leach, at least at the beginning of the flood, the radon-enriched soils. Then, concentration decreases because of a temporary impoverishment of the gas in the infiltration zone which has probably a small extent in the case of Violí spring [11].

The radon trend in Adou spring is not so clear. However, it seems that the radon content begins also to increase immediately as a consequence of a piston effect (fig. 2a), but for reaching a maximum only 15% greater than the basic level. It is probable that radon comes mainly from the materials laid down in the karstified parts of the aquifer, by erosion or by dissolution. Then, in Adou spring, a dilution effect takes place for two days approximately and the concentration is 30% lower than the basic level. It must be noted also that the turbulences in the spring during the flood were very important and the radon losses by degassing effects must be important. Laslty, three days after the maximum flow rate, the radon content goes back to the basic level.

The PRASSI device can be also a very useful tool to intercompare with other types of radon probes. During the flood, intensive sampling with PRASSI makes possible some comparison of the results with that from the Clipperton probes, which record radon levels every hour (fig. 3). In Violí spring, one of the probe does not seem to respond to the important radon input. In return, the other probe records a radon content rise of about 45%, but more delayed in time according to the PRASSI results; the radon decrease is also slower and more regular.

In Adou spring, the radon trend recorded by the Clipperton probe remains more or less constant. But the probe is located 100 m downstream from the spring and it is probable that the degassing phenomena hide the real radon variations at the spring.

4. – Conclusion

The PRASSI device which combines a portable and autonomous radon monitor with a high-precision scintillation cell technique gives a very reliable way to perform radon measurements in karstic waters, generally poor in this gas. Thus, it was possible to determine precisely the basic radon level in every spring of the studied karstic system, that constitutes a good basis for making assumptions about radon origins, in corroboration of the hydrological data. Though it is not possible until now to perform continuous radon measurements with this methodology, the interest of this last one was greatly confirmed during the flood study, thanks to an intensive radon sampling and sample analysis directly in the field. The results point out the great variability of radon levels, closely related to the variability of flow rates. Systematic studies of floods in karstic systems must give useful and precise information about radon origins and about the waters which carry the gas towards the outlets. In this case, comparison of the radon trend not only with the flow rate but also with the conductivity and the temperature is essential.

The results obtained during the flood pointed out the significative differences of the data trends from Clipperton probes and PRASSI monitor.

Finally, this study points out the great importance of the radon degassing phenomena in water. Firstly, it can be a serious problem for measuring accurately radon concentrations in springs with a lot of turbulence. Secondly, the measurements give an idea of the radon loss which can occur inside the karst itself, in particular within its more karstified parts where gas exchanges are very important.

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REFERENCES

[1] MONNIN M. and SEIDEL J. L., *Nucl. Instrum. Methods Phys. Res. A,* **314** (1992) 316.

[2] LEGRAND H. E, *Groundwater*, **25** (1987) 59.

[3] SURBECK H. and MEDICI F., *Int. Ass. Hydrol., Mem.*, **22** (1991).

[4] ANDREWS J. N. and WOOD D. F., *Inst. Min. Metall. Trans., Sect. B*, **81** (1972) 198.

[5] HOEHN E. and VON GUNTEN H. R., *Water Resources Res.*, **25** (1989) 1795.

[6] LAWRENCE E., POETER E. and WANTY R., *J. Hydrol.*, **127** (1991) 367.

[7] SURBECK H. and EISENLOHR L., *Radon as a tracer in hydrogeology; a case study*, in *Gas Geochemistry*, supplement to *Environ. Geochem. Health*, **16** (1995) 91-100.

[8] SURBECK H. and EISENLOHR L., *Radon as a naturel tracer to study transport processes in a karst system, An example in the Swiss Jura, C. R. Acad. Sci. Paris*, **321-IIa** (1995) 761-767.

[9] SURBECK H., *Nucl. Tracks Radiat. Meas.*, **22** (1993) 463.

[10] CURRIE L. A., *Anal. Chem.*, **40** (1968) 586.

[11] FREIXES A., GOURCY L. and RAMONEDA J., *The Bastareny karstic system*, final report of the European project, *A multidisciplinary global approach of groundwaters flows in karstic areas and its consequences for water resources and environment studies* (CHRX - CT94 - 0567), Recursos Hídrics Subterranis i Recerca, Junta d’Aigües de Catalunya (1997).

[12] KOBAL I., VAUPOTIC J., MITIC D., KRISTAN J., ANCIK M., JERANCIC S. and ŠKOFLJANEC M., *Environ. Internat.*, **16** (1990) 141.

[13] HUNYADI I., HAKL J., LÉNÁRT L., GÉCZY G. and CSIGE I., *Nucl. Track Radiat. Meas.*, **15** (1990) 321.