

A Wide Range Monitoring of Drinking Water Natural Radioactivity in Northern Italy

M. Forte*, R. Rusconi, S. Bellinzona, M.T. Cazzaniga and G. Sgorbati

ARPA Lombardia, Dipartimento Provinciale di Milano, via Juvara 22, 20129 Milano, Italy
E-mail: m.forte@arpalombardia.it

Abstract: During the latest years, the Regional Environment Protection Agency (ARPA) has been performing an extensive monitoring of tap waters in the Lombardia district of Italy. Natural radioactivity content was measured to check the compliance with recent European and Italian rules. Analyses were performed by an ultra low level scintillation counter equipped with an alpha-beta discrimination device. Specifically arranged procedures, requiring quick and easy pre-treatments, allowed to measure gross alpha and beta activity, ^{222}Rn , ^{226}Ra and uranium isotopes concentrations in more than 100 samples in a relatively short time. Method performances were carefully tested by both internal validation procedures and international intercomparison exercises.

At first, tap water of the 13 largest towns was examined. Then, 30 sampling points in smaller towns were chosen to take into account the geographical and geological unhomogeneity of Lombardia which is partly a flat and partly a mountainous district. Obtained results showed that in most cases gross alpha activity was lower than 0.1 Bq/kg and gross beta activity was lower than 1 Bq/kg. When these values were exceeded, a more detailed survey was planned. This was the case of Parabiago, a town in western Lombardia. The city of Milano, which is by far the largest one, deserved a special sampling program.

1. Introduction

In recent years, a great interest arose towards the natural radioactivity in drinking water. The European Council Directive 98/83/EC^[1], subsequently enforced in Italian^[2] law, pushed public authorities to organize tap water surveys. Parameter values have been fixed for tritium content (100 mBq/l) and for total indicative dose (0.1 mSv/year): the Directive points out that the total indicative dose must be evaluated excluding tritium, ^{40}K , ^{14}C , radon and its decay products, but including all other natural series radionuclides. Maximum concentration values for radon are separately proposed in a European Commission Recommendation^[3].

Since the calculation of the total dose requires the measurement of all dissolved natural radionuclides, World Health Organization guidelines for drinking water suggested to perform an indirect evaluation of committed dose by measuring alpha and beta gross activity and checking compliance to derived limit values^{[4][5]}. The proposed limit values are 0.1 Bq/l for gross alpha and 1 Bq/l for gross beta activity. Nevertheless, it is desirable to identify single radionuclides contribution to alpha and beta activity in order to perform more accurate evaluations of committed dose.

Liquid scintillation counting coupled to alpha/beta discrimination proved to be a very effective technique for both a quick screening of drinking waters and for single radionuclides determinations if suitable procedures are arranged. Easy and quick procedures are desirable for wide monitoring campaign, as in our case. Thus, a special effort was made in selecting, modifying and testing pre-treatment and measure protocols.

At first Lombardia 13 district largest towns were considered: tap water samples were drained by local ARPA laboratories and analysed for gross alpha and beta activity and for uranium isotopes concentrations^[6]. Lombardia district is geographically unhomogeneous: mountains are in the northern part while the southern part is mainly plain (Pianura Padana); hills are spread in the middle and in the south-western district corner. The district Health Agency (ASL) supported a more extensive monitoring program to take into account the geographical and geological variability of the area: 30 sampling points were chosen in small towns following a uniform geographical distribution principle.

This preliminary screening allowed to single out specific areas with unexpectedly high radioactivity concentration in water. This was the case of Parabiago, a town between Milano and the western border of Lombardia, marked by Ticino river. A deeper investigation was carried out in order to check the extension of the phenomenon and to understand its origin. Other places are currently under investigation, both in south-western part and in the very north area. A detailed sampling was established for Milano as well, which is by far the largest town in Lombardia.

2. Materials and methods

Liquid scintillation counting was performed by a Quantulus 1220 (Perkin Elmer) equipped with an alpha/beta discrimination device and a thermostated counting chamber (16 °C). Teflon coated polyethylene vials Zinsser SLD were always used. Liquid scintillation cocktails Optiphase Hisafe 3 and Optiscint were purchased from Perkin Elmer. For home-made scintillation cocktails, scintillation or spectrophotometric grade reagents were used. High-resolution semiconductor detectors (HPGe) were used for gamma ray analysis; typical values for 1173 keV relative efficiency ranged from 25 % to 35 %. All uncertainties are given as expanded uncertainties (coverage factor $k = 2$).

2.1. Gross alpha and beta

Water samples were acidified, to avoid losses due to precipitations, polymerizations, colloid formations, and preconcentrated by slow evaporation on hot plate. 15 M redistilled nitric acid was added to a 200 g sample up to pH 2,5 and the volume was reduced ten folds by heating: the pH drops to 1,5 and in the same time all the dissolved radon is desorbed. Finally 8 g of the concentrated sample is transferred in the scintillation vial and 12 ml of Optiphase Hisafe 3 (Perkin Elmer) cocktail is added. No quenching effect of nitric acid was observed. Detection efficiency was evaluated by measuring degassed pH 1,5 nitric solutions traced with ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ with activity concentrations similar to those of real samples.

The alpha beta discrimination parameter (PSA) was set by the mean of $^{90}\text{Sr}/^{90}\text{Y}$ standards as beta emitter and uranium isotopes (^{234}U , ^{235}U and ^{238}U) in natural proportions as alpha emitters. Uranium isotopes should be freshly cleaned from beta-emitters daughters by anionic resin separation^[7]. The detailed procedure for sample preparation, efficiency determination and PSA calculation is described elsewhere^[7]. Some authors^[8] suggest the use of ^{241}Am as alpha tracer for the alpha/beta discrimination setting. Nevertheless, since discrimination is energy dependent, the PSA parameter obtainable with americium is considerably different from that recovered from uranium and it may cause relevant alpha spillover when measuring uranium rich samples. The color or chemical quenching influence was found to be not so effective on PSA parameter^[6]. Pulses misclassification due to spillover effects was also considered in the evaluation of uncertainty components.

LSC method was tested by comparing its outcomes with the “thick source” procedure results^{[9] [10]} for 31 bottled and tap water samples and a good agreement was observed. (Fig. 1.).

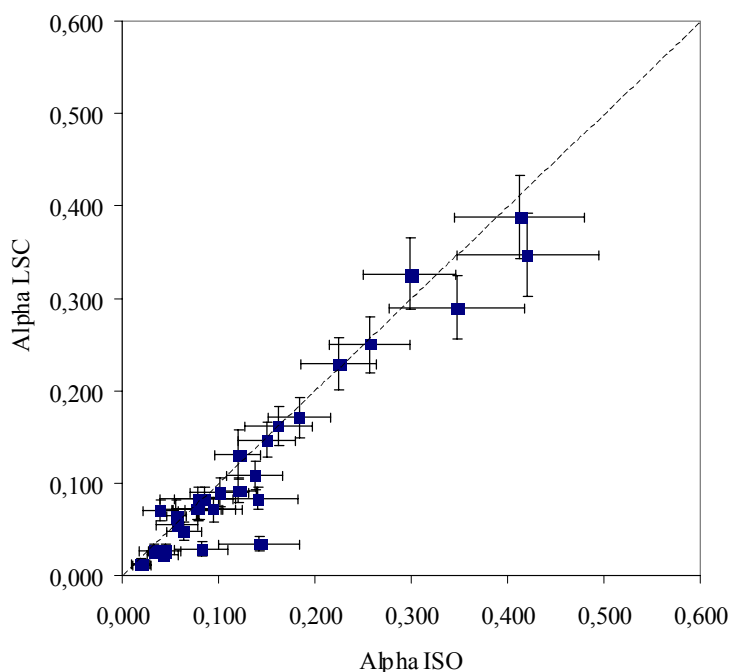


FIG. 1. Comparison of LSC and ISO methods results (activity in Bq/kg)

Natural uranium and $^{90}\text{Sr}/^{90}\text{Y}$ standards were used for the calibration of the “thick source method”, since uranium alpha efficiency is about 30% lower than americium one, due to different sample self-absorption.

The repeatability of liquid scintillation based procedure was tested in a ten fold replication experiment; alpha and beta measurement repeatability, as expressed by values distribution width, resulted to be 9% and 16% respectively. The LSC procedure was used in an international intercomparison exercise with a good agreement (Table I)^[11].

Table I. IRC-CEC intercomparison results

	Gross alpha (Bq/kg)	Gross beta (Bq/kg)
Our laboratory results	0.051 ± 0.010	0.519 ± 0.063
IRC reference values	0.057 ± 0.008	0.520 ± 0.047

2.2. Tritium

Tritium concentration was measured by liquid scintillation counting of the distilled sample^[12] only in Lombardia preliminary screening (3.1.). In all other cases, the evaluation of the gross beta spectrum was considered adequate to check concentrations higher than regulation parameter value (100 Bq/l)^[1]^[2].

2.3. Uranium isotopes

The water sample (1 kg) was acidified with 5 ml of 14 M in order to avoid uranium losses, then slowly evaporated on a hot plate to 100 ml; the final HNO_3 concentration is 0,7 M. The sample was then extracted twice, in a separatory funnel, with two portions of 10 ml each of a water immiscible scintillation cocktail containing bis-2-ethylhexyl-orthophosphoric acid (HDEHP). In the chosen conditions, extraction yields are close to 100%. The procedure was described in previous papers^[7]. Since it is known that dissolved oxygen seriously affects both resolution and α/β discrimination, all samples were degassed after the extraction by sparging them with argon. Samples were counted for 1000 minutes. Uranium measurements were made considering the alpha discriminated spectrum component (channels range 600-800). ^{238}U and ^{234}U content was evaluated applying spectral deconvolution of uranium alpha peaks; Canberra Genie 2k Interactive Peak Fit software was used to this purpose. ^{235}U contribution to total uranium was estimated to be lower than 2.5%, and was neglected when performing alpha spectra deconvolution.

The method was tested by comparison with alpha spectrometry and ICP-MS measurement of selected water samples^[7]. It has been verified, as well, in a interlaboratory study on ‘Determination of radium and uranium radionuclides in water’ promoted by the International Atomic Energy Agency (IAEA) in 2003^[13].

2.4. ^{222}Rn

Radon was measured following the ASTM test method^[14]. Water (abt. 10 g) was sampled by a gas tight syringe and injected in a scintillation vial containing 10 g of a water immiscible scintillation (Optiscint – Perkin Elmer). After a 3 hours rest for the ingrowth of radon daughters, the sample was counted for 60 minutes. The total spectrum (alpha + beta) was considered.

The method was tested by comparing the outcomes with those of emanometric method and gamma spectrometry. The measurement of the national standard of radon in water supplied by the National Agency for Alternative Energy (ENEA) gave good results^[15].

2.5. ^{226}Ra

A 10 g portion of the sample pre-concentrated for gross alpha and beta measurement, was transferred in a scintillation vial with 10 g of Optiscint (Perkin Elmer) scintillation cocktail. The vial was stored for 1 month for ^{222}Rn ingrowth, then shaken and counted for 1000 minutes. Best sensitivities were achieved by using only the alpha component of the spectrum, as alpha background contribution is lower and less variable than the full spectrum one (alpha + beta). The method was tested in the above mentioned IAEA interlaboratory study^[13].

3. Results

3.1. Lombardia district preliminary screening

Results of the gross alpha/beta and uranium screening performed on the 13 largest towns of Lombardia are shown in Table II. Tritium activity was always lower than 100 Bq/kg, as expected, so it is not reported. Lowest alpha and beta activity values were found in southern Lombardia (Pavia, Cremona, Mantova), in the valley of Po river while Milano and surrounding area exhibited highest radioactivity concentrations. In all cases the gross alpha activity was equal to the total uranium activity within experimental uncertainties.

The extended monitoring campaign (30 small towns) has been just completed and its results will be soon published in ARPA Lombardia website (www.arpalombardia.it).

Table II. Results of the tap waters screening in Lombardia district

Town	Gross α (mBq/kg)	Gross β (mBq/kg)	U total (mBq/kg)	^{234}U (mBq/kg)	^{238}U (mBq/kg)
Parabiago	349 ± 41	273 ± 48	372 ± 41	211 ± 24	161 ± 18
Lodi	94 ± 16	239 ± 45	110 ± 12	59 ± 7	52 ± 6
Milano	91 ± 16	118 ± 37	105 ± 12	59 ± 7	46 ± 6
Monza	78 ± 14	132 ± 38	97 ± 11	50 ± 6	47 ± 6
Sondrio	55 ± 12	140 ± 38	55 ± 6	30 ± 4	26 ± 4
Lecco	36 ± 11	136 ± 38	38 ± 4	20 ± 3	18 ± 3
Brescia	27 ± 10	81 ± 35	43 ± 5	25 ± 3	18 ± 3
Bergamo	23 ± 10	< 25	25 ± 3	14 ± 2	11 ± 2
Varese	20 ± 10	88 ± 35	21 ± 3	11 ± 2	10 ± 2
Como	< 8	81 ± 35	4.7 ± 0.8	3 ± 1	1.6 ± 1.0
Pavia	< 8	78 ± 35	0.6 ± 0.4	< 0.4	< 0.4
Cremona	< 8	65 ± 34	< 0.4	< 0.4	< 0.4
Mantova	< 8	88 ± 35	< 0.4	< 0.4	< 0.4

3.2. The monitoring of Parabiago water

The aqueduct of Parabiago town is fed by only 7 wells, so a single well sampling could be carried out. Moreover, 13 wells were chosen in the surrounding zone. In the whole area, wells draw water from three different layers. Water from the first layer is not suitable for human consumption, nevertheless we chose wells fed by each layer for a better knowledge of the aquifer.

For each sample gross alpha and beta activity, uranium isotopes, ^{226}Ra and ^{222}Rn concentrations were determined together with chemical and chemical-physical parameters (pH, conductivity, dry residue, cations and anions concentrations etc.); geological and hydrogeological information were evaluated as well.

Results are fully reported in the ARPA Lombardia website. 7 samples over 20 exhibit a gross alpha activity higher than 100 mBq/kg and 2 of them exceed 300 mBq/kg. The alpha activity is mostly due to uranium isotopes. In all samples ^{226}Ra concentration is lower than the minimum detectable activity (7 mBq/kg). Radon concentration is close to the expected one for centre-southern Lombardia (10 Bq/kg). A statistical treatment on both chemical and radiometric parameters made by principal components analysis (PCA) allowed to group parameters into 2 main classes with relevant internal correlation:

- Component 1: Well depth, $^{234}\text{U}/^{238}\text{U}$ ratio, pH, dry residue, anions, cations
- Component 2: Gross alpha, ^{234}U , ^{238}U , total U

Gross beta and radon lies in other two separate classes. Total activity seem not to be correlated with chemical features of water while uranium isotopes ratio could be a good marker of the water layer. Higher uranium activities were found in the second layer waters and, as geographic position is considered, activities grow going westward. In Fig. 2 total uranium activities are plotted versus the Gauss-Boaga X coordinates.

A survey of geological features of the area can offer a possible explanation of obtained results^[16]. The earlier Ticino river took origin from uranium rich gneiss and granite rocks. It ran more eastward than nowadays and crossed the present Parabiago area. Sediments of paleo-Ticino river lies now at a depth roughly corresponding to the second water bearing stratum. Thus, the second water layer should be markedly uranium rich.

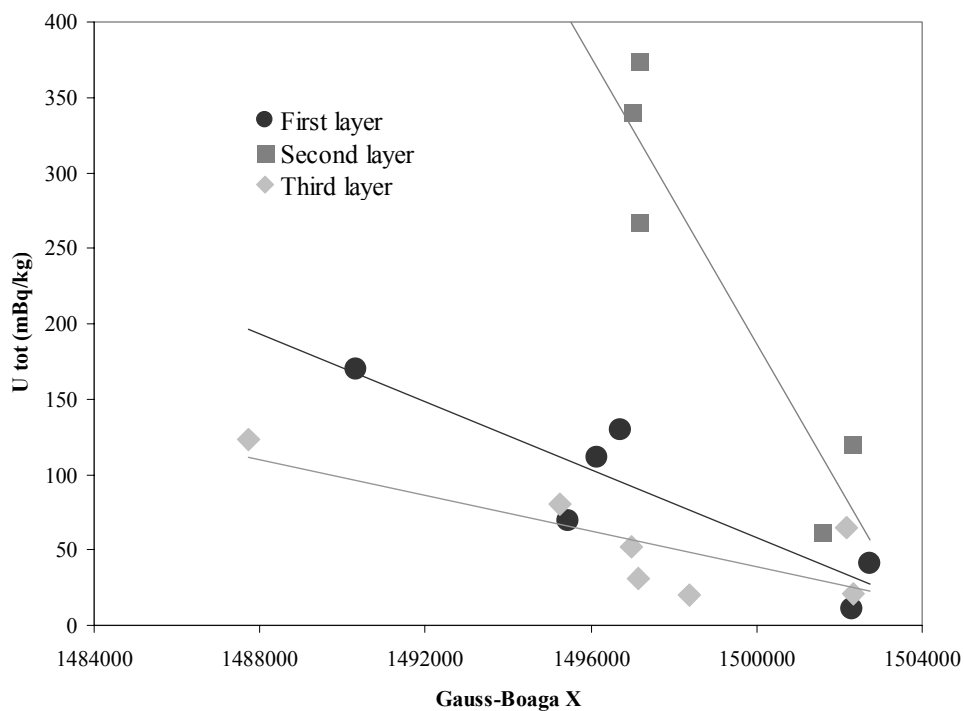


FIG. 2. Parabiago area: total uranium activity variation in eastward direction

3.3. The monitoring of Milano water

More than 500 wells, connected with 31 distribution stations supply Milano aqueduct, so a different sampling strategy was adopted. In order to ensure the representativeness of the investigation, we divided the town area in 31 square meshes 2.4 km large and, in each of them, we selected a public drinking fountain as sampling point. Gross alpha/beta activities, uranium and radium concentrations were measured..

Approximately 60% of samples exhibited a gross alpha activity higher than WHO reference level (100

mBq/kg. Gross beta activities were lower than the method sensitivity limit (60 mBq/kg) in 28 cases over 31 and never exceeded the WHO reference level (1 Bq/kg)^[8, 9].

Concentrations of ²²²Rn range between 0.3 and 12.8 Bq/kg with an average concentration of 6.8 Bq/kg. Lowest values were found close to distribution stations provided with water purification devices (active charcoals, aeration plants).

The first Milano mapping showed a wide variability of natural radioactivity in tap waters; as an example, gross alpha activity spatial distribution is shown in Fig. 3. As in above reported results, alpha activity is mostly due to uranium isotopes.

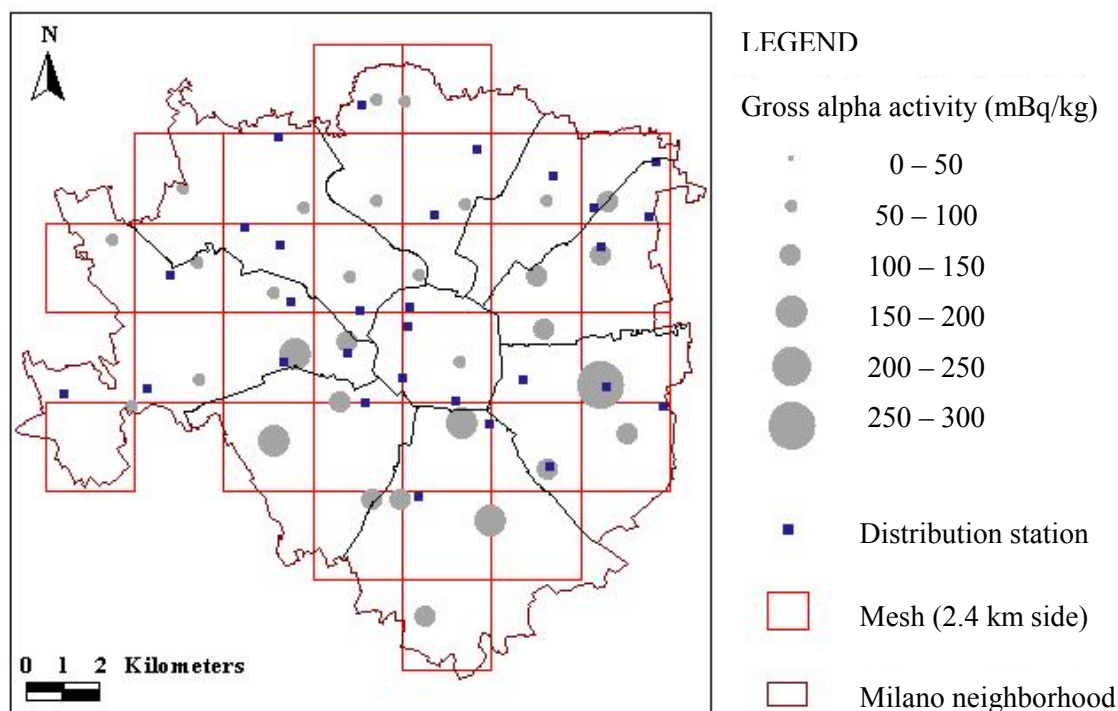


FIG. 3. Gross alpha activity in Milano drinking fountains

4. Conclusions

Liquid scintillation counting has proven to be a versatile and accurate tool for radiometric investigations. Gross alpha and beta, radon, tritium, uranium and radium isotopes activity can be measured with quick and simple procedures; reduced equipment requirements and relative readiness of radiochemical procedures make LSC an attractive technique which can be applied also by laboratories lacking specific radiochemistry facilities and experience.

With regard to the natural radionuclides content of waters, preliminary results on Lombardia tap waters showed the existence of critical areas where gross alpha activity content exceeds WHO proposed values. High values are usually due to uranium isotopes and the indicative dose reference value of 0.1 mSv/y proposed by Council Directive 98/83/EC was never exceeded. Nevertheless, previous works^[17] pointed out, in specific areas, a relevant dose contribution is due to radium isotopes, whose radiotoxicity is higher than those of uranium isotopes. A more detailed monitoring program in the whole Lombardia area was carried out in order to improve the knowledge of the radiometric characteristics of drinking waters.

Tap water of the town of Parabiago exhibits the highest uranium concentrations in Lombardia district. A detailed investigation showed that the second layer water is the most radioactive one. Statistical analysis of data did not highlight out any relation between chemical and radiological parameters, nevertheless a geological survey of the area offered some possible explanations.

The first Milano mapping showed a wide variability of natural radioactivity in tap waters. In particular, a single point sampling proved not to be fully representative of the whole urban area. When

large aqueducts, supplied by many wells, are considered, the spatial variability of the radioactivity content could be a critical factor and wider sampling programmes should be applied.

References

1. European Union, *Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption*, Official Journal L 330, 05/12/1998.
2. Decreto Legislativo 2 febbraio 2001, n. 31 *Attuazione della direttiva 98/83/CE relativa alle acque destinate al consumo umano*, Supplemento ordinario alla G.U. n. 52, 3 marzo 2001 (in Italian).
3. European Union, *Commission Recommendation of 20 December 2001 on the protection of the public against exposures to radon in drinking water supplies*, 2001/928/Euratom.
4. World Health Organization, *Guidelines for drinking-water quality - Vol 1: Recommendations*, Geneva (1993).
5. World Health Organization, *Guidelines for drinking-water quality - Vol 2: Health criteria and other supporting information*, Geneva (1996).
6. Forte, M., Rusconi, R., Bellinzona, S., and Sgorbati, G., *Natural radionuclides monitoring in Lombardia drinking water by liquid scintillation technique*. Proceedings of European IRPA Congress, Florence, October 2002.
7. Forte, M., Rusconi, R., Di Caprio, E., Bellinzona, S. and Sgorbati, G., *Natural radionuclides measurements in Lombardia drinking water by liquid scintillation counting*, Proceedings of 9th Symposium on Environmental Radiochemical Analysis. Maidstone (GB), September 2002.
8. Sanchez-Cabeza J.A. and Pujol L., *A rapid method for the simultaneous determination of gross alpha and beta activities in water sample using a low background liquid scintillation counter*, Health Physics 68 (5): 674-682 (1995).
9. International Organization for Standardization, *Measurement of gross alpha activity in non saline water. Thick source method*, ISO 9696 (1992).
10. International Organization for Standardization, *Measurement of gross beta activity in non saline water*, ISO 9697 (1992).
11. IRC-CEC, *Report of intercomparison concerning the measurement of the gross alpha, gross beta, tritium activities and potassium concentration in a drinking water sample* (2002).
12. International Organization for Standardization, *Water quality: Determination of tritium activity concentration – Liquid scintillation counting method*, ISO 9698 (1989).
13. International Atomic Energy Agency, *Interlaboratory study: determination of radium and uranium radionuclides in water*, IAEA (2003).
14. American Society for Testing and Materials, *Standard test method for radon in drinking water*, ASTM D 5072 (1998).
15. Forte, M., Rusconi, R., Abbate, G., Badalamenti, P., Bellinzona, S., Cazzaniga, M.T., Maltese, S., Palermo, M. and G. Sgorbati, *Metodi di misura del radon-222 nelle acque di rete: l'esperienza dell'ARPA Lombardia*, Internal Report, ARPA Lombardia (2003) (in Italian).
16. Bini, A., Zuccoli L., *Geologia del sottosuolo della valle Olona tra Malnate e Lonate*, Geologica Insubrica 6/2 (2001) (in Italian).
17. Sgorbati, G., Forte, M., Gianforma, G., Rusconi, R., Margini C., *Rilevazione delle concentrazioni di uranio-238 e radio-226 in acque destinate al consumo umano in Lombardia*, Internal Report, ASL Città di Milano (1998) (in Italian).