IL NUOVO CIMENTO Vol. 34 C, N. 5 Settembre-Ottobre 2011
DOI 10.1393/ncc/i2011-10985-7

Communications: SIF Congress 2010

Tritium measurements in water on Mt. Etna by liquid scintillation counting

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(ricevuto il 31 Dicembre 2010; revisionato il 23 Giugno 2011; approvato il 27 Giugno 2011;

Summary. — Tritium exists rather uniformly in the environment as a result of both natural production by cosmic-ray interaction with the upper layers of the atmosphere and residual fallout from nuclear-weapons tests carried out from 1952 till 1980. Naturally occurring tritium mainly reaches the Earth's surface in the form of precipitation, becoming part of the hydrological cycle. Nowadays, the possibility of measuring the low level of tritium radioactivity gives a chance to use tritium as a natural tracer in water systems. This paper presents results from a first survey carried out in the north-west flank of Mt. Etna and in the southern side of Nebrodi, in order to validate a procedure developed for the determination of tritium activity concentrations in water samples by liquid scintillation counting. The investigated areas show low tritium concentrations, much below the Italian limit of 100 Bq/ℓ for drinking water and even comparable with the minimum detectable activity value. The effective dose due to tritium consumption is also calculated.

PACS `92.40.qc` – Surface water quality.
PACS `92.40.kc` – Ground water quality.

1. – Introduction

Tritium (^{3}H, T), the radioactive isotope of hydrogen, decays into ^{3}He by beta decay and releases 18.6 keV of energy in the process, distributed between electron and antineutrino. Tritium has a relatively short half-life (12.33 years) and is both naturally occurring and manufactured.

Natural tritium, in particular, is continuously formed in the highest layers of the atmosphere by interaction of thermal neutrons, produced by primary cosmic radiation, with atoms of atmospheric nitrogen and is present in the environment at trace levels as

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(*) E-mail: `roberto.catalano@ct.infn.it` the outcome of the competition between formation and radioactive decay. The mean production rate is estimated to be around 0.25 atoms $\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$ [1], two thirds of it takes place in the stratosphere and one third in the troposphere.

About 99% of natural tritium oxidizes into water (tritiated water, HTO) and comes to the Earth's surface in the form of precipitation and atmospheric moisture, becoming part of the hydrological cycle. Thus, in general, measurements of tritium activity concentration in natural waters (precipitation, surface or ground waters) can be used as a very successful tool in hydrology and tritium can also be regarded as one of the most important natural tracers in ecologic, climatologic and meteorological investigations. Due to its characteristics, for example, tritium is useful for tracing groundwater movements in young hydrological systems and for determining the groundwater ages [2]. Tritium activity concentration is generally measured and recorded in tritium units (TU), where one tritium unit represents the ratio of one atom of tritium to 10^{18} atoms of ordinary hydrogen, corresponding to a concentration in water of 0.119 Bq/ℓ [3].

It is important to underline that, however, the largest amount of tritium activity in the atmosphere and in the whole hydrological cycle is of antropogenic origin, formed since 1952 by nuclear-weapon tests in the atmosphere. Concentrations up to about 6000 TU in precipitation on the northern hemisphere were observed between 1960 and 1963 [4]. After the Nuclear Test-ban Treaty, these levels decreased steadily to present values of about 5–10 TU [5], thanks to the relatively short half-life of tritium.

Fortunately, due to the low energy and the low range in the biological tissues of β-particles emitted by tritium decay, this isotope is potentially dangerous only if inhaled (HT) or ingested (HTO). When tritium is distributed through the organism, either as HTO or incorporated into biological molecules, its decay will result in internal irradiation which may cause several biological effects [6-8].

The low energy of the emitted β-particles makes their detection extremely difficult, so a very sensitive technique is needed. In this regard, liquid scintillation counting is the most commonly used technique for low-energy beta emitters.

In this paper, we report the results of a preliminary survey carried out, in the north-west flank of Mt. Etna and in the southern side of Nebrodi, to test the methodology for determining the activity concentration of tritium in water. The obtained activity values were also used to calculate the effective doses for inhabitants assuming water consumption of 2 ℓ per day (730 ℓ/year). The results were compared with the national recommendation limit of 100 Bq/ℓ for tritium activity concentration in drinking water [9].

2. – Material and methods

2˙1. *Sampling*. – The investigation area is Mt. Etna (reaching an altitude of about 3320 m a.s.l.), a typical strato-volcano, with diameter of about 40 km, located in eastern Sicily. In particular, the sampling was carried out in the north-west flank of Mt. Etna and in the southern side of Nebrodi (fig. 1).

The many lythologic types present in the Etna area show remarkable differences in permeability. Volcanic rocks, in fact, have generally a high permeability ($2.5 \cdot 10^{-7}$ to $2.9 \cdot 10^{-6}\,\mathrm{cm}^2$ [10, 11]), whereas the permeability of the sediments of Etna's basement is much lower (mean value of $10^{-10}\,\mathrm{cm}^2$ [12]). Such a large permeability range, together with the remarkable amount of water and snow precipitations characterizing the area, implies that the Mt. Etna volcano is also an important reservoir of groundwater (about $0.7\,\mathrm{km}^3$ of water available per year [13]). A considerable part of this volume of water is currently used for drinking by the local population. The circulation of groundwater

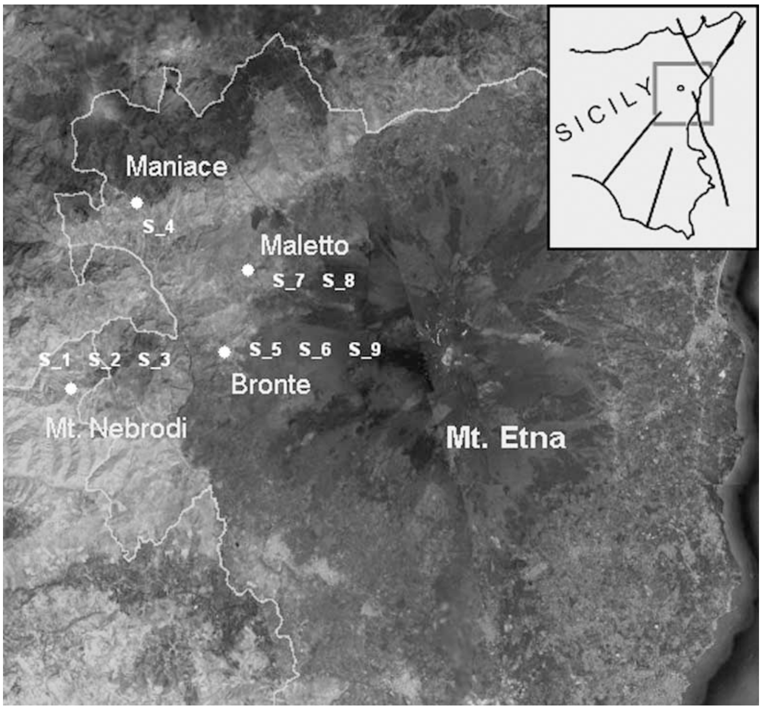

Fig. 1. – Investigated area and sampling sites.

inside Mt. Etna is strongly influenced by the morphology of the sedimentary basement of the volcano. In fact, most of the water that falls on the soil as rain or snow percolates through the permeable volcanic rocks and, once reached the impermeable basement, it moves along radial directions towards the outer boundaries of the volcanic edifice.

Otherwise, the Nebrodi Mountains represent the central sector of the Sicilian northern belt (reaching an altitude of 1817 m a.s.l.). They run from the Peloritani on the eastern part of Sicily to the foothill of the Madonie Mountains to the west, facing the Tyrrhenian Sea on the north, and are separated from Mt. Etna by the rivers Alcantara and Simeto. The Nebrodi belt is characterized by a considerable morphological and geological heterogeneity, including metamorphic terrains, flyschoid formations [14], clay rocks, arenites and limestones [15]. In terms of water distribution, the countryside is characterized by perennial lacustrine basins and springs, torrents and seasonal ponds, that form important hydrological systems. Nevertheless, the water circulation is generally very limited and the Nebrodi Mts. are acknowledged as a region with scarce water potential [16].

Different samples were collected, in July 2009, from nine sites in the north-west flank of Mt. Etna and in the southern side of Nebrodi as shown in fig. 1.

The sampling was carried out according to ISO 5667-1 and ISO 5667-2 [17, 18]. Each sample was collected in 1 ℓ borosilicate glass bottle, previously covered with black tape to avoid direct exposure to the sunlight, and kept at a constant temperature of 4 °C to minimize evaporation. During the sampling physical-chemical parameters of the investigated waters, *i.e.* total dissolved solids (TDS), pH, conductibility and temperature, were determined. The obtained values are reported in table I.

TABLE I. – *Physical-chemical properties of the investigated water samples and their description (MPS stands for Municipal Power Supplies).*

Sample code		Sample description	pH	T (°C)	Conductibility (mS)	TDS (mg/ℓ)
S_1	Sorgente Canalotto (Nebrodi)	Drinking water, used mainly for irrigation	7.25	11.0	0.63 (16.6 °C)	305
S_2	Sorgente Malacosta (Nebrodi)	Not distributed, drinking water at the intake	7.66	10.5	0.80 (16.5 °C)	384
S_3	Sorgente Sambuchello (Nebrodi)	Not distributed, drinking water at the intake	7.67	10.0	0.42 (16.5 °C)	200
S_4	“Biveri” - Maniace (Nebrodi)	MPS, local distribution only Maniace city	7.71	13.0	1.68 (16.7 °C)	825
S_5	Saragoddio - Bronte	MPS, local distribution only Bronte city	7.74	14.5	2.51 (16.9 °C)	1250
S_6	Contrada Cimitero - Bronte	MPS, not drinking water	7.87	14.5	2.53 (16.7 °C)	1260
S_7	Poggio Monaco - Maletto	MPS, local distribution only Maletto city	8.02	13.0	1.05 (16.4 °C)	510
S_8	Pozzo Avellina - Pietralonga	Private intake, used also for irrigation	7.53	12.5	2.59 (17.3 °C)	1290
S_9	Casa Orefice – Bronte	Private intake, drinking water	7.80	13.5	2.17 (16.7 °C)	968

2˙2. *Sample preparation.* – The sample preparation was performed according to the International Standard ISO 9698:1989(E) *Water quality - Determination of tritium activity concentration - Liquid scintillation counting method*, prepared by the Technical Committee ISO/TC 147, Water quality. This International Standard specifies a method for the determination of HTO activity concentration in water and is applicable, in general, to all types of water with tritium concentrations up to $10^6\,\mathrm{Bq\,m^{-3}}$.

For each sample $250\,\mathrm{m}\ell$ of water were collected. For each about 250 mg of sodium thiosulfate anhydrous ($Na_2S_2O_3$) to convert iodine into iodide, and about 500 mg of sodium carbonate anhydrous (Na_2CO_3) to make the sample alkaline, and some glass beads were added to prevent bumping. Afterwards, the samples were distilled by means of an apparatus consisting of a round bottom flask of capacity $500\,\mathrm{m}\ell$, a Vigreux distillation column, an adapter (bent type) and a condenser. After discarding the first 50–$75\,\mathrm{m}\ell$ of distillate, about $100\,\mathrm{m}\ell$ were collected in polyethylene bottles. With this procedure there was no significant isotopic fractionation in the distillation.

For each water sample a part of the distillate was mixed with a scintillation solution (sect. **2**˙3) in a counting vial. Under optimal counting conditions, the scintillation solution (ULTIMA Gold$^{\mathrm{TM}}$ uLLT from Perkin Elmer, Inc.) can incorporate up to about 40% of water, corresponding to a volume of $8\,\mathrm{m}\ell$ for ordinary counting vials of $20\,\mathrm{m}\ell$. In order to minimize the diffusion of organic solvents through the walls teflon-coated polyethylene vials were used, that give a lower background counting rate than glass vials [19].

The minimum detectable activity (sect. **2**˙5) was determined using a blank sample obtained by deep underground water with tritium activity concentration as low as possible and maintaining the proportion 8:12 with the scintillation solution in the counting vial.

2˙3. *Measurement methodology.* – Liquid scintillation counting today is the most sensitive and widely used technique for the detection and quantification of low-level radioactivity.

As already mentioned above, the radioactive sample to be measured is dissolved into a scintillation cocktail, *i.e.* a mixture of an organic solvent, an emulsifier which ensures proper mixing of aqueous samples in the organic solvent and a fluorescing substance. The light produced from the excitation of the cocktail by the charged particles is directed to photomultiplier tubes, which then convert the light into a measurable electrical pulse, proportional to the energy of the charged particles. In order to discriminate between true radioactive decay events and the electrical background noise of the multiplier tubes, a coincidence unit allows the measurement of those events occuring simultaneously at both photomultiplier tubes. The pulses from the photomultiplier tubes are analyzed, converted to digital and stored in a multichannel analyzer, according to the particle energy.

2˙4. *Quenching corrections.* – In general, the *quenching* effect, due to anything added to a counting vial, can reduce the efficiency of the scintillation process so the measured counts per minute (CPM) may differ significantly from the true radioactive decay rate (disintegrations per minute, DPM) [20].

So, preliminarily, *quench curves*, which trade on the relationship between counting efficiency and *quench indicating parameters* (QIPs), were constructed to correct the measured CPM to DPM. This required the use of a quenched series of ten standards, supplied by Perkin Elmer Inc., in which the absolute radioactivity per vial is constant (280200 DPM) and the amount of quenching agent (nitromethane, CH_3NO_2) increases from vial to vial over the range of 0–$66\,\mu\ell$ per $20\,\mathrm{m}\ell$ of scintillating cocktail.

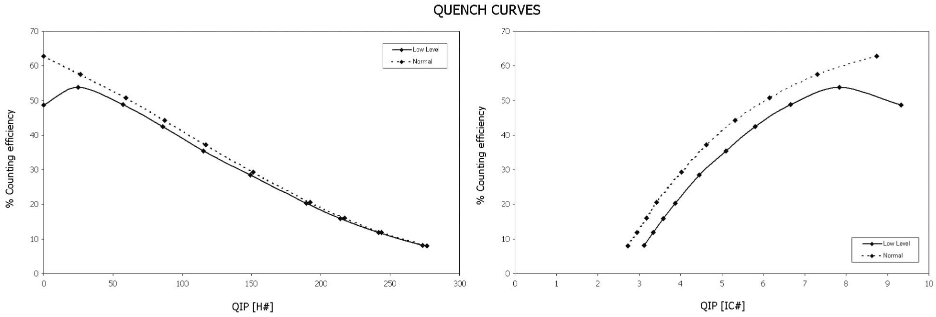

Fig. 2. – Quench correction curves for tritium based on the quench indicating parameters H# (left picture) and IC# (right picture). Dashed curves are their respective "low level".

In particular, in order to asses quench levels we applied two different methods to determine the QIP, both by using tritium spectrum analysis, based on the changes in spectral shape caused by quenching.

The first method uses the IC# parameter, which is a sample activity quench monitor and is defined as [21]

$$\mathrm{IC\#} = \frac{\sum_{i=L}^{U} i N_i}{\sum_{i=L}^{U} N_i}\,,$$

where N_i is the number of counts in the i-th channel and L and U are the lowest and uppermost limits, respectively, of the sample pulse height spectrum.

The second method uses the H# quench parameter, the so-called "external standard" method, based on the analysis of a specific region of the Compton spectrum generated by γ-rays emitted by a ^{137}Cs source near the scintillation vial. The H-parameter is the difference in the spectrum between the inflection point of the unquenched standard and of the sample. For each correction a *low-level* quench curve was obtained by reducing of 50% the background counts caused by cosmic-ray interaction with glass in the counting chamber of the liquid scintillation counter (LSC).

The obtained quench curves for tritium, using both IC# and H# parameters as QIP, are shown in fig. 2 as a function of the counting efficiency (%). The low-level quench curves follow the same pattern of their respective "normal" ones, although at an efficiency of about 54% they show a maximum and begin gradually to move away from them. It is important to underline that, however, they always remain below the "normal" quench curve, providing a higher value of DPM for a given QIP.

In order to obtain reliable concentration values, we chose to refer to the low-level quench curve, since we expected both low tritium activity and low counting efficiency for unknown water samples, and used H# parameter as QIP because it ensures a better accuracy (an average discrepancy of only 0.39% from the expected value for known samples).

2˙5. *LSC setup.* – For the determination of tritium activity concentration we used a Beckman Coulter LS6500 liquid scintillation counter. The LSC system calibration was performed with a set of radioactive sources consisting of two unquenched ^{3}H and ^{14}C (both beta emitters) standards and was repeated once a month during the entire period of measurements.

In order to reach a better sensitivity, recording only counts due to tritium in the sample, we identified three well-defined regions of beta particles spectrum corresponding to three intervals of energy: A (0–18.6 keV) enclosing the whole spectrum, B (0.4–4.5 keV) which only considers the peak, C (0–14.5 keV) which takes into account the *spill over* with ^{14}C occurring for energies close to $E_{\max}$. The optimum "counting window" selection was based on the signal-to-background ratio, expressed as the square of the detection efficiency divided by the background (E^2/B) and termed figure of merit (FOM). By averaging on four unquenched standards, the best FOM was obtained for the counting window C, with an efficiency of 63.48% and mean background of 19.13 counts per minute.

The minimum detectable activity (MDA), which expresses the detection sensitivity for the tritium analysis method, was determined in the optimal window and with a counting time of 12 hours (also used for unknown samples) by [22]

$$\mathrm{MDA} = \frac{4.65 \cdot u_{CB} + 2.71}{\varepsilon \cdot T \cdot V} \cdot 1000,$$

where u_{CB} is the count uncertainty in blank sample, ε is the counting efficiency (expressed as a decimal), T is the counting time in seconds and V is the volume of blank sample in mℓ. The obtained MDA was 3.40 Bq/ℓ.

3. – Results and discussion

The International Standard ISO 9698 suggests to count the vial series during repeated short counting times in order to provide a better control of stability of the samples. Nevertheless, since we expected to detect very few counts, we opted for one long counting time to improve statistics and to lower the detection limit. Anyhow, before counting we left the vials in the liquid scintillation counter overnight to adapt to temperature and to reduce the residual luminescence while counting.

In order to promptly identify possible system malfunctioning or any problem arising from used chemical substances (*e.g.*, scintillation cocktail) that could affect the accuracy of the measurements, the counts distribution was routinely checked by means of a χ^2 test.

Since most of the investigated water samples were drinking water (see table I), directly taken from the intakes or distributed into homes through water supply systems, effective doses due to tritium consumption were also extracted. We considered that people consume 2 ℓ of water per day, as estimated by the World Health Organization and Environmental Protection Agency [23], corresponding to 730 ℓ per year and assuming a dose conversion factor of $1.8 \cdot 10^{-11}$ Sv/Bq [24].

The results of tritium activity concentrations in the investigated water samples are shown in table II, together with their respective effective doses due to tritium consumption.

As expected tritium activity concentrations are quite low if compared to the National recommendation of 100 Bq/ℓ for drinking water and, in particular, three samples show values less than MDA. These concentration values are also lower than those observed in other surveys carried out in some regions of Italy [25, 26], but higher than those obtained in a previous investigation on Mt. Etna both in rainwater and groundwater samples [27]. The evaluated effective radiation doses from tritium vary from 4.57 to $6.06 \cdot 10^{-8}$ Sv/year.

Moreover, it is interesting to emphasize that by comparing tritium levels measured in the north-west flank of Mt. Etna and in the southern side of Nebrodi, these values

Table II. – *Activity concentrations of tritium in Bq/ℓ and TU and extracted effective doses due to tritium consumption in Sv/y (NC stands for Not Calculated).*

Sample code	Tritium concentrations		Effective doses(Sv/Bq)
	(Bq/ℓ)	TU	
S_1	3.48 ± 1.16	29.2 ± 9.7	$4.57 \cdot 10^{-8}$
S_2	< MDA	< MDA	NC
S_3	3.96 ± 2.17	33.3 ± 18.2	$5.20 \cdot 10^{-8}$
S_4	4.05 ± 0.94	34.0 ± 7.9	$5.32 \cdot 10^{-8}$
S_5	4.61 ± 1.27	38.7 ± 10.7	$6.06 \cdot 10^{-8}$
S_6	< MDA	< MDA	NC
S_7	3.87 ± 1.46	32.5 ± 12.3	$5.09 \cdot 10^{-8}$
S_8	< MDA	< MDA	NC
S_9	4.61 ± 1.89	38.7 ± 15.9	$6.06 \cdot 10^{-8}$

result comparable with each other within experimental errors, showing that they are likely independent from the local geolithological situation.

4. – Conclusions

We report on the experimental procedure to determine tritium activity concentrations in water samples using a low background liquid scintillation system. Particular care was taken in the chemical preparation of samples, in the quenching corrections, as well as in the optimization of the counting methodology in order to reach a better sensitivity. To validate the adopted procedures, we carried out a first survey of natural radioactivity due to tritium on the basis of water samples collected from nine sites in the north-west flank of Mt. Etna and in the northern side of Nebrodi.

All water samples showed tritium activities lower than the Italian limit of 100 Bq/ℓ for drinking water and even comparable with the value of MDA (3.40 Bq/ℓ), which expresses the detection sensitivity. Hence, the analyzed waters may be classified as low-tritium waters, with activity concentrations up to 4.61 ± 1.89 Bq/ℓ. From the activity concentration values the effective radiation doses, due to tritium ingestion with drinking water (4.57–$6.06 \cdot 10^{-8}$ Sv/year) were also extracted, assuming an annual consumption of 730 ℓ for adults.

Furthermore, the concentrations of tritium in water, as resulted from the present work, seem not so related to local geology. The extension of the survey to the whole volcanic edifice of Mt. Etna could allow in future to confirm this result and/or to establish possible correlations with other local parameters.

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Special thanks to the other authors of this work: Prof. Giuseppina Immè, Dr. Daniela Morelli and Dr. Anna Brogna.

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