

Tritium activity levels in environmental water samples from different origins

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Abstract

Tritium activity was determined in environmental waters from different areas of Catalonia, using a distillation procedure before liquid scintillation counting. The developed method was validated by analysing two samples from proficiency tests.

In most of water samples (from rivers, rain, mineral bottled waters and tap waters) analysed, the activity values were lower or close to the minimum detectable activity (MDA) for our method which has a value of 0.6 Bq/l. However, the Ebro river samples had a mean activity around 3.6 ± 0.6 Bq/l. The nuclear power station of Ascó, which is located on the banks of this river, can be a source of tritium production and introduction into the environment, so a more exhaustive study of these waters was carried out. Tritium activities in this river were a long way above the normative limit in Spain for waters intended for human consumption, which is 100 Bq/l.

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1. Introduction

Tritium is a radioactive isotope that emits low-energy beta particles, with a maximum energy of 18.6 keV, and with a half live of 12.6 years (UNSCEAR, 1982). It is found in nature and it can also be produced by human activities. The natural origin is associated to the interaction of cosmic rays with the atmosphere. However, the environmental levels of this radionuclide were enhanced between 1945 and 1963 during nuclear weapon tests. Nowadays tritium is also produced in nuclear reactors that provide electricity, mainly of the pressurised water reactors type (PWR), as a by-product of the fission of uranium, which is a significant source of tritium in the environment (Pujol, 1996).

Tritium shows only slight differences in the chemical and physical characteristics in comparison with ^1H ; for this reason, it can replace hydrogen atoms in water. When it is taken into living tissues, it can metabolise, resulting in

organically bound tritium. Consequently, it is important to evaluate its radioactive impact in environmental samples, and in particular those that are for human consumption. The health criteria applicable to waters used for human consumption in Spain were published in 2003 in decree no. 140/2003, which established the maximum allowed values for some radioactive parameters. The maximum stipulated for tritium activity was 100 Bq/l (Real Decreto 140/2003).

Liquid scintillation counting (LSC) is the most commonly used technique for measuring low-energy beta emitters. However, it suffers from an effect known as quenching, which reduces the efficiency of detection. To overcome this problem pretreatment step is usually applied to the sample to remove the interferences which can affect the counting step. One of the pretreatments often used is a distillation process (Hisamatsu et al., 1989; Baeza et al., 2002). Another pretreatment process is electrolytic enrichment which can be used with or without a previous distillation step. This procedure also decreases detection limits, but is more laborious than distillation (Villa and Manjón, 2004; Schäfer et al., 2000; Gröning and Rozanski, 2003).

In this study we have developed a method that uses a distillation process as the pretreatment step and then

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measures the tritium activity with a Wallac Quantulus 1220, an ultra-low-level liquid scintillation system, in an attempt to determine this hydrogen isotope at environmental levels activities lower than 10 times the maximum allowed tritium activity for drinking water in Spain (100 Bq/l). The parameters affecting the performance of the detection (scintillation liquid, sample volume, vial material and counting time) were optimised in order to get the maximum counting efficiency and the lowest detection limits.

The method developed was validated by participating in two proficiency tests. One then was organised by Environmental Resource Associates (ERA) from the United States, and the other by the Consejo de Seguridad Nuclear (Nuclear Safety Council) (CSN) from Spain. Finally, the performance of the method was investigated by analysing water samples from different environmental origins: rain, bottle, tap, well and river. The samples from the Ebro river were taken from several sampling points upstream and downstream of where the nuclear power plant is located so its possible influence on the activity levels of tritium could be studied. This is of special importance since the water from the Ebro river is destined for human consumption after it has been treated (Real Decreto 140/2003; Hisamatsu et al., 1989; Baeza et al., 2002).

2. Experimental procedure

2.1. Standards, reagents and materials

A calibrated solution of ^3H provided by CIEMAT from Madrid, Spain, with a nominal activity concentration of 10.00 ± 0.09 Bq/mg, was used to determine the tritium detection efficiency.

In order to validate the method, we analysed two samples provided by certified institutions. Both were water samples with a known activity concentration of tritium established by the reference laboratory. One of the samples was provided by ERA from USA with a certified activity of 90.28 ± 9.03 Bq/l. The other one was provided by the CSN from Spain, with an activity of 10.13 ± 1.21 Bq/l. In both cases, three aliquots of the original samples were analysed.

In the distillation process, KMnO_4 (99.0–100.5%) and NaOH (98%), both supplied by J.T. Baker from Deben-ture, Holland, were used. After distillation, 8 ml of the sample was introduced into a 20 ml polyethylene scintillation vial supplied by Sarstedt from Nümbrecht, Germany, with 12 ml of the liquid scintillation cocktail (Optiphase Hifase™ 3) supplied by Wallac from Turku, Finland.

2.2. Instrumentation

Tritium was determined by ultra-low-level LSC in a Quantulus 1220™ from Turku, Finland. This spectrometer is specifically designed for determining very low activities. The detector has a multi-channel analyser (MCA) that separates tritium signals in the sample from those produced

by chemiluminescence in two different spectra. The window for tritium was set between 60 and 250 channels. The counting was performed for 2 cycles of 500 min and the tritium activity was calculated by averaging the results.

2.3. Procedure

Samples were distilled before they were measured by LSC to remove any impurities, to reduce quenching and to prevent the introduction of other radionuclides which might adulterate the results. Distillation was performed by adding 0.1 g of KMnO_4 and 1 g of NaOH to a volume of 100 ml of the water samples. An aliquot of 8 ml from the second 10 ml fraction of the distillate was placed in a 20 ml polyethylene scintillation vial, and mixed with 12 ml of Optiphase Hifase™ 3 scintillator cocktail.

All the samples, before the distillation, were passed through a 45 μm internal diameter Whatman filter (Maidstone, England) to remove suspension material.

2.4. Samples

Different types of water samples were analysed. Tap water was taken directly from the public water supply of Tarragona, in the south of Catalonia (Spain). The mineral bottled water samples selected were some of the most commonly produced and consumed bottled waters in Catalonia and they were all purchased from local supermarkets in the area of Tarragona. Other samples were from wells and other sources. Rainwater samples were also analysed and they were collected in Tarragona, during the period of the investigation.

River waters were also analysed. Ter, Llobregat and Noguera Pallaresa river water samples (Spain) were provided by other laboratories. In the case of the Ebro river, samples were taken from different points along the river (see Fig. 1) in an area near to a nuclear power station, Ascó. Samples were taken in different months: October 2005 and February 2006. Water samples were collected using a 2-l polyethylene bottle and were then taken to the laboratory.

2.5. Calibration

Calibration was performed monthly and basically consisted of determining the detector efficiency and background for tritium. Detector efficiency was evaluated by measuring a tritiated water standard of known activity (100 Bq/l) prepared by a certificate standard supplied by CIEMAT, Madrid, Spain. As a blank sample mineral bottled water (Font Vella) was used.

The yield of the distillation was measured monthly with two different tritium standards. One of them was prepared by distilling a water sample of known tritium activity and the other one was prepared by adding the same tritium activity but without the distillation stage. The distillation yield was calculated by measuring both samples by LSC.



Fig. 1. Sampling points on the Ebro river selected for this study. The sampling points correspond to: (1) Riba-Roja d'Ebre, (2) Flix, (3) Vinebre, (4) Móra la Nova, (5) Miravet and (6) Tortosa. Point (A) is the nuclear power station of Ascó. (CR) is the sampling point in Camp Redó, which is where the average samples were taken in 2005 and (TP) is the sampling point of the treatment plant in L'Ampolla.

2.6. Expressions

The minimum detectable activity (MDA) is usually used to discriminate a measurement from the background. MDA was evaluated using the following expression (Curie, 1968):

$$MDA \text{ (Bq/l)} = \frac{3.29 \cdot \sqrt{cpm_{bk}/t_{bk} + cpm_{bk}/t_s}}{60 \cdot \varepsilon \cdot V \cdot R_d},$$

where the parameters used are: cpm_{bk} is the net count rate of the background sample, t_{bk} and t_s are the background (1000 min) and sample (500 min) counting time, respectively, the V is the volume of the sample contained in the counting vial in litres, ε is the counting efficiency and R_d is the distillation yield.

The used expression to determine the efficiency of counting is as follows:

$$\varepsilon = \frac{cpm_{st} - cpm_{bk}}{60 \cdot A_{st}}.$$

The detection efficiency depends on the counts per minute of the blank (cpm_{bk}), the counts per minute of the tritium standard (cpm_{st}) and the activity of the standard (A_{st}).

The sample activity is obtained by the following expression:

$$A \text{ (Bq/l)} = \frac{cpm_s - cpm_{bk}}{60 \cdot \varepsilon \cdot R_d \cdot V},$$

where cpm_s is the net count rate of the analysed sample.

The uncertainty is evaluated using a confidence level of 95% ($K = 2$) using the following expression:

$$\sigma \text{ (Bq/l)} = \frac{2}{60 \cdot \varepsilon \cdot V \cdot R_d} \cdot \sqrt{\frac{cpm_s}{t_s} + \frac{cpm_{bk}}{t_{bk}}}.$$

3. Results and discussion

3.1. Optimisation process

The determination of tritium activity in environmental samples can be affected by different parameters. In the first

stage of this study, we optimised the parameters that directly affected the radioactive counting so that the detection was as efficient as possible, and then we optimised the pretreatment of the sample (distillation).

3.1.1. Parameters affecting LSC

First, the various parameters that affected the LSC efficiency and background were optimised. Some of the parameters we checked were the influence of the vial material, the scintillation cocktail and the ratio between the volume of the sample and the scintillator cocktail. The reagents used in the distillation and measurements did not present any tritium content.

3.1.1.1. Liquid scintillation cocktail. The first parameter evaluated was the scintillation cocktail. The influence of the cocktail on the efficiency of detection was investigated. To do so, we used a standard sample of tritium of known activity and a scintillator. Several commercially available scintillation cocktails have been used for tritium determination (Vallés, 1994; Pujol, 1996). We compared two of the most common ones: Instagel (Packard) and Optiphase Hisafe™ 3 (Wallac).

To achieve maximum counting efficiency, it is of vital importance that the mixture between the scintillation cocktail and the sample be stable and homogeneous. Table 1 shows the results obtained in the study for different sample–cocktail ratios for the two scintillators evaluated. For higher sample volumes (11 and 12 ml), a white mixture was obtained for both cocktails. When Instagel was used, and the sample volume decreased, a precipitate was formed and some samples turned white, which can cause quenching effects and decrease the efficiency. Instagel also contains the solvent pseudocumene which can give rise to problems of diffusion and permeability with the conventional vials if the counting time is long. For Optiphase Hisafe™ 3 the solvent is diisopropyl naphthalene (DIN), which does not have any of the problems reported with the previous cocktail. Optiphase Hisafe™ 3 is more soluble in the sample, hardly diffuses on the walls of the vials used and is not very toxic. For all these reasons it was the cocktail selected in this study. The results agree with the

bibliography, because several studies recommend that this scintillator be used (Kaiholo, 1993).

The next step was to optimise the ratio between the sample and the scintillation liquid volumes. This parameter was optimised to obtain the lowest value possible for the MDA. It is extremely important for this value to be low, particularly for the analysis of environmental samples, which present very low tritium contents. The MDA decreases as the water volume increases and results were best with a volume ratio of 8:12 (sample:scintillation cocktail). This ratio provides the lowest MDA value for tritium, around 0.6–2.6 Bq/l, but it should be pointed out that these values depend on the counting time (180–1000 min). Our results agree with those reported by other authors, who also used the above-mentioned ratio. For them, the MDA values were 1.2–2.2 Bq/l (Thomson, 2005).

Blank samples: The next step was to study which was the best sample to be used as the blank so that we could define the background of the detector. This selection can be very difficult since the tritium content of environmental waters can depend on their exposure and origin. For a suitable blank to be selected, it is necessary to find water that has received no tritium for a period of time equivalent to more than 10 of its half lives (12.6 years). This water can be obtained, for example, from petroliferous wells. Because of the difficulty in getting this type of water, we considered analysing a variety of commercial mineral bottled waters and using the one that had the lowest tritium content as the blank sample. Table 2 shows the activity values of some of the bottled water analysed. As can be observed, the activities for some of the samples were below the MDA (0.6 Bq/l) and similar to those reported in the bibliography (Pujol, 1996; Vallés, 1994). We finally chose Font Vella water, since it was easily obtainable and it is also one of the most consumed mineral waters in the area under study.

Vials: We tested how the material of the vial that held the sample–scintillator mixture affected the background of the counting. We evaluated two types of materials: polyethylene covered with Teflon and high-density polyethylene. Other common materials such as glass with a low potassium content and Teflon were discarded, on the basis of previous results reported in the literature (Pujol, 1996).

Table 1
Comparison of the performance of Instagel and Optiphase Hisafe 3 for different volume ratios of sample and liquid scintillation cocktail

Sample volume	Instagel	Optiphase Hisafe 3
12 ml	White transparent	White opaque
11 ml	White transparent	White opaque
10 ml	Optimum	White opaque
9 ml	Optimum but after stabilisation time converts to solid	Optimum
8 ml	Solid	Optimum
7 ml	Solid	Optimum

Table 2
Specific tritium activities (in Bq/l) obtained for bottled mineral waters used for selecting the blank

Samples	Specific tritium activity (Bq/l)
Viladrau (Montseny, Girona)	<0.6
Font Vella (St. Hil. Iari de Sacalm, Girona)	<0.6
Cardó (Benifallet, Tarragona)	<0.6
Ribes (Ribes de Freser, Girona)	0.9 ± 0.4
Font d'Or (St. Hil. Iari de Sacalm, Girona)	<0.6
Auchan (St. Hil. Iari de Sacalm, Girona)	0.7 ± 0.4
Montseny (St. Esteve de Palautordera, Barcelona)	0.9 ± 0.5

The uncertainty is calculated using a confidence level of 95% ($K = 2$).

Blank samples were prepared with Font Vella mineral water. The results obtained for each vial were compared. For the polyethylene covered with Teflon vials the average value was 0.31 counts per minute (cpm) and for the high-density polyethylene it was 0.30 cpm. We selected the high-density polyethylene vials for further analyses, since they are less expensive than polyethylene covered with Teflon, and the MDA obtained were very similar (approximately 0.6–0.7 Bq/l) in both cases.

Counting time: The counting time required to measure the activity of the samples was also evaluated. The MDA value is affected by this parameter as can be observed through the corresponding formula which is in algorithms section. We can observe in this formula how this parameter influences the value and the uncertainty because an increase in the counting time decreases the other parameters. In environmental samples, tritium activity is usually very low, so the best option is to select long measurement times so that MDA values are as low as possible.

This study covers activities that range from 5.26 to 105.12 Bq/l, and the periods of time used for the LSC measurement ranged from 90 to 1000 min. The counting time selected will depend on the type of sample that has to be analysed and on the desirable MDA values. We selected a counting time of 500 min for which the MDA value was 0.6 Bq/l. Pujol and Sánchez-Cabeza (2000) used a shorter counting time (360 min) but the MDA values were higher (2.6 Bq/l). As one of the main objectives of our study was to analyse environmental waters, we selected a longer time.

Detection efficiency: Efficiency was determined by measuring 8 ml of tritium standard of 100 Bq/l (specific tritium activity 0.8 Bq, A_{st}) and a blank and using the expression in Section 2.6. After the blank and the standard have been measured, the efficiency obtained oscillates around 27%, and the successive calibrations show no significant differences. This value agrees with other values reported in the bibliography.

3.1.2. Distillation process

In the analysis of tritium activity some substances in the sample can produce luminescence and quenching that interfere in the transfer of the energy between the scintillation cocktail and the sample.

To prevent luminescence in the vial that contains the sample, it is recommended to store the sample for a minimum of 24 h in the dark before it is measured. To eliminate the quenching, it is usually necessary to introduce a pretreatment step before the LSC, which removes the radioactive non-volatile interfering substances and other possible volatile organic substances that interfere in the transfer of energy. The most commonly used pretreatment stage is a distillation process (ASTM D 4107-98, 2002; Kaihola, 2000; UNE 73350-3, 2003).

To determine the optimum conditions for the distillation process, we prepared a tritium standard of 20 Bq/l in 100 ml of Font Vella water and then we used the procedure

previously described in the experimental section to proceed with the distillation. We studied which was the most suitable fraction of the distilled water to be measured by LSC. We collected 10 ml fractions after distillation and then 8 ml of each one was placed in a vial containing 12 ml of Optiphase Hisafe™ 3. Fig. 2 shows the tritium activity of each 8 ml fraction of distilled water. The first fraction gave a lower tritium activity value, whereas the values of the other fractions were similar. In the different sample fractions obtained after the distillation process, the obtained quench parameter (SPQ(E)) was very similar so no differences were observed. So from this point it should be pointed out that any of the fractions (except the first one, which gave lower activity values) could be a good selection to measure the tritium activity. Therefore, we selected the second fraction of the distillate to measure tritium activity, because the bibliography recommends that neither the first ones nor the last ones be used since they contain more impurities (ASTM D 4107-98, 2002; Kaihola, 2000; UNE 73350-3, 2003).

The distillation recovery was also evaluated by comparing the results of measuring 100 Bq/l tritium standards. Ten of them were prepared with distilled Font Vella bottled water (10 ml), of which 8 ml was measured directly in the liquid scintillation detector. The other 10 standards were prepared with Font Vella bottled water (100 ml) and then distilled. Then 8 ml of the second 10 ml fraction of distillate was measured. All the standards were counted for 500 min. The results enabled the activity (Bq/l) for each standard (distilled and directly measured) to be determined. The distillation yield in % was calculated from the relationship between the activity obtained for the distilled and directly measured standards. The results showed that the recuperation was practically 100% in all cases.

3.2. Validation

To validate the method developed, we analysed samples distributed by two official institutions: ERA and CSN. They organised interlaboratory studies to determine the

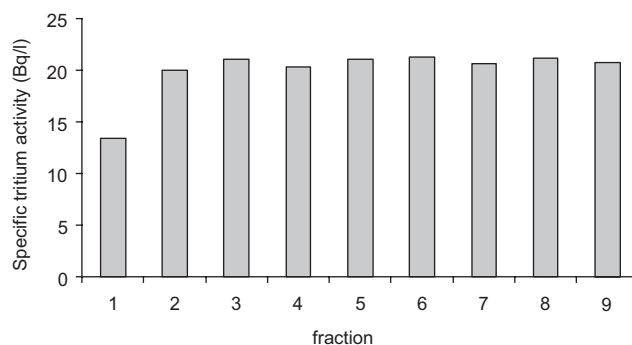


Fig. 2. Specific tritium activities measured in successive 10 ml fractions after distillation of 100 ml standard tritium of 20 Bq/l prepared in Font Vella bottled water.

radioactivity parameters in water samples, one of which was the tritium content.

CSN used the *Z*-score test to evaluate the results provided by the various laboratories that took part in the exercise. This test evaluates the experimental result, the certified result and the uncertainty associated with the latter in such a way that if *Z* is above 3, the laboratory has not applied a suitable analytical procedure, and if *Z* is below 2, it has.

ERA intercomparison establishes warning and control limits in accordance with the USEPA's guidelines, so that both intercomparison exercises could be compared through the same parameter; our laboratory also applied the *Z*-score test in this exercise from ERA.

The sample from ERA was tritiated water with a tritium activity of 90.28 ± 9.03 Bq/l, and the sample from CSN was water spiked with tritium and alpha and beta radionuclides, with a tritium activity of 10.13 ± 1.21 Bq/l. Three aliquots of each sample were analysed by the method developed. Table 3 shows the results and the corresponding associated uncertainty.

The value of the parameter *Z* in both cases was below 2, which indicates that the method developed provides satisfactory results. So the optimised method was validated.

3.3. Application to real samples

The validated method was applied to the analysis of real samples, in an attempt to verify the tritium activity in waters from different environmental origins (rivers or rain) or waters intended for human consumption (tap or bottled mineral water).

In the case of samples from the Ebro river, we selected several sampling points along the river so that we could study the possible radioactive impact of the nuclear power plant of Ascó which is located on its banks.

3.3.1. Rain water

The International Atomic Energy Agency (IAEA), with the cooperation of the World-wide Meteorological Organisation, established a world-wide network of stations to collect precipitation samples monthly, and to determine their isotopic composition. Tritium can be formed naturally (in the high atmosphere) or artificially (thermonuclear or industrial tests). Then the tritium oxidises (HTO) and enters the water cycle. Tritium distribution in precipitation

depends on latitude, proximity to the sea and distances from artificial sources or thermonuclear test zones. These factors and its radioactive decay mean that tritium can be used to determine how long water has been present in aquifers (OIEA-RLA/8/031, 2001; Dapeña and Panarello, 2004).

The precipitation samples were collected several times during the study in the city of Tarragona. For all these samples, the tritium activity found was lower than the MDA (0.6 Bq/l). Dapeña and Panarello (2004) found tritium activities between 0.08 and 2.09 Bq/l in the rain-water of Buenos Aires.

3.3.2. Springs and wells

Atmospheric precipitations can deposit tritium in superficial waters. The tritiated water deposited on the ground can filter through to internal layers. The extent of this infiltration depends on such factors as the type and permeability of the ground, water content, organic matter, etc. Therefore, different tritium levels are found in different waters. To study the tritium content of this kind of samples, we analysed waters from different wells and springs in Catalonia. As expected, the tritium activity of most of the samples was below MDA, meaning that they are not directly exposed to a direct contribution of this isotope. The tritium activity of the rest of the samples was between 0.7 and 1.2 Bq/l, which is very close to the MDA. The results confirmed that the underground waters and sources analysed receive a low tritium contribution (with activities below our MDA, 0.6 Bq/l) from the outside or human activities.

3.3.3. Mineral water and tap water

Spanish legislation (law decree no. 140/2003) regulates the parameters that drinking waters must comply with if they are to be considered as suitable for human consumption. These parameters include restrictions on radioactivity. Tritium activity is limited to a maximum of 100 Bq/l. Radioactive parameters are excluded from the regulation governing the quality of bottled mineral waters so they are only affected by the geology of their source aquifer (Real Decreto 1744/2003).

To determine tritium levels in waters intended for human consumption, we selected several samples from Catalonia: some were bottled mineral water and the rest were from different water treatment plants.

Table 3

Certified values and obtained tritium activity values in the intercomparison exercises organised by ERA and CSN

Intercomparison exercise	Obtained values (Bq/l)	Certified values (Bq/l)	<i>Z</i>
ERA (Environmental Resource Associates)	90.3 ± 0.9	90.3 ± 9.0	0.0
CSN (Consejo de Seguridad Nuclear)	10.8 ± 0.7	10.1 ± 1.2	0.5

The uncertainty is calculated using a confidence level of 95% ($K = 2$).

Most of the bottled water samples analysed had tritium activity values lower than the MDA (0.6 Bq/l). The rest presented activity values above the MDA, in the range 0.7–0.9 Bq/l. However, these values are a long way from the established legal limit (100 Bq/l). These results agree with previously reported results in the literature (Vallés, 1994).

Tap-water samples from different water treatment plants in Catalonia were analysed. In particular, these samples were taken once a month throughout 2005 from plants located in the area of the rivers Ter, Llobregat and Ebro. These rivers provide most of the water for purposes of consumption in Catalonia. The results are shown in Fig. 3. Tritium activity levels were higher in the samples from the Ebro river while the activities of the samples from other rivers were below the MDA. In the case of the Ebro river the average activity was 6.44 ± 0.63 Bq/l. Vallés' thesis obtained activity values between 2 and 18 Bq/l and between 1.6 and 2.1 Bq/l in tap-water samples from the Ebro and Llobregat–Ter rivers, respectively, in the period 1990–1993. The higher tritium activity in samples from the Ebro may be due to the nuclear power station located on the banks of this river. As reported, nuclear power plants are one of the main sources of the artificial production of tritium and in order to determine whether this kind of industry affects tritium levels, we analysed water samples from this river, and compared the activities for other rivers that did not have a nuclear plant along their course. This study is discussed below. However, it should be pointed out that the levels found are a long way from the maximum for tritium permitted by current legislation (Real Decreto 140/2003).

3.3.4. River water

Several rivers in Catalonia that were not affected by the presence of a nuclear power plant were selected and their tritium levels determined. These rivers were the Ter, Llobregat and Noguera Pallaresa. We compared the tritium activity of these rivers with the activity of the Ebro, on the banks of which the nuclear power plant of Ascó is located. Fig. 4 shows the results of this study as the average values of the 1-year period (2005). The results of the three rivers not affected by the presence of a nuclear

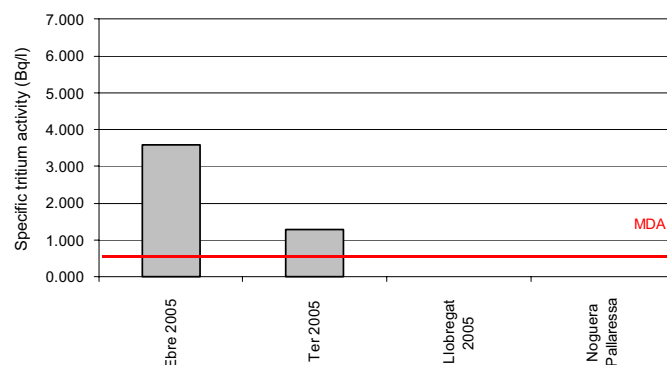


Fig. 4. Average tritium activity from different rivers of the region of Catalonia obtained during 2005.

power station are also shown in this figure and it can be seen that the activity of the Ter was slightly above the MDA, whereas activities of the other rivers were below this value. The average activity of the Ebro was 3.60 ± 0.56 Bq/l. In this case, it should be pointed out that the sample was taken at the point marked CR (Camp Redó) in Fig. 1, which is a long way from the nuclear power plant but, even so, the tritium level was higher than that of the other rivers. So, the nuclear power station may be a source of artificial tritium along the course of this river. However, it should be pointed out that the value is considerably lower than the one established by the regulations (100 Bq/l). In a previous study, Pujol and Sánchez-Cabeza (1999) found similar or even higher tritium activities (<1.6–23.6 Bq/l) when they analysed tritium levels in the nuclear power plant's zone of influence. All of these studies make it clear that the values depend not only on the sampling point but also on when the sample is taken.

We observed differences between the activities of tap-water samples from the Ebro river (6.44 ± 0.63 Bq/l) and the activities of the Ebro river samples (3.60 ± 0.56 Bq/l). This may be due to the different sampling points, which are located at different points along the river. Tap-water samples were taken at the exit to a water treatment plant, marked TP (treatment plant) in Fig. 1, and river water samples were taken at point CR in the same figure.

Since the results obtained for the Ebro river were higher than the ones obtained for the other rivers studied, another of our aims was to evaluate the potential radioactive impact of the nuclear power plant on the river. For this reason, we selected 7 different sampling points along the river; some of them were in the area surrounding the nuclear power station while others were in the area near the water treatment plant. Fig. 1 shows the points selected, the points 1 and 2 are upstream the nuclear power plant and the points 3–6 are downstream the nuclear power plant.

The samples were taken in two different months: October 2005 and February 2006. Table 4 shows the results. All the samples presented low tritium activities,

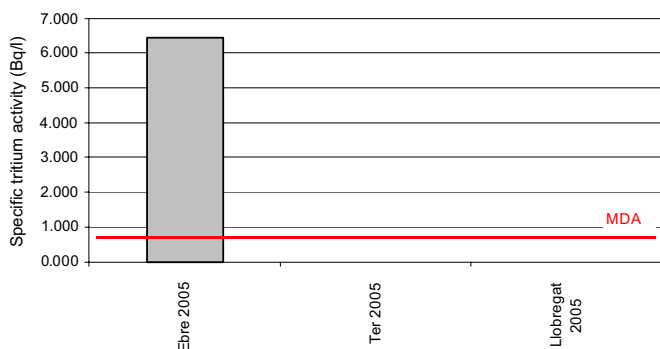


Fig. 3. Average tritium activity of tap water from different treatment plants in Catalonia during 2005.

Table 4

Tritium activity in the Ebro river at different points around the nuclear power station of Ascó in October 2005 and January 2006

	Sampling point	Samples	October (Bq/l)	February (Bq/l)
Upstream nuclear power plant	1	Riba-Roja d'Ebre	0.71 ± 0.48	0.93 ± 0.51
	2	Flix	0.92 ± 0.49	<0.6
Downstream nuclear power plant	3	Vinebre	<0.6	<0.6
	4	Mora d'Ebre	<0.6	0.95 ± 0.51
	5	Miravet	<0.6	1.04 ± 0.52
	6	Tortosa	<0.6	0.86 ± 0.51

The uncertainty is calculated using a confidence level of 95% ($K = 2$).

close to the MDA, between 0.71 and 1.04 Bq/l. These values are a long way from the value of 100 Bq/l established by the legislation (Real Decreto 140/2003). The differences between the tritium contents reported in Fig. 4 and Table 4 can be attributed to the different times at which the samples were taken. In Fig. 4, the values are the averages of a 1-year period (2005), whereas in Table 4 the values are from two different months, as previously reported. The tritium activity values upstream seem to be higher than the tritium activity values downstream to the nuclear power plant. Moreover, taking into account these activities and their uncertainties, and comparing them to the MDA value, we could not conclude there is a difference in the activities upstream and downstream Ebro river.

In the present study, the tritium activity values detected in the Ebro river are similar to those reported by other authors who analyse different Spanish river waters also affected by nuclear installations. Thus, Baeza et al. (2002) found values between 1.4 and 36.5 Bq/l for the Alcántara reservoir and between 0.35 and 8.3 Bq/l for the Guadiloba reservoir. The Tajo river is the main water supplier of these reservoirs, and the relatively high tritium activities can be attributed to the nuclear power plants located upstream of this river: Zorita, Trillo and Almaraz.

4. Conclusions

LSC is a quick method for determining tritium in environmental samples. A distillation step before the radioactive measurement was included to prevent quenching. We validated the method by participating in two different intercomparison exercises organised by ERA and CSN and, in both cases, we found that the results were satisfactory. The MDA was 0.6 Bq/l, which was a suitable value for analysing environmental water samples, 100 times below the normative limit (100 Bq/l) for drinking water.

Our study confirmed that waters analysed have a low tritium content. Most of the samples analysed (rainwater, mineral water, tap water and river water) presented activities lower than the MDA. Some samples mainly those from the Ebro river and the tap water from this river showed higher activities than the rest of the samples analysed (between 0.71 and 6.44 Bq/l), although they were still a long way from the limit established by Spanish

legislation for waters intended for human consumption (100 Bq/l). So it can be concluded that the nuclear station of Ascó does not significantly affect the tritium levels in the river, so this water is appropriate for human consumption after treatment.

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