Journal of Environmental Radioactivity 192 (2018) 143–149

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Monitoring of tritium concentration in Hanoi's precipitation from 2011 to 2016

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ARTICLE INFO

Keywords:
Tritium (^{3}H)
Precipitation
Hanoi
Liquid scintillation analyzer

ABSTRACT

Tritium is a radioisotope of hydrogen and a component of the water molecule. It is a marker for reservoirs such as the stratosphere, troposphere, and oceans involved in the hydrological cycle. Tritium monitoring is an essential research tool in hydro-climate, dating for water and recharge groundwater. The Isotope Hydrology Laboratory has collected monthly precipitation samples in Hanoi for tritium concentration analysis. This paper reports the tritium concentrations in precipitation in the city from 2011 to 2016. The results show that monthly tritium concentration reached a maximum of 7.07 Tritium Units (TU) in August 2011. The mean annual tritium concentration stabilized from 2.03 to 3.36 TU. It suggests that tritium in monitoring station precipitation is predominantly natural. The seasonal variation trend of ^{3}H in precipitation at the Hanoi station is similar to those monitored at the Hong Kong station. The correlation of tritium and rainfall was also estimated.

1. Introduction

Tritium (^{3}H, T) is the radioactive isotope of hydrogen and an emitter of soft beta radiation with 18.6 keV energy. The recently re-evaluated half-life value of tritium equals 4500 ± 8 days corresponding to 12.32 ± 0.02 tropical years (Lucas and Unterweger, 2000). It may be of either natural and human-made origin.

Tritium is naturally produced due to nuclear reactions in the upper atmosphere between atmospheric nitrogen and high-energy cosmic rays. The mean rate of natural tritium production is estimated to be 0.25 atoms $cm^{-3}s^{-1}$, which corresponds to an annual natural production of about 0.20 kg tritium or 7.0×10^{16}Bq (Craig and Lal, 1961; Lebaron-Jacobs et al., 2009). It is estimated that 55% of the natural production of tritium occurs in the stratosphere (Masarik and Beer, 1999). Tritium is rapidly oxidized into tritiated water (HTO) and transferred into the troposphere where it is removed by precipitation (Ehhalt et al., 2000). It comes to the Earth in the form of precipitation and atmospheric moisture and is then transported in the environment through the hydrological cycle.

Tritium is also produced anthropogenically by a variety of nuclear activities. One example was the atmospheric testing of nuclear weapons between 1945 and 1963 which released approximately 650 kg (2.3×10^{20} Bq) of tritium. However, most of the tritium introduced into the environment between 1945 and the late 1960s has disappeared by radioactive decay and dilution in the world oceans (Cauquoin et al., 2015).

Nuclear facilities that release tritium into the environment include pressurized water reactors, irradiated fuel reprocessing and recycling plants and reactors dedicated to tritium production. Tritium in irradiated fuel is mainly retrieved during reprocessing when the fuel is sheared. It is found in the form of tritiated water in liquid effluent most of which is released into the sea (Lebaron-Jacobs et al., 2009).

Tritium is a useful environmental tracer. It is a marker for reservoirs such as the stratosphere, troposphere, and oceans involved in the hydrological systems. It is widely applied as a semi-quantitative tool for the identification of modern recharge, dating, infiltration condition and groundwater balance (Allison and Hughes, 1975; Huang and Pang, 2010; Zhang and Ye, 2011; Yangui et al., 2012). Recently, tritium is increasingly being applied to calibrate and validate three-dimensional groundwater flow and solute transport models of aquifer systems at the regional scale (Povinec et al., 2010; Zuber et al., 2011). Tritium is used for understanding and quantification of the processes determining the flow of water through the soil-plant-atmosphere system. It is, therefore, an essential prerequisite for modeling ^{3}H transfers in terrestrial ecosystems to help improve management of irrigation or water utilization in agriculture (Connan et al., 2015).

Tritium dating of groundwater in the Hanoi region was conducted in the Institute for Nuclear Science and Technology (INST) Isotope Hydrology Laboratory. It has been used to study the hydraulic interaction between Holocene and Pleistocene aquifers in the south of Hanoi. The tritium data have been used to characterize hydrogeological features of groundwater. Several studies on arsenic mobilization in

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https://doi.org/10.1016/j.jenvrad.2018.06.009
Received 20 November 2017; Received in revised form 29 May 2018; Accepted 8 June 2018

groundwater were conducted in the Hanoi region with the use of tritium tracer. Tritium dating could allow for estimating the As mobilization rate from sediment into groundwater (Nhan et al., 2006; Postma et al., 2007; Larsen et al., 2008).

The concentration of tritium activity is commonly expressed as tritium units (TU); one TU corresponds to 0.11919 ± 0.00021 Bq/kg of water (Gröning and Rozanski, 2003). The concentration of tritium in precipitation is monitored by the Global Network of Isotopes in Precipitation (GNIP), and the database is available through the IAEA. In the course of the GNIP activities, monthly precipitation samples were collected from over 1000 stations in more than 125 countries in the past and Hanoi was one of them.

The Hanoi monitoring station has been set up at the Institute for Nuclear Science and Technology since 2003 and has contributed data from 2004 to 2007 to the GNIP. Tritium data obtained from the IAEA database is used to model the global distribution of tritium (Doney et al., 1992; Zhang and Ye, 2011; Cauquoin et al., 2015) and a detailed study of tritium in precipitation over Australia was published by Tadros et al. (2014). Results from previous research have shown that tritium in precipitation has been decreasing toward natural levels, which are less than 10 TU (Cartwright and Morgenstern, 2012; Michel, 2015; Cauquoin et al., 2015; Harms et al., 2016).

This paper presents the concentration of tritium in precipitation in Hanoi collected from 2011 to 2016 ($21^0 04' 53.5''$N, $105^0 79' 86.7''$E) to determine the concentration of tritium in recent times; how this value compares to natural tritium levels; how tritium concentration changes seasonally and how the precipitation amount effects the concentration of tritium. The results provide tritium reference data for future environmental and hydrological studies in Hanoi.

2. Material and methods

Our study included 70 precipitation samples collected between January 2011 and December 2016 in Hanoi. The construction of the precipitation sampling device and the procedure used for rainwater collection were based on sampling procedures for the IAEA's isotope hydrology of water resource program. Precipitation was sampled on a monthly basis and also randomly by event, i.e. as soon as possible after each rain event. Collected samples were poured into 5-liter plastic bottles with tight caps to avoid evaporation. Samples were labeled with codes, dated and kept in a cool, dark place. At the end of the month, all the water from the 5-liter containers was mixed and shaken before refilling it to 500 mL bottles which were then tightly capped for further treatment and measurement of tritium concentration.

As the concentration of tritium in rainwater was expected to be low, in the laboratory, tritium was subject to electrolytic enrichment in order to improve the precision of the beta activity counting. The electrolytic enrichment of tritium in water samples is described in detail elsewhere, e.g. K. Rozanski (2000), Plastino, et al. (2007). The procedure applied is described below.

Tritium activity of the precipitation samples was enriched using an electrolytic enrichment system. It has 20 cells of volume 500 mL and an electrolysis control unit that were supplied by IAEA. The electrolysis occurred in the electrolyzed medium NaOH, at the maximum current of 10A, for a time of 190 h and a total electric charge of 1426 Ah/sample. Prior to enrichment, the water samples were distillated until dryness for the elimination of all minerals present. We checked pH and electrical conductivity values of each distilled sample with Seven Multi Metter Toledo, pH around 7.0, EC < 30.0 μS/cm. If these pH and EC target values were not reached, samples were distilled again. Each enrichment sequence comprised 15 precipitation samples, 2 samples of dead water, and 3 samples of spike water that were diluted based on the NIST-SRM4926E reference with certificate issues date 07 February 2011 (Radioactivity, 2011). The use of standard and dead water is necessary to correct for the enrichment efficiency and for the background. Dead water was groundwater taken from a well outside Hanoi city at a depth of 140 m and its tritium concentration was < 0.2 TU, as checked at the IAEA Isotope Hydrology Laboratory (Vienna, Austria) and at the Bhabha Atomic Research Center (BARC, India). The enrichment efficiency of the equipment was better than a factor of 25.

After tritium enrichment, the water samples, usually reduced to 10–13 ml. The samples were transferred into round bottom glass flasks and mixed with 6 g of anhydrous PbCl2 to neutralize the alkaline material, and then to distillation to remove the precipitate. These enriched and alkaline free water samples were mixed with 10 ml of Ultima Gold LLT - low level of tritium cocktail (PerkinElmer) and then subject to counting for the tritium activity in a liquid scintillation analyzer, LSC (TriCarb 3170 TR/SL-Packard). Counting efficiency of the LSC was corrected using the external standard channel ratio (ESCR) method and it was better than 55% for tritium. The counting time for samples was set to 100 min and repeated 10 times for each sample to ensure that counting precision would be better than 10% for an activity range below 10 TU.

Evaluating the measurement data and calculating the tritium concentration in the samples were guided by Gröning and Rozanski's method (Gröning and Rozanski, 2003). The lower limit of detection of the analysis is $A_T = 0.46$ TU. Measurement uncertainty was up to 20% with samples $A_T \leq 1.0$ TU and less than 10% with $A_T > 1.0$ TU. Data presented for the mean annual tritium concentration has been weighted by the amount of precipitation and calculated using the method outlined by the IAEA (Technical report series No. 331, 1992).

3. Result and discussion

3.1. Statistical distribution and sources of tritium in precipitation

The results for tritium in precipitation at monthly intervals are given in Table 1. The mean of month tritium concentration in precipitation samples that were collected in 6 years at Hanoi station was 2.54 ± 1.28 TU. The highest tritium concentration value, 7.07 ± 0.65 TU, was found in Aug 2011 and the lowest value, 0.51 ± 0.11 TU, was found in June 2011.

The tritium values distribution is represented on a histogram and can be approximated by a Gaussian distribution and frequency curve has R^2 of 0.94 with $P < 0.0002$ (Fig. 1). The results of test distribution using a normal Q-Q plot show that the regression line has an R^2 of 0.88 with $P = 2.27*10^{-33}$ (Fig. 2). In both of figure, frequency distribution and Q – Q plots show that the tritium concentration data follow a Gaussian distribution. This result of tritium distribution agrees fully with Harms's report about precipitation in California published in 2016 (Harms et al., 2016).

The results show that 90% of the values of tritium concentration in Hanoi's precipitation are less than 5 TU, this value is approximately equivalent to the natural distribution of tritium activity in precipitation (less than 10 TU). In tropical regions tritium concentrations are around and less than 5 TU, mostly due to the cosmogenic tritium production term and the transport process of radionuclides in the tropic known as the Hadley cell (Cauquoin et al., 2015; Paul Martin & John L. Mc Bride, 2012; Begemann and Libby, 1957). The average annual values for tritium concentration in precipitation between 2011 and 2016 are presented in Fig. 3. Precipitation in Hanoi has low tritium concentrations, most of the values are around 2–3 TU, and some values are very low, less than 1 TU. This can be explained as a large fraction of the Hanoi precipitation is from water evaporation of oceanic origin, particularly the Indian Ocean, with the concentration less than 1 TU (Povinec et al., 2010). Water vapor over the ocean is depleted in tritium due to the relatively reduced transfer of HTO compared with non-tritiated water by evaporation exchange from the ocean. Therefore precipitation at the sampling sites is affected by coastal proximity where rainwater has lower tritium concentration owing to a large fraction of the precipitation being diluted by molecular exchange of tritium between the rain droplets and ocean water evaporation. Some values are larger than 5