Journal of Environmental Radioactivity 162-163 (2016) 56–67

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

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

Measurement of tritium in the Sava and Danube Rivers

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ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form
3 May 2016
Accepted 14 May 2016

Keywords:
Tritium
Rivers
Nuclear power plant
Dose

ABSTRACT

Two nuclear power plants (NPP), the KrškoNPP (Slovenia) on the Sava River and the Paks NPP (Hungary) on the Danube River, are located in the immediate vicinity of Croatia and Serbia. Some of the radioactivity monitoring around the NPPs involves measuring tritium activity in the waters of rivers and wells. The authors present the tritium measurement results taken over several years from the Sava and Danube Rivers, and groundwater. The measurements were carried out in two laboratories including an impact assessment of the tritium released into the rivers and groundwater. The routine methods for determining tritium (with/without electrolytic enrichment) were tested in two laboratories using two different instruments, a Tri-Carb 3180 and Quantulus 1220. Detection limits for routine measurements were calculated in compliance with ISO 11929 and Currie relations, and subsequently the results were compared with those determined experimentally. This has shown that tritium can be reliably determined within a reasonable period of time when its activity is close to the calculated detection limit. The Krško NPP discharged 62 TBq of tritium into the River Sava over a period of 6 years (23% of permitted activity, 45 TBq per year). The natural level of tritium in the Sava River and groundwater is 0.3–1 Bq/l and increases when discharges exceed 1 TBq per month. Usually, the average monthly activity in the Sava River and groundwater is maintained at a natural level. The maximum measured activity was 16 Bq/l in the Sava River and 9.5 Bq/l in groundwater directly linked to the river. In the majority of water samples from the Danube River, measured tritium activity ranged between 1 and 2 Bq/l. The increased tritium levels in the Danube River are more evident than in the Sava River because tritium activity above 1.5 Bq/l appears more frequently on the Danube River. All measured values were far below the allowed tritium limit in drinking water. Dose assessment has shown that tritium released from NPPs contributes negligibly to annual doses in comparison to natural sources.

1. Introduction

Tritium is a radioactive isotope of hydrogen created in nature by cosmic rays interacting with the atmosphere. The average natural concentration of tritium in environmental waters has been estimated to range from 0.12 Bq/l to 0.9 Bq/l (Mook, 2001; Palomo et al., 2007; Baeza et al., 2001). Although occurring naturally on Earth, significant amounts of tritium are also generated through human activity, including the operation of nuclear power plants, manufacture of nuclear weapons, and atomic bomb testing. Nuclear power plants routinely and accidentally release tritium into the air and water in gas (HT) or water (HTO) form. No economically feasible technology exists to filter tritium from gaseous and liquid emissions from a nuclear power plant into the environment. Routine releases and accidental spills of tritium from nuclear power plants is a growing concern for public health and safety. Given that nuclear power plants release most of the tritium into the natural water recipients, such as internal waterways and seas, there is concern that tritium enters into drinking water in wells. This issue is exceptionally important when nuclear power plant are located on rivers or lakes near water wells that supply drinking water to the population (Jean-Baptiste et al., 2007; Hanslik et al.,. 2005, 2009; Bolsunovsky and Bondareva, 2003). More specifically, exposure to tritium has been clinically proven to cause cancer, genetic

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http://dx.doi.org/10.1016/j.jenvrad.2016.05.014
0265-931X/

mutations, and birth defects in laboratory animals. In studies conducted by the Lawrence Livermore Laboratory, a comprehensive review of the carcinogenic, mutagenic, and teratogenic effects of tritium exposure has revealed that tritium packs 1.5 to 5 times more relative biological effectiveness (RBE), or biological change per unit of radiation, than gamma radiation or X-rays (Straume, 1993; Hill and Johanson, 1993). These effects relate to high tritium exposures. Tritium levels in the environment are generally far lower downstream of releases from NPPs. Consequently, similar biological effects are not expected. However, international and national regulations require the constant control in releasing tritium from nuclear power plants into the environment, especially into natural waters.

There are two nuclear power plants located in our immediate vicinity, the Krško NPP (Slovenia) on the Sava River and the Paks NPP (Hungary) on the Danube River. The cities supplied with drinking water from water reservoirs which are close to the rivers are located on the banks of both rivers. These rivers pass through Croatia and Serbia. The primary task is environmental protection and sustainable use of water resources that requires continual environmental monitoring. Part of this programme involves monitoring radioactivity and measurement tritium activity in river waters and reservoirs.

The routine control of releases from NPPs requires rapid, simple and reliable methods for determining radionuclides. To that end, determining tritium in water often utilises the liquid scintillation technique. The development of modern LS counters and the use of safer scintillation cocktails enables reliable determination of tritium activity almost to the 5 Bq/l limit, without sample pretreatment. Below this limit, determining tritium is more difficult and requires low level background instruments, such as Tri-Carb2770/3180 and Quantulus 1220, as does equipments for tritium enrichment (Morgenstern and Taylor, 2009; Varlam et al., 2009; Jakonić et al., 2014). On the other hand, nuclear power plants release tritium directly into the environment and its concentration in water can vary widely, generally with the highest levels closer to the release point. It follows that the measurement routines must be reliable subject to a wide range of activities for improving environmental impact assessments. In view of the above, the aim of this paper is twofold. The first is to verify compliance of methods used to determine tritium in two laboratories using different instruments, the Tri-Carb 3180 and Quantulus 1220. Secondly, the aim is also to present the results tritium measurements in groundwater, and in the Sava and Danube Rivers, over a period of several years and carried out in two laboratories. This also involves assessing the possible impact of tritium released into the environment.

2. Methodology

Tritium measurements along the Sava and Danube Rivers are routinely carried out through environmental monitoring in Serbia and monitoring by NPPs in Croatia. For this reason, this paper will present an overview of tritium measurement methodologies carried out in two laboratories, the Laboratory for Low Radioactivity Measurements or LLRM (University of Novi Sad, Serbia) and Laboratory for Radioecology or LRE (Ruder Bošković Institute in Zagreb, Croatia). The authors intend to review sample preparation techniques, describe the methodologies and instruments, and compare measurement results. Further, the results of determining tritium levels in the Sava and Danube Rivers linked to the NPPs are also provided. The LLRM implements procedures in line with the ASTM method (ASTM International D 4107–08, Standard Test Method for Tritium in Drinking Water (2006)) and the direct method as proposed by (Pujol and Sanchez–Cabeza, 1999). The LRE uses an "in-house method for determining tritium and is based on a procedure described in the IAEA 295 and 246 reports (IAEA 295, 1989, IAEA TEC-DOC 246, 1981) and ISO 9698 procedure (ISO 9698, 2010).

Equipment: Liquid scintillation counters, the Quantulus 1220 and TriCarb-3180 TR/SL, were used for sample counting. An electrolytic enrichment system comprising 12 cells (mild steel and stainless steel cathode-anode (IAEA type) and home-made electronic current control were used for enriching tritium. A calibrated precise electronic balance, the Sartorius GP3202 (measurement range 0–3200 g, relative uncertainties below ±0.05% in the whole range), was used for weighing cells. A calibrated electronic analytical balance, the Metller Toledo AX205 (measurement range 0–220 g, relative mass uncertainties below ±0.02% in the entire range), and automatic calibrated pipettes, the Rainin (volume 0–1 ml, relative uncertainty ±0.2% at 0.5 and 1 ml, volume 1–10 ml, relative uncertainty ±0.1% at 5 and 10 ml) were used for comparing sample preparations.

Sampling location: Proximate sampling locations are shown in Fig. 1. Jesenice station is located (GPS 45° 51′ 40,7"N, 015° 41′ 14,6"E) on the right bank of the Sava River, 20 km from the Krško NPP. The station receives water from the riverbed some 50 m from the right bank. The Medsave reservoir is located (GPS 45° 50′ 00,4"N, 015° 43′ 10,6"E) on the right side of the Sava, about 25 km from the Krško NPP and 50 m from the riverbed. The Šibice reservoir is located (GPS 45° 51′ 17,0"N, 015° 43′ 10,6"E) on the left side of the Sava River, about 25 km from the Krško NPP and 2 km away from the riverbed. Sremska Mitrovica is located on the right side of the Sava River about 300 km from the Krško NPP (GPS 44° 58′ 35" N, 19° 36′ 44" E). The sampling position on the Danube is located a few kilometres north of Batina-Bezdan rural settlement on the Serbian-Croatian border (Batina is the Croatian and Bezdan the Serbian name given to the settlement) (GPS 44° 58′ 35" N, 19° 36′ 44" E). This location is about 60 km from the Paks NPP.

Sampling: Water from the Sava River at the Jesenice site was sampled 24 h a day continuously using an automatic sampler (2 L of water samples taken every hour between 00 and 24 h). The sample was taken on a daily basis and filtered to remove suspended matter (filter with pore sizes of 0.45 μm). The average monthly sample was obtained as a composite sample by taking an aliquot of 100 ml daily samples. Preparation of the composite sample required storing the daily samples in a refrigerator (polyethylene bottle at 4 °C). Groundwater (well) samples at the Medsave and Šibice locations were taken only once and at the start of the month. An aliquot of 1 l was taken for the purpose of analysing tritium which had been filtered and stored as described above. The composite sample of Danube water on the Croatian side of the river (sampling location at Batina-Bezdan) was obtained by sampling water near the banks and in the middle of the river (3 × 5 l). The sample was filtered to remove suspended matter and an aliquot of 1 l was used for analysis. On the Serbian side of the river, a 10 L composite sample of Danube water (sampling location also at Batina-Bezdan) and Sava water (sampling location at Sremska Mitrovica) was taken from water stochastically on certain days in a month. The liquid discharge samples from the Krško NPP were monthly composite samples obtained by taking an aliquot of each release.

Preparation of the water sample: Samples were distilled at the LLRM based on the ASTM D 4107–08 method (ASTM International D 4107–08, 2006). Tritium was determined as described in recent papers (Nikolov et al., 2013; Jakonić et al., 2014). At the LLRM, 8 ml of sample was mixed with 12 ml of the scintillation cocktail (Ultima Gold LLT) in a 20 ml low diffusion polyethylene vial (PE). At the LRE, tritium levels in the water samples were determined after electrolytic enrichment. Prior to measurement and/or enrichment, the water sample was filtered through a slow depth filter (cellulose nitrate filter with a pore size of 0.45 μm) and deionised using