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Tritium in river waters from French Mediterranean catchments: Background levels and variability

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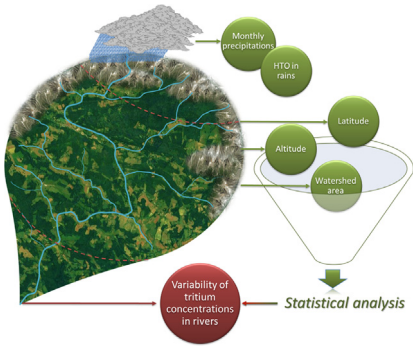
HIGHLIGHTS

- Tritium contents in river waters are lower than in rain waters.
- Contrarily to rain waters no seasonality is demonstrated for river waters.
- Variation of tritium concentrations in rivers depends on various parameters.
- Tritium inputs by rainfall, altitude, basin surface are the main parameters involved.
- Tritium fluxes delivered to the Mediterranean Sea are estimated.

GRAPHICAL ABSTRACT



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ABSTRACT

Tritium background levels in various environmental compartments are deeply needed in particular to assess radiological impact, especially in river systems where most of releases from nuclear facilities are performed. The present study aims to identify the main environmental factors that influence tritium background levels in rivers at the regional scale. 41 samples were collected from 2014 to 2016 along 17 small rivers in the south of France. All were located out of the influence of direct releases from nuclear facilities. Tritiated water (HTO) concentrations measured in water samples ranged from 0.12 ± 0.11 to 0.86 ± 0.15 Bq L^{-1} and HTO concentrations in rains were modelled between 2015 and 2016 over the study period referring to time series acquired from 1963 to 2014 at Thonon-les-Bains monitoring station. The results of tritium concentrations in rivers studied present a significant variability and are more than twice lower than forecasted values in rain. Multiple linear regressions allowed identifying that HTO concentration in rains, watershed area and altitude were the main tested parameters that are linked to the variability of HTO concentrations in the studied rivers. Finally, HTO fluxes delivered to the Mediterranean Sea by French coastal rivers out of influence of nuclear releases were estimated. The results highlight that those account for around 1% of HTO exported while 99% are transferred by the nuclearized Rhone River.

1. Introduction

Tritium is the radioactive hydrogen isotope characterized by a half-life of 12.32 years, a low energy beta emitter (average energy of

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5.7 keV) decaying to the stable element ^{3}He. Tritium is naturally produced in the environment mainly by nitrogen (^{14}N) atoms absorbing neutrons from cosmic rays in the upper atmosphere, a production significantly higher than its telluric production. These natural processes lead to a rather constant amount of 1EBq at equilibrium at the global scale (Eisenbud et al., 1979; Zerriffi, 1996). Tritium had been also artificially produced since the middle of the last century by the atmospheric nuclear weapon testings from 1945 to 1980, with peaking releases in 1958 and 1962. Explosions from nuclear tests led to tritium emissions in the atmosphere as tritiated hydrogen (HT) and methyl tritium gas (CH_3T) that were rapidly oxidized and converted into tritiated water molecules (HTO). Those inputs generated tritium concentrations in rains more than one hundred times above natural levels during the peaking emissions in 1963 (UNSCEAR, 2000).

Among contemporary anthropic sources of tritium, reprocessing plants release most quantities. For example, nuclear discharges of AREVA NC La Hague (France) are about 10 times larger than releases of all French Nuclear Power Plants (NPP) (IRSN, 2009). Currently, tritium is the major radionuclide, with ^{14}C, to be released in both liquid and gaseous effluents by Nuclear Power Plants (Gontier and Siclet, 2011). Tritium is additionally released to a lesser extent by tritium production facilities and other plants using tritiated compounds regarding their luminescent properties or for medical research purposes. At the global scale about 0.1 EBq per year are released by the nuclear installations (UNSCEAR, 2000); i.e., 10 fold less that the natural production at equilibrium.

Tritium exchanges very quickly with hydrogen or water molecules and is thus extremely mobile and ubiquitous in all compartments of the environment. It is encountered in gaseous forms (HT, CH_3T), liquid form (HTO), as well as associated with naturally-occurring organic compounds (Organically Bound Tritium - OBT), or with man-made organic molecules (Croudace et al., 2012; Krejci and Zeller, 1979) or refractory sub micrometric particles (El-Kharbachi et al., 2014). HTO is by far the predominant form in the environment and thus closely follows the whole water cycle and the water mass dynamics. Consequently, it is generally encountered in various components of the hydrosphere including atmosphere, rivers, marine waters, underground waters, interstitial water in soils and sediments and tissue free water within organic compounds.

Tritium was widely used in the field of hydrogeology for its tracing properties enabling to estimate origin, residence time, dynamic, mixing, storage volumes of groundwater and their zone of discharge in surface waters (Gusyev et al., 2016; Mayer et al., 2014; Michel, 1992; Michel, 2004; Mundschenk and Krause, 1991; Ravikumar and Somashekar, 2011; Subbotin et al., 2013). Tritium was also widely used like tracer in the frame of marine studies (Andrie and Merlivat, 1988; Bailly du Bois et al., 2002; Broecker et al., 1986; Bush, 1988; Butzin and Roether, 2004; Göte Östlund, 1994; Göte Östlund et al., 1974). Finally, various studies were performed in order to investigate the radiological impact of tritium releases from nuclear facilities on the environment referring to pre-testing baseline levels (Dinçer and Davis, 1984; Eyrolle-Boyer et al., 2014; Mundschenk and Krause, 1991; Vakulovskii et al., 1978). Tritium behavior and fate were often studied close to military, industrial or nuclear research center areas such as Semipalatinsk Nuclear Test Site (Mitchell et al., 2008; Subbotin et al., 2013), NPP (Ciffroy et al., 2006; Gontier and Siclet, 2011; Kotzer and Workman, 1999; Mundschenk and Krause, 1991; Péron et al., 2016) or more rarely after the Fukushima Dai-ichi NPP accident (Kakiuchi et al., 2012; Matsumoto et al., 2013; Ueda et al., 2015). Some studies contributed to establish long time series for tritium concentrations in various hydrosystems and generally allowed to determine tritium activity in the nearest influenced zone close to those sites, i.e., the amount of anthropogenic tritium at the downstream part of nuclearized rivers (Bondareva and Rubailo, 2016; Ciffroy et al., 2006; Marang et al., 2011; Pujol and Sanchez-Cabeza, 2000; Tomášek and Wilhelmová, 1996; Varlam et al., 2012).

In this context, tritium baseline levels are deeply needed in the various environmental compartments in order to characterize the environmental impact of nuclear releases and to identify potential sources of tritium other than nuclear facility discharges. It is known that tritium baseline (HTO form) in rivers varies according to physical, climatic and geographic parameters spreading from regional to global scales within the hydrosphere. Therefore, in order to assess to the variability of tritium concentrations in rivers, water samples were collected among various French Mediterranean catchment located out of the influence of atmospheric and liquid nuclear releases. Statistical approaches were performed in order to identify the most sensitive parameters accounting for the variability of HTO concentrations in rivers. Finally, tritium fluxes delivered from these different rivers to the northwestern part of the Mediterranean Sea were estimated and compared to those calculated for the nuclearized Rhône River.

2. Materials and methods

2.1. Location of sampling areas

Sampling stations were mainly selected in South-Eastern France, in rivers out of influence of atmospheric or liquid radioactive releases from nuclear facilities in agreement with Eyrolle-Boyer et al. (2014) (Fig. 1). All nuclear power plants and a reprocessing plant (Marcoule) were taken into account in order to avoid any impact of direct atmospheric and liquid releases.

In order to identify these areas, GIS software (ARCGIS) were used to target rivers. Various upstream and downstream stations were selected and sampled to study variations of tritium concentrations in freshwater.

2.2. Sampling

This step was manually carried out using a sampling rod to sample in the center of the river (in the middle of the water column after the depth has been estimated) in order to enhance the representativeness and limit remobilization of particles from bottom sediments and banks. All samples were taken after at least 7 days without rainfalls and flood events. Samples were filtered directly in-situ with GVS® filters (0.22 μm). The filtered water was immediately stored in previously dried (40 °C) amber glass vials then stocked in a cooler to the laboratory. Then, samples were packaged in aluminized bags under vacuum in order to avoid any exchange with the surrounding atmosphere and stored at 4 °C until analysis.

2.3. Analytical method

Two analytical methods were used to quantify tritium concentrations in river water samples.

- Samples filtered in the field then distilled in laboratory. 70 mL of water sample with 70 mL of scintillation cocktail (Ultimagold LLT – PerkinElmer) in a polythene antistatic vial before scintillation counting with Hitachi ALOKA LSC-LB7. The mean uncertainty is equal to 57%.
- 500 mL of water sample distilled then concentrated by electrolytic enrichment during 9 days to obtain an average enrichment factor of 25. In a second part, added 12 mL of scintillation cocktail (Ultimagold uLLT – PerkinElmer) with 8 mL of the sample enriched and neutralized with lead chloride in a polythene antistatic vial before scintillation counting with Tricarb 3180 TR/SL. The mean uncertainty is equal to 7%.

2.4. Other data sets

Tritium concentrations in rainfall in Thonon-les-Bains (France) near Geneva (Switzerland) (altitude: 385 m; latitude: 46.3708°) (Fig. 1) are produced for the International Atomic Energy Agency (IAEA) and available in the Wiser Data base (Global Network of Isotopes in Precipitation (GNIP)) from 1953 until 2012. Rain water samples measured between