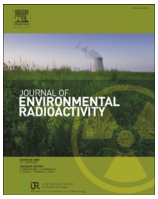
Journal of Environmental Radioactivity 136 (2014) 162–168

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

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



Short communication

Apparent enrichment of organically bound tritium in rivers explained by the heritage of our past

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ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form
15 January 2014
Accepted 23 May 2014
Available online

Keywords:
Tritium
Rivers
Sediments
Biomass
Global fallout
Freshwaters

ABSTRACT

The global inventory of naturally produced tritium (3H) is estimated at 2.65 kg, whereas more than 600 kg have been released during atmospheric nuclear tests (NCRP, 1979; UNSCEAR, 2000) constituting the main source of artificial tritium throughout the Anthropocene. The behaviour of this radioactive isotope in the environment has been widely studied since the 1950s, both through laboratory experiments and, more recently, through field observations (e.g., Cline, 1953; Kirchmann et al., 1979; Daillant et al., 2004; McCubbin et al., 2001; Kim et al., 2012). In its “free” forms, [i.e. 3H gas or 3H hydride (HT); methyl 3H gas (CH3T); tritiated H2O or 3H-oxide (HTO); and Tissue Free Water 3H (TFWT)], tritium closely follows the water cycle. However, 3H bound with organic compounds, mainly during the basic stages of photosynthesis or through weak hydrogen links, is less exchangeable with water, which explains its persistence in the carbon cycle as re underlined recently by Baglan et al. (2013), Jean-Batiste and Fourré (2013), Kim et al. (2013a,b). In this paper, we demonstrate that terrestrial biomass pools, historically contaminated by global atmospheric fallout from nuclear testing, have constituted a significant delayed source of organically bound tritium (OBT) for aquatic systems, resulting in an apparent enrichment of OBT as compared to HTO. This finding helps to explain concentration factors (tritium concentration in biota/concentration in water) greater than 1 observed in areas that are not directly affected by industrial radioactive wastes, and thus sheds light on the controversies regarding tritium ‘bioaccumulation’. Such apparent enrichment of OBT is expected to be more pronounced in the Northern Hemisphere where fallout was most significant, depending on the nature and biodegradability of terrestrial biomass at the regional scale. We further believe that OBT transfers from the continent to oceans have been sufficient to affect tritium concentrations in coastal marine biota (i.e., near river inputs). Our findings demonstrate that the persistence of terrestrial organic ^{3}H explains imbalances between organically bound tritium and free ^{3}H in most river systems in particular those not impacted by releases from nuclear facilities.

1. Introduction

Tritium production from naturally occurring processes lead to a global inventory at equilibrium of 2.65 kg, which corresponds to approximately 9.6×10^5 TBq (NCRP, 1979; Zerriffi, 1996). Tritium is mainly produced in the atmosphere and has a relatively short half-life (12.32 years), inducing no accumulation of this isotope from this origin over a centennial time scale and a very low natural abundance (Lucas and Unterweger, 2000). Like most artificial radionuclides, man-made tritium was first introduced into the environment as a result of atmospheric nuclear testing, starting in 1945. The last atmospheric testing carried out by China in 1980. Tritium inputs peaked from 1954 to 1958 and again from 1961 to 1962, when numerous tests were performed. The total tritium production from these past events has been estimated at 1.86×10^8 TBq (UNSCEAR, 2000) taking into account both theoretical estimations (Miskel, 1973) and field observations (Bowen and Roether, 1973; Schell et al., 1974; Mitchel, 1976). Most of the tritium released by nuclear explosions, initially present in the form of hydrogen gas (HT) and methyl tritium gas (CH_3T), was oxidized to water (HTO) in the stratosphere and then progressively washed out from the atmosphere during precipitation events. In the early 1960s, acute increases in tritium concentration were recorded in northern hemisphere rainwater, reaching levels up to 1000 times

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http://dx.doi.org/10.1016/j.jenvrad.2014.05.019
0265-931X/

the natural background level (IAEA/WMO, 2012). Since the maximum global atmospheric radioactive fallout in 1963, environmental tritium concentrations have gradually decreased, and current concentrations in precipitation and surface waters have almost returned to pre-testing levels, i.e. 1–2 Bq L^{-1} (Palomo et al., 2007; IAEA, 2012). Industrial and medical applications are other anthropogenic sources of ^{3}H, however, their releases to the environment are several orders of magnitude lower than those from atmospheric fallout (UNSCEAR, 2000), even though ^{3}H is expected to be increasingly introduced into the environment by existing or new nuclear technologies (e.g. heavy water reactors such as CANDU nuclear reactors, pressurized water reactors (PWRs), fusion energy production).

Due to its ease of exchange among chemical species containing hydrogen, anthropogenic tritium is extremely mobile and has become ubiquitous in all biological and geochemical systems through mixing, transfer, chemical reaction and dilution processes associated with the water cycle and to some extent to the carbon cycle through its organically bound form (OBT) as recently synthesized by Kim et al. (2013b). Over the past ten years, an increasing amount of interest and controversy has focused on OBT accumulation in various biological compartments, mainly since significant disequilibrium between OBT and HTO has been increasingly observed but with widely varying explanations as it will be thoroughly described further on in this paper with associated references. In this context, we present new findings on the causes of OBT enrichment in environmental samples from aquatic systems based on data set chronicles acquired in metropolitan French river systems and subsequent specially designed modelling.

2. Review of current knowledge

2.1. Behaviour and fate of tritium in aquatic systems

A large number of studies have addressed the presence of tritium in plants and aquatic organisms, as well as tritium sampling and measurement techniques, and tritium transport and cycling processes in the environment (e.g. NCRP, 1979; Belot, 1986; Diabaté and Strack, 1997; Murphy, 1993; Wood et al., 1993; Pointurier et al., 2004; Galeriu et al., 2005, Cossonnet et al., 2009; Kim and Korolevych, 2013; Kim et al., 2013b). Tritium behaviour in aquatic systems is influenced by its various forms and exchanges among key components of the biogeochemical cycle as we describe in Fig. 1. HTO is the most abundant form of ^{3}H in the environment. It has been estimated to be 25 000 times more radiotoxic to human beings than HT, mainly due to its longer residence time in biota tissues and abiotic components (e.g., soils and rivers) (ASN, 2011). In addition to its "free" forms (i.e. HT, CH$_3$T, HTO and TFWT), which are closely linked to the water cycle, ^{3}H is also linked to the carbon cycle through the two major metabolic processes (photosynthesis and cellular respiration). Tritium is bound to dissolved, colloidal or particulate organic compounds either through exchange reactions or enzymatically catalysed reactions. In the case of exchange reactions, tritium is bound to oxygen, sulphur, phosphorus or nitrogen atoms (i.e., hydroxides, thiols, phosphides and amines) through

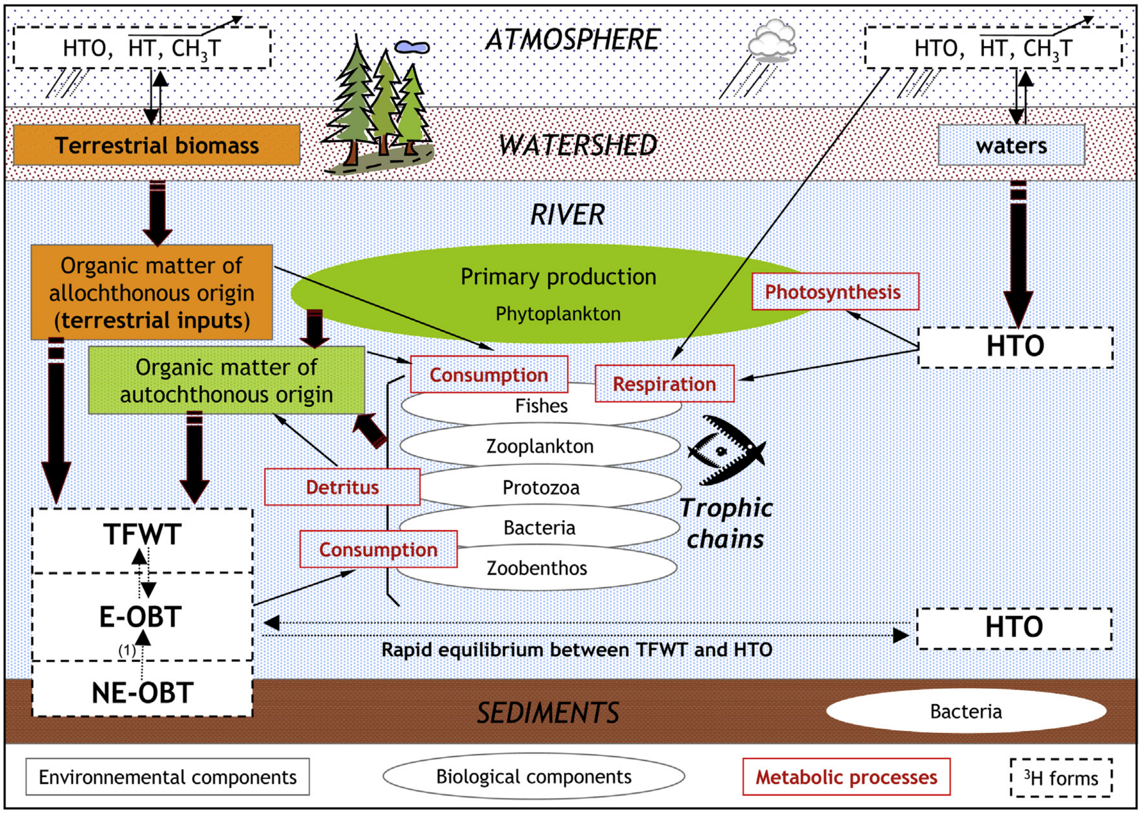

Fig. 1. Tritium (^{3}H) behaviour in aquatic systems and its various forms; HT (^{3}H gas or ^{3}H hydride); CH$_3$T (methyl ^{3}H gas); HTO (tritiated water or ^{3}H oxide); TFWT (Tissue Free Water ^{3}H); E-OBT (Exchangeable Organically Bound ^{3}H); NE-OBT (Non Exchangeable Organically Bound ^{3}H). TFWT exchanges rapidly with ambient HTO and, to a lesser extent, with E-OBT. The NE-OBT form in fresh or detrital autochthonous organic matter mirrors contemporary ^{3}H levels in water and, in most cases, is in close equilibrium with tritiated water (HTO). In allochthonous naturally occurring organic compounds, however, it contains past contamination from the terrestrial biomass. Biological components in the aquatic trophic chain and bacteria fix ^{3}H from allochthonous organic compounds labelled in the past through consumption. (1) NE-OBT is expected to produce E-OBT during the biodegradation of organic compounds.