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Review

Isotopic fractionation of tritium in biological systems

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ABSTRACT

Isotopic fractionation of tritium is a highly relevant issue in radiation protection and requires certain radioecological considerations. Sound evaluation of this factor is indeed necessary to determine whether environmental compartments are enriched/depleted in tritium or if tritium is, on the contrary, isotopically well-distributed in a given system. The ubiquity of tritium and the standard analytical methods used to assay it may induce biases in both the measurement and the signification that is accorded to the so-called fractionation: based on an exhaustive review of the literature, we show how, sometimes large deviations may appear. It is shown that when comparing the non-exchangeable fraction of organically bound tritium (neOBT) to another fraction of tritium (e.g. tritiated water) the preparation of samples and the measurement of neOBT reported frequently led to underestimation of the ratio of tritium to hydrogen (T/H) in the non-exchangeable compartment by a factor of 5% to 50%. In the present study, corrections are proposed for most of the biological matrices studied so far.

Nevertheless, the values of isotopic fractionation reported in the literature remain difficult to compare with each other, especially since the physical quantities and units often vary between authors. Some improvements are proposed to better define what should encompass the concepts of exchangeable and non-exchangeable fractions.

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1. Theoretical background

Tritium is the only natural radioactive isotope of hydrogen. As hydrogen is a major element in the biosphere (as a component of water, mineral or organic matter) and as tritium is one of the most released radionuclides by the nuclear industry in the environment, tritium is ubiquitous in every environmental compartment. Tritium transfer from release compartments to biological organisms (microorganisms, plants, animals) along the food chains is a key question in radioecology of tritium. Taking into account the methods of sample treatment and measurement of tritium specific activities, some cautions have to be taken when interpreting results. The aims of this article are to review works dealing with flows of tritium in the environment and to propose some improvements in the analysis and presentation of the results.

1.1. Sources of tritium in the environment and the pathways in which it is involved

Most of tritium is produced in the high atmosphere (from 10 to 30 km of altitude) by the action of cosmic particles (protons and neutrons) on ^{14}N and ^{16}O. Tritium produced in these conditions reacts mainly with atoms of ^{1}H to form tritiated hydrogen (HT) (Belot et al., 1996). In lower layers of the atmosphere, tritium is incorporated into water molecules and forms tritiated water, also called tritium oxide (HTO) (Balonov et al., 1974). Natural production of tritium is estimated at 200 g y^{-1} and the natural stock of tritium at 3.5 kg (Okada and Momoshima, 1993).

Anthropic tritium is mainly released into the environment as HT or HTO by nuclear facilities (nuclear power stations, fuel reprocessing plants, military applications, tritium extraction plants) and as volatile tritiated compounds in minor quantities (essentially CH_3T). At the world scale, these sources are equivalent to about one third of natural emissions (UNSCEAR, 2008).

As HT and CH_3T are taken up very slowly by the different compartments of the environment, it is assumed that their oxidation into HTO (in particular by soil microorganisms) is their main environmental fate (Galeriu et al., 2008). On the other hand, HTO is ubiquitous in abiotic or biotic compartments. Its transport and transfer in the environment follow the general water cycle (IAEA, 1981), with the exception of a few fractionation effects.

1.2. Biological incorporation

As HTO follows the water cycle, plants and animals incorporate it. The part of tritium in living organisms that remains as HTO is termed Tissue Free Water Tritium (TFWT) (Spencer, 1984). TFWT in plants soon reaches equilibrium with water of its environment (water in soil and in the atmosphere) because plant, soil and atmosphere constitute a continuum (Boyer et al., 2009b). For example, the half-life of TFWT is estimated at 20–30 min in sunflower (*Helianthus annuus*) (Koranda and Martin, 1972). In animals, TFWT results from the drinking water, the water in food and the water that is produced by the catabolism of organic molecules. It has a short biological half-life (Pinson, 1951): in humans, the average half-life of TFWT is about 10 days (Moghissi et al., 1971, 1972).

In plants, animals and in most environmental compartments, the hydrogen of water and labile hydrogen (hydrogen bonded with atoms of oxygen, nitrogen or sulphur, accounting for approximately a third of the hydrogen in organic molecules) reach a quasi-instantaneous equilibrium. This kind of tritiation is termed "exchangeable Organically Bound Tritium" (eOBT) (Diabaté and Strack, 1993). Nevertheless, some labile hydrogen can stay "buried" in the core of macromolecules and thus remain inaccessible to isotopic exchange until the macromolecule "breathes" (following enzymatic action for example) (Baumgärtner and Donhaerl, 2004). This latter situation can influence measures of tritium in biological matrices (see Section 4.1).

Plants produce organic matter from HTO essentially through the photosynthesis cycle. When this leads to a tritium atom bound to an atom of carbon, the tritium is termed as "non-exchangeable OBT" (neOBT) because it is assumed to remain bound until the catabolism of the tritiated molecule (Diabaté and Strack, 1993).

The sum of eOBT and neOBT is called total OBT (tOBT).

Animals can also integrate tritium into their tissues and fluids by consuming tritiated food. The integrated fraction of ingested OBT[1] depends on the form in which it occurs (Taylor, 2008). When animals take up tritiated organic compounds, the absorption rate and the retention time depend on the organic molecules involved and their function in the body: Diabaté and Strack indicate that the retention time and the incorporation into the dry matter of tissues/organs are generally higher for constitutive and storage molecules than for water (Diabaté and Strack, 1993).

1.3. Isotopic effects and isotopic fractionation: some theoretical considerations

The isotopic substitution affects translational, rotational and vibrational motions of a substrate relative to the transition state or product of a reaction. Two kinds of isotopic effects might arise from these modifications: kinetic isotopic effects and equilibrium isotopic effects (Klinman, 2006).

First, the difference of mass between isotopes leads to variation of molecular speed, the heaviest isotope having a lower molecular speed than the lightest. It conduces to a slower diffusion for the molecule marked by the heavy isotope and a less frequent collision with other molecules. This latter point explains why molecules with light isotopes generally react faster (IAEA, 2000).

Secondly, the activation energy of a reaction is also dependant on the mass of the atoms involved in the reaction due to the effect of the mass variation on the force constant of the vibrating bond. In the normal isotopic effect, the heaviest isotope has a higher binding energy and reacts less than the lightest isotope. The difference of vapour pressure between $^{1}H^{3}H^{18}O$ or $^{1}H^{2}H^{16}O$ and $^{1}H_2^{16}O$ illustrates well this case. Nevertheless, inverse isotope effects are also observed, especially in polyatomic molecules or in reactions involving hydrogen atoms (Bigeleisen and Wolfsberg, 1958).

As the equilibrium isotopic effect is reversible, it is generally significant only when chemical intermediates in a given reaction can reach equilibrium, as in some enzymatically catalyzed reactions. In nature, kinetic and equilibrium isotopic effects are combined.

Lastly, by the transition of a compound from one state to another (liquid water to water vapour for example), the condensed phase get enriched in the heaviest isotope as described by the means of the Rayleigh equation (Rayleigh, 1902). Under equilibrium, this effect can be described by the vapour pressure isotope effect (Van Hook, 1968). Concerning tritium, this phenomenon has been observed at world scale geochemistry (Hoefs, 2009) as in laboratory conditions (Baumgärtner and Kim, 1990, 2000; Baumgärtner et al., 2001; Kim and Baumgärtner, 1997; Le Goff et al., 2014).

All these mechanisms might lead to modifications of the isotope ratio (R which is the ratio of number of atoms of one isotope to the number of atoms of another isotope of the same chemical element in the same system) along processes. These modifications of the isotopic ratios are termed as isotopic fractionation (IAEA, 2000). As isotopic fractionation in nature is the result of both kinetic and equilibrium isotopic effects, it should be referred as to non-equilibrium fractionation.

The changes in isotopic composition between reactant and product can be measured by the isotopic fractionation factor (α) which is the ratio of R of products to R of reactants. The isotopic fractionation (ε) is defined as $\alpha - 1$ and is useful when discussing distributions of isotopes

[1] In this article OBT is only used when it can be termed tOBT, neOBT or eOBT.