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https://doi.org/10.5109/5909112

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 8, pp.330-334, 2022-10-20. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University
バージョン：

Proceedings of the 8th International Exchange and Innovation Conference on Engineering & Sciences (IEICES 2022)

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Abstract: *Organically bound tritium (OBT) is radiologically relevant for radiation protection purposes due to its persistence and relatively long effective half-life (80 days). Estimation of doses due to OBT requires analysis of key environmental matrices that serves as pathway for ingestion. Studies on vegetation and soil exposed to tritium or deuterium has been done with models to predict future doses. Tritiated water has been identified as the chemical species of interest due to its ease of incorporation into biological tissues. Estimation of tritium doses has been done with a variety of techniques including Liquid Scintillation Counting, mass spectrometry. Environmental tritium models such as BIOMOVS, BIOMASS and EMRAS has been widely adopted by countries for radiation safety assessment.*

Keywords: Organically Bound Tritium; Liquid Scintillation Counting; Radiation Safety

1. INTRODUCTION

Tritium (^{3}H or T) is the only radioactive isotope of the element hydrogen. It is a beta emitter with a physical and biological half-life of 12.3 years and about 10 days (min.) respectively. It has been noted to associate with water molecules and easily transported within ecosystems hence its ease of incorporation into organic molecules.

Tritium is incorporated in different chemical forms in humans, animals, and plants. Models for studying their dynamics has been based on assumptions that tritium is largely transferred in the form of tritiated water and therefore assumes equilibrium steady state with the environment. Dose estimates due to tritium exposure based on the assumption of steady state equilibrium is done using the specific activity of the source. However, in organic molecules where tritium behaves differently (and in non-equilibrium), the dose estimate is higher than when the specific activity model is used [1]. Organic fractions of tritiated molecules have been identified to be more persistent in ecosystems than tritiated water hence the need to include the contributions of so-called Organically Bound Tritium (OBT) in dose estimations.

In recent times, research attention on OBT has increased due to the risk associated with human radiation dose from OBT in biological tissues and organs of plants and animals [2] [3] [4]. It has been investigated that atmospheric tritium can be transferred to plants and subsequently converted into OBT making it available in the soil [5]. However, OBT concentration in soil is not well understood due to the limited data, limited methods of soil analysis for OBT and varying tritium values which are difficult to explain [6].

1.1 Tritium sources

Generally, tritium sources can be grouped in three namely: natural sources, weapons testing and accidental/planned releases from nuclear facilities. Future sources could be that from fusion reactors like International Thermonuclear Experimental Reactor (ITER) which uses deuterium/tritium as fuel and from accelerators.

Naturally, tritium is produced by cosmic interactions between fast moving neutrons and nitrogen as shown below:

$$^{14}N + {}^{1}n \rightarrow {}^{12}C + {}^{3}H \qquad (1)$$

Also, a minute percent of natural inventory is due to neutron capture by ^{6}Li in the earth's crust similar to Li neutron capture processes in fission/fusion reactors.

Tritium from past weapons testing persists in the atmosphere. Examples include the accidental tritium release in the Dayton nuclear lab in 1989 in the USA [7] in addition to other weapons testing in the 1960s. Nuclear facilities produce a large percentage of tritium from processes such as nuclear fuel processing, nuclear power reactors and tritium production plants. A few of the man-made tritium sources are discharges from medical usage and research-based institutions. With active proposed fusion reactors such as the ITER project and advanced accelerators being developed, the tritium inventory is expected to increase. Generally, tritium is produced when there is a target with which fast neutrons can interact with hence the ease of tritium production.

1.2 Biological risks related to tritium

Tritium is a beta emitter with an electron energy of 0.018 MeV. Characteristic of beta particles, they can be stopped by thin sheet of paper hence do not pose dangerous effects outside biological tissues. However, internal deposition of beta particles may cause significant health risks and has been the basis for radiation protection measures concerning tritium exposures.

Currently, there is no concerted agreement on the effects of tritium in human and plant cells. Studies had been done on animals from which detrimental effects are assumed for humans. Epidemiological studies done on next generation related to radiation workers or on pregnancy outcome in places associated with tritium releases do not contain enough detail to estimate risks from tritium exposure [8].

2. TRITIUM IN THE ENVIRONMENT

Tritium exists in the atmosphere as either tritiated gas (HT) or tritiated water (HTO). Its behavior in the atmosphere is like other radionuclides in terms of transport and dispersion, however, HTO is re-emitted by plants and soil into the air [4]. Geleriu et al. [6], found out HT is not incorporated by plants due to its low dry deposition velocity. Further, it has a low dose per unit intake during inhalation therefore do not pose significant risk. Tritium is however biochemically converted by microorganisms in the soil into HTO and transported to

soil biota including plants resulting in significant intakes and a pathway of interest [9].

HTO in the atmosphere is also trapped by plants during photosynthesis and incorporated into tissues. Lighter protium atoms are substituted with the more heavier tritium atoms, the extent to which depends on the surrounding tritium concentration and the conditions necessary for efficient photosynthesis [5].Ingestion of contaminated plant tissues is a significant pathway of radiological interest therefore the emergence of several models to estimate exposure doses.

Tritium safety studies in the past three decades has focused on tritium differentiation in biological tissues. Generally, the two types of tritium fractions are the loosely bound tissue free water tritium (TFWT) and the atomically bound organically bound tritium (OBT) [2] [3] [4] [10]. TFWT is found to be tritium on the surfaces or part of internal water stream of biological tissues. They can be easily removed by rinsing or isotopic exchange reactions. Tritium in OBT is bound to atoms such as O, C, S, N and P and are persistent in biological tissues [10]. Stability of these bonds play a crucial role in determining its ease of release. The tritium in O-T, S-T, P-T and N-T were found to be easily replaced by protium atoms thereby the exchangeable OBT (eOBT) classification. That in C-T is relatively stable and is difficult to be exchanged with protium hence a non-exchangeable OBT classification (neOBT). OBT has an effective half-life of about 10-80 days therefore it is of high relevance to radiation protection practitioners.

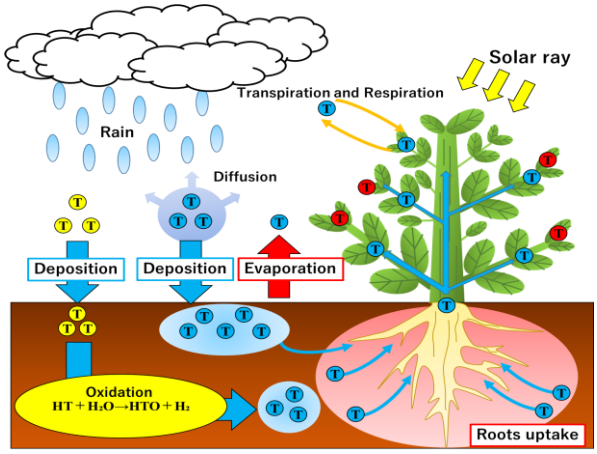

Fig. 1. Tritium pathways and transfer to plants.

Table 1: Some Tritium detection and measurement techniques

	Analysis of samples containing tritium			
	Technique	**Advantages**	**Limitations**	**Areas of Use**
Liquids	Liquid Scintillation Counting (LSC)	• Liquid samples containing tritium can be analyzed. • Water-soluble gases and solids containing tritium can be analyzed. • Suitable for low tritium concentrations (0.1 Bq/L)	• No direct analysis of solids and gases. • Relatively low detection ranges	• Environmental monitoring • Nuclear waste repositories • Research laboratories
Gases	Ionizing chamber	• Detect and quantify tritium gases • High detection limits ($2.5kBq/m^3$-$1.6 *10^5$ Bq/m^3)	• Not suitable for solids and liquids • Not specific to only Tritium • Does not work under vacuum	• Process monitoring in tritium breeding/production facilities • Nuclear waste repositories
	Scintillation Crystal detectors	• Total %mole of tritium in sample • Reusable scintillator	• Not suitable for low T-concentration samples • Less sensitive compared to LSC	• Process monitoring in tritium breeding/production facilities • Nuclear waste repositories
	Mass spectrometry	• Discriminates between tritium species	• Very expensive • Requires very high resolution	• Assaying laboratories • Research laboratories
	Gas chromatography	• Discriminates between tritium species • Low detection limits	• Low pressures required for tritium gases	• Assaying laboratories • Research laboratories
	Raman spectroscopy	• Non-destructive	• Optimization required	• Quality control for in-line processes
Solids	calorimetry	• Non-destructive • High tritium detection limit	• Not specific to only Tritium	• Tritium inventory in tritium production facilities
	Pyrolysis	• High tritium yield	• Destructive technique	• Assaying laboratories • Research laboratories

2.1 Tritium detection and measurement

Tritium is a beta emitter and quite difficult to measure due to its ubiquitous nature, its existence as gas, liquid or

trapped in solids, and its short range in air (~6 mm). The choice of measurement depends on the scale of exposure and existing phase.

Liquid Scintillation Counting (LSC) is a common technique for analysing liquid tritium-containing samples. Solid samples cannot be effectively analysed directly by LSC without significant sample preparation (e.g. pyrolysis) which is destructive. In LSC, samples are mixed with scintillation cocktails which absorb energies and convert them to detectable pulses.

Tritium in gases comes in different forms including HT, T_2, CH_3T etc. and detectors in current use can not differentiate between these fractions. Detectors in use now include ionization chambers, proportional counters, ^{3}He mass spectrometry, gas chromatography, etc. Solid samples can be analysed by calorimetry or pyrolysis. For tritium inventory analysis in a nuclear waste facility for example, calorimetric techniques may be deployed due to its non-destructive nature and high detection limit. Due to this, it has favourable use in industry compared to environmental monitoring where detection limits can be low. Table 1 summarizes some tritium detection and analysis techniques.

2.2 Sample treatment

Literature on tritium safety has been focused on OBT studies using different approaches. For academic and commercial research labs that uses active tritium sources, these are done in low level radioactivity labs. This may be different for nuclear waste repositories and may require stricter regulatory controls. To circumvent the problems of tritum leakages, some researchers used deuterium as substitutes [11] [12] [13]. The basic principle in OBT detection and measurement involves quantification of both eOBT and neOBT. Decision on including TFWT to the total dose has split opinion within the tritium research community with those against it arguing that the ease of TFWT removal implies its reduced availability to dose contribution.

2.2.1 TFWT and exchangeable-OBT

Due to its availability on surface matrices such as soil, stem, leaveas and fruits, TFWT can be sampled by simply rinsing such surfaces with tritium-free deionised water [14]. However, eOBT is in equilibrium with TFWT which in itself in equilibrium with the surrounding atmospheric water. Extraction of eOBT had been done by freeze drying where gas is passed over the sample and the tritium is cold-trapped [15]. Others also used immersion methods where samples were soaked in tritium-free water and LSC analysis done on immersion water. Atarashi-Andoh and Momoshima [12] [11] extracted deuterium-water from samples by microwave heating after which collected water was analysed for deuterium using gas chromatography.

The use of cold traps is essential in the above techniques as it converts liberated tritiated gases into tritiated water via isotope exchange reactions over suitable catalysts e.g. platinum.

$$HT_{(g)} + H_2O_{(l)} \rightarrow HTO_{(l)} + H_{2(g)} \qquad (2)$$

2.2.2 Non-exchangeable OBT

For solid samples, tritium has to first be liberated from the matrix and converted into liquid form for easier analysis. Basically, samples are combusted under a steady stream of oxygen gas (Fig.2). For organic samples such as leaves, the end product is CO_2 and $H_2O/D_2O/HDO$.

Below is a schematic for the analysis of various tritium fractions in vegetation and soil.

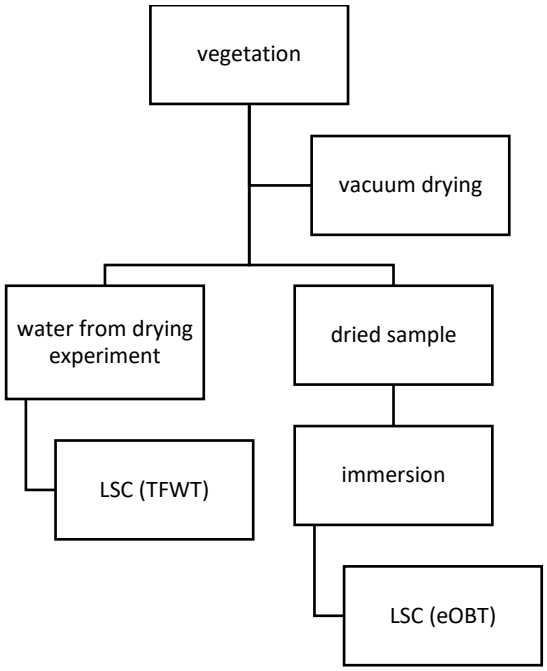

Fig. 2. Scheme for ^{3}H in vegetation analysis.

3. RADIATION PROTECTION MEASURES

Generally, dose estimation for radionuclides is based on either specific activity models or dilution models. Environmental assessment is normally done based on specific activity (SA) models which assumes that tritium is transferred within the environment and is transferred into living tissues through its interaction with water molecules. However, the now widely acceptable presence of OBT means the SA model is underestimating tritium exposure doses hence the need for improved models [1]. International Commission on Radiological Protection (ICRP) generally recommends a reference dose limit of 0.1 mSv per annum with guidance reference levels set by countries based on local exposure situations [16].

^{3}H was considered in the *BIO*spheric *MO*del *V*alidation *S*tudy (BIOMOVS II) model which was based on a short-term release of tritium vapor into the atmosphere [17]. Its limitation was the lack of data on deposition and re-emission from soil below plant canopies. The BIOsphere Modelling and ASSessment (BIOMASS) model was an enhancement on BIOMOVS II with the focus on long term continuous tritium releases [18]. The Environmental Modelling for Radiation Safety (EMRAS) model consolidated the earlier ones and included three additional perspectives: Radioactive Release Assessment, Remediation of Sites with Radioactive Residues and, Protection of the Environment [19].

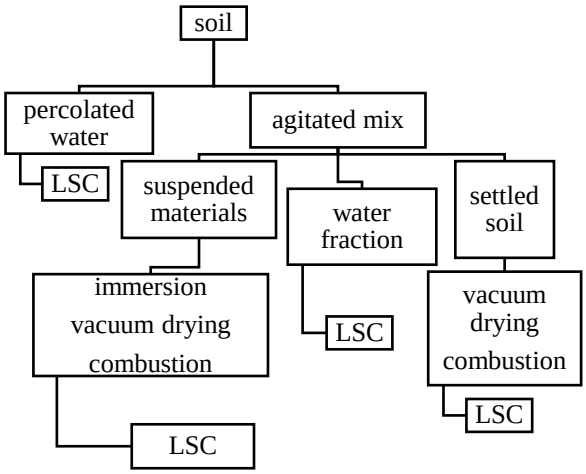

Fig. 3. Schenme for ^{3}H in soil analysis.

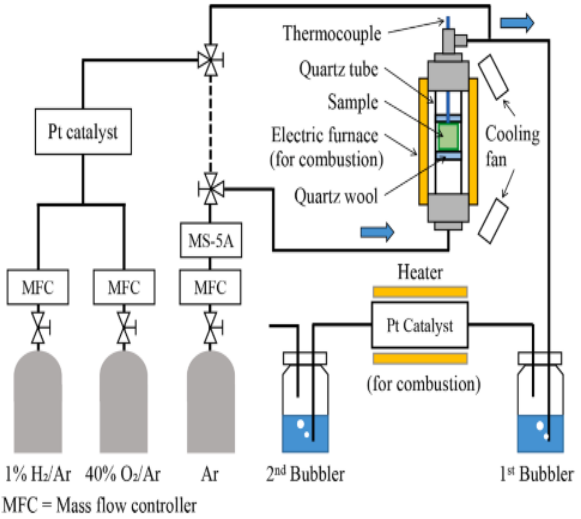

Fig. 4. Diagramatic scheme for combustion (Matano et al., 2021).

4. GAPS

Several studies had been done on tritium behavior in soil, vegetation, and atmosphere with an increased focus on OBT. Its behavior in soil is one determinant of its ultimate transfer into plants (through its roots), re-emission into the atmosphere and interaction with other living organisms. However, it is not known if OBT is released into the soil when contaminated plants rot.

5. CONCLUSION

Tritium safety and containment is one critical work which needs to be done to continuously provide sufficient information on the safety of existing and planned nuclear uses. Models based on real data have been developed using critical safety parameters. As an evolving area, new data on unknown parameters will enhance robustness of models, further deepening the nuclear safety principles. OBT assessment still requires some critical attention with regards to tritium dynamics in soil.

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