INTRODUCTION AND REVIEW OF EARLIER WORK

1.1 Introduction

1.1.1 Tritium: Physical Properties and Applications

Of the three isotopes of Hydrogen viz Protium (\(^1\)H), Deuterium (\(^2\)H) and Tritium (\(^3\)H), only tritium is radioactive. It decays with a half life of 12.3 years to Helium (\(^3\)He) by beta emission. The emitted beta particles have a maximum energy of 18 Kev and an average energy of 5.7 keV. The betas emitted have a maximum range of 1.3 cm in air\(^1\). Specific activity of tritium is approximately 9600 curies/g.

Tritium has an atomic weight of 3.01689±.000011 g as compared to 1.008142±.000003 g and 2.01475±.000006 g for protium and deuterium respectively\(^2\). The thermodynamic properties of the oxides of hydrogen isotopes are given in Table 1.1\(^3\). The maximum density of T\(_2\)O is 1.215 g/cm\(^3\) at 13.4°C as compared to 1.105889 at 11.2°C and 0.99997 at 3.98°C for D\(_2\)O and H\(_2\)O respectively\(^2,4\).

Since tritiated water behaves in the same manner as ordinary water\(^5,6\), tritium is used as a tracer in water turnover and fixation studies in animals and
Table 1.1

Thermodynamic Properties of The Oxides of Hydrogen Isotopes

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>D₂O</th>
<th>T₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point °C</td>
<td>100.00</td>
<td>101.42</td>
<td>101.51</td>
</tr>
<tr>
<td>Triple point temp. °C</td>
<td>0.01</td>
<td>3.82</td>
<td>4.49</td>
</tr>
<tr>
<td>Triple point pressure mm Hg</td>
<td>4.58</td>
<td>5.02</td>
<td>4.87</td>
</tr>
<tr>
<td>Heat of evaporation kcal/mole</td>
<td>9.72</td>
<td>9.9</td>
<td>10.1</td>
</tr>
<tr>
<td>Entropy at 298.16 °K (in eu)</td>
<td>18.75</td>
<td>18.9</td>
<td>19.0</td>
</tr>
</tbody>
</table>

plants, for studying distribution and movement of water in lakes, streams, rivers etc., and for evaluating moisture distribution in the environment. However large mass difference between protium and tritium gives different metabolic rates in biological specimens thereby giving an opportunity to study metabolic and other reactions of the system under study.

Due to the short range of its beta particles\(^7,8\), tritium is essentially an internal hazard i.e. only when it enters the body by ingestion, inhalation and/or percutaneous absorption, its beta particles transfer the energy to the internal organs and can cause damage. Due to the very low energy of its beta emission, tritium has the highest tolerance limit. Further, this limit also
depends on chemical form in which tritium enters the body. Tritiated water gets absorbed and causes much damage while elemental tritium is not at all absorbed by the body. Because of this, the tolerance limit for elemental tritium in air is about 100 times as that of tritiated water vapour.

1.2 Natural Production and Man-made Tritium

The main tritium producing process in nature is the bombardment of atmospheric nitrogen by cosmic ray particles. Besides this natural process, tritium is generated in nuclear reactors, particularly in those using heavy water as moderator and coolant. Thermonuclear explosions produce large quantities of tritium. In both the cases tritium eventually gets released to atmosphere.

The thermo-nuclear explosions have resulted in significantly increased tritium content of atmosphere. Prior to these explosions, it was estimated that in nature only one atom of tritium existed for every $10^{18}$ hydrogen atoms. This ratio of $3^\text{H}:1^\text{H} (10^{-18})$ was referred to as Tritium Unit (TU) and concentration of tritium was expressed in this unit. (International Commission on Radiation Units and Measurements had objected the usage of word TU and instead recommended the use of the word Tritium Ratio (TR) instead. However, TU continues to
be in use and tritium content even now is reported in terms of TU.) Equivalence of 1 TU in various media at 25°C is given in Table 1.2³.

**Table 1.2**

*Equivalence of One Tritium Ratio in Various Media at 25°C*

<table>
<thead>
<tr>
<th>Medium</th>
<th>Atoms/cm³</th>
<th>Dis/sec/cm³</th>
<th>uCi/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$6.7 \times 10^4$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$3.20 \times 10^{-9}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>$4.1 \times 10^4$</td>
<td>$7.2 \times 10^{-5}$</td>
<td>$1.95 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>49</td>
<td>$8.7 \times 10^{-8}$</td>
<td>$2.35 \times 10^{-12}$</td>
</tr>
<tr>
<td>Ethane</td>
<td>149</td>
<td>$2.65 \times 10^{-7}$</td>
<td>$7.17 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

In heavy water reactors tritium is produced by $^2\text{H}(n,\gamma)^3\text{H}$ reaction. Due to the large quantity of tritium present in water in these reactors and due to the fact that it is not practicable to seal off all the leaks and make the reactor system leak proof, some tritium always escapes. It is assessed that under normal operation of a heavy water reactor, radiological problems due to tritium alone are more than the problems due to all other radio-isotopes put together¹⁴,¹⁵.
Tritium is also produced in ternary-fission. Tritium thus produced, besides being of very low yield, gets lodged inside the fuel and is released essentially during reprocessing of the fuel.

To meet the requirements of large quantities of tritium for research, and industrial applications like self-luminous paints etc., it is produced in highly concentrated form by nuclear reactions. Though a large number of activation reactions are possible, normally used reaction is $^6\text{Li}(n,\alpha)^3\text{H}$, because of its high thermal neutron cross section (940 barns).

1.3 Movement of Tritium in the Environment

The natural production of tritium is essentially confined to higher atmosphere. Most (~65%) of the cosmic ray produced tritium and that produced by high altitude thermonuclear explosions is introduced directly into the stratosphere, where inter-altitude mixing is very slow. In the case of low altitude thermonuclear explosions in tropical regions, tropopause acts as a trap for the sizable fraction of water vapour of the environmental atmosphere that is entrained by the ascending air current created by the explosion and prevents it from entering into stratosphere. The ice particles formed at tropopause fall back quickly into the troposphere. However in polar regions, the natural
water vapour content of the air is relatively low and much of the tritium from detonations in polar regions penetrate into the stratosphere and move to lower latitudes before moving into troposphere. The stratospheric tritium is slowly released to troposphere, preferentially in mid latitude region of 30° - 50° with a maxima in spring. Once in troposphere, the flushing effect of rainfall causes more rapid removal of tritium as water vapour. The vertical mixing in the troposphere is quite pronounced and the tritiated water is flushed down with a residence time of about a month as compared to its residence time of the order of a few years in the stratosphere. Since present tritium levels are mainly due to thermonuclear explosions and since these explosions were confined mainly to the northern hemisphere, one can expect variation in tritium distribution in northern hemisphere from north down to equator, with a maxima in 30°N - 50°N latitude region.

Tritium produced by natural or artificial processes is oxidised in atmosphere and thus the most abundant form of tritium in nature is tritiated water. This gets mixed with water from other sources and follows the water cycle. The global dispersion model can be represented as in Figure 1.35.
1.4 Detection and Measurement of Tritium

Due to the short range of the tritium betas, conventional detection methods such as counting by Geiger-Mueller counters, etc are not feasible. They can be detected by either gas-filled counters or by liquid scintillation detectors. Further, the concentration present in nature\(^{10,41-43}\), inspite of its increase due to thermonuclear explosions, results in a very low specific activity. Table 1.3 gives estimated tritium levels in natural waters, prior to explosion, immediately after explosion and at present. These levels are well below the detection limit of most of the detection systems. As such, to detect tritium at the
level present in natural waters, it would be necessary to quantitatively enrich the sample with respect to its tritium content. As the mass difference between protium and tritium is large and their chemical properties identical, most of the enrichment methods are based on differences in their physical properties.

1.5 Review of Earlier Work on Tritium distribution and application

Since discovery of tritium in 1939 by Alvarez and Corong, number of workers have used tritium as a tracer to study different branches of science.

Thompson and others have used it to study metabolical processes and hydrogen fixation in different organs of rats and mice. Similar studies have been made by Muller and Yousef on other animals. Krichman, Muller and Kistner have made similar studies on
cow's milk using both labelled water and labelled fodder. Mullay\textsuperscript{60} has made studies in hen and on the amount of tritium that gets fixed in egg.

Krishnamoorthy\textsuperscript{61} and Iyengar\textsuperscript{62} have studied tritium pick up by different types of cereals and vegetation. They have used both static and dynamic modes of foliage exposure so as to determine transfer of tritium from atmosphere to plants. Some of these studies\textsuperscript{63,64} have been made to study soil-plant relationships where as others\textsuperscript{56} are useful in food chain studies. Krichman\textsuperscript{56-58} and Sadarangani\textsuperscript{65} have investigated the fraction of sprayed tritium picked up by grass. Some of these workers have used soil exposure to determine migration from soil to plants. In all these studies, attempts have been made to determine fraction of picked up activity that remains in tissue free water (TFWT) and the fraction that remains in organically tissue bound (TBT). All these studies are climate - dependent.

International Atomic Energy Agency (I.A.E.A.) had organised a co-ordinated research programme to make such studies under different climates. A number of institutions from ten countries made these studies, keeping different factors in mind and their findings are summerised in I.A.E.A.'s technical report\textsuperscript{66}. 
Kirchman and others have indicated existence of a third fraction which can easily exchange with TFWT and TBT and they termed it as labile fraction. During studies on succulent plants, Krishnamoorthy has found that in cacti tritium residence time is very large (approximately 120 days) and this is expected since in succulent plants water turnover rate is expected to be small.

Some workers have used tritium as a tracer to study water circulation through trees. With the help of tritiated water, Kline and Ovington have estimated bio-mass in different forests.

Martin and Hatch made studies on tritium pickup by rats and other desert animals, tritium migration etc from Sedan Crater ejecta. From these studies with the help of soil-tritium content, they have attempted to calculate total amount of tritium ejected and have determined half value distance (HVD) to be about 200 ft from crater lip. Further from their studies on trapped animals, they conclude that the biological tritium residence in small animals reflects the residence time of tritium in the desert soil, as the tritium content in body of these animals soon attains equilibrium with tritium content of surroundings. Stead and Culler have studied movement of underground explosions produced...
tritium. The studies under CANE (chemical applications of nuclear explosions) program using Gnome nuclear event show that the entire tritium released will be oxidised and released to the atmosphere in tritiated water form. Miskel \textsuperscript{82} has reported some studies on tritium produced by atmospheric tests and concludes that contribution due to fission explosions is negligible as compared to fusion explosions and that the main contribution in fusion explosions comes from atmospheric tests.

Garland \textsuperscript{78} has used tritium for studying the exchange of water with atmosphere. He has studied precipitation from and evaporation to the atmosphere and effect of rain on migration of deposited tritium. According to him precipitation is more on bare soil as compared to vegitated soil and that rain helps in downward migration of the absorbed tritium. Sarma \textsuperscript{83} and Horton \textsuperscript{84} have reported evaporation losses from tritiated water pools. The authors have studied exchange between experimental pool and atmosphere and conclude that the condensation and evaporation processes taking place at water surface are dependent upon water column depth, humidity and temperatures of both water and air. Horton's studies show that when relative humidity is greater than 8\%, there is a net depletion of tritium in water since the atmospheric moisture is virtually tritium free. Barry \textsuperscript{85} has conducted similar experiments
on Pearch lake to understand process of heat exchange between atmosphere and earth's surface, water lost from and heat economy of earth's surface. Tritium tracer studies have also been made in hydrology and for underground water movement.

Bogen has reported atmospheric tritium concentrations in New York city where as Suess found that the precipitation rate of tritium is different during different seasons, maximum being in spring and early summer which he calls as 'spring leak'. According to him similar studies have been made with other radionuclides also. He reports that the tritium flux from stratosphere is almost one order of magnitude higher in spring and early summer than in fall and winter and this results in higher tritium content in precipitation in spring. These variations give rise to annual oscillations in the tritium content in precipitation. In northern hemisphere amplitude of these oscillations decreases from north to south as most of the tritium was introduced to the stratosphere at high northern latitudes. Usually tritium content gradient with latitude is greater over continents and is much greater in northern hemisphere than in the southern hemisphere. Libby has reported that there exists N-S and seasonal effects in natural precipitation. This is also expected on the basis of
nonuniformity of the stratospheric radioactive fall out pattern relative to latitude. In northern hemisphere precipitation is expected to be maximum in $30^\circ - 50^\circ$ latitude and minimum in polar and equitorial regions. His studies on tritium distribution during the three years moratorium on nuclear testing indicate that the bomb and the natural tritium distributions are roughly proportional, indicating that the same factors control these distributions. His studies further indicate that (a) tritium stratospheric fallout shows a peak at middle latitudes, (b) maximum appears in the tropospheric moisture over continents in summer and down wind therefrom and (c) that the principal mechanism for water movement over the world is wind. The rain water samples studied by him show a very low tritium content in southern hemisphere compared to that of northern hemisphere. This can be attributed to the fact that most of the bomb produced tritium is released in the northern hemisphere. A number of workers$^{34,93-97}$ have studied environmental releases of tritium from heavy water reactors and their dispersion in the vicinity of different nuclear installations. These studies show that at present the operating nuclear facilities do not release significant amount of tritium. The aquatic samples in vicinity of one of the installation$^{34}$ show a slight increase in their tritium activity.
In order to assess radiation dose received from tritium, different workers have made studies on turnover rates in animals\textsuperscript{55,98,99} and also in humans\textsuperscript{100-102}. During such studies Rudran\textsuperscript{103} and Lawrence\textsuperscript{104} have reported multi component elimination, different components having different biological half lives. In his studies Sadarangani\textsuperscript{101} did not find multi component elimination.

Deo\textsuperscript{105} has reported that tritium built up in plants in vicinity of nuclear installations can be used for environmental surveillance, but more studies have to be made to determine relationship between releases from an installation and the build up in plants in it's neighbourhood.

Ostlund\textsuperscript{106}, Bainbridge\textsuperscript{107,108}, Michel\textsuperscript{109} and Roether\textsuperscript{110} have made studies in the Pacific Ocean waters and Weiss\textsuperscript{111} has reported tritium concentration values in the Atlantic waters. From these studies Roether has suggested depth vs tritium concentration profile in oceans and concludes that in the upper layer of about 150 meters, tritium concentration remains constant and thereafter rapidly decreases with depth. Bainbridge from his studies concludes, on the assumption that the tritium concentration in the surface layer is only due to precipitation, that the top surface layer thickness
is only about 40 m. Michel from his inventory studies in the region 51°N - 60°S latitude concludes that the highest inventory is in the north of 20°N, drops rapidly from 20°N to 10°N and is constant from 10°N southwards in the top 500 m layer. From his studies on the Pacific Ocean, he has extrapolated values for the Indian Ocean whereas Fine112 has used Indian Ocean tritium data collected under Geosecs113 (Geochemical Ocean Sections) programme for predicting transport of water in upper 300 meters from the Pacific Ocean to the Indian Ocean. Fine112 has conducted studies to determine flow from the Pacific to the Indian ocean. From his studies on the Indian ocean, he has determined the tritium content on the surface and at 200 m depth in Indian ocean.

1.6 Present Work

In the present study, the distribution of tritium in water bodies in different parts of India has been studied with the following objectives:

(i) mapping the land water tritium levels in the different regions of the country.

(ii) establishing the base line data for different regions. This is of special significance to India's nuclear power programme since it provides base line data for comparision of any increase in the tritium in the environment due to reactor
operations.

(iii) determination of tritium levels present, both at surface and at different depths, in Arabian sea in the region from west coast of India to east coast of Somalia.

An attempt has also been made to project calculated tritium values present in land surface waters and ocean surface waters and to see if these values can be correlated with experimentally determined average values.