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The Influence of the Rate of Conversion of HT to HTO on Projected Radiation Doses from Release of Molecular Tritium

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ABSTRACT

Releases of tritium in the past have been largely in the form of tritiated water and the projected radiation doses could be estimated by assuming tritium behavior to parallel that of water. There is increasing interest in potential releases of tritium in the form of HT because of significant recent advances in fusion reactor research.

Several recent studies have shown that bacteria containing the enzyme hydrogenase can catalyze the conversion of HT to HTO at rates several orders of magnitude faster than the rates measured in atmospheric systems. Rates of conversion in the soil have been combined with estimates of rates of permeation of HT into the soil and with global and local models depicting tritium transport and cycling. The results suggest that for the anticipated conversion rates, the impact on projected radiation doses should be relatively minor.

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INTRODUCTION

It is generally assumed for estimates of environmental radiation exposure that tritium released into the environment is in the form of water vapor and would rapidly assume the same distribution as natural tritium. This has largely been true with the exception of several rather large releases of molecular tritium from the Savannah River Plant Production facility and the Lawrence Livermore Laboratory weapons program. Recent and anticipated advances in fusion research portend numerous future facilities each with inventories of tritium comparable to the natural inventory of 7 to 14 kg. We note that a fusion power plant may contain up to 10 kg (10^8 curies) of molecular tritium. Although limitation of release rates to $\sim$1 to 10 Ci/day seem technically possible, there is not yet any definitive information concerning the economic feasibility of such release rates. Hence it is appropriate to understand potential effects of chronic releases of tritium gas into the environment.

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An adequate understanding of the potential radiological effects to man from a release of tritium involves several considerations. Not only must one understand the global movement and distribution of tritium depending on its form of release and the location of discharge, but knowledge is also required of the local effects as a function of form at release. Tritiated water is more readily incorporated into the human body than is molecular tritium [1], and the maximum permissible concentration of HTO in air for nonoccupational exposure is lower by a factor of 200 than for HT [2]. Thus, potential processes and rates of conversion should be considered in developing models for assessment of releases of tritium gas.

CONVERSION PROCESSES AND RATES

Physical Conversion

Eakins and Hutchinson [3] measured the conversion of HT to HTO at a concentration of 2×10^{-2} mCi/cm^3 in the presence of various metal surfaces and estimated reaction half-times, extrapolated to a concentration of 3.4×10^{-2} μCi/cm^3, ranging from 4 years in the presence of platinum to 1150 years for glass. Phillips and Easterly [4] reported a first order reaction rate constant of $\sim 10^{-5}$ h^{-1}, which yields a reaction half-time of about 8 years; this is consistent with the range of 6-10 years residence time of HT in the atmosphere estimated by Mason [5].

Biological Conversion

The ability of enzyme systems of certain bacteria to catalyze the reduction of specific compounds to molecular hydrogen has been known since the 1930's [6] and metabolic oxidation of tritium gas was observed in the early 1950's [7,8]. However, not much attention has been paid to the role of metabolic conversion of tritium as it relates to a potential increase in radiation doses to humans. Rates of oxidation have been measured in various systems, from bacterial suspensions to whole mammals. Smith and Marshall [7] observed the conversion in 24 h of 41 of the 43 mCi of tritium introduced into a 100 ml suspension of *Azotobacter vinelandii* containing 4 mg cellular nitrogen per ml, demonstrating that bacteria containing hydrogenase are potential catalysts for tritium conversion.

Studies with several plants and soils have shown increasing evidence that soils, and in particular, the bacteria in soils, are important in catalyzing the oxidation process [9,10,11,12]. Liebl [13] reported rates of H_2 incorporation into soil of 2×10^{-12} to 4×10^{-12} g H_2/cm^2·s. Comparable rates of oxidation of HT in soil columns was found by McFarlane *et al* [12]. If these rates are integrated over the land surface of the earth - excluding the polar regions - the conversion of H_2 would be about 114×10^{12} g/a, which is about 71.5% of the tropospheric inventory [14]. Such a rapid conversion rate is not consistent with the chemical decay constant of 10.2 to 15.5% per year for HT estimated on the basis of interhemispheric exchange [5].

McFarlane *et al* [12] also have presented data indicating that HT in immediate contact with soil can be converted to HTO at a rate of about 20% per hour; their more recent data [15] shows a range in the conversion rates for various soils of 12 to 66% per hour or conversion half-times of 0.6 to 5.4 hours. Other laboratory data obtained with plants and soils suggest conversion half-times up to about 24 hours [9,12].

Diffusion of Tritium Gas into the Soil

Although these rates of conversion appear to be quite rapid, one must consider them in the context of the rate of penetration of HT into the soil from the atmosphere. The coefficient of diffusion of hydrogen gas in air is 0.611 cm^2/s(NTP) [16]. Heavier gases diffuse at rates inversely proportional to the square root of their density. Using the relationships presented in the Chemical Engineer's Handbook [17], it is estimated that the coefficient for diffusion of HT in air should be approximately 0.42 cm^2/s(NTP). In a porous medium, corrections must be made for porosity and for the tortuous path the molecule must follow to move around the solid particles. The effective diffusion coefficient is given by:

$$D_{eff} = \frac{D\theta}{\tau}$$

where D is the molecular diffusion coefficient in the gaseous phase, θ is the effective porosity of the porous medium, and τ is the tortuosity factor. In our estimate we assume $D = 0.4$ cm^2/s, $\theta = 0.2$ and $\tau = 1.5$, yielding an effective soil diffusion coefficient of $\sim$ 0.05 cm^2/s.

The mean penetration into the soil in a given time is given by:

$$\bar{x} = \sqrt{2D_{eff}t} \quad .$$

For a three-hour time period, the half-time for a conversion rate of 20% per hour, this corresponds to a mean penetration of about 30 cm. If this rate of penetration represents the average, it is estimated that the global rate of biological conversion in soil would be about 0.7% of the atmospheric inventory per year.

Conversion of HT in Vegetative Cover

Tritium gas can be converted to tritiated water in vegetative cover as well as in soils [9,10,11,12,18]. However, the rates of conversion appear to be significantly lower than in soil systems;

McFarlane *et al* [12] report conversion of about 1% in a 48 h exposure period. Even assuming a relative accessible surface area for vegetative cover over the earth's surface of ten times that of the land area occupied, it seems doubtful that conversion in the vegetative cover would be as great as in the underlying soil.

Conversion of HT in the Oceans

The solubility of hydrogen gas in water is fairly low, on the order of 2% of that in an equivalent volume of air in direct contact. Assuming rapid mixing and saturation of the surface 75 meters of the ocean, the inventory of HT in the ocean would be about $1.5\times10^{-2}\%$ of that in the atmosphere. The mixing time of the ocean surface 75 meters is about 3.5 years [18], so that we can estimate an upper limit for the rate of conversion in the oceans of about $4\times10^{-3}\%$ of the atmospheric inventory per year, if all tritium entering the ocean were converted to HTO. Actually, the surface waters of the oceans are generally supersaturated with respect to H_2, indicating that they serve as a source rather than a sink for hydrogen gas [14].

Summary of Sources and Sinks for HT Conversion

Schmidt has attempted to estimate the magnitude of various sources and sinks for hydrogen conversion [14]. His values, based on measurements, are summarized in Table 1. Based upon his estimates of sources and a tropospheric inventory of 160×10^{12}g H_2, he estimates a tropospheric residence time for H_2 of 6.1 to 7.4 years. This agrees quite well with the range of 6 to 10 years estimated by Mason on the basis of measurements of interhemispheric exchange of HT [5] and with the rates of HT to HTO conversion measured by Phillips and Easterly [4]. However, Schmidt's estimated rate of conversion of H_2 to H_2O in the soil seems much too high, both when compared to the total sources of H_2 and when converted to residence time. He points out that field conversion rates are likely to be much lower than the rates measured in the laboratory by Liebl [13]. This is born out by the later studies of McFarlane *et al* [12]. To balance the sources, the rate of conversion in the soil should be of the order of 15×10^{12} to 20×10^{12}g H_2/a. Estimates based on rates of conversion measured by McFarlane *et al* [12,15], limited by diffusion into the soil, are on the order of 1.1×10^{12}g H_2/a.

MODELS FOR ENVIRONMENTAL CYCLING OF TRITIUM

Global Model

A generalized model for tritium cycling, based on the hydrological cycle, has been employed by Easterly and Jacobs [19] to estimate the effect on the collective radiation dose to the world population following discharge of tritium into various environmental compartments. A schematic of the cycle is presented in Figure 1. The water compartments are assumed to mix uniformly and instantaneously and to interact with each other in a linear manner. For a set of conditions (for example, a globally uniform input of tritiated water into one or more compartments), the equations can be solved and evaluated for the relative compartmental distributions at subsequent times. From this model, it is estimated that tritiated water releases to the atmosphere would give rise to collective radiation doses less by a factor of 10 than releases into surface waters (See Table 2). The projected collective dose for atmospheric release of tritium gas is within a factor of two of that for tritiated water vapor, when atmospheric conversion half-times of up to 10 years are considered. If the primary compartment for conversion is the soil, the tritiated water formed may be in closer contact with man and the projected collective dose slightly higher, perhaps up to a factor of two. Both the preliminary data of Phillips and Easterly [2] and atmospheric residence time estimates of Mason [3] indicate a slow conversion in the atmosphere with half-times on the order of 5 to 10 years. Hence for the global scale, if releases are to the atmosphere, estimates of population dose are little affected by uncertainties in the conversion rate.

Local Model

Although our estimates indicate that the rate of conversion of HT to HTO does not have a major impact upon projected radiation doses from tritium releases when considered on a global scale, the same question needs to be addressed from a local perspective.

The calculations of radiation dose downwind from a molecular tritium release depends on numerous imprecisely known variables. The greatest uncertainties lie in the relative HTO/HT dose conversion factors and the rate of HT to HTO conversion. To test the sensitivity of the conversion rate, an atmospheric transport computer code, ACRA-II [20], was modified to include the conversion of HT to HTO. The code uses a three-dimensional normal distribution (Gaussian) model to simulate transport of material through the environment. The conversion rate is assumed to follow a first-order law; this is simulated by means of a pseudo-radioactive decay of HT with the daughter product being HTO. Sample calculations have been made for various conditions of stability, height of release, wind-speed, and rates of conversion.

The relative risks resulting from a release of HT from heights of 0 and 100 m are shown in Figures 2 and 3, respectively, for HT to HTO conversion rates of 0, 0.1, 1 and 10% per day. We feel that it is unlikely that more than 10% of the tritium gas released from an elevated source would come into immediate contact with the soil daily due to the limitations imposed by atmospheric mixing. The relative risk for 0% per day conversion is numerically equal to χ/Q in s/m^3. Numerical values of relative risk are related to dose by a constant factor. The hazard from HTO is taken to be a factor of 200 times that for HT based upon ICRP recommendations [2].

Values along the conversion curves are found by multiplying the HTO concentration by 200 and adding the product to the remaining concentration of HT. Thus, each curve represents the total relative risk for that conversion rate.

Doses can be calculated by multiplying the relative risk index by the HT release rate (Ci/s), the exposure time (s), and the dose conversion factor for HT (rem Ci^{-1} s^{-1} m^3), which we have assumed to be a factor of 200 lower than that for HTO.

From Figures 2 and 3, it is seen that for distances up to 5 km from the point of release, the difference in risk at any point between 10% per day conversion and no conversion is less than a factor of two; at 100 km the difference is a factor of 14. Virtually the same results are obtained for both 0 and 100m release heights and the difference caused by a deposition velocity for HTO of 1 cm/s compared to 0 cm/s is at most 15%. This occurs at a distance of 100 km where the concentration has been reduced about 9 orders of magnitude below the initial concentration.

If one further considers the land area affected, as an approximation of the number of people potentially exposed, the difference in risk between 0 and 10% conversion per day is less than a factor of 2 within 10 km and a factor of 5 within 100 km.

On the basis of our assumptions, we conclude that the rate of conversion of HT to HTO does not have a significant impact on projected radiation doses to the population near the point of release (within 10 km) nor on a global scale. The relative impact may be greatest in the region from 10 km up to the point where deposition into the ocean becomes significant.

SUMMARY

Recent studies have shown that biological systems, particularly the bacteria in soils, can catalyze the oxidation of HT to HTO at rates which are several orders of magnitude faster than the rates measured in atmospheric systems. However, the movement of HT from the atmosphere into contact with the soil is likely to be the rate limiting step. When the anticipated ranges of conversion rates are incorporated into models for global or local transport and cycling, it appears that the impact on projected radiation dose is relatively minor.

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CAPTIONS

Table 1. Global Molecular Hydrogen Budget Data

Table 2. Relative Percent of Tritium in Various Hydrologic Compartments After 100 Years' Continuous Release of Tritiated Water into the Atmosphere or Surface Waters

Figure 1. Global Hydrologic Cycle with Respect to Man

Figure 2. Relative Risk for HT and HTO vs. Distance for Varying Conversion Rates for a Release Height of 0 m, a Wind Speed of 1.7 m/sec and C-stability

Figure 3. Relative Risk for HT and HTO vs. Distance for Varying Conversion Rates for a Release Height of 100 m, a Wind Speed of 1.7 m/sec and C-stability

Table 1. Global Molecular Hydrogen Budget Data*

Sources of H_2	(10^{12}g H_2/a)
Anthropogenic activity	13.0
Oceans	4.0
Photochemistry (atmosphere)	4.6 - 9.2
Volcanoes	0.1
	21.7 - 26.3
Sinks for Conversion of H_2 to H_2O	
Photochemistry (atmosphere)	3.7 - 7.3
Soils	114
	117.7 - 121.3

*Adopted from Reference [14].

Table 2

RELATIVE PERCENT OF TRITIUM IN VARIOUS HYDROLOGIC COMPARTMENTS AFTER 100 YEARS' CONTINUOUS RELEASE OF TRITIATED WATER INTO THE ATMOSPHERE OR SURFACE WATERS

HYDROLOGIC COMPARTMENT OF ACCUMULATION	COMPARTMENT OF RELEASE	
	ATMOSPHERE	SURFACE WATER
Atmosphere	0.22	0.022
Vadose water*	0.87	0.090
Deep groundwater	5.6	0.57
Surface water	0.017	0.19
Ocean surface	46.0	49.0
Deep ocean	47.0	50.0
Man	2.5×10^{-6}	1.5×10^{-5}

*Water in earth's crust above the permanent water table.

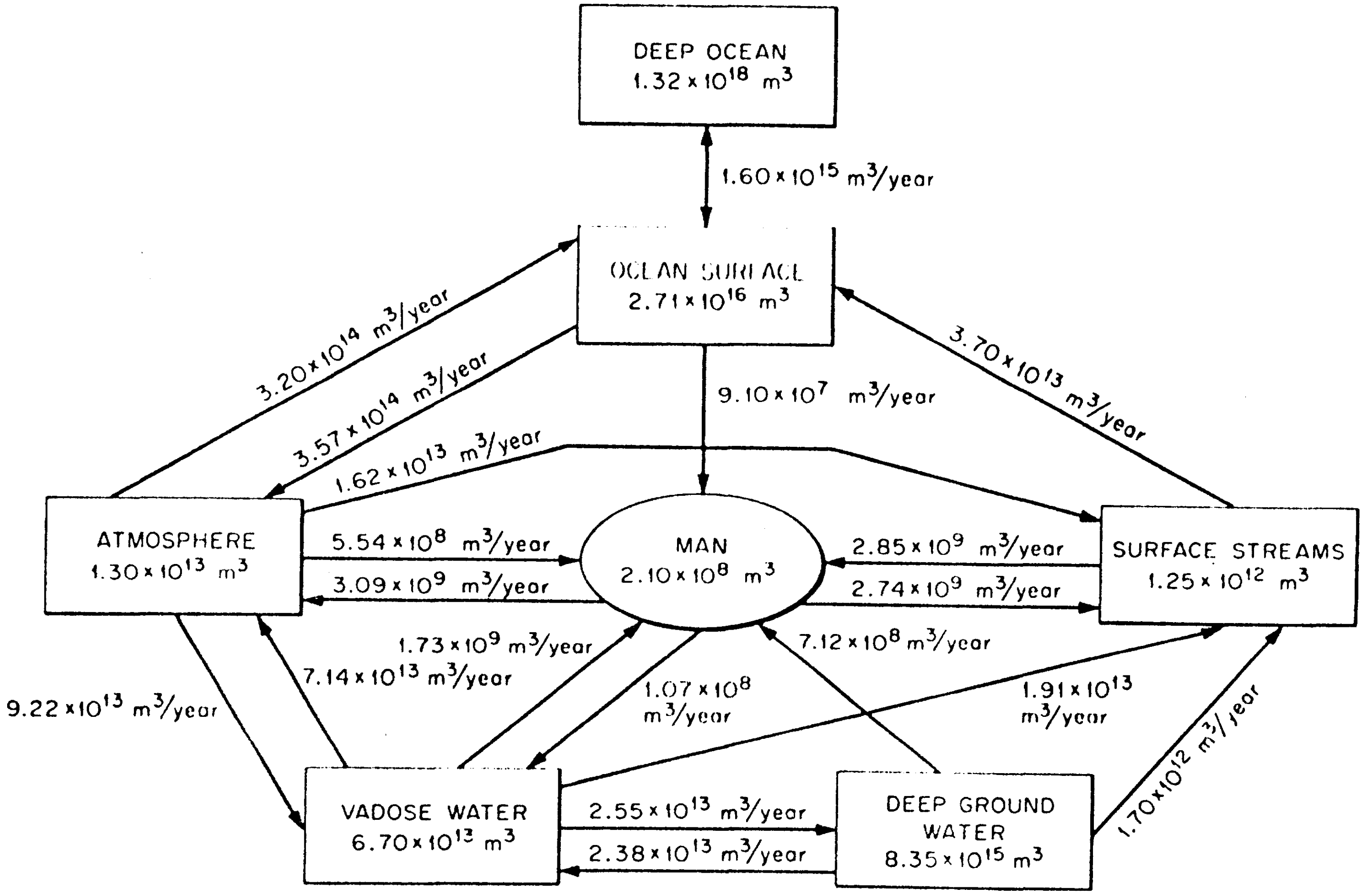

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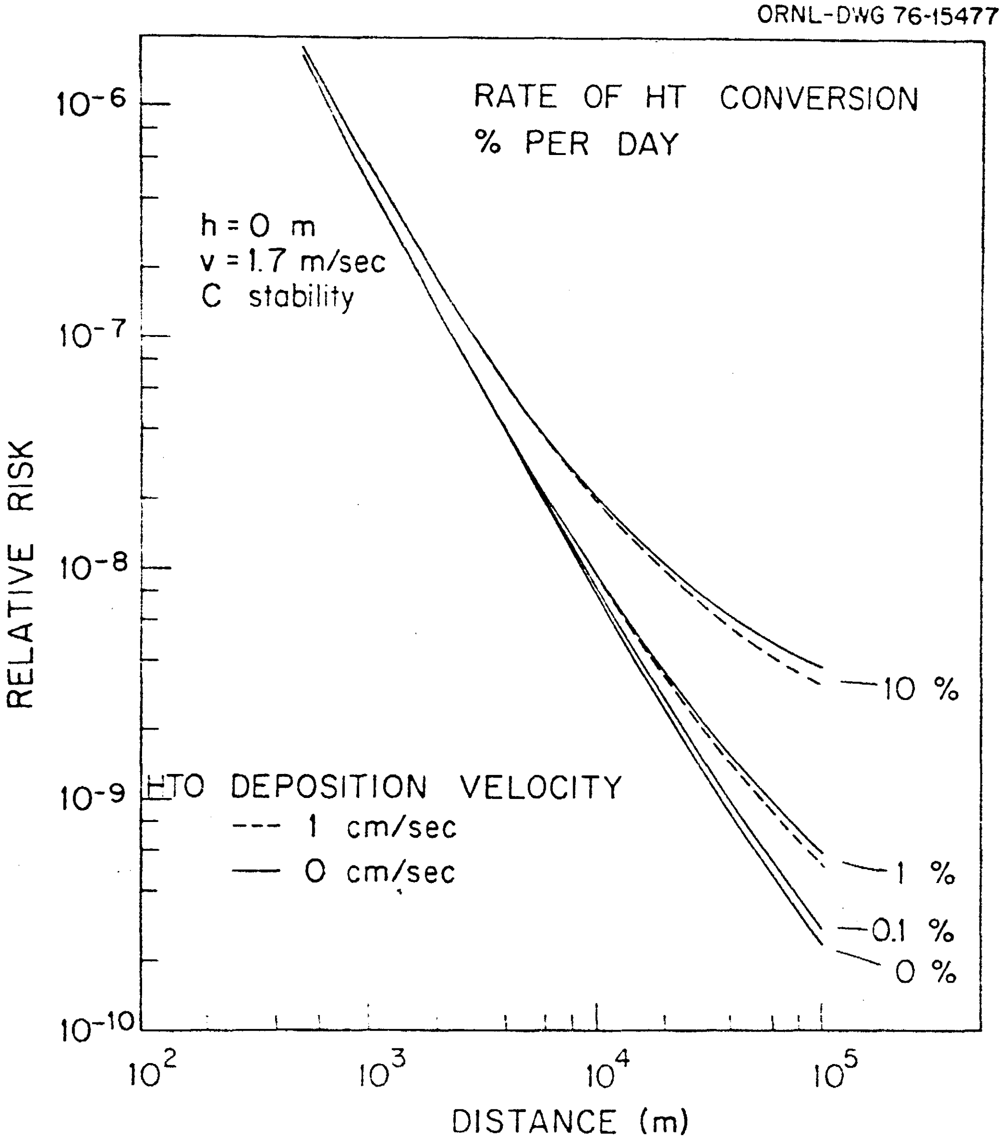
Fig. 1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RATE OF HT CONVERSION
% PER DAY
h = 0 m
v = 1.7 m/sec
C stability
HTO DEPOSITION VELOCITY
--- 1 cm/sec
— 0 cm/sec
10 %
1 %
0.1 %
0 %
RELATIVE RISK
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^2
10^3
10^4
10^5
DISTANCE (m)

Fig. 2

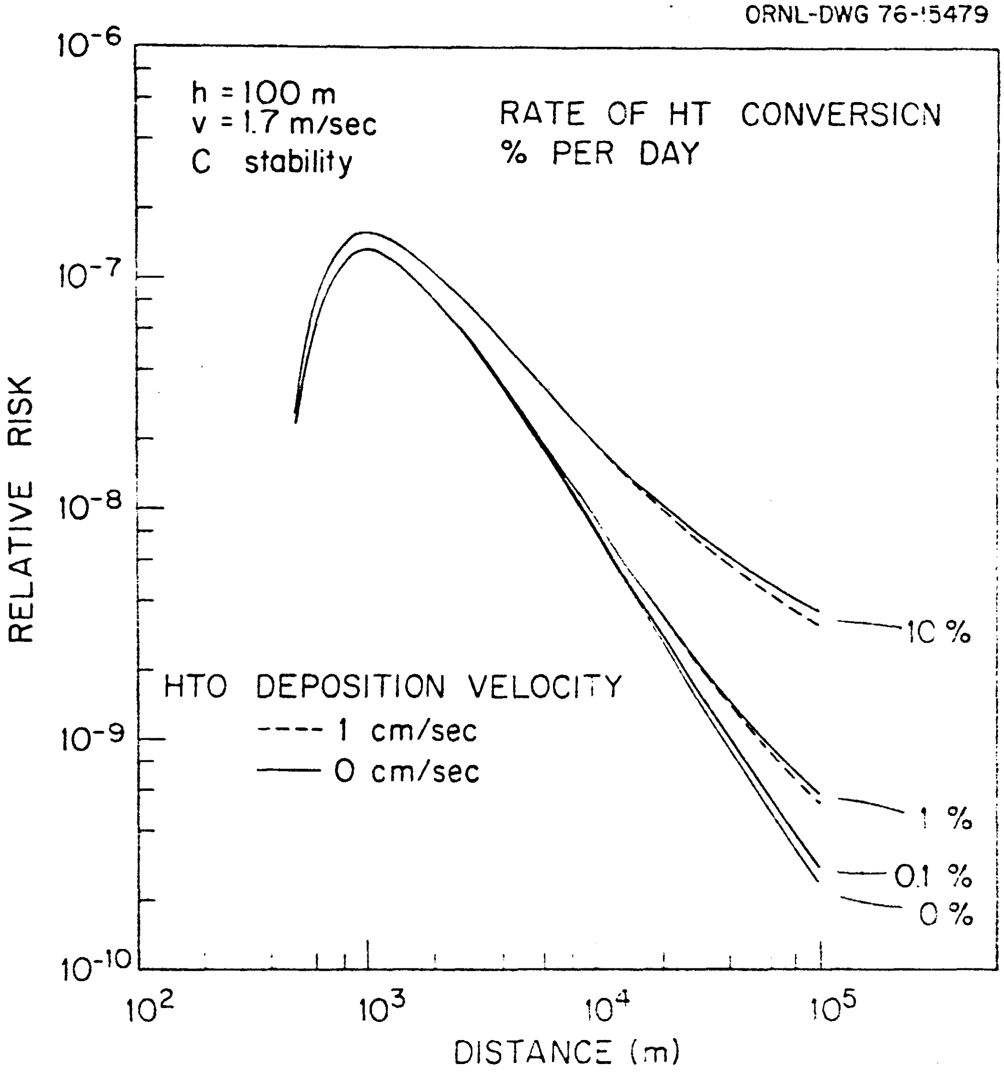
ORNL-DWG 76-15479
h = 100 m
v = 1.7 m/sec
C stability
RATE OF HT CONVERSION
% PER DAY
HTO DEPOSITION VELOCITY
---- 1 cm/sec
—— 0 cm/sec
10 %
1 %
0.1 %
0 %
RELATIVE RISK
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{2}
10^{3}
10^{4}
10^{5}
DISTANCE (m)

Fig. 3