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Studies of HTO transport and oxidation in unsaturated soil

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Abstract. A paper presents results of studies of HTO transport in unsaturated soil in the vicinity of long-term emission source and tritium oxidation by soil microorganisms. The objective of the first study was to determine the vertical profile of tritium from surface to 10m-depth using boreholes. The boreholes were sampled every 1m for measurements of tritium in the soil water. The objective of the second study was to determine tritium oxidation activity of soil in laboratory environment depending on temperature, tritium activity, humidity, etc. A special apparatus in which a mixture of air, water vapour and tritium gas is pumped through the soil material under study was used to determine soil oxidation activity. The amount of HT converted into HTO in the soil sample during a certain period of time was used to determine the tritium reaction rate. This rate varies, depending on the catalytic and/or biological activity of the material. The knowledge of the reaction rate can help to estimate HT deposition rate of HT onto the surface of an undisturbed soil sample. A theoretical treatment based on simplifying assumptions has shown that the deposition rate can be expressed by the reaction rate and the effective diffusion coefficient of HT in the porous material.
The studies are performed in frame of ISTC project 654.

1. INTRODUCTION

When HT is emitted into atmosphere its major amount is oxidized in the surface ground layer. The elementary tritium (HT) when entering the soil is known to oxidize to become HTO and then it can enter the depth of the unsaturated soil area.

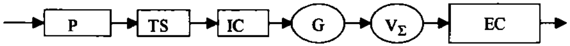
Tritium oxidation in the surface ground layer was studied in papers [1-9]. The mechanism and accelerated oxidation of hydrogen isotopes, HT included, are caused by biochemical reactions involving hydrogen bacteria available in soils [3, 6, 9]. The above studies conducted in laboratory and field conditions resulted in obtaining a number of values of HT deposition rates, HT [1, 2], oxidation constants [4-6, 9] and periods of HT semi-washing out of the gaseous phase [1, 6]. These data demonstrate that the oxidation process of HT in soil depends on a variety of factors, including the type and the bedding depth of the soil, its humidity and temperature, the degree of its treatment, the affect of a number of chemical and physical factors on it.

The aim of the current work was to develop the technique and to conduct investigations with the view of determining constants of effective rates of oxidation of (HT) to (HTO) in the local (regional) soil samples.

2. EXPERIMENTAL PART

In the papers [1-9], to research into tritium deposition processes and oxidation in the soil, use was made of the techniques based on exposure of a sample (or a ground section) in closed volume, containing air with the pre-determined initial tritium concentration. During experiments conducted with the use of these techniques, the process of HT diffusion in soil is always available to a certain extent in experiments. Strictly speaking, the process constants obtained at that (deposition rates, the oxidation rate constant, the period of semi-washing out) are just a few of effective constants characterizing the overall oxidation process: (HT) → (HTO) including the process of HT supply (by diffusion) to the given point and the oxidation process proper.

To maximally decrease the diffusion effect in experiments, to simplify processing and the following interpretation of results, we have selected a technique based on forced blowing of soil samples through with air, at the tritium concentration of $\approx 1{,}5\times10^{-9}$ Ci/l being constant during the experiment. The constant tritium concentration was maintained by using an ad hoc fabricated tritium source. The layout of the 2-channel installation allowing the experiment concurrently using two samples both in the mode of blowing through and close loop is presented in fig.1.



P – pump; TS – tritium source; IC – ionization chamber; G – rotameter;
V_Σ - air flow meter; EC – experimental cell with the soil sample.

Figure 1: The Block diagram of one channel of the installation.

Soil samples to be studied were selected from the top layer of soil (0-5 cm), cleaned of plants' visual roots and were stored in refrigerators at the temperature of 10^0C till the experiment. Soil humidity was measured by collecting ~ 15 g samples with their following drying at $t=+110^0$C until their weight became constant.

A soil sample of bulk density was placed into the working cell between two filters. When conducting experiments, the temperature, air consumption, tritium concentration in airflow, the volume of the air passed were recorded. The amount of tritium converted to HTO and deposited in soil, was estimated by using thermal vacuum desorption of soil water from the sample and the following measuring of its activity with the liquid scintillation counter.

The constant of effective tritium retention rate in the soil sample under investigation was calculated by using the formula:

$$K_{eff} = \frac{\left(C_1^{soil} - C_0^{soil}\right)\cdot m_s \cdot \varphi_s}{V \cdot C^{air} \cdot \tau}, \qquad (1)$$

where K_{eff} – is the constant of effective tritium retention rate in soil, %/min; C_0^{soil}, C_1^{soil} -is HTO concentration in soil water before and after the experiment, respectively, Ci/g; m_S -is the sample mass, g; φ_S - is the relative water content in soil, mass % ; V –is the volume of the air passed through the sample, l; C^{air} –is the tritium concentration in the air flow at the entrance to the working cell; *Ci/l*; τ - is the time of blowing the sample through, min.

To select modes, at which the effect of HTO diffusion and removal from the sample with water would be minimal, a number of experiments were conducted. The results of these experiments are presented in tables 1, 2.

Table 1 presents the results illustrating the difference of tritium retention rates in dynamics (during blowing the samples through with air) and static (without blowing through, with the diffusion effect available). While conducting these experiments, the tritium concentration was maintained constant, equal to ~ 1.5×10^{-9} Ci/l.

Judging by the results presented, at an ordinary contact of samples with still air, with tritium contained in the air brought into the sample through diffusion, the tritium retention rate in soil is by 8 to 10 times lower than that during blowing through. At that, the contact area of samples with air, during the experiments conducted in static conditions, was ≈ 16 times higher than the piping section through which the air was brought in conditions of dynamics. This clearly shows that the rate constants of the process HT→HTO, obtained in the experiments involving no pumping of air/HT mixtures through the sample, represent, strictly speaking, some approximation to constants of oxidation rates rather than being themselves proper.

Table 1. Tritium retention in samples under dynamic and static conditions

Mass of soil samples, g	Air consumption, l/min	Time, min	C, Ci/g of soil
200	4.5	25	1.5×10^{-10}
200	-«-	-«-	1.44×10^{-10}
150	4.6	-«-	1.37×10^{-10}
200	static	-«-	0.12×10^{-10}
166	static	-«-	0.20×10^{-10}

Table 2 represents the results concerning assessment of the effect of soil samples' blowing on variation in their humidity during the course of the experiments.

Table 2. Variation in relative content of soil water in samples when being blown through with air

Weight of soil sample, g	Initial humidity of soil, mass %	Air consumption, l/min	Humidity of air pumped through, %	Pumping time, min	Humidity decrease, relative %.
200	13.7	8	85	30	6.7
200	16.8	8	70	30	7.7
55	6.85	4.5	25	5	2
55	6.85	4.5	-«-	5	2.1
55	9.8	4.5	-«-	5	2.9
55	9.8	4.5	-«-	5	2.8
55	20	8	-«-	5	4
55	20	8	-«-	5	3.9

It follows from the results presented in table 2 that the minimal bringing out of soil water is implemented with sample's weight of 55 g and air consumption of ~ 4.5 l/min.

To maximally decrease the diffusion effect and HTO bringing out with water from the sample, the following parameters were selected: the sample's weight of 55 g, the air consumption of ~ 4.5 l/min and the blowing time of 5 minutes.

3. RESULTS AND DISCUSSIONS

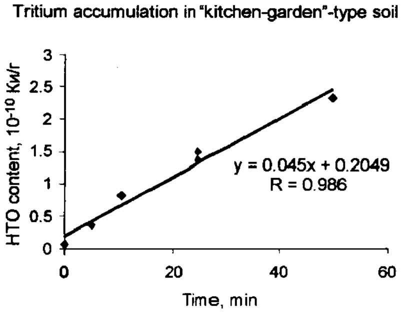
Table 3 presents the constant values of effective rates for tritium retention in soil samples under investigation selected from a variety of places.

Table 3. Constants for effective rates of tritium retention in soil samples selected from a variety of regional places

Soil type	Sampling point	Humidity, mass %	K_{eff}, %
Vegetable-garden	«1»	13.65	1.9 ± 0.4
	«2»	16.8	3.8 ± 0.9
	«3»	16.1	2.3 ± 0.6
Sand, forest	«4»	5.03	4.3 ± 0.9
	«5»	4.66	12.7 ± 3.2
	«6»	4.6	7.5 ± 1.9
	«7»	4.53	6.2 ± 1.5
	«8»	5.25	5.5 ± 1.6

As one can see from table 3, the values of constants obtained K_{eff} represent a wide range for the given region (1.9-13) %/min and agree in value with the data of papers [1, 4], according to which $K = (1\text{-}20)$ %/min.

Fig.2 presents the dependences of tritium retention in samples on time when being blown through with air, at the tritium constant concentration of ~ 1.5×10^{-9} Ci/l. These graphs represent the equations of the straight line approximating the results and indicate the correlation factor (R).


Tritium accumulation in "kitchen-garden"-type soil

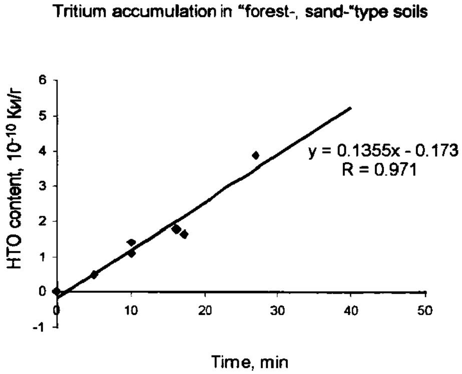

Tritium accumulation in "forest-, sand-"type soils

Figure 2: Dependence of tritium concentration in samples on time when being blown through with air at the tritium constant concentration of ~ 1.5×10^{-9} Ci/l.

As one can see from fig.2, tritium accumulation within the time range under investigation actually occurs according to the linear law. The linear law testifies to the fact that the oxidation process takes place in the initial section of the curve, therefore, the use of the formula (1) to calculate K_{eff} is quite possible. It should be mentioned that the tritium retention rate in forest ground is by a factor of 3 higher than in treated (kitchen-garden) soil. This fact testifies to the different biochemical activity of soils and agrees with the data earlier obtained in [1,4].

Fig. 3 presents the dependence of K_{eff} on soil humidity. Arithmetical mean values are indicated in graphs by markers; n is the number of experiments conducted at the same humidity. Humidity variation in soil samples selected in the same place was achieved by their drying or by adding distilled water into them.

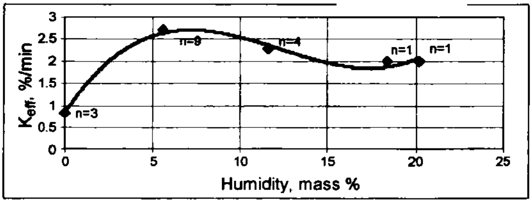


Figure 3: Constants' dependence of the effective rate of tritium retention on soil humidity (sand-forest)

As one can see from fig.3, a weakly pronounced peak in observed at φ_S = 5-8%. Such a form of the curve is in qualitative agreement with the results of the paper [4] and can be caused by decrease of the concentration and biochemical activity of aerobic hydrogen bacteria depending on the soil humidity, both with the soil being dried and with soil pores being filled with water.

Judging by the above results, one can make the following conclusions:

1. The technique and equipment developed can be used to determine kinetic interaction constants for tritium (retention) oxidation process in soils.
2. The constants of effective rates for tritium retention in soils can be treated in the first approximation as constants of HT oxidation rates. The K_{eff} values obtained for soils of the studied region in laboratory conditions constitute (2-13) %/min and agree with the results of the papers [1,4].

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