

## OXIDATION OF HT-GAS IN THE SYSTEM AIR/SOIL

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## 1. INTRODUCTION

Tritium is a nuclide with a natural geochemical pathway: It is produced nearly exclusively in the higher atmosphere, oxidised at least to water and buried once in the groundwater and oceans until it decays. The calculation of the global inventory depends on the velocity of the supplying reactions: The range between  $10^{18}$  to  $10^{19}$  Bq seems to be the best one /1/. As a rough number about 10 kg tritium seems to be the natural global tritium inventory. It is predominantly bound to water and therefore part of the natural water cycle.

The major anthropogeneous tritium sources are bomb produced tritium, reactor technology and special applications (dyes, lamps). Further sources of HT and HTO are reprocessing of fuel elements, pilot projects in fusion technology and solid-state physics experiments.

Ten years ago a remarkable high content of tritium has been found in the atmospheric hydrogen compared to the water vapour. From experiments with inactive hydrogen and geochemical considerations it has been concluded that the soil organisms are the most important sink for gaseous tritium under natural conditions /2/. Further studies /3/ and experiments /4/ had focussed again the attention to the soil as the main sink of HT. In an air volume, which contains HT, its oxidation to HTO seems to be a very slow process, especially if the radioactivity is low /5/. The next step of interest in the radioecological pathway of tritium is the contact with the surface of plants and of soil. A first set of soil experiments was conducted to study the velocity of HT-conversion under well-defined conditions in a gastight experimental setup.

## 2. EXPERIMENTAL PROCEDURE

HT is taken from a glass container (1.1 L) with a stock supply of about  $4 \times 10^9$  Bq HT (Amersham TRG 1). The container is sealed by a silicone stopcock, which is covered with mercury. The gas volume must be kept free from oxygen. The HT is taken by a syringe and fed into the reaction circuit through a silicone sealed injection stopcock. The volume difference is replaced by helium. About  $2 \times 10^6$  Bq are used for each test run (reproducibility  $\pm 5$  %).

The soil samples were taken from an air-dry stored parabraunerde (loess-type; Eschweiler, North-Rhine Westphalia, Fed. Rep. Germany). Some characteristic data are /6/: pH(CaCl<sub>2</sub>) 5.9/1.4 % C(organic)/12.0 % clay, 28.4 % silt, 58.3 % fine sand. The maximum water holding capacity is about 46 %, during the experiment it was adjusted between 18 and 19 %. The moist soil was transferred into the reaction vessel (12 cm diameter). While increasing the amount of soil the surface area remained constant. Four soil treatments were compared: sterilisation in an autoclav (120 °C), moistening with deionized water, addition of either a filtrate or a suspension of a garden soil. Moist soil has been stored two days in darkness.

The closed experimental circuit (see Figure 1) has a volume of 2.6 L and is made from glass and stainless steel. Some fittings contain either teflon or grease sealings. The soil in the reaction vessel (up to 1.0 kg) is kept under constant conditions (temperature 22 °C, relative humidity 75 %, air turnover in the circuit  $40 \text{ l h}^{-1}$ ). After its contact with the soil the HT-concentration

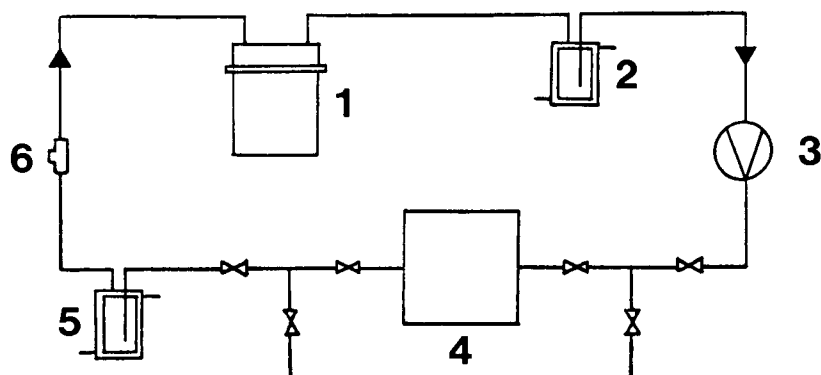


Figure 1: Scheme of the experimental circuit (1: reaction vessel containing soil, 2: cooling trap, 3: pump, 4: ionisation chamber, 5: dew point trap for air humidity, 6: injection point).

of the air is measured continuously by an ionisation chamber. Before entering the chamber the air must be dried by cooling traps, to separate HT and its reaction product HTO. The self-constructed ionisation chamber (stainless steel, 500 V, 65 mm diameter, 0.25 l volume, aluminium barrier to lengthen pathway) has an efficiency of 95 %, a sufficiently short response time, and no noticeable memory effect. The resistance of the ionisation chamber can be read from a teraohmmeter Knick H 12 (range:  $5 \times 10^6$  to  $10^{16}$  ohm, detection range:  $0.2$  to  $1 \times 10^6$  Bq  $l^{-1}$ ). The air stream (driven by a metal bellows pump) is detected by a flowmeter. Leaving the ionisation chamber and the flowmeter the relative humidity of the air is adjusted by a dew point trap.

The tritium activity of all samples (air, water, organic material in the soil) is measured as water by LSC. Gas and organic material are burned in a stream of oxygen. The tritium content of HTO and of the organically-bound fraction are defined in the following manner: HTO is the portion, which can be extracted by a twofold vacuum distillation of water (second distillation after addition of inactive fluid). The remaining tritium burned in the oxygen stream is assumed to be the organically-bound fraction. After calibration of the oxidation all samples can be compared directly to get a tritium balance, to detect unnoticed losses or sinks within the reaction circuit.

### 3. RESULTS

After a twofold sterilization of the soil the HT-concentration in the experimental setup shows only a very slow decrease during the first hours after HT-injection. Afterwards the HT-content of the air remains constant.

The loss of HT from the gas above the non-sterilized soil can be described by a simple exponential function ( $A$  : HT-activity);

$$A_t = A_0 e^{-kt}, \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k}. \quad (2)$$

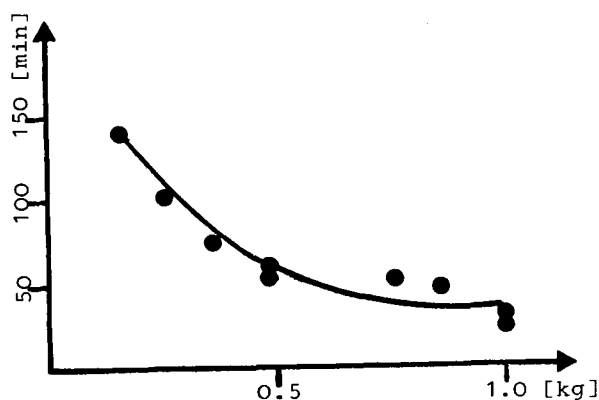


Figure 2:

Dependence of the half-time from the amount of soil in the reaction vessel (theoretical curve by least square method drawn as solid line) (soil moistened with deionized water).

This means, the HT-loss is proportional to the HT-concentration in the air. Also, only one reaction should be responsible for the HT-turnover. For there are different values of  $A_0$  (e.g. individual adjustment of the pressure in the circuit, differences in the amount of injected HT) only the half-time  $t_{1/2}$  was taken as a measure of the turnover velocity. The half-time of the reaction in the presence of the biologically active soil should be

$$t_{1/2} \propto 1/Q, \quad (3)$$

where  $t_{1/2}$ : half-time (min),  $Q$ : amount of soil (kg). The experimental results, using soil simply moistened with deionized water after storage under air-dryness, fit the equation (4):

$$t_{1/2} = 7.8 + 25 \times 1/Q \quad (r = 0.98). \quad (4)$$

The equation proposed above assumes a well-mixed gaseous atmosphere in the soil and consequently a homogeneously distributed reaction in the soil column. The limit of 7.8 minutes is significant from zero at the level of 80 %. This may be due to an incomplete mixing with the soil gas volume, or may be the limit of the whole experimental arrangement.

To support this consideration the profile of the resulting HTO in a soil column was analyzed (Table 1). The data show only a slow decrease of concentration in HTO with increasing soil depth. This leads to the conclusion, that the constant in equation (4) of about 8 minutes can be considered as the result of experimental limitations.

Table 1: HTO-activity (kBq/g dry soil) after reaction of soil (moistened with deionized water) with HT gas. Four segments of soil were taken in the center and near the border of the vessel from top (1) towards the bottom (4).

segment	sample from			
	center		border	
	activity	%	activity	%
1	2.1	100	2.1	100
2	1.8	86	1.6	76
3	1.8	86	1.5	71
4	1.6	76	1.5	71

Only less than 1 % was found as organically-bound fraction. Nearly all of tritium gas was converted to tritiated water as the primary reaction product. This water remains mainly at its reaction site during the observation period. Only  $1.7 \pm 0.9$  % of the total tritium could be detected in the cooling period finally.

The addition of a filtered soil extract did not enhance the half-time of the reaction (Table 2), while a test run with a suspension of garden soil showed a rapid reaction velocity, which was in the range of the experimental detection limit.

Table 2: Half-time of the HT-conversion (min) in dependence from different treatments of the soil.

amount of soil (kg)	deionized water	garden soil filtrate	garden soil suspension
0.5	26 28	37	—
1.0	52 58	53	10.5

#### 4. DISCUSSION AND CONCLUSIONS

Under laboratory conditions a rapid conversion of HT to HTO from air moving over a soil has been observed. This is in accordance with former results /3/, /4/. The HT is lost into the whole soil column, remarkable loss of HTO back to the air humidity is observed.

Our results are in accordance with the literature /7/: The most intensive HT/HTO-conversion has been observed by warm, moist loam. The addition of formaldehyde vapour lowered, the addition of nutrient solution or microorganismic cultures enhanced the HT/HTO-reaction in the soil. These results also confirm the role of soil organisms as major site the HT/HTO-conversion. Our observation did not include plants. For beans preliminary results reported a conversion of HT to HTO, but not to organic material, too /8/. In the next future one should test the dependence of the HT/HTO-turnover in soil from environmental conditions (e.g. temperature), and should confirm the role of microorganisms in contrast to pure chemical reactions by stimulation and inactivation procedures.

#### 5. LITERATURE

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