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**Experimental measurements of the bacterial oxidation of HT in soils:
impact over a zone influenced by an industrial release of tritium in HT
form.**

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Experimental measurements of the bacterial oxidation of HT in soils: impact over a zone influenced by an industrial release of tritium in HT form.

Abstract

Tritium is a radionuclide released to the atmosphere by nuclear industries in various forms, mainly HTO and to a lesser extent HT. However, some nuclear sites may emit predominantly HT in the atmosphere. The HT is oxidized to HTO essentially in the top cm of soils, and that the formed HTO is then possibly released into the atmosphere. HTO is an assimilable form by plants. Therefore, it is important to understand the environmental behaviour of HT.

In this work, we adapt the bacterial oxidation model of HT in soils of Ota *et al.* (2007) by laboratory experiments on soils typical of western France, and we have in particular adapted the frequency factor A and the Michaelis-Menten enzymatic reaction parameter (Km) on the basis of an Arrhenius equation in function of the porosity of the soil.

We then applied this model to the environment near the reprocessing plant of Orano la Hague (France), which emits a significant amount of HT. Based on the adapted model, and knowing the atmospheric variations of HTO and HT over the period 2013-2016, we estimated that the mean HTO activity in soil due to atmospheric HT reached 0.6 Bq.L^{-1} (with a peak value of 5 Bq.L^{-1}) while the mean value with all sources taken into account is 6.2 Bq.L^{-1} . Then, in an environment such as that surrounding the Orano La Hague plant, where near-field atmospheric HT activity is very high, the bacterial oxydation contribution to produce HTO in the soil can be considered as approximately 10%. The flux to the atmosphere from these source representing approximately $1.5 \text{ Bq.m}^{-2}.\text{d}^{-1}$. If we consider an area of 2 km around the plant (i.e. 13 km^2), we estimate 218 Bq.s^{-1} of HTO was released by the soil, representing less than 0.1% of the direct atmospheric release of HTO around the site. From this work, it appears clear that this secondary source term from the soil is insignificant at this specific site.

Keyword : HT, bacterial oxydation in soil, soil texture, reprocessing plant.

29 **1. Introduction**

30 Tritium (^3H) is a low energy β -emitting radionuclide with a half-life of 12.32 years. Tritium is
 31 produced by naturally-occurring processes through the interaction of gases and cosmic
 32 radiation. Natural abundance is estimated at about 4.5 kg of tritium, produced at an average
 33 rate of $0.32 \text{ atom cm}^{-2}\text{s}^{-1}$ of earth surface (Masarik and Beer, 2009, UNSCEAR, 2016),
 34 corresponding to $\approx 258 \text{ g y}^{-1}$ (Oms *et al.*, 2019). Atmospheric tests of nuclear weapons
 35 between 1945 and 1980 led to an estimated release of 668 kg, corresponding to about 242×10^6
 36 TBq during that period (Okada and Momoshima, 1993; UNSCEAR, 2000); in 2016, the
 37 tritium remaining from the fallout from atmospheric nuclear weapons testing is estimated to
 38 be 22-23.5 kg (Oms *et al.*, 2019). Today, ^3H is mainly released into the environment by
 39 nuclear power plants, military nuclear facilities and nuclear reprocessing plants (CNSC, 2009;
 40 ASN, 2010). Atmospheric releases of tritium to the world's nuclear power plants range from
 41 500 to 600 TBq.y^{-1} ($1.4\text{-}1.7 \text{ g.y}^{-1}$). At country scale, for example in France, the 58 reactors
 42 (PWR Pressurized Water Reactor) from nuclear power plants release approximately 34
 43 TBq.y^{-1} ($\sim 0.1 \text{ g}$) of tritium gas and 1000 TBq.y^{-1} ($\sim 3 \text{ g}$) of tritium liquid (Oms *et al.*, 2019).
 44 Spent fuel reprocessing plants (Orano La Hague in France, Sellafield in UK, Tokai-Mura in
 45 Japan) released approximately 200 to 300 TBq.y^{-1} in gaseous form between 1995 and 2007
 46 (IRSN, 2009). These three plants in the world contribute proportionally strongly to the release
 47 of tritium to the atmosphere if we compare with the large number of Nuclear Power plants.
 48 Since 2010, Orano La Hague (France) has released 64 TBq.y^{-1} of gaseous tritium annually on
 49 average, and a major part of this release is in HT form (85%, Connan *et al.*, 2017). Many
 50 facilities other than nuclear power plants and fuel reprocessing plants may release tritium in
 51 gaseous form, such as military weapons manufacturing plants, or tritium plants in the
 52 luminescent product industry (mainly in Canada). For the luminescent produce industry, in
 53 2006, gaseous releases were estimated at 300 TBq.y^{-1} (ASN, 2010). Military weapons plants
 54 can also release gaseous tritium. Thus in France, the Valduc and Marcoule factories releases
 55 about 200 TBq.y^{-1} (IRSN, 2018). In the future, the construction of new nuclear facilities (e.g.
 56 European Pressurized Reactor, International Thermonuclear Experimental Reactor ITER) as
 57 well as changes in nuclear fuel management may lead to an increase in ^3H released from the
 58 nuclear industry. For example, ITER in the south of France could release between 220 and
 59 900 TBq.y^{-1} (Cortes, 2015) and we cannot exclude, on a global scale, the possibility of HT

releases related to tritium production and underground tests by countries that are actively developing nuclear weapons programs.

While the HT form is not the dominant content of these releases, it is important to understand the behaviour of this HT form when oxidized in the top cm of soils, because this tritium can then be released into the atmosphere in assimilable HTO form. The HT form is not directly bio-available in the ecosystem for plants, but becomes bio-available after oxidation into HTO (Sweet and Murphy, 1981, Conrad *et al.*, 1983, Dunstall *et al.*, 1985, Bunnenberg *et al.*, 1986, Spencer and Vereecken-Sheehan, 1994, Golubev *et al.*, 2001, Peterson and Davis, 2002, Kim *et al.*, 2014). In HTO form, tritium can be readily exchanged with hydrogen atoms in the environment, thus entering the hydrological cycle, and then can enter the human/biological body through ingestion and inhalation (Belot, 1986).

HT can oxidize into HTO in the environment at atmospheric level (Clerc *et al.*, 1988, Ota *et al.*, 2007, Ehalt and Rohrer, 2009) and on the surface of a plant leaf (Cline, 1953, Dunstall *et al.*, 1985, Ichimasa *et al.*, 1989, 1995). However, HT mainly oxidizes in the top centimeters of soil due to bacterial action (McFarlane *et al.*, 1978, Schuler and Conrad, 1991, Spencer et Dunsdall, 1986, Kim *et al.*, 2014) and, to a lesser extent, under the effect of abiotic enzymes in the soil (Conrad et Seiler, 1981, Schuler et Conrad, 1991).

HT bacterial oxidation can be anaerobic or aerobic (Popelier *et al.*, 1985, Schuler et Conrad, 1991, Libert *et al.*, 2000, Piché-Choquette *et al.*, 2016), but it has been shown that, in soil, aerobic bacteria are the most active type (Schuler et Conrad, 1991). Ota *et al.* (2007) proposed an empirical equation to quantify the oxidation of HT into HTO in soil. This reference equation for the scientific community is based on deuterium oxidation works carried out in controlled laboratory conditions for a given soil type. However, it has been shown that the oxidation rate of HT varies depending to the soil type (Conrad *et al.*, 1983, Golubev *et al.*, 2001, Kim *et al.*, 2014) and it is important to adapt the work of Ota *et al.* (2007) to soils corresponding to all existing environment.

In this study, to begin with, we started with laboratory experiments focusing on the oxidation of HT to HTO for several soil types typical of north-west France, and corresponding to the soils we found around the Orano La Hague spent fuel reprocessing plant. We particularly attempted to better integrate the influence of the soil texture on the rate of HTO production from atmospheric HT. The aim was to improve the precision of the current bacterial oxidation

equation used by Ota *et al.* (2017) and, in addition, to generally apply this equation to any soil type depending on porosity estimated from soil fractions (silt, loam, clay).

Our subsidiary and more operational aim was to improve forecasts for HTO stock potentially "generated" in the soils in the immediate environment of the Orano La Hague plant, which could be available for atmospheric release based on precise available information on variation in HT activity. The idea behind the work is, as the Orano la Hague plant releases 85% of tritium in HT form, to estimate the ability of soils to convert this HT form into HTO, and to compare this "new stock" of HTO from bacterial oxidation with usual direct atmospheric releases of HTO.

2. Modelling HT oxidation in soil and expressing the frequency factor A as a function of soil porosity

HT oxidation in soil is mainly driven by the hydrogen oxidation enzymes (hydrogenesis) contained in the streptomyces (Komuro *et al.*, 2002). The generation of HTO by HT oxidation is considered as an enzymatic reaction (Ota *et al.*, 2007), and the kinetics are described by the Michaelis-Menten equation (Quinlan, 1981):

$$V_{oxi} = V_{max} \cdot \frac{[HT]}{[HT] + K_M} \quad (1)$$

The terms of the equations in this section are described in Table 1. It has been proven that the bacterial oxidation of HT depends on temperature, water content, porosity and the vertical distribution of oxidizing micro-organisms (bacterial concentration gradient) in the soil profile (Sweet and Murphy, 1981, Conrad *et al.*, 1983, Dunstall *et al.*, 1985, Bunnenberg *et al.*, 1986, Spencer and Vereecken-Sheehan, 1994, Peterson and Davis, 2002, Ota *et al.*, 2007). These different factors affect the rate of an enzymatic reaction V_{max} and were defined by Ota *et al.* (2007) using the equation (2). The parameters $f_W(\theta)$, $f_T(T)$, $f_Z(Z)$ are defined in Table 1 and readers should refer to Ota *et al.* (2007) for a detailed parametrization of these factors.

$$V_{max} = V_{ref} \cdot f_W(\theta) \cdot f_T(T) \cdot f_Z(Z) \quad (2)$$

The Michaelis-Menten enzymatic reaction parameter (Km) for equation 1 is expressed as a function of the temperature on the basis of an Arrhenius equation (Quinlan, 1980, Ota *et al.*, 2007) according to equation (3):

$$K_M = A \cdot e^{\left(\frac{-E}{RT}\right)} \quad (3)$$

In the model of Ota *et al.* (2007), the parameters A and E are determined by adjusting according to experiments for a given soil type. The activation energy of the bacterial reaction of the HT (noted E) exclusively depends on the type of catalysing enzyme and the substrate (Triebwasser-Freese *et al.*, 2015, Bock *et al.*, 2019). We postulate that E is identical for all pedological soil types as, for our study, hydrogenesis is assumed as the type of catalysing enzyme and HT is assumed for the substrate, for all soil types (Conrad *et al.*, 1983). A is defined as a frequency factor, integrating steric effects and the probability of collision between an oxidizing enzyme and HT (Hupp et Weaver, 1983, Weilandt et Hatzimanikatis, 2019). On this basis, parameter A will depend on soil porosity and type and is likely to differ depending on the pedological characteristics of the soil: this parameter A must be adjusted to refine the oxidation model.

The process applied in this context, to express frequency factor A for any soil type, includes several stages:

- Measuring particle distribution and expressing soil porosity;
- Performing bacterial oxidation laboratory experiments with HT for different soil types, using soils from our local environment and air enriched in HT sampled from the Orano La Hague plant stack plume;
- Calculating the value of A according to equation (3) by adjusting the outputs from the model (equation 1) and the HTO activity produced based on experimental measurements;
- Expressing A as a function of soil porosity.

3. Experimental design and methodology

3.1 Soil samples

The soils used for laboratory experiments were taken *in situ* in zones outside of the influence of the sites releasing tritium in the north-west region of France (Table 2) in order to obtain initial HTO activity values less than 1 Bq.L⁻¹. Samples were taken using PVC tubes with a diameter of 10 cm, and a depth varying between 5 and 15 cm. Each soil sample (see characteristics in Tables 2 and 3) corresponds to a meadow type farming soil, planted with

ray-grass. The granulometric characteristics of the 5 soil types studied can be found in Table 2. Analyses were performed according to standards NF ISO 11464 and NF X 31 107 by an external laboratory (National Institute of Agronomical Research, INRA, France).

During this study, three types of soil cores were systematically sampled at each site:

- One core intended to check the absence of HTO in the sample;
- One core containing grass intended to determine the bacterial oxidation of HT in the top centimetres of soil, in laboratory conditions;
- One core without grass intended to study the bacterial oxidation of HT for bare soil (soil in which the top 4 cm, corresponding to grass roots, have been removed).

The cores are isolated from the environment by attaching a sleeve (PVC) to the "root" end of the core sampling tube and a parafilm to the "surface" end of the core sampling tube. Once the core has been isolated from contact with ambient air, it is stored in a chiller during transport, and then in a freezer prior to use in laboratory experiments.

3.2 Calculating soil porosity

The soil porosity index for our 5 experiments was calculated in several stages. The apparent bulk density of the soil, noted $density_{bulk}$, and expressed in $kg.m^{-3}$, corresponding to the mass of soil contained in a given volume, including the volume of interstitial air, is determined using equation 4.

$$density_{bulk} = fraction_{clay} \cdot density_{clay} + fraction_{silt} \cdot density_{silt} + fraction_{sand} \cdot density_{sand} \quad (4)$$

Where the term fraction corresponds to the share of a type of particle i (i = clay, silt, sand) in $kg_i.kg \text{ soil}^{-1}$ and $density_i$ is the apparent density of a particle i. The different types of soil particle (Clay, Silt, Sand) and their apparent densities can be found in the website (Density of Sand, dry in 285 units and reference information (aqua-calc.com) ; Table A1).

The density of a soil particle ($density_{particle}$) corresponding to the mean mass of a soil particle per unit of volume is then calculated. Schjønning *et al.* (2017) propose equation 5 to determine $density_{particle}$ from the fraction of clay in the soil ($fraction_{clay}$).

$$density_{particule} = fraction_{clay} \cdot 2.86 + (1 - fraction_{clay}) \cdot 2.65 \quad (5)$$

Finally, porosity (equal to the volume of porous space per volume of soil) stated in m³ space m⁻³ soil) is determined from the two terms calculated earlier, $density_{bulk}$ and $density_{particule}$ by equation 6 (Chaudhari *et al.*, 2013).

$$porosity = 1 - \frac{density_{bulk}}{density_{particule}} \quad (6)$$

3.3 Sampling of air enriched with HT

The aim in this context is to circulate air enriched with tritium in HT form in the laboratory in order to observe the incorporation of HT in the soil and oxidation into HTO. The volumes of air containing high concentrations of atmospheric HT are sampled in the environment near to the Orano La Hague (France) spent fuel reprocessing plant, which releases tritium in HT and HTO forms (Connan *et al.*, 2017) during its industrial processes. These tritium releases are concomitant with the ⁸⁵Kr releases. This gas can be measured in real time, which allows samples to be specifically taken during periods with high HT activity. Air samples containing HT were therefore taken downwind from the Orano la Hague plant, making sure that the air sampled was enriched in tritium thanks to the ⁸⁵Kr measurements, using an air compressor (Bauer compressor Junior). Several B20 type (4 m³) gas cylinders were prepared with a vacuum prior to sampling for the purposes of these experiments; the air sampled for our experiments contained HT levels between 1 and 23 Bq.m⁻³. Due to the compression sampling technique, ambient humidity (water vapour containing tritium in HTO form) is eliminated and the air only contains HT.

In order to determine the exact HT content of the air used for the experiments, the protocol described by Connan *et al.* (2017) was applied; For HT measurements, the volume of air collected in the pressurized container was transferred to gas treatment lines in order to obtain the HT concentration after transformation to HTO. The air passed successively at a rate of 20 L.h⁻¹ through an activated charcoal trap made of two carbon canisters (ACR, Agilent technologies), which trap volatile organic compounds; two first bubblers (Bubbler N°1 and N°2) filled with 150 cm³ of tritium-free water (Abatilles spring water) are used to eliminate any residual tritiated water vapor after compressing while sampling. A heated 200°C catalysis oven (palladium pellets SDEC, France) was then used to oxidize the HT to HTO (Bubblers

N°3 and N°4). After the passage of a volume of about 500 L of air (depending on the expected level), air without ^3H was injected (flow: 30 L.h^{-1}) to purge the pipes and ovens of all traces of ^3H in order to prevent any cross-contamination between the different samples. During this step, which lasts 60 minutes, both ovens were heated to a temperature of 450°C . Then, after these different steps, a volume of water was collected from the bubbler for measuring purposes. After storage in darkness at 4°C prior to analysis, water (10 mL) was mixed with a liquid scintillator (10 mL) to allow for measurements by liquid scintillation counting.

3.4 HT bacterial oxidation chamber

The experimental set-up includes a leaktight bag containing soil cores, and HT is injected into this bag at a constant rate (0.2 L.min^{-1}). The oxidation kinetics of HT driven by soil bacteria is quantified by measuring the HTO produced in the soil core after a given period. The experimental set-up is described in Figure 1. The oxidation chamber consists of a $300 \times 400 \times 500 \text{ mm}^3$ airlock in leaktight Tedlar in which the soil cores taken from the environment are introduced. The full length of the bag is open so that cores can be added or removed, and a clip system is used to ensure leaktightness. The HT is injected into the experimental set-up using a B20 (4m^3) cylinder with known HT activity (see table 6 for HT activities in the cylinder). The injection flow is controlled by a pressure gauge to maintain a constant pressure at equilibrium. To avoid any contamination of the bag by traces of HTO, an upstream bubbler-type system containing Abatilles spring water is inserted between the gas cylinder and the bag. This ensures that only the HT hydrogen form is injected into the bag. The same set-up is placed downstream of the bag to prevent external air backflow and to evacuate any extra air inside the oxidation chamber. During the experiments, temperature and humidity sensors (WATCHDOG, SDEC France) are placed in the soil cores and in the oxidation chamber to track temperature and water-content changes. A beta radioactivity meter (LB123, Berthold Technology Germany) is also placed against the bag to track ^{85}Kr activity (present in the air injected containing the HT) in real time. The real time ^{85}Kr measurements can be used, by analogy, to monitor and avoid any sudden change in HT activity in the bag.

3.5 Processing soil after exposure to HT:

After a few days, when the HT soil contamination experiments have been completed, the core(s) are removed from the bag (cores can be removed at different times as part of the same experiment). The soil sample is then wrapped in parafilm and temporarily stored in a cold chamber at 4°C. Each core is then opened and placed on an aluminium tray with a diameter of 20 cm, and then vacuum packed to avoid any contamination, and frozen for 48h at -80 °C. This freezing phase optimises the upcoming lyophilization process. Samples are then lyophilized (ThermoElectron HETO PowerDry PL3000) in order to remove the HTO from the soil produced during HT oxidation. After 24 to 72 h of lyophilization, the water from the soil is recovered and the HTO will be measured by liquid scintillation counting of 10 mL of water (Maro *et al.*, 2017).

3.6 Tritium measurements

Tritium activity (HTO) was measured by liquid scintillation counting (TRI-CARB 3180 TRSL, PerkinElmer) with a counting time of 16 hours per sample. For HTO measurements, a volume of 10 cm³ of collected water was placed in a vial with 10 cm³ of liquid scintillation cocktail (Ultima gold LTT). Measurement uncertainty depends on the counting time and level of activity. Typically, for the levels to be measured, uncertainty was 3-10%. The background count rate and counting efficiency were 2.09 cpm and 14.9%. Our measurement practices are regularly validated by comparison exercises between French and international laboratories. Limit of detection are 1 Bq.L⁻¹.

3.7 Application of the methodology to the Orano La Hague reprocessing plant site

The Orano La Hague reprocessing plant (49.677 °N, -1.883°W) is located in North-West France, in the Normandy region. Reprocessing releases ³H into the environment, mainly through two main discharge stacks at the UP2-800 and UP3 plants. For example, in 2016, 66 TBq of tritium was released into the atmosphere, with 85% in HT form and 15% in HTO form (Connan *et al.*, 2017). As part of earlier works, for an experimental study site around the Orano site, located at 2 km from the plant (Plateforme Technique Instrumenté de La Hague (La Hague Instrument-fitted Technical Platform), PTILH, 49.694°N, -1.873°W), we developed tools which can be used to reconstruct atmospheric variation in HT and HTO activity, over specific time periods, by measuring ⁸⁵Kr, HTO and HT activity at minute, weekly and monthly intervals respectively, as these elements are discharged simultaneously at the main stacks (Maro *et al.*, 2017, Le Dizès *et al.*, 2017, Renard, 2017). On this basis, we can access highly precise timelines for some past periods. Further to the adjustments made, based

on these experiments, to the relationship between soil porosity and factor A used to complete the oxidation model proposed by Ota *et al.* (2017), we attempted to calculate the variation in HTO activity induced by bacterial oxidation in soil in the immediate environment around the Orano plant, when ambient HT activity is known. We used the TOCCATA- χ transfer model for ^3H (and ^{14}C) in terrestrial ecosystems, developed by the IRSN (Radiation Protection and Nuclear Safety Institute) (Le Dizès *et al.*, 2017, Renard, 2017), for this purpose. This compartmented model covers specific time periods and integrates the day/night cycle inherent in the physiological behavior of plants based on a simplified grassland model (Riedo *et al.*, 1998, Le Dizès *et al.*, 2017). The pool of tritium in soil is considered to exclusively comprise tritiated water dissolved in the unsaturated soil compartment. Soil HTO activity concentration is expressed as a function of (1) a (net) exchange process with an exchange velocity rate at the soil/air interface, (2) percolation (downward migration) of rainwater in soil, (3) root uptake of soil HTO and (4) soil HT oxidation. Similarly, soil water content results from the integration of precipitation over time minus water losses by percolation and root uptake, which is estimated using the Penman-Monteith model (Allen *et al.*, 1998) and a soil water stress factor that also possibly affects stomatal conductance (Le Dizès *et al.*, 2017, Renard, 2017).

4. Results and discussion

4.1 Soil granulometry

The different proportions of clay, total loam and total sand can be used to characterize the soil type with reference to the texture triangle proposed by USDA (Table 4, United States Department of Agriculture, USDA). The soils we focused on were loam or silt loam type, with clay content of less than 19%, sand content varying between 25 and 51% and loam content varying between 40 and 57%.

4.2 Porosity of the soil types studied

The porosities of the soil types covered by our study have been estimated using equations 4, 5 and 6 and the respective proportions of clay/loam/sand measured (Table 5); we also ran the same calculations for various works found in the literature, as mentioned in table 5, and which allow us to complete this project by extending the soil types considered. Porosity varies from

0.43 to 0.44 for the soil types covered by our experiments. For the studies in the literature mentioned in this paper for the purpose of comparison, porosities vary from 0.39 to 0.46.

4.3. Determining the frequency factor A

Frequency factor A (defined by equation 3) was calculated for our soil types based on the rate at which HTO is generated by soil bacteria (V_{oxi}) calculated using equations 1, 2 and 3, and which depends, in situ, on the HTO activity measured at the end of the HT exposure experiments. The oxidation rate is initially determined by measuring the HTO activity in the water in the soil produced by bacterial HT oxidation (Table 6) at the end of the experiment, with a known period of exposure given in hours (Table 3 and 6). It has been demonstrated that the rate of bacterial HT oxidation varies linearly over time (Piché-Choquette *et al.*, 2016).

During our experiments with soils with initial HTO values $< 1 \text{ Bq.L}^{-1}$, the activity measured at the end of the experiments reached values between 6.6 and 32 Bq.L^{-1} , directly influenced by HT activity (from 1.1 to 23.0 Bq.m^{-3}) and exposure time (224 to 1224 h). The rate of production of HTO in soil in the experimental system of HTO varied from 8 to 64 $\text{mBq.L}^{-1}.\text{h}^{-1}$, which is equivalent to 0.2-1.54 $\text{Bq.L}^{-1}.\text{d}^{-1}$.

The frequency factor A is then calculated by minimizing errors between the model (equation 1) and the measurements (Table 6) using an Excel solver. The frequency factors for our experiments vary between 6.97×10^4 and $3.06 \times 10^5 \text{ ppm.mol.m}^{-3}$.

For soil types from the same sampling site (Experiments 1, 4 and 5), the frequency factors A obtained are similar, despite different core coverage (Table 3). The minor variation in A between these 3 soil types sampled at the same location indicate that the plant cover does not play a significant role in the rate of bacterial oxidation of HT.

This methodology was applied to data taken from the literature if sufficient experimental details were available in the original publications. Table 7 combines different values for frequency factor A calculated using the associated soil types.

According to Table 7, the highest A values are found in sandy soils and the lowest A values are found in loamy to silt-loam soils. According to equations 1 and 3, this means that the rate of HT oxidation by soil bacteria is faster in loamy soils than in sandy soils in equal experimental conditions (temperature, water content, HT concentration, soil depth, plant

cover). This pedological variability in the frequency factor reflects the impact of soil porosity on A:

- For a soil with low porosity levels (e.g. sandy soil): steric repulsion and the probability of collision between an oxidizing enzyme and HT will be high;
- For a soil with high porosity levels (e.g. very fine loamy/silty soil): steric repulsion and the probability of collision between an oxidizing enzyme and HT will be low.

4.4. Relationship between frequency factor A and soil porosity

The frequency factor was plotted as a function of soil porosity (Figure 2) using the data in tables 5 and 7 (porosity calculated for all soil types in our study and in the literature and A calculations). By using data from the literature and our experimental data, we cover a soil porosity range of 0.39 - 0.46, and a second degree polynomial type equation is proposed (Figure 2). This equation can also be written in canonical form as equation 7): on this basis, the minimum theoretical value of A is 8.19×10^4 ppm.mol.m⁻³ (calculated as the minimum of the regression function in Figure 2), which is reached when soil porosity is equal to 0.44.

$$A = 4.43 \times 10^9 \cdot (\text{porosity} - 0.44)^2 + 8.19 \times 10^4 \quad (7)$$

By using this equation, which depends on the soil porosity calculated according to Eq. 6 with standard particle density values for each soil type listed according to USDA (Table 5), we can estimate the frequency factor A for each potential existing soil type (Table 4). The frequency factor will vary by a factor of 46 between the sand, which has the highest factor A (1.00×10^7 ppm.mol.m⁻³), and the Silty Clay, which has the lowest factor A (2.19×10^5 ppm.mol.m⁻³).

5. Operational application in the Orano La Hague environment

Our operational aim behind this experiment was to determine the ability of the soil in the immediate environment around the Orano La Hague reprocessing plant to "generate" HTO from release of HT. As previously mentioned, tritium is released into the atmosphere during the process as gaseous HTO (15%) but mostly HT form (85%) representing about 60 - 70 TBq.y⁻¹ (Connan *et al.*, 2017).

5.1 Theoretical simulation for air HT activity = 1 Bq m⁻³, for all soil types

In this environment with a high ambient HT activity, it is worth preparing a report and estimating if the HTO stock generated by bacteria in soil is significant on an annual scale, and must be considered (as this stock could be re-released to the atmosphere) or if, on the contrary, it can be ignored versus the HTO already present in the soil (from a different origin). We calculated the formation of HTO in soil by the bacterial oxidation of HT for this purpose, based on equations (1), (2) and (3) and the data from Table 4.

To begin, the calculation was run assuming a constant atmospheric HT activity of 1 Bq.m⁻³ (Table 8), for all potential soil types (including types which are not present in the immediate environment around the plant, Figure 3), using mean water density and temperatures for 4 seasons (Table 8) obtained in previous works (Maro *et al.*, 2017). On this basis, equation 8 can be used - after calculating the oxidation rate - to convert a mole of HT in the soil (mol HT.kg⁻¹ dry soil) into a mole of HT per surface area depending on soil type (mol HT.m⁻²).

$$V_{oxi_surface} = V_{oxi} \cdot density_{bulk} \cdot z \quad (8)$$

Where z is the depth of soil (we use a value of $z = 0.05$ m to represent the top cm of soil, corresponding to the soil thicknesses on which we based our experiments, and because this slice contains nearly 70% of oxidizing soil bacteria, Komuro et al 2002) and $V_{oxi_surface}$ is the oxidation rate for superficial HT (mol.m⁻²). $density_{bulk}$ is determined using equation (5).

The HTO formation values obtained vary from 0.14 to 5.86 Bq.m⁻².d⁻¹ during the winter and from 0.15 to 6.86 Bq.m⁻².d⁻¹ during the summer (Table 8), i.e. the differences between the seasons are minor, however significant deviations are recorded depending on soil types. Figure 3 shows HTO activities obtained by bacterial oxidation (for 1 Bq.m⁻³ of HT) for a temperature of 12°C and a soil water content of 22.5% by volume, to illustrate the clear differences between soil types. SiC (Silty Clay) type soil is the most productive in terms of HTO formation by bacterial oxidation, followed by SiCL (Silty Clay Loam) and L (Loam) soils. The most common soil types are Loam and Silt Loam in our focus area.

5.2 Simulation for real ambient HT activities over the 2013-2016 period

For the 2013-2016 period, hourly atmospheric HT content varied from 0.01 to 28.7 Bq.m⁻³ around the industrial site covered (Maro *et al.*, 2017). We also considered a Loam soil type with porosity of 0.428 and a frequency factor of 3.92x10⁵. Soil temperatures and water content per volume are taken from data measured for each time period (Maro *et al.*, 2017). Bacterial oxidation calculations (improved by this work) using the TOCCATA- χ model were initially performed exclusively using this source of atmospheric HT, and after we carried out an identical simulation, but added to the atmospheric HT the contents for atmospheric HTO and HTO in rainwater (the atmospheric concentrations of the various tritiated forms present on the La Hague site from 2013 to 2016 are present Appendix 2). The results can be found in Figure 4. If we exclusively consider HT and therefore bacterial production, it appears that a significant percentage of HTO is produced in this way (blue line), but we can see that the HTO in the soil is mainly from other atmospheric sources (HTO and rainwater, black line). Over the 2013-2016 period, the mean HTO activity from atmospheric HT reached 0.57 Bq.L⁻¹ (with a peak value of 5 Bq.L⁻¹) while the mean value for all sources is 6.21 Bq.L⁻¹ with peak values in excess of 20 Bq.L⁻¹. Over this period, the contribution of atmospheric HT to the HTO value in Bq.L⁻¹ in soils is calculated as 9.1%. In an environment such as that surrounding the Orano La Hague plant, where near-field atmospheric HT activity is high, the contribution of the oxidation of HT to HTO in soil represents only about 10% of the total available HTO stock in soil.

The aim of this work is to allow for the quantification of the impact of atmospheric HT once converted into HTO and then re-released to the atmosphere, if necessary. The contribution of HT to the radiation dose is lower than that of HTO, therefore it is worth obtaining information on the conversion of HT into HTO in the soil and then subsequently on re-release to the atmosphere as HTO. For the 2013-2016 period, and on the basis of data on HTO in soils produced by the bacterial oxidation of HT (blue line, Figure 4), we used the TOCCATA- χ model to calculate the HTO exchanged at the soil-atmosphere interface (calculation with the limiting condition that the air contains no prior HTO). Figure 5 shows the results obtained, which indicate mean ambient release levels from the soil of 1.5 Bq.m⁻².d⁻¹ with occasional peak values of 15 Bq.m⁻².d⁻¹ over some periods.

This HTO flow released by the soil representing approx. 1.5 Bq.m⁻².d⁻¹ must be compared with the annual quantities of HTO released directly into the atmosphere from plant stacks.

Over the 2012-2019 period, the Orano La Hague fuel reprocessing plant discharged 66.7 TBq.y⁻¹ ($\pm 11\%$) of tritium on average. Based on weekly measurements at outlets in 2014-2015, mean HTO and HT sources are evaluated at 3.9×10^5 Bq.s⁻¹ and 1.7×10^6 Bq.s⁻¹ respectively over this period. Soil release of HTO generated by the bacterial oxidation of HT was compared with this mean value for the direct ambient release of HTO; for this purpose, we considered a circular surface area with a 2 km radius around the site (i.e. 12.57 km²), which appeared a pertinent value in view of the sea to the north, south and west, at a distance of approximately 2 km. For 12.57 km², 218 Bq.s⁻¹ of HTO was released by the soil, representing only 0.06% of available ambient stock. If we refer to the maximum possible releases from the soil (15 Bq.m⁻².d⁻¹) and we extrapolate to produce a constant release over time, the influence of the soil would represent 0.6% of available ambient stock around Orano La Hague. Although this calculation is clearly subject to extensive uncertainty (with respect to the soil surface area to be considered, and the fact that releases in the form of plant transpiration are also ignored), it appears clear that this secondary source term from the soil is insignificant at this specific site, due to the relatively abundant levels of existing HTO in the atmosphere and despite high HT releases, compared to other nuclear sites, which could reach the soil.

6. Conclusions

This work was started in order to improve our ability to forecast the bacterial oxidation of HT in soils for all soil types. Our second aim was to quantify the amount of HTO produced in soils, and then re-released into the air around a nuclear site generating high levels of atmospheric HT activity (Orano La Hague spent fuel reprocessing plant, North west France, Europe) and to compare this amount with existing HTO activity in the atmosphere and considered in impact calculations.

To begin with, and on the basis of the model prepared by Ota *et al.* (2007) and laboratory experiments, we proposed an equation which can be used to estimate the frequency factor for bacterial oxidation after calculating soil porosity. These porosity and frequency factor parameters are suitable for the soils found in our working environment and were entered as input for the TOCATTA- χ model (Le Disez *et al.*, 2017, Renard, 2017) used by our teams. To begin with, this work demonstrated that bacterial oxidation is the dominant factor, for exposure to a constant value of HT, for a Silty Clay (SiC) soil type, followed by Silty Clay

Loam (SiCl), Loam (L) and Silt loam (SiL) with HTO values produced for ambient HT activity of 1 Bq m^{-3} in excess of 2 Bq HTO.m^{-2} for soil activity. For the most frequent soil types around the Orano La Hague nuclear plant (Loam and Silt Loam), using the actual HT activities measured over the 2013-2016 period, mean inducted HTO activity exclusively attributable to bacterial oxidation represents 0.6 Bq.L^{-1} on average in the soil, with peak values of approx. 5 Bq.L^{-1} . These values represent approx. 10% of the HTO activity measured in Bq.L^{-1} in these soils. In other words, even in this environment where ambient HT activity is high versus HTO activity (85% of total tritium, i.e. factor 6), the HTO contribution (via the atmosphere and rain) remains dominant over the activity measured in the soil. Secondly, thanks to the TOCATTA- χ model, we were able to calculate bacterial HTO released from the soil into the atmosphere during the 2013-2016 period, in $\text{Bq.m}^{-2}.\text{d}^{-1}$, by clearly taking a circular area with a 2 km radius around the nuclear site studied. Using this approach, we were able to compare this secondary soil source with the main source of HTO released directly into the atmosphere by the Orano La Hague site. This secondary source is insignificant and represents less than 0.1% of the main source, and less than 1% if we use the highest possible values. These results ultimately reflect the low level of HT converted to HTO, approximately 1%, and are consistent with the results proposed by Kim *et al.* (2014), even if the approach is not entirely identical.

Our works showed that the soil is not a significant secondary source of HTO for the atmosphere, on a preliminary basis, in the immediate environment of the Orano la Hague reprocessing plant. It is now necessary to focus on a possible marine source. Liquid releases in the marine environment are higher than atmospheric releases. Very low emission levels at the sea - atmosphere interface could be increase HTO activity on the coast.

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7. References

- Allen R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop Evapotranspiration: Guidelines for Computing Crop Water Requirements. FAO Irrigation and Drainage Papers, Rome, Italy, p. 328
- ASN, 2010. French Nuclear Safety - Livre blanc du tritium (http://livre-blanc-tritium.asn.fr/fichiers/Tritium_CHAP_5-5.pdf) 278p.
- Belot, Y., 1996. Comportement du tritium dans l'environnement. In: Belot, Y., Roy, M., Metivier, H., Le tritium de l'Environnement à l'Homme. Editions de Physique, Paris, pp. 39-76.
- Bunnenberg, C., Feinhals, J., & Wiener, B., 1986. Differences in the Behaviour of HTO and H₂O in Soil After Condensation from the Atmosphere and Conversion of HT to HTO and OBT in Soil Relative to Moisture Content and Pore Volume. Radiation Protection Dosimetry, 16(1-2), 83-87.
- Bock, C., Zollmann, T., Lindt, K.A., Tampé, R., Abele, R., 2019. Peptide translocation by the lysosomal ABC transporter TAPL is regulated by coupling efficiency and activation energy. Scientific Reports 9(1), 1-12.
- Chaudhari P.R., Ahire D.V., Ahire V.D, Chkravarty M., Maity M. 2013. Soil Bulk Density as related to Soil Texture, Organic Matter Content and available total Nutrients of Coimbatore Soil. International Journal of Scientific and Research Publications, 3, 2, 2250-2258.
- Clerc, H., Calando, J., Paillard, P., Gros, R., Hircq, B., 1988. The experimental determination of the oxidation rate of tritium in the atmosphere, Radiation protection practice.
- Cline, J.F., 1953. Absorption and metabolism of tritium oxide and tritium gas by bean plants. Plant Physiology, 28: 717-723.
- CNSC, 2009. Rejet de tritium et conséquences sur les doses au Canada en 2006. INFO-0793. 48pp.
- Connan O, Hebert D., Solier L., Maro D., Pellerin G., Voiseux C., Lamotte M., Laguionie P., 2017.. Atmospheric tritium concentrations under influence of AREVA NC La Hague reprocessing plant (France) and background levels. Journal of Environmental Radioactivity, 177, 184-193.
- Conrad R., Seiler W., 1981. Decomposition of atmospheric hydrogen by soil microorganisms and soil enzymes. Soil. Biol. Biochem. 13, 43-49.
- Conrad, R., Weber, M., Seiler, W., 1983. Kinetics and electron transport of soil hydrogenases catalyzing the oxidation of atmospheric hydrogen. Soil Biology and Biochemistry 15, 167-173.
- Cortes, P., 2015. Rejets liquides et gazeux de l'installation expérimentale ITER en fonctionnement de routine. SFRP, Paris, 5-6 Novembre 2015.
- Dunstall, T., Ogram, G.L., Spencer, F., 1985. Elemental tritium deposition and conversion in the terrestrial environment. Fusion Science and Technology 8, 2551-2556.
- Ehhalt, D.H., Rohrer, F., 2009. The tropospheric cycle of H₂ a critical review. Tellus 61B, 50-535.
- Golubev, A., Glagolev, M., & Misatyuk, C., 2001. Studies of HTO transport and oxidation in unsaturated soil. ECORAD, Aix-en-Provence, France, September, 3-7.
- Hupp, J., Weaver, M., 1983. The frequency factor for outer-sphere electrochemical reactions. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 152(1-2), 1-14.
- Ichimasa M., Ichimasa Y., Akita Y., 1989. In vivo fixation of atmospheric tritium gas in pine and Zelkova trees and their surroundings. J. Radiat. Res. 30, 330-337.

513 Ichimasa Y., Ichimasa M., Jiang H., Katsuno K., Noguchi H., Yokoyama S., Amano H., Atarashi M.,
514 1995. In vitro determination of HT oxidation activity and tritium concentration in soil and vegetation
515 during the chronic HT release experiment at Chalk river. *Fusion Technol.* 28, 877-882.

516 IRSN, 2009. Le tritium dans l'environnement : synthèse critique des connaissances et perspectives de
517 recherches. Rapport IRSN/DEI, 105 pp.

518 IRSN, 2017. Actualisation des connaissances acquises sur le tritium dans l'environnement « 7 ans
519 après le livre blanc de l'ASN : que sait-on de plus et que reste-il à faire ? », Rapport PRP-
520 ENV/SERIS/2017-004.

521 IRSN, 2018. Bilan de l'état radiologique de l'environnement français de 2015 à 2017., 354 pp.

522 Kim, S.B., Stuart, M., Bredlaw, M., Festarini, A., Beaton, D., 2014. HT to HTO conversion and field
523 experiments near Darlington Nuclear Power Generating Station (DNP GS) site. *J. Environ. Radioact.*
524 132, 73-80.

525 Komuro, M., Ichimasa, Y., Ichimasa, M., 2002. HT oxidation in soils in Ibaraki and isolation,
526 identification of HT oxidizing soil bacteria. *Fusion science and technology* 41, 422-426.

527 Le Dizès, S., Aulagnier, C., Maro, D., Rozet, M., Vermorel, F., Hébert, D., Voiseux, C., Solier, L.,
528 Godinot, C., Fievet, B., Laguionie P., Connan O., Cazimajou O., Morillon M., 2017. The VATO
529 project: Development and validation of a dynamic transfer model of tritium in grassland ecosystem.
530 *Journal of Environmental Radioactivity* 171, 83-92.

531 Libert, M., Sellier, R., Marty, V., Camaro, S., 2000. Development of hydrogen oxidizing bacteria
532 using hydrogen from radiolysis or metal corrosion.

533 Maro D., Vermorel F., Rozet M., Aulagnier C., Hebert D., Le Dizes S., Voiseux C., Solier L.,
534 Cossonnet C., Godinot C., Fievet B., Laguionie P., Connan O., Cazimajou O., Morillon M., Lamotte
535 M., 2017. An original methodology to study the transfer of tritium as HT and HTO in grassland
536 ecosystem. *Journal of Environmental Radioactivity*, 167, 235-248.

537 Masarik, J., Beer, J., 2009. An updated simulation of particle fluxes and cosmogenic nuclide
538 production in the Earth's atmosphere. *Journal of Geophysical Research: Atmospheres*, 114(D11).

539 McFarlane, J.C., R.D. Rodgers and D.V. Bradley Jr. 1978. Environmental tritium oxidation in surface
540 soil. *Environ. Sci. Technol.*, 12: 590-593.

541 Okada S., Momoshima N., 1993. Overview of tritium : characteristics, sources, and problems. *Health*
542 *Physics*, 6, 595-609.

543 Oms P.E., Bailly Du Bois P., Dumas F., Lazure P., Morillon M., Voiseux C., Le Corre C., Cossonet
544 C., Solier L., Morin P., 2019. Inventory and distribution of tritium in the oceans in 2016. *Science of*
545 *the Total Environment*, 656, 1289-1303.

546 Ota, M., Yamazawa, H., Moriizumi, J., Iida, T., 2007. Measurement and modeling of oxidation rate of
547 hydrogen isotopic gases by soil. *Journal of environmental radioactivity* 97, 103-115.

548 Peterson, S. R., Davis, P. A., 2002. Tritium doses from chronic atmospheric releases: a new approach
549 proposed for regulatory compliance. *Health Physics*, 82(2), 213-225.

550 Piché-Choquette, S., Tremblay, J., Tringe, S.G., Constant, P., 2016. H₂-saturation of high affinity H₂-
551 oxidizing bacteria alters the ecological niche of soil microorganisms unevenly among taxonomic
552 groups. *PeerJ* 4, e1782.

553 Popelier, F., Liessens, J., Verstraete, W., 1985. Soil H₂-uptake in relation to soil properties and
554 rhizobial H₂-production. *Plant and soil* 85, 85-96.

555 Quinlan, A. V., 1980. The thermal sensitivity of Michaelis-Menten kinetics as a function of substrate
556 concentration. *Journal of the Franklin Institute*, 310 (6), 325-342.

557 Renard, H., 2017. Modélisation à pas de temps horaire des transferts de tritium au sein d'un
558 écosystème prairial (in French), Thesis, Université d'Aix-Marseille.

559 Riedo M., Grub, A., Rosset, M., Fuhrer, J., 1998. A pasture simulation model for dry matter
560 production and fluxes of carbon, nitrogen, water and energy. *Ecol. Model.*, 105, pp. 141-183

561 Schuler, S., Conrad, R., 1991. Soils contain two different activities for oxidation of hydrogen. *FEMS*
562 *Microbiol. Ecol.* 73, 77-84.

563 Spencer F.S., Dunstall T.G., 1986. Molecular tritium conversion in vegetation, litter and soil. *Radiat.*
564 *Prot. Dosimetry* 16, 89-93.

565 Spencer F.S., Vereecken-Sheehan L., 1994. HTO Concentration Relationships Between Air, Soil and
566 Vegetation and Seasonal Dependence of HT Deposition to Soil. Ontario Hydro Technologies, Report
567 No. A-NBP-94-36-K.

568 Sweet, C.W., Murphy, C.E., 1981. Oxidation of molecular tritium by intact soils. *Environmental*
569 *Science & Technology* 15, 1485-1487.

570 Triebwasser-Freese, D. J., Tharayil, N., Preston, C. M., Gerard, P. G., 2015. Catalytic kinetics and
571 activation energy of soil peroxidases across ecosystems of differing lignin
572 chemistries. *Biogeochemistry*, 124(1), 113-129.

573 UNSCEAR, 2016. Sources, effects and risks of Ionizing Radiation. In Annex C, biological effects of
574 selected internal emitters, tritium, UNSCEAR United Nations Scientific Committee on the Effects of
575 Atomic Radiation, 122 pp.

576 UNSCEAR, 2000. Sources and effects of ionizing radiation, Vol 1 Sources: United Nations Scientific
577 Committee on the effects of Atomic Radiation. UNSCEAR United Nations Scientific Committee on
578 the Effects of Atomic Radiation, 659 pp.

579 USDA (U.S. Department of Agriculture), web.
580 https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_054167.

581 Weilandt, D., Hatzimanikatis, V., 2019. Particle-based simulation reveals macromolecular crowding
582 effects on the Michaelis-Menten mechanism. *Biophysical journal*, 117(2), 355-368.

583

Figure 1 : Schematic representation of the experimental oxidation device. a: HT air canister; b: upstream bubblers (trapping of HTO traces); c: core soil samples (5 cm); d: clip; e: ^{85}Kr detector (LB123); f: reading acquisition station (^{85}Kr , temperature, water content); g: downstream bubbler.

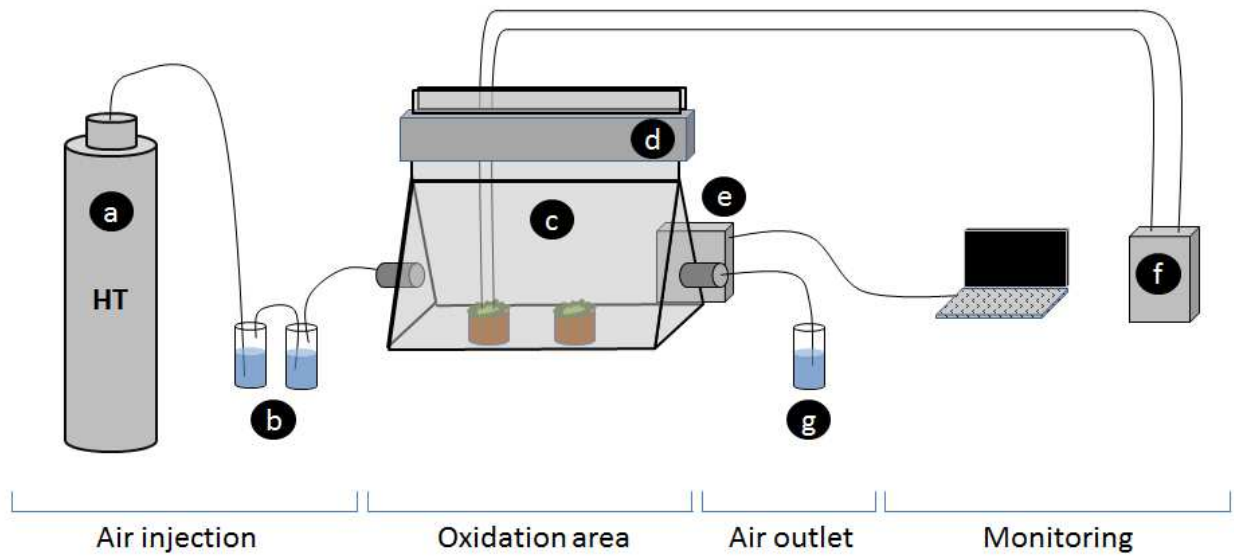


Figure 2 : Expression of frequency factor A as a function of soil porosity. White circles are data from this study. Grey squares are data from the literature.

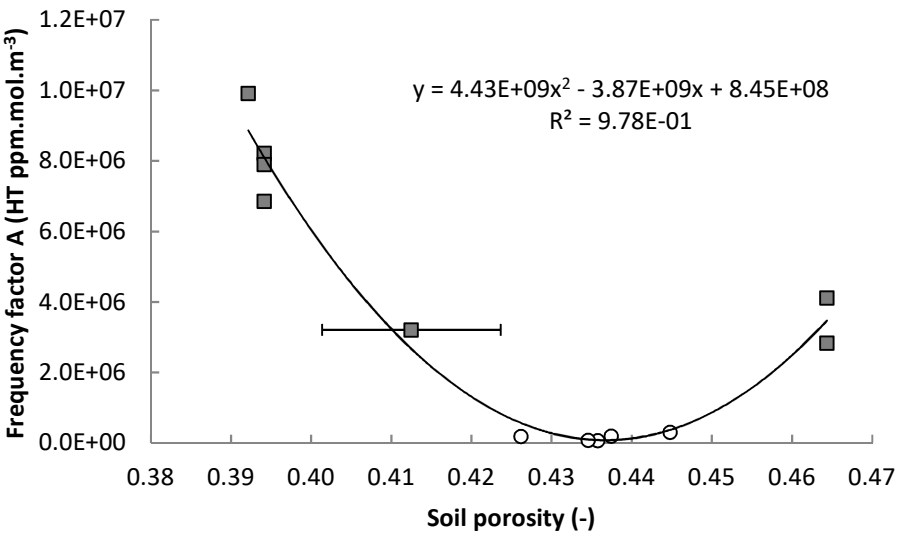


Figure 3 : Modelling of annual production of HTO by bacterial oxidation of 1 Bq.m⁻³ HT in air, with average annual soil water content and temperature for different type of soil (C= Clay, SC= Sandy Clay, CL= Clay Loam, SiCL= Silt Clay Loam, SiC= Silt Clay, SCL= Sandy Clay Loam, L= Loam, SL= Sandy Loam, SiL= Silty Loam, Si= Silty, LS= Loamy Sand, S=Sand).

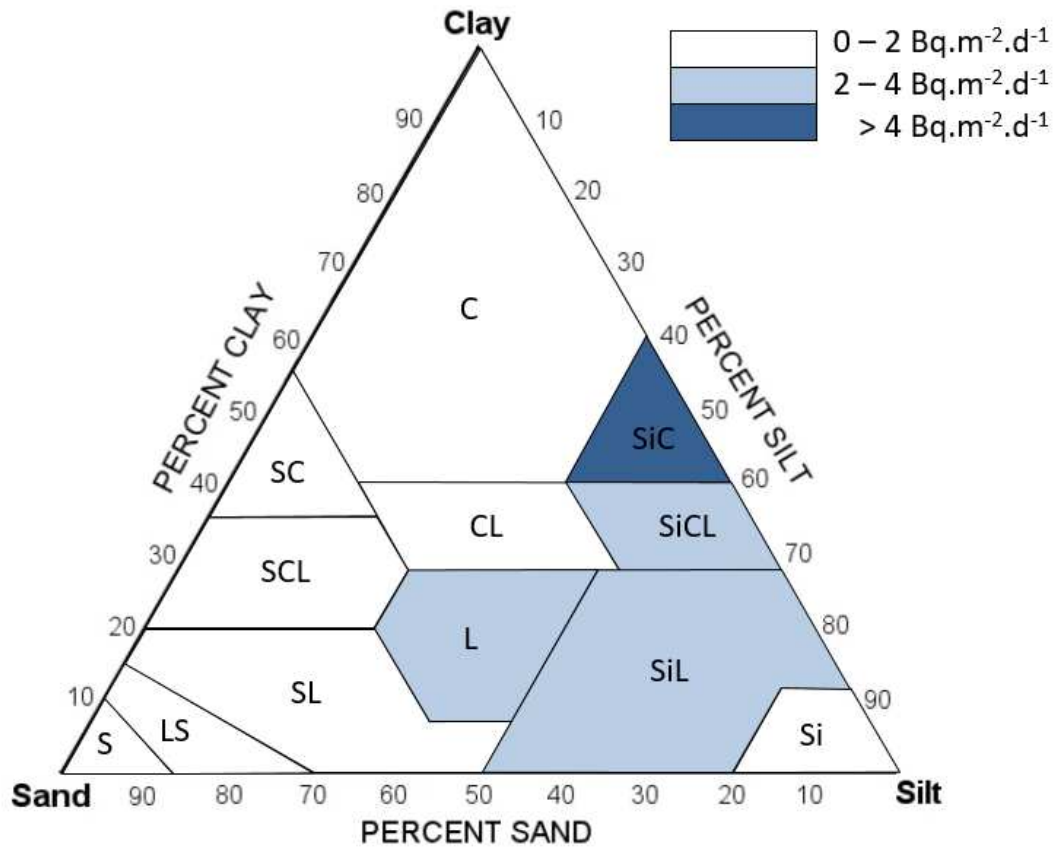


Figure 4 : Evolution of HTO in soil (Bq.L^{-1}) for 2013-2016 period, calculate from TOCATTAX model, taken into account only atmospheric measurements of HT in air (blue line) and taken into account all sources of tritium (HTO and HT in air, HTO in rainwater, black line) for site 2 km from Orano La Hague reprocessing plant.

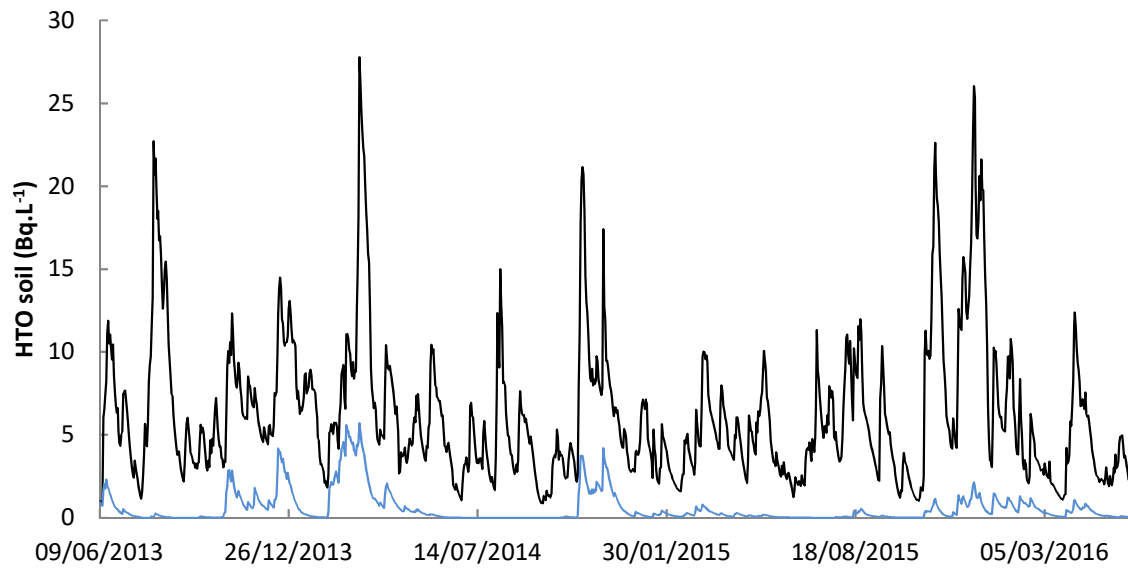


Figure 5 : Exchange of HTO between soil and atmosphere ($\text{Bq.m}^{-2}.\text{d}^{-1}$) for 2013-2016 period, calculate from TOCATTA- χ model, with only atmospheric measurements of HT in air for site 2 km from Orano La Hague reprocessing plant. Positive values indicate flux of HTO from soil to atmosphere, and negative values indicates flux of HTO from atmosphere to soil.

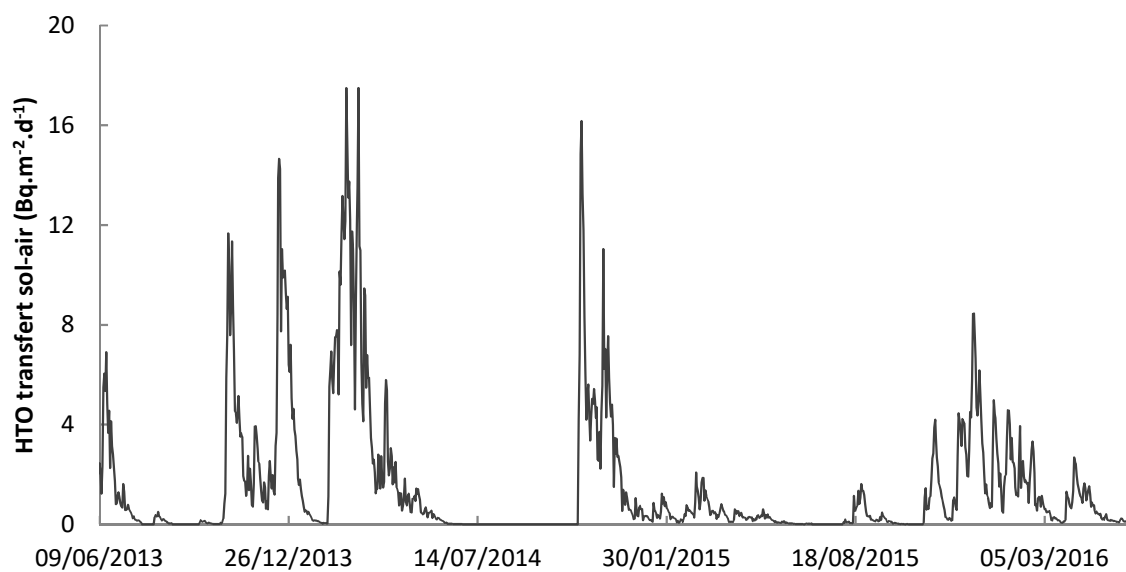


Table 1 : Description of the parameters used to calculate the oxidation rate of HT in HTO in soils.

Symbol	Meaning	Units
$[HT]$	HT concentration in soil air	mol.m^{-3}
A	frequency factor	ppm.mol.m^{-3}
E	reaction activation energy	J.mol^{-1}
$f_T(T)$	soil temperature-dependant weighting factor	-
$f_W(\theta)$	soil water content-dependant weighting factor	-
$f_Z(Z)$	soil depth-dependant weighting factor	-
K_M	Michaelis-Menten parameter	ppm.mol.m^{-3}
R	gas constant	$\text{J.mol}^{-1}.\text{K}^{-1}$
T	absolute temperature	K
V_{max}	initial maximal HT oxydation velocity	$\text{mol.kg}^{-1} \text{ dry soil.s}^{-1}$
V_{oxi}	actual HT oxydation velocity	$\text{mol.kg}^{-1} \text{ dry soil.s}^{-1}$
V_{ref}	reference HT oxydation velocity	$\text{mol.kg}^{-1} \text{ dry soil.s}^{-1}$

1 **Table 2: Characteristics of the core sampling of the soils used for the oxidation laboratory experiments.**

Experiment	Sampling date	Latitude/longitude (DD)	Location Name	Clay content ($\text{kg}_{\text{sands}} \cdot \text{kg}_{\text{dry soil}}^{-1}$)	Total loam content ($\text{kg}_{\text{sands}} \cdot \text{kg}_{\text{dry soil}}^{-1}$)	Total sand content ($\text{kg}_{\text{sands}} \cdot \text{kg}_{\text{dry soil}}^{-1}$)	Type of soil
1	25/05/2016	49.618°N/-1.351°W	Le Vast (France)	0.183	0.476	0.341	Loam
2	29/06/2016	49.646°N/-1.644°W	Equeurdreville (France)	0.090	0.399	0.511	Loam
3	04/04/2016	48.781°N/-0.678°W	Fresnes (France)	0.189	0.567	0.244	Silt loam
4	15/11/2018	49.618°N/-1.351°W	Le Vast (France)	0.170	0.472	0.358	Loam
5	19/11/2019	49.618°N/-1.351°W	Le Vast (France)	0.169	0.501	0.330	Loam

Table 3: Experimental characteristics measured during the laboratory testing of HT bacterial oxidation in the first centimeters from natural soil.

Experiment	Sample surface	soil	Duration	Massique soil water content	Average Air temperature	Sample height	Sample depth from surface
-	-		hour	kg.kg ⁻¹	°C	cm	cm
1	Grass		264.0	0.176	20.3	5	0
2	Grass		576.0	0.188	20.9	5	0
3	Grass		305.4	0.265	19.6	5	0
4	Bare soil		504.0	0.133	22.0	5	4
5	Bare soil		1224.0	0.168	17.0	5	4

Table 4: Granulometric characteristics, porosity (according to Eq 6) and frequency factor A (according to Eq 5) of the different soils.

Soil type	Clay content	Silt content	Sand content	Soil porosity	Frequency factor A
-	%	%	%	-	HT ppm.mol.m ⁻³
Clay	60	20	20	0.416	1.94x10 ⁶
Silty Clay	45	50	5	0.442	2.19x10 ⁵
Sandy Clay	40	5	55	0.398	6.75x10 ⁶
Clay Loam	35	30	35	0.421	1.14x10 ⁶
Silty Clay Loam	35	55	10	0.446	4.23x10 ⁵
Sandy Clay Loam	30	10	60	0.401	5.81x10 ⁶
Loam	20	40	40	0.428	3.92x10 ⁵
Silt Loam	15	60	25	0.447	5.56x10 ⁵
Silt	5	90	5	0.475	6.68x10 ⁶
Sandy Loam	10	25	65	0.412	2.89x10 ⁶
Loamy Sand	5	10	85	0.396	7.57x10 ⁶
Sand	4	4	92	0.389	1.00x10 ⁷

Table 5: Estimation of soil porosity from apparent density and theoretical particle density for soils resulting from HT bacterial oxidation experiments in this study or present in the literature.

Source	Bulk density	Theoretical particule density	Soil porosity
-	kg.m ⁻³	kg.m ⁻³	-
Experiment 1	1.52x10 ³	2.69x10 ³	0.44
Experiment 2	1.53x10 ³	2.67x10 ³	0.43
Experiment 3	1.49x10 ³	2.69x10 ³	0.44
Experiment 4	1.52x10 ³	2.69x10 ³	0.43
Experiment 5	1.51x10 ³	2.69x10 ³	0.44
Conrad <i>et al.</i> , 1982	1.44x10 ³	2.69x10 ³	0.46
Conrad <i>et al.</i> , 1982	1.44x10 ³	2.69x10 ³	0.46
Conrad <i>et al.</i> , 1982	1.61x10 ³	2.66x10 ³	0.39
Conrad <i>et al.</i> , 1982	1.61x10 ³	2.66x10 ³	0.39
Dong et Layzell 2001	1.62x10 ³	2.66x10 ³	0.39
Ota <i>et al.</i> , 2007	1.61x10 ³	2.66x10 ³	0.39
Piché-Choquette <i>et al.</i> , 2016	1.57x10 ³	2.67x10 ³	0.41

Table 6: Tritium activity measured during the laboratory experiments of HT bacterial oxidation.

Experiment	Air HT activity in the bag	Initial HTO activity in soil water	Final HTO activity in soil water	Rate of HTO production in soil water
-	Bq.m ⁻³	Bq.L ⁻¹	Bq.L ⁻¹	Bq.L ⁻¹ .h ⁻¹
1	1.1± 0.1	<1	8.4±0.9	3.2x10 ⁻² ±3.4x10 ⁻³
2	1.1±0.1	<1	6.6±1.4	1.2x10 ⁻² ±2.4x10 ⁻³
3	5.8±0.3	<1	7.0±0.9	2.3x10 ⁻² ±3.0x10 ⁻³
4	23.0±1.4	<1	32.2±1.5	6.4x10 ⁻² ±3.0x10 ⁻³
5	7.8±0.7	<1	10.3±1.2	8.4x10 ⁻³ ±9.8x10 ⁻⁴

Table 7: Soil particle size and A-frequency factor from HT bacterial oxidation experiments in soil conducted in this study or from the literature.

Source	Sand content	Loam content	Clay content	Soil type	Frequency factor A
	%	%	%	-	HT ppm.mol.m ⁻³
Experiment 1	34	48	18	Loam	6.97x10 ⁴
Experiment 2	51	40	9	Loam	1.85x10 ⁵
Experiment 3	24	57	19	Silt Loam	3.06x10 ⁵
Experiment 4	36	47	17	Silt Loam	7.89x10 ⁴
Experiment 5	33	50	17	Silt Loam	1.99x10 ⁵
Conrad <i>et al.</i> , 1982	5 ^b	77 ^b	18 ^b	Silt Loam	2.84x10 ^{6a}
Conrad <i>et al.</i> , 1982	5 ^b	77 ^b	18 ^b	Silt Loam	4.12x10 ^{6a}
Conrad <i>et al.</i> , 1982	88 ^b	9 ^b	3 ^b	Loamy Sand	8.22x10 ^{6a}
Conrad <i>et al.</i> , 1982	88 ^b	9 ^b	3 ^b	Loamy Sand	6.86x10 ^{6a}
Dong et Layzell 2001	90 ^e	7 ^e	3 ^e	Sand	9.92x10 ^{6a}
Ota <i>et al.</i> , 2007	88 ^c	9 ^c	3 ^c	Sand	7.90x10 ⁶
Piché-Choquette <i>et al.</i> , 2016	64 ^d	26 ^d	10 ^d	Loamy Sand	3.21x10 ^{6a}

^aTemperature is assumed to be 25°C if not indicated in the literature; ^bSeiler *et al.*, 1977; ^cSince the soil in this study is physically apparent to that described by Conrad et Seiler (1982), this soil is considered to have the same particule size composition; ^dAverage value for this particule size range; ^eThe type of land is issued by Info-sols.ca and the location of the soil sample indicated. The fraction of silica added to the mixture (1/3) is assimilated to pure sand particles.

Table 8 : Estimated production of soil HTO (Bq.m⁻²) for different soil types under a La Hague climate type following the 24-hour presence of a HT plume with a concentration of 1 Bq.m⁻³.

Soil Type	Bulk density	Soil HTO			
	Kg.m ⁻³	Bq.m ⁻² .d ⁻¹			
	Season	Spring ^a	Summer ^b	Autumn ^c	Winter ^d
Clay (C)	1621	0.73	0.65	0.73	0.68
Silty clay (SiC)	1530	6.23	6.26	6.16	5.86
Sandy clay (SC)	1646	0.20	0.16	0.20	0.14
Clay loam (CL)	1576	1.15	1.00	1.09	0.62
Silty clay loam (SiCL)	1510	3.19	3.23	3.15	2.99
Sandy clay loam (SCL)	1626	0.24	0.24	0.23	0.18
Loam (L)	1539	3.51	3.58	3.46	3.29
Silt loam (SiL)	1483	2.39	2.46	2.36	2.25
Silt (Si)	1396	0.19	0.19	0.18	0.18
Sandy loam (SL)	1572	0.49	0.49	0.48	0.45
Loamy sand (LS)	1608	0.19	0.19	0.19	0.18
Sand (S)	1623	0.15	0.15	0.14	0.14

^atemperature and average volumic water content of soil: 12.6°C and 21.5%; ^btemperature and average volumic water content of soil: 16.6°C and 15.2%; ^ctemperature and average volumic water content of soil: 11.3°C and 24.5% ; ^dtemperature and average volumic water content of soil: 7.5°C and 28.8% . The data mentionned ^a, ^b, ^c and ^d come from hourly measurements over the period 2013 to 2019 (Maro *et al.*, 2017).