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

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1 **Experimental measurements of the bacterial oxidation of HT in soils:**
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3 **form.**

4 **Abstract**

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

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

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

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

27

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 $0.32 \text{ atom cm}^{-2}\cdot\text{s}^{-1}$ 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 $\text{TBq}\cdot\text{y}^{-1}$ ($1.4\text{-}1.7 \text{ g}\cdot\text{y}^{-1}$). At country scale, for example in France, the 58 reactors
42 (PWR Pressurized Water Reactor) from nuclear power plants release approximately 34
43 $\text{TBq}\cdot\text{y}^{-1}$ ($\sim 0.1 \text{ g}$) of tritium gas and 1000 $\text{TBq}\cdot\text{y}^{-1}$ ($\sim 3 \text{ g}$) 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 $\text{TBq}\cdot\text{y}^{-1}$ 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 $\text{TBq}\cdot\text{y}^{-1}$ 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 $\text{TBq}\cdot\text{y}^{-1}$ (ASN, 2010). Military weapons plants
54 can also release gaseous tritium. Thus in France, the Valduc and Marcoule factories releases
55 about 200 $\text{TBq}\cdot\text{y}^{-1}$ (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 $\text{TBq}\cdot\text{y}^{-1}$ (Cortes, 2015) and we cannot exclude, on a global scale, the possibility of HT

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

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

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

77 HT bacterial oxidation can be anaerobic or aerobic (Popelier *et al.*, 1985, Schuler et Conrad,
78 1991, Libert *et al.*, 2000, Piché-Choquette *et al.*, 2016), but it has been shown that, in soil,
79 aerobic bacteria are the most active type (Schuler et Conrad, 1991). Ota *et al.* (2007) proposed
80 an empirical equation to quantify the oxidation of HT into HTO in soil. This reference
81 equation for the scientific community is based on deuterium oxidation works carried out in
82 controlled laboratory conditions for a given soil type. However, it has been shown that the
83 oxidation rate of HT varies depending to the soil type (Conrad *et al.*, 1983, Golubev *et al.*,
84 2001, Kim *et al.*, 2014) and it is important to adapt the work of Ota *et al.* (2007) to soils
85 corresponding to all existing environment.

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

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

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

100

101 **2. Modelling HT oxidation in soil and expressing the frequency** 102 **factor A as a function of soil porosity**

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

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

107

108 The terms of the equations in this section are described in Table 1. It has been proven that the
109 bacterial oxidation of HT depends on temperature, water content, porosity and the vertical
110 distribution of oxidizing micro-organisms (bacterial concentration gradient) in the soil profile
111 (Sweet and Murphy, 1981, Conrad *et al.*, 1983, Dunstall *et al.*, 1985, Bunnenberg *et al.*, 1986,
112 Spencer and Vereecken-Sheehan, 1994, Peterson and Davis, 2002, Ota *et al.*, 2007). These
113 different factors affect the rate of an enzymatic reaction V_{max} and were defined by Ota *et al.*
114 (2007) using the equation (2). The parameters $f_W(\theta)$, $f_T(T)$, $f_Z(Z)$ are defined in Table 1 and
115 readers should refer to Ota *et al.* (2007) for a detailed parametrization of these factors.

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

116 The Michaelis-Menten enzymatic reaction parameter (Km) for equation 1 is expressed as a
117 function of the temperature on the basis of an Arrhenius equation (Quinlan, 1980, Ota *et al.*,
118 2007) according to equation (3):

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

119 In the model of Ota *et al.* (2007), the parameters A and E are determined by adjusting
120 according to experiments for a given soil type. The activation energy of the bacterial reaction
121 of the HT (noted E) exclusively depends on the type of catalysing enzyme and the substrate
122 (Triebwasser-Freese *et al.*, 2015, Bock *et al.*, 2019). We postulate that E is identical for all
123 pedological soil types as, for our study, hydrogenesis is assumed as the type of catalysing
124 enzyme and HT is assumed for the substrate, for all soil types (Conrad *et al.*, 1983). A is
125 defined as a frequency factor, integrating steric effects and the probability of collision
126 between an oxidizing enzyme and HT (Hupp et Weaver, 1983, Weilandt et Hatzimanikatis,
127 2019). On this basis, parameter A will depend on soil porosity and type and is likely to differ
128 depending on the pedological characteristics of the soil: this parameter A must be adjusted to
129 refine the oxidation model.

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

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

140

141 **3. Experimental design and methodology**

142 **3.1 Soil samples**

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

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

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

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

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

161 **3.2 Calculating soil porosity**

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

166

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

167

168 Where the term fraction corresponds to the share of a type of particle i (i = clay, silt, sand) in
169 $kg_i.kg \text{ soil}^{-1}$ and $density_i$ is the apparent density of a particle i. The different types of soil
170 particle (Clay, Silt, Sand) and their apparent densities can be found in the website (Density of
171 Sand, dry in 285 units and reference information (aqua-calc.com) ; Table A1).

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

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

175 Finally, porosity (equal to the volume of porous space per volume of soil) stated in m³ space
 176 m⁻³ soil) is determined from the two terms calculated earlier, $density_{bulk}$ and
 177 $density_{particule}$ by equation 6 (Chaudhari *et al.*, 2013).

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

179

180 **3.3 Sampling of air enriched with HT**

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

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

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

212 **3.4 HT bacterial oxidation chamber**

214 The experimental set-up includes a leaktight bag containing soil cores, and HT is injected into
215 this bag at a constant rate ($0.2 \text{ L}\cdot\text{min}^{-1}$). The oxidation kinetics of HT driven by soil bacteria is
216 quantified by measuring the HTO produced in the soil core after a given period. The
217 experimental set-up is described in Figure 1. The oxidation chamber consists of a
218 $300\times 400\times 500 \text{ mm}^3$ airlock in leaktight Tedlar in which the soil cores taken from the
219 environment are introduced. The full length of the bag is open so that cores can be added or
220 removed, and a clip system is used to ensure leaktightness. The HT is injected into the
221 experimental set-up using a B20 (4m^3) cylinder with known HT activity (see table 6 for HT
222 activities in the cylinder). The injection flow is controlled by a pressure gauge to maintain a
223 constant pressure at equilibrium. To avoid any contamination of the bag by traces of HTO, an
224 upstream bubbler-type system containing Abatilles spring water is inserted between the gas
225 cylinder and the bag. This ensures that only the HT hydrogen form is injected into the bag.
226 The same set-up is placed downstream of the bag to prevent external air backflow and to
227 evacuate any extra air inside the oxidation chamber. During the experiments, temperature
228 and humidity sensors (WATCHDOG, SDEC France) are placed in the soil cores and in the
229 oxidation chamber to track temperature and water-content changes. A beta radioactivity meter
230 (LB123, Berthold Technology Germany) is also placed against the bag to track ^{85}Kr activity
231 (present in the air injected containing the HT) in real time. The real time ^{85}Kr measurements
232 can be used, by analogy, to monitor and avoid any sudden change in HT activity in the bag.

233 **3.5 Processing soil after exposure to HT:**

235 After a few days, when the HT soil contamination experiments have been completed, the
236 core(s) are removed from the bag (cores can be removed at different times as part of the same
237 experiment). The soil sample is then wrapped in parafilm and temporarily stored in a cold
238 chamber at 4°C. Each core is then opened and placed on an aluminium tray with a diameter of
239 20 cm, and then vacuum packed to avoid any contamination, and frozen for 48h at -80 °C.
240 This freezing phase optimises the upcoming lyophilization process. Samples are then
241 lyophilized (ThermoElectron HETO PowerDry PL3000) in order to remove the HTO from the
242 soil produced during HT oxidation. After 24 to 72 h of lyophilization, the water from the soil
243 is recovered and the HTO will be measured by liquid scintillation counting of 10 mL of water
244 (Maro *et al.*, 2017).

245 **3.6 Tritium measurements**

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

254 **3.7 Application of the methodology to the Orano La Hague reprocessing plant site**

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

267 on these experiments, to the relationship between soil porosity and factor A used to complete
268 the oxidation model proposed by Ota *et al.* (2017), we attempted to calculate the variation in
269 HTO activity induced by bacterial oxidation in soil in the immediate environment around the
270 Orano plant, when ambient HT activity is known. We used the TOCCATA- χ transfer model
271 for ^3H (and ^{14}C) in terrestrial ecosystems, developed by the IRSN (Radiation Protection and
272 Nuclear Safety Institute) (Le Dizès *et al.*, 2017, Renard, 2017), for this purpose. This
273 compartmented model covers specific time periods and integrates the day/night cycle inherent
274 in the physiological behavior of plants based on a simplified grassland model (Riedo *et al.*,
275 1998, Le Dizès *et al.*, 2017). The pool of tritium in soil is considered to exclusively comprise
276 tritiated water dissolved in the unsaturated soil compartment. Soil HTO activity concentration
277 is expressed as a function of (1) a (net) exchange process with an exchange velocity rate at the
278 soil/air interface, (2) percolation (downward migration) of rainwater in soil, (3) root uptake of
279 soil HTO and (4) soil HT oxidation. Similarly, soil water content results from the integration
280 of precipitation over time minus water losses by percolation and root uptake, which is
281 estimated using the Penman-Monteith model (Allen *et al.*, 1998) and a soil water stress factor
282 that also possibly affects stomatal conductance (Le Dizès *et al.*, 2017, Renard, 2017).

283

284 **4. Results and discussion**

285 **4.1 Soil granulometry**

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

291

292 **4.2 Porosity of the soil types studied**

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

297 0.43 to 0.44 for the soil types covered by our experiments. For the studies in the literature
298 mentioned in this paper for the purpose of comparison, porosities vary from 0.39 to 0.46.

299

300 **4.3. Determining the frequency factor A**

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

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

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

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

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

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

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

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

333

334 **4.4. Relationship between frequency factor A and soil porosity**

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

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

342

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

348

349 **5. Operational application in the Orano La Hague environment**

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

355 **5.1 Theoretical simulation for air HT activity = 1 Bq m⁻³, for all soil types**

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

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

368

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

369

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

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

382

383 **5.2 Simulation for real ambient HT activities over the 2013-2016 period**

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

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

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

415 Over the 2012-2019 period, the Orano La Hague fuel reprocessing plant discharged 66.7
416 TBq.y⁻¹ ($\pm 11\%$) of tritium on average. Based on weekly measurements at outlets in 2014-
417 2015, mean HTO and HT sources are evaluated at 3.9×10^5 Bq.s⁻¹ and 1.7×10^6 Bq.s⁻¹
418 respectively over this period. Soil release of HTO generated by the bacterial oxidation of HT
419 was compared with this mean value for the direct ambient release of HTO; for this purpose,
420 we considered a circular surface area with a 2 km radius around the site (i.e. 12.57 km²),
421 which appeared a pertinent value in view of the sea to the north, south and west, at a distance
422 of approximately 2 km. For 12.57 km², 218 Bq.s⁻¹ of HTO was released by the soil,
423 representing only 0.06% of available ambient stock. If we refer to the maximum possible
424 releases from the soil (15 Bq.m⁻².d⁻¹) and we extrapolate to produce a constant release over
425 time, the influence of the soil would represent 0.6% of available ambient stock around Orano
426 La Hague. Although this calculation is clearly subject to extensive uncertainty (with respect to
427 the soil surface area to be considered, and the fact that releases in the form of plant
428 transpiration are also ignored), it appears clear that this secondary source term from the soil is
429 insignificant at this specific site, due to the relatively abundant levels of existing HTO in the
430 atmosphere and despite high HT releases, compared to other nuclear sites, which could reach
431 the soil.

432

433 **6. Conclusions**

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

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

447 Loam (SiCl), Loam (L) and Silt loam (SiL) with HTO values produced for ambient HT
448 activity of 1 Bq m^{-3} in excess of 2 Bq HTO.m^{-2} for soil activity. For the most frequent soil
449 types around the Orano La Hague nuclear plant (Loam and Silt Loam), using the actual HT
450 activities measured over the 2013-2016 period, mean inducted HTO activity exclusively
451 attributable to bacterial oxidation represents 0.6 Bq.L^{-1} on average in the soil, with peak
452 values of approx. 5 Bq.L^{-1} . These values represent approx. 10% of the HTO activity measured
453 in Bq.L^{-1} in these soils. In other words, even in this environment where ambient HT activity is
454 high versus HTO activity (85% of total tritium, i.e. factor 6), the HTO contribution (via the
455 atmosphere and rain) remains dominant over the activity measured in the soil. Secondly,
456 thanks to the TOCATTA- χ model, we were able to calculate bacterial HTO released from the
457 soil into the atmosphere during the 2013-2016 period, in $\text{Bq.m}^{-2}.\text{d}^{-1}$, by clearly taking a
458 circular area with a 2 km radius around the nuclear site studied. Using this approach, we were
459 able to compare this secondary soil source with the main source of HTO released directly into
460 the atmosphere by the Orano La Hague site. This secondary source is insignificant and
461 represents less than 0.1% of the main source, and less than 1% if we use the highest possible
462 values. These results ultimately reflect the low level of HT converted to HTO, approximately
463 1%, and are consistent with the results proposed by Kim *et al.* (2014), even if the approach is
464 not entirely identical.

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

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473

474 **7. References**

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

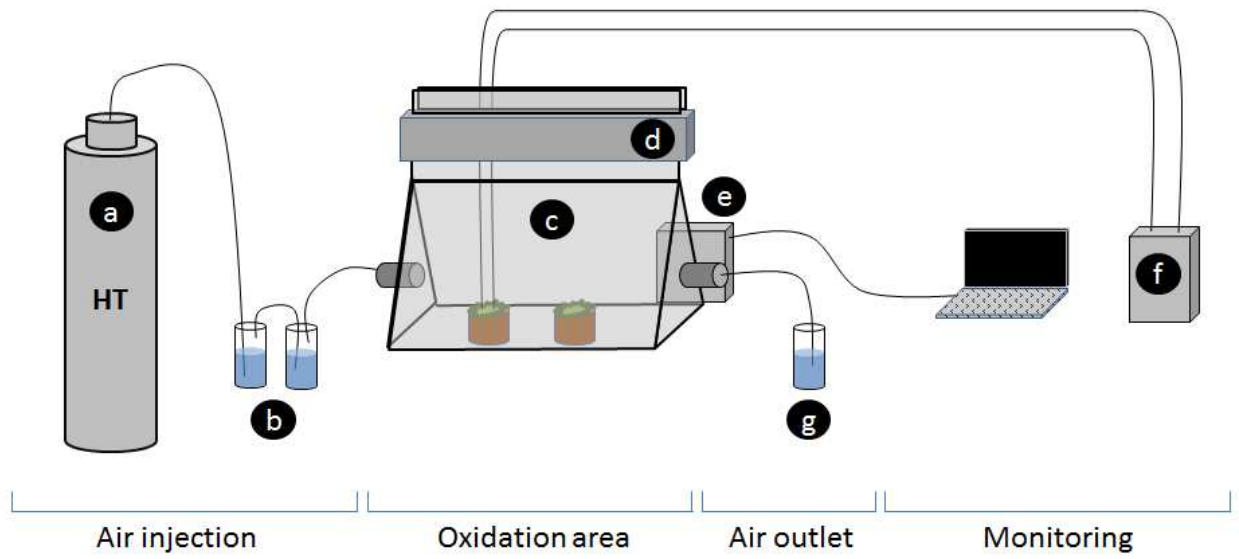


Figure 2 : Expression of frequency factor A as a function of soil porosity. White circles are data from this study. Grey squares are data from the literature.

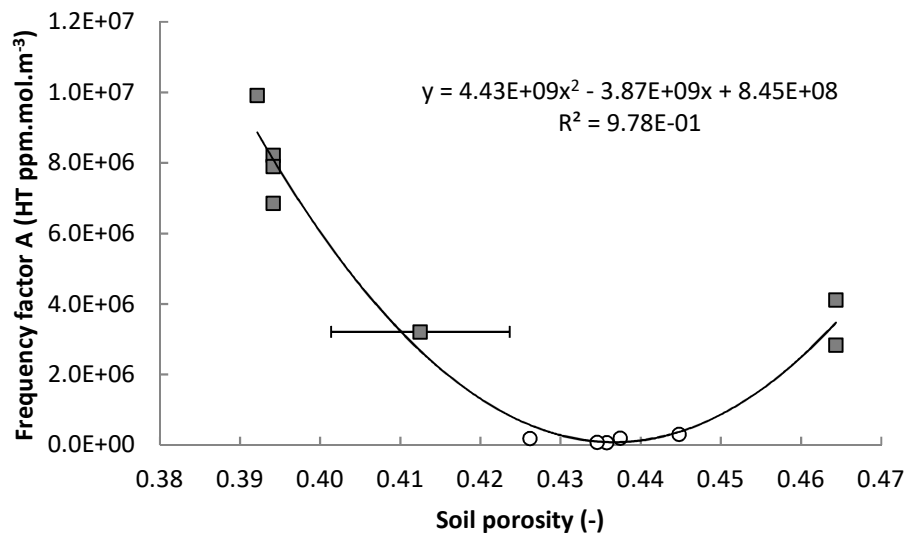


Figure 3 : Modelling of annual production of HTO by bacterial oxidation of 1 Bq.m⁻³ HT in air, with average annual soil water content and temperature for different type of soil (C= Clay, SC= Sandy Clay, CL= Clay Loam, SiCL= Silt Clay Loam, SiC= Silt Clay, SCL= Sandy Clay Loam, L= Loam, SL= Sandy Loam,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

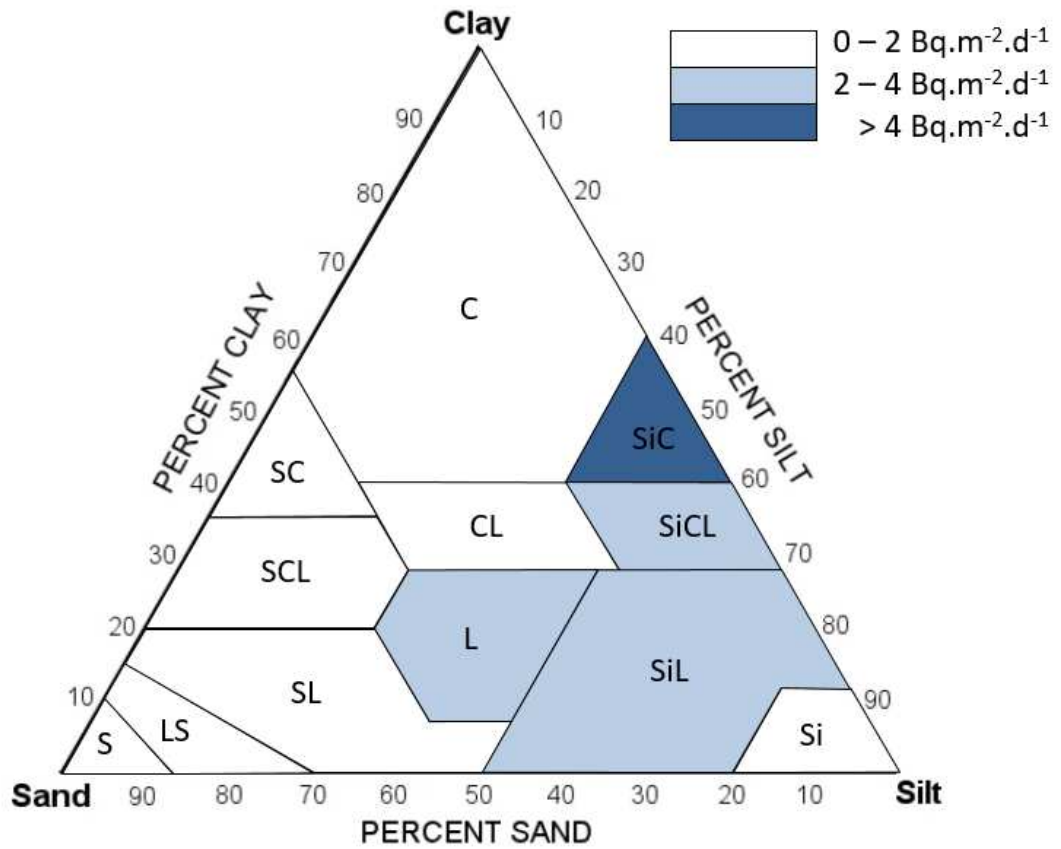


Figure 4 : Evolution of HTO in soil (Bq.L^{-1}) for 2013-2016 period, calculate from TOCATTA- χ model, taken into account only atmospheric measurements of HT in air (blue line) and taken into account all sources of tritium (HTO and HT in air, HTO in rainwater, black line) for site 2 km from Orano La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

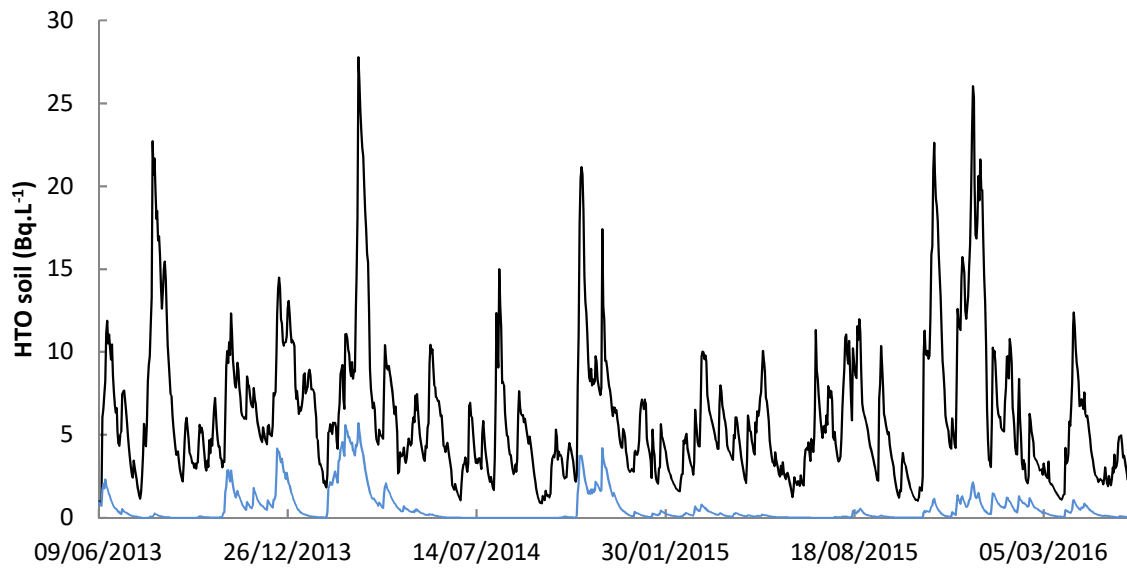


Figure 5 : Exchange of HTO between soil and atmosphere ($\text{Bq}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) for 2013-2016 period, calculate from TOCATA- χ model, with only atmospheric measurements of HT in air for site 2 km from Orano La Hague reprocessing plant. Positive values indicate flux of HTO from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

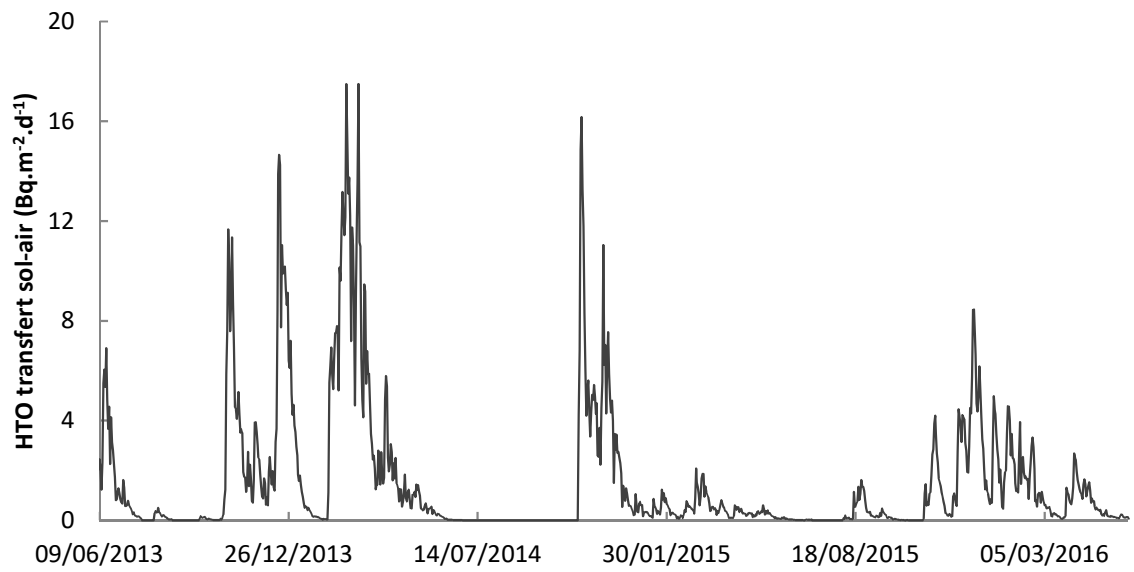


Table 1 : Description of the parameters used to calculate the oxidation rate of HT in HTO in soils.

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 (kg _{sands} .kg _{dry soil} ⁻¹)	Total loam content (kg _{sands} .kg _{dry soil} ⁻¹)	Total sand content (kg _{sands} .kg _{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 soil surface	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 particules.

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 Kg.m ⁻³	Soil HTO Bq.m ⁻² .d ⁻¹			
		Season	Spring ^a	Summer ^b	Autumn ^c
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 mentioned ^a, ^b, ^c and ^d come from hourly measurements over the period 2013 to 2019 (Maro *et al.*, 2017).