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Spatial and temporal variation of tritium concentrations during a dam flushing operation

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Abstract

Tritium is a radionuclide commonly observed worldwide in riverine systems. In the Rhône River downstream the Lake Geneva (Switzerland and France), its occurrence is also related to its use for its luminescent properties in watchmaking paints. In fact, tritium is regularly observed at anomalous levels in this river and extreme events such as flushing operations might conduct to its transport downstream. In the Rhône River, characterized by 21 dams downstream the Geneva Lake, such operations are regularly organized to remove the sediments and limit problematic consequences such as siltation and increased flooding hazards. The consequences of dam flushing operations on tritium concentrations were thus investigated. Samples of Suspended Particulate Matter (SPM) and water were collected in the Rhone River downstream of Geneva in June 2012, during a planned flushing operation of three upstream reservoirs (Verbois, Chancy-Pougny and Génissiat). The concentrations of tritiated water (HTO) and organically bound Tritium (OBT) were measured and compared to reference concentrations. The flushing operations had no impact on the HTO concentration while the increases observed were related to the authorized releases of HTO from a nuclear power plant located downstream the dams. High increases of OBT concentrations in SPM were observed at two stations (Creys-Malville and Jons) without clear spatial or temporal trends. These anomalous peaks could be explained by the heterogeneous spatial distribution of technogenic tritium leading to large variations of tritium concentrations within the samples even though collected in areas close to each other. The results highlight the need to investigate the amount of such technogenic tritium currently stored in the upstream Rhone River as it might be significant.

Keywords	Radionuclide; Technogenic tritium; organically bound Tritium; sediment; suspended particulate matter; watchmaking paint
Taxonomy	River Basin Management, Environmental Science, Environmental Radioactivity
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Comments from reviewer	Answers from corresponding author	Correction in the manuscript
Reviewer 1	<p>Explanation for the use of SPM and sediment in the manuscript:</p> <ul style="list-style-type: none"> • SPM is used to characterize the particles that are transported by the river. It is what we sampled to measure the OBT. • Sediment characterized the particles stored either in the studied dams or along the river. <p>Sediment could be resuspended (for example during the flushing operations) and thereafter considered as SPM as well as SPM could be stored by sedimentation and considered as sediment.</p> <p>Since the reviewers 2 and 3 did not complain on that point, we did not changed the terminology of SPM and sediments.</p>	
- Line 12: Insert (SPM)	Added	Samples of Suspended Particulate Matter (SPM) and water were collected in the Rhone River downstream of Geneva in June 2012 [...]
- Line 18: High increase of OBT concentration from SPM or sediment? I am confused between sediment and SPM through whole manuscript. Is SPM a part of sediment?	<p>See first comment for SPM and sediment definition.</p> <p>Although the increase was observed in the SPM sampled at two of the four stations, it was directly related to the resuspension during the flushing operations of the sediments stored in the dams or in the river.</p>	High increases of OBT concentrations in SPM were observed at two stations (Creys-Malville and Jons) without clear spatial or temporal trends.

<p>- Line 36: “the nuclear sector is allowed to release low-activity liquid effluent into rivers”. Is it including SPM or OBT? If yes, insert a reference.</p>	<p>Nuclear industries release radionuclides as dissolved species only. No particles are released. However, dissolved species can fix to suspended solid particles transported by the river. Tritium is transferred in the environment predominantly as dissolved free HTO and is known to be a conservative radionuclide during water mass transfer and mixing. Part of tritium can associate to particulate organic matter during photosynthesis (OBT).</p>	
<p>- Line 40: These forms?</p>	<p>OBT – corrected in the text</p>	<p>Part of OBT do not easily exchange with the surrounding water molecules and persist in the environment until organic compounds are biodegraded.</p>
<p>- Line 56: 0.6×10^9. Is it suspended or precipitated in the bottom?</p>	<p>It is particles that were suspended but got stored by sedimentation.</p>	
<p>- Line 61-62: What is a difference between contaminated sediments and SPM?</p>	<p>See first comment for SPM and sediment definition. Sediments stored in the dam might be either contaminated or depleted so as the SPM.</p>	
<p>- Line 71: soil washout by rain?</p>	<p>Soil erosion. Corrected</p>	<p>[...] or finally progressively transferred due to soil erosion (Schürch et al., 2003).</p>
<p>- Line 99-110: Format error? All stations (A,B,C,D) have different sampling periods from 6 days to 30 days. Do you have any specific reason?</p>	<p>Unfortunately, due to logistic constraint, periods of sampling differed depending on the stations. Sampling at station A and B needed specific authorization due to safety rules during the flushing operations and sampling were only authorized during the flushing of the closest dams. Detail added to the manuscript.</p>	<p>To characterize the impact of the dam flushing operations on the concentrations of HTO (water samples) and OBT (SPM samples), samples were collected at four stations (Figure 1, Table 1) with different sampling periods due to logistic constrain</p>

<p>- Line 118: For SPM sampling, is any water depth related to?</p>	<p>At Station A B and D, Particle Trap were set in the bottom of the river while for Station C, the sampling were conducted approx. 50cm below the surface in order to side step potential heterogeneity of SPM throughout the river cross-section. Detail added to the manuscript.</p>	<p>Due to logistic constrain, the PT were set on the bottom of the river at Stations A, B and D while at Station C it was approx. 50 cm below the surface.</p>
<p>- Line 132: detection limit of HTO and OBT?</p>	<p>With used detection limit and detection threshold to determine the concentration in our samples as described in Currie (1968). For both methods, detection limit was approx. 0.6 Bq.L⁻¹ with a detection threshold of approx. 1.2 Bq.L⁻¹. Information added in the manuscript.</p>	<p>For both methods, detection limit was approx. 0.6 Bq.L⁻¹ with a detection threshold of approx. 1.2 Bq.L⁻¹ (Currie, 1968; Eyrolle et al., 2018).</p>
<p>- Line 182: How much tritium released annually from the NPP?</p>	<p>In the Rhône River, almost 80% of HTO come from the NPP, it is the most released radionuclide in term of quantity (Eyrolle-Boyer et al., 2015). In 2012, almost 210 TBq of HTO were released in the Rhône River (with 200 TBq only by NPP).</p>	
<p>- Line 224: What is the relationship between sediment and SPM?</p>	<p>Corrected, OBT is heterogeneously distributed in the sediments.</p>	<p>However, OBT is heterogeneously distributed in sediments of the Rhône River and large amounts of this radionuclide are still stored in the Upper Rhône sediments.</p>
<p>- Table S1: In C station, MDA is 1.2 or 1.5 but in D station, can be detected up to 0.6 Bq/L. Are they use the same technique?</p>	<p>The same technique was used, it depended not only on the detection limit but also on the detection threshold. See information on detection limit in the comment above.</p>	
<p>Reviewer 2</p>		

<p>1. In order to determine how turbid in the river water collected in this study, please indicate and explain the SPM amount (mg/L) of the river water.</p>	<p>The discharge of the river and its SPM concentration were investigated in a thesis in French (Launay, 2014), while the data are available online (Thollet et al., 2018). A specific focus on Jons was conducted in Lepage et al. (2020). These references and additional information were added in the manuscript and in the electronic supplementary materials.</p>	<p>Discharge varied from $129 \text{ m}^3 \text{ s}^{-1}$ to $631 \text{ m}^3 \text{ s}^{-1}$ in the vicinity of Chancy-Pougny during the flushing periods (Figure ESM1 in electronic supplementary materials). Discharge increased from upstream to downstream and reached maximal values ($1600 \text{ m}^3 \text{ s}^{-1}$) at Jons (Station D in Figure 1) on the 06/14, which correspond to discharges observed for biennial flood (Lepage et al., 2020). SPM concentration reached 16.6 g L^{-1} near Génissiat during its flushing and the highest SPM concentration was observed during the flushing of Verbois and Chancy-Pougny with 48.6 g L^{-1} observed at Chancy-Pougny (Figure ESM1 in electronic supplementary materials). The SPM concentrations decreased with distance and the maximum concentrations observed at Jons was 0.9 g L^{-1}. It has to be noted that floods occurred in two tributaries (Ain and Fier - Figure 1) with a limited impact on the transport of SPM (Launay, 2014; Lepage et al., 2020).</p>
<p>2. Can you estimate the tritium load into a downstream using the amount of sediment released during flushing operations of 3 dams and data of OBT concentration in SPM? You should describe the effect of tritium on the downstream caused by the dam flushing operation.</p>	<p>Fluxes of SPM related to these flushing operations were calculated in Lepage et al. (2020) and might be used to estimate the flux of OBT. However due to its heterogeneous distribution in the SPM it is difficult to evaluate an accurate load of OBT exported.</p>	
<p>3. Please add information such as organic matter quantity (TOC, TN, etc.) to clarify the composition in SPM.</p>	<p>The particulate organic carbon and grain size distribution were added in the Table S2 and in the manuscript (in Mat & Met., Results and Discussion)</p>	

<p>4. By the way, are there an impact of high-concentration tritium SPM on ecosystems? Is there bioaccumulation through the food chain by SPM? If so, please describe in the "introduction", "discussion" or "conclusion".</p>	<p>To our knowledge, any investigation was conducted on the radiotoxicity of the technogenic tritium observed in the Rhône River. Additional information was added to the manuscript.</p>	<p>The radiotoxicity of free tritium (HTO) or organically bound tritium to naturally occurring organic compounds (OBT) are low comparing to most other natural or artificial radionuclides. Nevertheless, the specific radiotoxicity of organically bound tritium to synthetic organic particles are unknown to our knowledge as well as their transfer rates toward living organisms.</p>
<p>5. Precipitation information is needed to distinguish the effects of dam flushing and precipitation. Provide information about precipitation during the observation period and please write that the SPM in the river water is not affected by precipitation.</p>	<p>During the flushing operations, floods occurred in two upstream tributaries (Ain and Fier rivers), downstream Stations A and B (Figure 1). Their impacts remained low as the input of SPM by these tributaries was strongly lower than the flux from the flushing operations (Launay. 2014; Lepage et al., 2020).</p>	<p>It has to be noted that floods occurred in two tributaries (Ain and Fier – Figure 1) with a limited impact on the transport of SPM (Launay, 2014; Lepage et al., 2020).</p>
<p>1. Change from unit of "Bq.L-1" to "Bq L-1" in manuscript. No period required.</p>	<p>Corrected for the whole manuscript.</p>	
<p>2. Line 45: Change from "coastal rivers" to "mountainous rivers".</p>	<p>Corrected</p>	<p>[...] HTO concentrations in two small mountainous rivers were shown to be higher during flood events than in baseflow conditions (Ueda <i>et al.</i>, 2015) [...]</p>
<p>3. It is easier to understand if you insert tritium concentration ranges in the river water and sediments of the Rhone River in Figures 2 and 3. For example, see Fig. 3 of Science of the Total Environment Eyrolle et al (2018) Vol 643, pp40-51.</p>	<p>Ranges of HTO and OBT concentrations were added to the figures 2 and 3.</p>	
<p>Reviewer 3</p>		
<p>- The graphical abstract looks inconsistent with the findings. Heterogeneous distribution of OBT is the key finding in my understanding. If so, the</p>	<p>Graphical abstract was improved</p>	

<p>heterogeneity should be illustrated in the graphical abstract.</p>		
<p>- More information is needed for heterogeneity for OBT. I remember that the author(s) don't have the data for the bed sediment, but how about the concentration of SPM (kg/L) in river water? That information helps the division of heterogeneity of SPM concentration and heterogeneity of OBT concentration (probably the unit should be Bq/kg instead of Bq/L in this case). I'm not familiar with the Rhone river but imagine heterogeneity of SPM concentration is large during such dam flushing operations.</p>	<p>Variation of discharge and SPM concentration were added in the electronic supplementary materials and in the manuscript. However, it is difficult to link the OBT to the SPM as the samples were collected during several hours in order to get a sufficient amount of SPM to realize the analysis.</p> <p>The Bq L⁻¹ of combustive water as described in our paper directly express the content of tritium associated with organic compounds. Bq kg⁻¹ can conduct to erroneous interpretation of OBT results because it doesn't consider organic matter content in suspended or deposited sediment samples. However, results in Bq kg⁻¹ were added in the ESM in the Table ESM2</p>	<p>This result highlights that these tritiated particles most probably come from the sediment stored in the dams and flushed during the operations. It also confirms their heterogeneously distribution as such increase of OBT concentration was not observed in Stations A and B.</p>

1 Spatial and temporal variation of tritium concentrations during a 2 dam flushing operation

3 Abstract

4 Tritium is a radionuclide commonly observed worldwide in riverine systems. In the Rhône
5 River downstream the Lake Geneva (Switzerland and France), its occurrence is also related to
6 its use for its luminescent properties in watchmaking paints. In fact, tritium is regularly
7 observed at anomalous levels in this river and extreme events such as flushing operations
8 might conduct to its transport downstream. In the Rhône River, characterized by 21 dams
9 downstream the Geneva Lake, such operations are regularly organized to remove the
10 sediments and limit problematic consequences such as siltation and increased flooding
11 hazards. The consequences of dam flushing operations on tritium concentrations were thus
12 investigated. Samples of Suspended Particulate Matter (SPM) and water were collected in the
13 Rhone River downstream of Geneva in June 2012, during a planned flushing operation of three
14 upstream reservoirs (Verbois, Chancy-Pougny and Génissiat). The concentrations of tritiated
15 water (HTO) and organically bound Tritium (OBT) were measured and compared to reference
16 concentrations. The flushing operations had no impact on the HTO concentration while the
17 increases observed were related to the authorized releases of HTO from a nuclear power plant
18 located downstream the dams. High increases of OBT concentrations in SPM were observed
19 at two stations (Creys-Malville and Jons) without clear spatial or temporal trends. These
20 anomalous peaks could be explained by the heterogeneous spatial distribution of technogenic
21 tritium leading to large variations of tritium concentrations within the samples even though
22 collected in areas close to each other. The results highlight the need to investigate the amount

23 of such technogenic tritium currently stored in the upstream Rhone River as it might be
24 significant.

25 **Keywords**

26 Radionuclide; Technogenic tritium; organically bound Tritium; sediment; suspended
27 particulate matter; watchmaking paint

28 **Introduction**

29 Tritium (^3H - half-life = 12.3 years) is a radionuclide commonly observed for several
30 decades in the environment (Eisenbud et al., 1979). In rivers, ^3H can be liquid (tritiated water
31 - HTO) or incorporated in particulate organic compounds (Organically Bound Tritium - OBT)
32 (Kim et al., 2013). The HTO is the predominant form of tritium in the environment and it closely
33 follows the water cycle (Ciffroy et al., 2006; Eyrolle-Boyer et al., 2015). It is commonly used as
34 a tracer in hydrogeology and marine studies (Ducros *et al.*, 2018). The HTO is also the most
35 released aqueous radionuclide from nuclear facilities, with levels of activity currently 1000
36 times higher than the sum of artificial gamma emitters discharged (Eyrolle *et al.*, 2018). In fact,
37 in compliance with the legislation, the nuclear sector is allowed to release low-activity liquid
38 effluent into rivers. The OBT is part of the organic matter cycle and has been measured in
39 sediments and suspended particulate matter (SPM) for decades (Eyrolle *et al.*, 2018). Some of
40 ~~these forms~~the OBT do not easily exchange with the surrounding water molecules and persist
41 in the environment until organic compounds are biodegraded. These forms of tritium are
42 expected to be stored in sediments associated with particulate organic matter (Eyrolle-Boyer
43 *et al.*, 2014) and might be affected by extreme events such as flood events or dam flushing
44 operations. In fact, these events strongly affect the behavior of dissolved and particulate
45 contaminants including tritium. For example, after the deposition of tritium following the

46 Fukushima accident in march 2011, HTO concentrations in two small ~~coastal~~ mountainous
47 rivers were shown to be higher during flood events than in baseflow conditions (Ueda *et al.*,
48 2015) but decreased rapidly the following years to reach background concentration in 2014.
49 Dams on rivers considerably impact SPM transport, by reducing flow velocity and increasing
50 SPM deposition (Syvitski *et al.*, 2005) and that of their related contaminants (Lepage *et al.*,
51 2020). Contaminants associated with deposited sediments may also be resuspended and
52 disseminated (Peter *et al.*, 2014) or transferred to the dissolved phase (Bretier *et al.*, 2019;
53 Kalnejais *et al.*, 2010).

54 In France, the Rhône River is characterized by the presence of 21 hydropower plants
55 and is one of the most nuclearized rivers in the world, with 5 nuclear power plants (NPP)
56 including one in dismantlement, nuclear fuel production, reprocessing plants and research
57 laboratories. From 0.2 to 0.6 10⁹ kg of SPM are stored each year along the Rhône River
58 (Bravard and Clémens, 2008), mostly in dam reservoirs (Provansal *et al.*, 2014). Resuspension
59 processes, such as dam flushing operations, are regularly organized to remove stored
60 sediments and limit problematic consequences such as siltation and increased flooding
61 hazards (Brown, 1944; Peteuil *et al.*, 2013). Such dam operations lead either to the
62 resuspension of contaminated sediments stored in the dams, or to the dilution of
63 contaminated SPM by flushing non-contaminated sediments (Lepage *et al.*, 2020).

64 Moreover, in the past century, most of the OBT was originate from other industrial
65 plants present in the Rhône River and especially in its upstream part that produced
66 luminescent paint used in watches (Eyrolle *et al.*, 2018; Jean-Baptiste *et al.*, 2018). These
67 companies have released fine particles of tritiated compounds (usually tiny tritiated
68 polystyrene spherules a few tens of microns in diameter) used in luminous paints (Jean-
69 Baptiste *et al.*, 2007; Krejci and Zeller, 1979; Schürch *et al.*, 2003). In fact, these tritiated

70 technogenic particles (hot tritiated particles) could have been released directly into the river
71 by the industrial plants, or transferred into the environment during the waste incineration
72 process, or finally progressively transferred due to soil ~~washout~~erosion (Schürch et al., 2003).
73 These refractory particles that accumulate in sediments are expected to persist in the
74 environment for a very long time (Eyrolle et al., 2018; Morereau et al., in prep.) and have also
75 been observed in the Mediterranean Sea near the outlet of the Rhône River (Jean-Baptiste *et*
76 *al.*, 2018). Although a recent review written by Eyrolle *et al.* (2018) summarized results on its
77 specific behavior in the Rhône River, reports on the impact of hydrological events on OBT
78 concentrations remain rare especially its dynamics during dam flushing operations.

79 This field study was conducted in the Rhône River downstream the Lake Geneva during
80 the flushing operations of several dams in June 2012. Water and SPM samples were collected
81 at different locations for different periods. The tritium concentrations were characterized and
82 the results were then compared with the contents recorded before the event.

83 **Materials and Method**

84 ***Dam location and description of the flushing operations***

85 This study was conducted along the Upper Rhône River in France and Switzerland,
86 downstream the Lake Geneva (Figure 1). This basin (95,600 km² at Beaucaire station)
87 constitutes the main SPM input flowing into the Western Mediterranean Sea with a mean SPM
88 flux of 6.5 Mt_{year}⁻¹ from 2000 to 2015 (Poulier *et al.*, 2019). This work focuses on flushing
89 operations conducted in June 2012 in three reservoirs located downstream of Lake Geneva in
90 Switzerland (Figure 1): Verbois, Chancy-Pougny, and Génissiat. These flushing operations are
91 described in Lepage *et al.* (2020). In brief, the water level of the three dams was lowered
92 following the drawdown flushing method (Fruchard and Camenen, 2012) in order to remove

93 stored sediments. The large-volume Génissiat reservoir located downstream of the two other
94 dams was flushed first (4-12 June 2012) in order to compensate for the deposition of the SPM
95 released from the Chancy-Pougny (9-16 June 2012) and Verbois dams (9-22 June 2012).
96 Discharge varied from 129 m³ s⁻¹ to 631 m³ s⁻¹ in the vicinity of Chancy-Pougny during the
97 flushing periods (Figure ESM1 in electronic supplementary materials). Discharge increased
98 from upstream to downstream and reached maximal values (1600 m³ s⁻¹) at Jons (Station D in
99 Figure 1) on the 06/14, which correspond to discharges observed for biennial flood (Lepage et
100 al., 2020). SPM concentration reached 16.6 g L⁻¹ near Génissiat during its flushing and the
101 highest SPM concentration was observed during the flushing of Verbois and Chancy-Pougny
102 with 48.6 g L⁻¹ observed at Chancy-Pougny (Figure ESM1 in electronic supplementary
103 materials). The SPM concentrations decreased with distance and the maximum
104 concentrations observed at Jons was 0.9 g L⁻¹. It has to be noted that floods occurred in two
105 tributaries (Ain and Fier - Figure 1) with a limited impact on the transport of SPM (Launay,
106 2014; Lepage et al., 2020).

107 ***Sampling and samples***

108 To characterize the impact of the dam flushing operations on the concentrations of
109 HTO (water samples) and OBT (SPM samples), samples were collected at four stations (Figure
110 1, Table 1) with different sampling periods due to logistic constrain:

- 111 • Station A at Pougny, in the downstream vicinity of Chancy-Pougny and Verbois
112 dams. Samples were collected from the 06/09/2012 to the 06/20/2012 during
113 the flushing operations of these two dams.
- 114 • Station B at Seyssel, downstream Génissiat dam and during its flushing
115 operation with samples collected from the 06/04/2012 to the 06/10/2012.

- 116 • Station C at Creys-Malville in a monitoring station used to supply the regulatory
117 control of the releases from NPPs (IRSN, 2015) and used in this study for
118 temporal comparison. Sampling was conducted before, during and after the
119 flushing operations, from the 05/25/2012 to the 07/01/2012.
- 120 • Station D at Jons in a monitoring station (Masson *et al.*, 2018; Thollet *et al.*,
121 2018) located downstream a NPP (Figure 1) with samples collected for the main
122 period of flushing operations, from the 06/04/2012 to the 07/03/2012.

123

124 Two different sampling methods were used to collect water samples (Table 1).
125 Instantaneous water samples were obtained manually using a stainless-steel bucket (approx.
126 4 L) at stations A, B and D, and by an Automatic Water Sampler (AWS) at station C. The AWS
127 used for water sampling was a Bühler 4011 (HachLange, Germany) and set to collect 10 mL
128 every 65 minutes to constitute time integrated raw water samples (6 days) stored in glass
129 bottles. Samples were all stored in dark glass bottles at 4°C until analyses.

130 For OBT measurement, SPM samples were collected using Particle Trap (PT). These
131 samplers were built following the German Environmental Specimen Bank model (Masson *et*
132 *al.*, 2018; Schulze *et al.*, 2007). Water flows through the high-quality stainless steel box and its
133 velocity is reduced by two baffles. SPM settle in two sedimentation basins in the box. Samples
134 were collected every 1 to 4 days (see Table ESMS1 in electronic supplementary materials).
135 Due to logistic constrain, the PT were set on the bottom of the river at Stations A, B and D
136 while at Station C it was approx. 50 cm below the surface. Prior to analysis, SPM samples were
137 stored in the dark at 4°C, deep-frozen, freeze-dried, and homogenized through a 2 mm
138 stainless steel sieve. Dried samples were then immediately sealed under soft vacuum in

139 aluminized bags until analyses in order to avoid the exchange of water molecules with the
140 atmosphere.

141 **Grain-size distribution**

142 For the measure of volumetric grain size distribution, a representative aliquot of each
143 wet sample was taken before processing and was analyzed on a CILAS 1190 laser particle size
144 analyzer (Masson et al., 2018) according to the ISO 13320 standard method (AFNOR, 2009).
145 Clay (<1.95 µm), Silt (<63 µm) and Sand (<2000 µm) were estimated.

146 **Particulate Organic Carbon analysis**

147 The determination of Particulate Organic Carbon (POC) in SPM samples was performed
148 using a carbon analyzer (Thermo Electron, CHN Flash 2000) by INRA laboratory (Arras, France).
149 Decarbonation was completed using hydrochloric acid according to the NF ISO 10694 standard
150 method (AFNOR, 1995). The limit of quantification (LQ) was estimated to be 0.05 g kg⁻¹ and
151 analytical uncertainty varied between ~3% and ~6% (k=2), depending on the POC
152 concentration.

153

154 ***Tritium analyses***

155 The concentrations of the two main forms of tritium (HTO and OBT) were investigated.
156 The HTO analyses were performed on 20ml of filtered water (< 0.2 µm) either directly filtered
157 in the field for punctual samples or in the laboratory for time-integrated ones sampled by
158 AWS. Filtered waters were analyzed by classical scintillation counting for HTO content (Tricarb
159 3180 TR/SL), by taking an aliquot of 10 mL and adding 10 mL of scintillation liquid (UltimaGold
160 LLT).

161 OBT analyses were conducted using the Helium-3 ingrowth method after placing the
162 sample in a vacuum (10^{-6} mbar) and storing it for 3 to 4 months (Cossonnet *et al.*, 2009). The
163 Helium-3 is a decay product of tritium—and its concentration is measured by mass
164 spectrometry (Jean-Baptiste *et al.*, 2010). OBT concentrations were converted in Becquerel
165 per liter of combustion water ($\text{Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$) by using the percentage of hydrogen measured in
166 each sample by a CHNS elemental analyzer (Elementar, vario MICROcube).

167 For both methods, detection limit was around 0.6 Bq L^{-1} with a detection threshold of
168 1.2 Bq L^{-1} (Currie, 1968; Eyrolle *et al.*, 2018). All the measured concentrations were corrected
169 for radioactive decay to the sampling date.

170 **Results**

171 **Variation of HTO contents**

172 The concentrations of HTO measured during this study were similar at Stations A and
173 B (Figure 2; Table [S4-ESM1](#)) with respectively a mean HTO concentration of $1.1 \text{ Bq}\cdot\text{Bq L}^{-1}$ (with
174 standard deviation $\text{sd} = 0.3 \text{ Bq}\cdot\text{Bq L}^{-1}$) and $1.2 \text{ Bq}\cdot\text{Bq L}^{-1}$ ($\text{sd} = 0.2 \text{ Bq}\cdot\text{Bq L}^{-1}$). At station C, the
175 only value observed above the detection limit ($0.8 \pm 0.7 \text{ Bq}\cdot\text{Bq L}^{-1}$) was not significantly
176 different to the two upstream stations. The HTO concentration at this station remained very
177 low as several values were lower than the detection limit. For these three stations, no
178 significant variation of HTO contents were observed during the flushing operations. At station
179 D, two significant increases were observed during the flushing operation the 06/05/2012 and
180 the 06/16/2012 with respectively $13.1 \pm 1.0 \text{ Bq}\cdot\text{Bq L}^{-1}$ and $11.8 \pm 1.0 \text{ Bq}\cdot\text{Bq L}^{-1}$. The other
181 concentrations measured at station D were similar to the values observed at the other stations
182 with $1.1 \text{ Bq}\cdot\text{Bq L}^{-1}$ ($\text{sd} = 0.3 \text{ Bq}\cdot\text{Bq L}^{-1}$).

183 **OBT**

184 During the period studied, OBT contents ranged from $180 \pm 40 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ to $11,700 \pm$
185 $2,300 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ (Figure 3 - Table S3ESM2) with a mean value of $1,640 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ (sd = $2,600$
186 $\text{Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$). The mean OBT concentration at stations A and B were similar with respectively
187 $850 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ (sd = $320 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$) and $890 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ (sd = $330 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$) while significant
188 variations of OBT were observed at the two other stations. At station C, the first value
189 measured was significantly higher than the other with $11,700 \pm 2,300 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ observed the
190 06/09/12, then decreased to reach similar level than the upstream stations A and B. At station
191 D, a high concentration of OBT was observed 48h afterwards that of station C ($6,670 \pm 340$
192 $\text{Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$ the 06/11/12). The other values measured during dam flushing operations (mean
193 = 680 sd $400 \text{ Bq}\cdot\text{Bq L}^{-1}_{\text{cw}}$) were similar to those of station A and B.

194 Silt particles always constituted the major part of the SPM whatever the station with
195 proportions ranging from 35.8 to 94.2% (Table ESM2). Sand particles were mostly observed at
196 stations A and B, close to the studied dams. Those particles were rapidly stored in the Upper
197 Rhône River as the proportion of sand were very low at Stations C and D. The POC
198 concentration observed at Station A and C remained constant while some variations were
199 observed at the two other stations (Table ESM2). Maximal concentration was observed at
200 Station D with $36.0 \pm 1.8 \text{ mg kg}^{-1}$.

201

202 Discussion

203 Most of the HTO concentrations measured at the four stations were similar to those
204 observed from 2003 to 2015 by the Swiss Federal office of public health (OFSP, 2015) in water
205 samples collected near station A ($1.03 \text{ Bq}\cdot\text{Bq L}^{-1}$ with sd = $0.41 \text{ Bq}\cdot\text{Bq L}^{-1}$) and not affected by
206 NPP releases. Furthermore, the concentrations remained in the range of values observed for

207 the natural background in waters of French pristine rivers (Ducros *et al.*, 2018). Although, the
208 increases observed at station D was strictly related to the releases of HTO by the NPP and not
209 related to the dam flushing operations. As mentioned in the introduction, NPPs are allowed
210 to release radionuclides into river systems conforming to liquid flow rate thresholds. The
211 sampling performed at station D for this study was conducted during short radionuclide
212 release operations with 12 events from 3 to 12 hours (Electricité De France, personal
213 communication). The absence of higher HTO concentrations in the other samples of station D
214 was due to the time lapse between the NPP's release operations and the samplings,
215 performed 10 hours after the end of the operations. The transit time between the NPP and
216 the sampling station has been validated by modeling using the hydrological model CASTEAUR
217 (Beaugelin-Seiller *et al.*, 2002). The increase was only observed at station D as the NPP is
218 downstream the other stations (Figure 1). Overall, the values measured during this NPP's
219 operations were similar to the mean concentrations recorded during radionuclide release
220 operations at this NPP from 2011 to 2014 ($12 \text{ Bq} \cdot \text{Bq} \cdot \text{L}^{-1}$) (IRSN, 2015). Therefore, despite the
221 input of high quantity of water from the flushing operations and characterized by a lower level
222 of HTO than from the NPP releases, no significant effect of dilution was observed. In the Upper
223 Rhône River, dam flushing operations do not affect HTO concentrations in the water column
224 and, in the absence of NPP releases, these concentrations remain similar from upstream to
225 downstream. Thus, in contrast with certain trace metals remobilized during such events such
226 as arsenic (Bretier *et al.*, 2019; Monnin *et al.*, 2018), no significant transfer of tritium from
227 sediment remobilization to the dissolved phase was observed. Moreover, these results did not
228 show any significant contribution of tritium either from HTO potentially stored in the pore
229 waters of remobilized sediments, or from OBT associated to fine particles ($<0.45\mu\text{m}$) towards
230 waters.

231 Despite the high concentrations of OBT observed at stations C and D, all the
232 concentrations remained in the same range as those reported by Eyrolle *et al.*, (2018) (from
233 4 to 30,200 $\text{Bq}\cdot\text{Bq}\cdot\text{L}^{-1}_{\text{cw}}$) and confirmed the high variability due to the presence of tritiated
234 technogenic particles in the Rhône River. In fact, OBT concentrations are generally expected
235 to be rather close to HTO concentrations in most other cases (Eyrolle-Boyer *et al.*, 2015). For
236 example, in the sediments of the Rhône's tributaries not affected by luminous paints,
237 background values were lower than 10 $\text{Bq}\cdot\text{Bq}\cdot\text{L}^{-1}_{\text{cw}}$ (Eyrolle *et al.*, 2018). Since neither
238 significant temporal nor spatial trends were observed in OBT concentrations, we hypothesize
239 that these results can be explained by the heterogeneous distribution of technogenic tritium
240 in suspended or deposited sedimentary particles leading to large variations of tritium
241 concentrations within the samples even though collected in areas close to each other. Also,
242 this result is confirmed by the absence of relation between OBT and POC concentrations. In
243 the Rhône River, OBT is not only bound to organic matter of natural origin, but would very
244 likely be trapped inside fine polystyrene particles from technogenic tritium (Eyrolle *et al.*,
245 2018). Regarding grain size, any specific relation was observed but the highest level of OBT at
246 Jons (6670 $\text{Bq}\cdot\text{L}^{-1}_{\text{cw}}$) was observed in a sample characterized by a high level of sand (42.2%)
247 (Table ESM2). This result highlights that these tritiated particles most probably come from the
248 sediment stored in the dams and flushed during the operations. It also confirms their
249 heterogeneously distribution as such increase of OBT concentration was not observed in
250 Stations A and B. Furthermore, with the evolution of technologies and the introduction of
251 guidelines for the protection of the environment (Morereau *et al.*, in prep.), OBT should no
252 longer be emitted at this level in the environment and its occurrence should be mainly related
253 to its long-time presence in the sediments of the Rhône River (Eyrolle *et al.*, 2018). The highest
254 concentrations observed below the dams might be related to the resuspension of old

255 contaminated sediments stored in the studied dams as observed for PAHs by Lepage et al.
256 (2020). The OBT is expected to be transported downstream and its concentration should
257 decrease from upstream to downstream in the following decades.

258

259 **Conclusion**

260 The consequences of dam flushing operations on tritium concentrations were
261 investigated in the Rhône River downstream Lake Geneva by characterizing ~~the~~ HTO and OBT
262 concentrations respectively in filtered water and suspended particulate matter (SPM) samples
263 collected downstream three dams flushed in June 2012. Our results demonstrate that dam
264 flushing operations do not significantly affect tritium concentrations in the water column as
265 they remained similar to those previously recorded during normal flow conditions. Analyses
266 of OBT in the SPM demonstrated ~~transient~~ increases in concentration during ~~the~~ dam flushing
267 operations. ~~This increase was~~ Those are most probably ~~linked~~ explained by the resuspension
268 of fine tritiated particles from watchmaking activities. As the increases were transient and not
269 observed at all the stations, no significant temporal nor spatial trend following dam flushing
270 operations can be drawn clearly ~~trend could be linked to the dam flushing operations.~~
271 However, OBT is heterogeneously distributed in sediments of the Rhône River and SPM ~~and a~~
272 large amounts of OBT ~~this radionuclide are still~~ might be currently stored in the Upper Rhône
273 River sediments. Extreme events and could be redistributed following extreme events such as
274 dam flushing operations can redistribute these storages to the downstream part of the River.
275 The radiotoxicity of free tritium (HTO) or organically bound tritium to naturally occurring
276 organic compounds (OBT) are low comparing to most other natural or artificial radionuclides.
277 Nevertheless, the specific radiotoxicity of organically bound tritium to synthetic organic
278 particles are unknown to our knowledge as well as their transfer rates toward living organisms.

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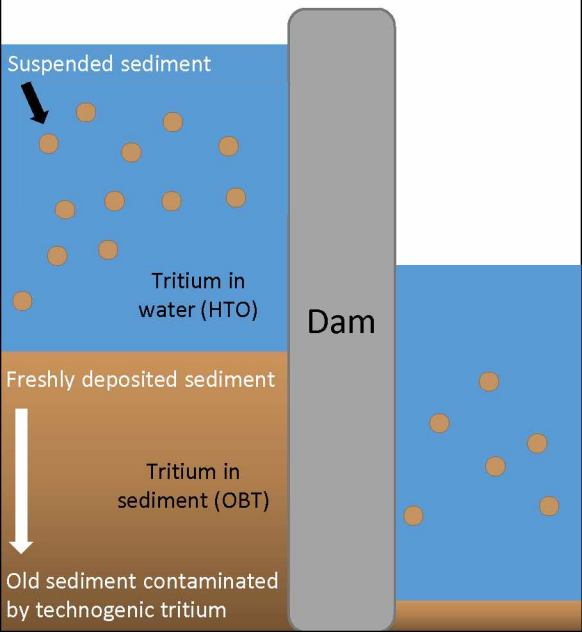
Highlights

- Tritium were monitored during dam regulations in the Rhone River.
- Dam flushing operations had no impact on HTO concentration in water.
- Increase of HTO contents were only related to the releases from a nuclear plant.
- Flushing operations resuspended contaminated sediments by watches industries.
- Sporadic high OBT contents in SPM reflect its heterogeneous distribution.

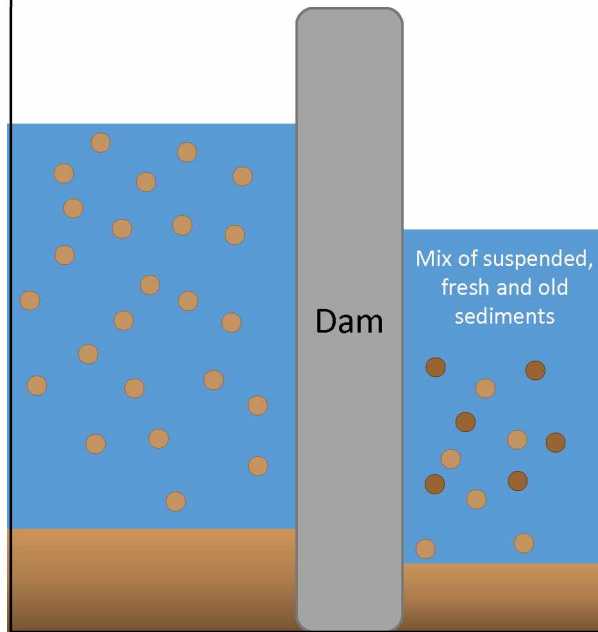
Abstract

Tritium is a radionuclide commonly observed worldwide in riverine systems. In the Rhône River downstream the Lake Geneva (Switzerland and France), its occurrence is also related to its use for its luminescent properties in watchmaking paints. In fact, tritium is regularly observed at anomalous levels in this river and extreme events such as flushing operations might conduct to its transport downstream. In the Rhône River, characterized by 21 dams downstream the Geneva Lake, such operations are regularly organized to remove the sediments and limit problematic consequences such as siltation and increased flooding hazards. The consequences of dam flushing operations on tritium concentrations were thus investigated. Samples of Suspended Particulate Matter (SPM) and water were collected in the Rhone River downstream of Geneva in June 2012, during a planned flushing operation of three upstream reservoirs (Verbois, Chancy-Pougny and Génissiat). The concentrations of tritiated water (HTO) and organically bound Tritium (OBT) were measured and compared to reference concentrations. The flushing operations had no impact on the HTO concentration while the increases observed were related to the authorized releases of HTO from a nuclear power plant located downstream the dams. High increases of OBT concentrations in SPM were observed at two stations (Creys-Malville and Jons) without clear spatial or temporal trends. These anomalous peaks could be explained by the heterogeneous spatial distribution of technogenic tritium leading to large variations of tritium concentrations within the samples even though collected in areas close to each other. The results highlight the need to investigate the amount of such technogenic tritium currently stored in the upstream Rhone River as it might be significant.

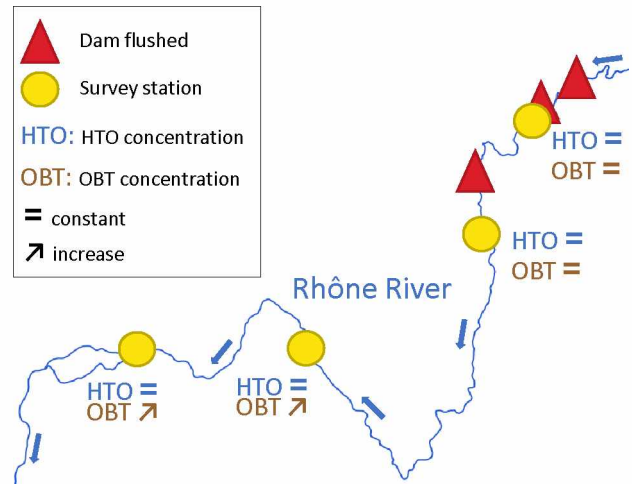
Before dam flushing operation



After dam flushing operation



Spatial variation of tritium during the flushing operations



Dam flushing operations:

- Had no impact on HTO concentration
- Confirmed the heterogeneous distribution of OBT

1 **Spatial and temporal variation of tritium concentrations during a**
2 **dam flushing operation**

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4

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1 **Spatial and temporal variation of tritium concentrations during a** 2 **dam flushing operation**

3 **Abstract**

4 Tritium is a radionuclide commonly observed worldwide in riverine systems. In the Rhône
5 River downstream the Lake Geneva (Switzerland and France), its occurrence is also related to
6 its use for its luminescent properties in watchmaking paints. In fact, tritium is regularly
7 observed at anomalous levels in this river and extreme events such as flushing operations
8 might conduct to its transport downstream. In the Rhône River, characterized by 21 dams
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15 water (HTO) and organically bound Tritium (OBT) were measured and compared to reference
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17 increases observed were related to the authorized releases of HTO from a nuclear power plant
18 located downstream the dams. High increases of OBT concentrations in SPM were observed
19 at two stations (Creys-Malville and Jons) without clear spatial or temporal trends. These
20 anomalous peaks could be explained by the heterogeneous spatial distribution of technogenic
21 tritium leading to large variations of tritium concentrations within the samples even though
22 collected in areas close to each other. The results highlight the need to investigate the amount

23 of such technogenic tritium currently stored in the upstream Rhone River as it might be
24 significant.

25 **Keywords**

26 Radionuclide; Technogenic tritium; organically bound Tritium; sediment; suspended
27 particulate matter; watchmaking paint

28 **Introduction**

29 Tritium (^3H - half-life = 12.3 years) is a radionuclide commonly observed for several
30 decades in the environment (Eisenbud et al., 1979). In rivers, ^3H can be liquid (tritiated water
31 - HTO) or incorporated in particulate organic compounds (Organically Bound Tritium - OBT)
32 (Kim et al., 2013). The HTO is the predominant form of tritium in the environment and it closely
33 follows the water cycle (Ciffroy et al., 2006; Eyrolle-Boyer et al., 2015). It is commonly used as
34 a tracer in hydrogeology and marine studies (Ducros *et al.*, 2018). The HTO is also the most
35 released aqueous radionuclide from nuclear facilities, with levels of activity currently 1000
36 times higher than the sum of artificial gamma emitters discharged (Eyrolle *et al.*, 2018). In fact,
37 in compliance with the legislation, the nuclear sector is allowed to release low-activity liquid
38 effluent into rivers. The OBT is part of the organic matter cycle and has been measured in
39 sediments and suspended particulate matter (SPM) for decades (Eyrolle *et al.*, 2018). Some of
40 the OBT do not easily exchange with the surrounding water molecules and persist in the
41 environment until organic compounds are biodegraded. These forms of tritium are expected
42 to be stored in sediments associated with particulate organic matter (Eyrolle-Boyer *et al.*,
43 2014) and might be affected by extreme events such as flood events or dam flushing
44 operations. In fact, these events strongly affect the behavior of dissolved and particulate
45 contaminants including tritium. For example, after the deposition of tritium following the

46 Fukushima accident in march 2011, HTO concentrations in two small mountainous rivers were
47 shown to be higher during flood events than in baseflow conditions (Ueda *et al.*, 2015) but
48 decreased rapidly the following years to reach background concentration in 2014. Dams on
49 rivers considerably impact SPM transport, by reducing flow velocity and increasing SPM
50 deposition (Syvitski *et al.*, 2005) and that of their related contaminants (Lepage *et al.*, 2020).
51 Contaminants associated with deposited sediments may also be resuspended and
52 disseminated (Peter *et al.*, 2014) or transferred to the dissolved phase (Bretier *et al.*, 2019;
53 Kalnejais *et al.*, 2010).

54 In France, the Rhône River is characterized by the presence of 21 hydropower plants
55 and is one of the most nuclearized rivers in the world, with 5 nuclear power plants (NPP)
56 including one in dismantlement, nuclear fuel production, reprocessing plants and research
57 laboratories. From 0.2 to 0.6 10⁹ kg of SPM are stored each year along the Rhône River
58 (Bravard and Clémens, 2008), mostly in dam reservoirs (Provansal *et al.*, 2014). Resuspension
59 processes, such as dam flushing operations, are regularly organized to remove stored
60 sediments and limit problematic consequences such as siltation and increased flooding
61 hazards (Brown, 1944; Peteuil *et al.*, 2013). Such dam operations lead either to the
62 resuspension of contaminated sediments stored in the dams, or to the dilution of
63 contaminated SPM by flushing non-contaminated sediments (Lepage *et al.*, 2020).

64 Moreover, in the past century, most of the OBT was originate from other industrial
65 plants present in the Rhône River and especially in its upstream part that produced
66 luminescent paint used in watches (Eyrolle *et al.*, 2018; Jean-Baptiste *et al.*, 2018). These
67 companies have released fine particles of tritiated compounds (usually tiny tritiated
68 polystyrene spherules a few tens of microns in diameter) used in luminous paints (Jean-
69 Baptiste *et al.*, 2007; Krejci and Zeller, 1979; Schürch *et al.*, 2003). In fact, these tritiated

70 technogenic particles (hot tritiated particles) could have been released directly into the river
71 by the industrial plants, or transferred into the environment during the waste incineration
72 process, or finally progressively transferred due to soil erosion (Schürch et al., 2003). These
73 refractory particles that accumulate in sediments are expected to persist in the environment
74 for a very long time (Eyrolle et al., 2018; Morereau et al., in prep.) and have also been observed
75 in the Mediterranean Sea near the outlet of the Rhône River (Jean-Baptiste *et al.*, 2018).
76 Although a recent review written by Eyrolle *et al.* (2018) summarized results on its specific
77 behavior in the Rhône River, reports on the impact of hydrological events on OBT
78 concentrations remain rare especially its dynamics during dam flushing operations.

79 This field study was conducted in the Rhône River downstream the Lake Geneva during
80 the flushing operations of several dams in June 2012. Water and SPM samples were collected
81 at different locations for different periods. The tritium concentrations were characterized and
82 the results were then compared with the contents recorded before the event.

83 **Materials and Method**

84 ***Dam location and description of the flushing operations***

85 This study was conducted along the Upper Rhône River in France and Switzerland,
86 downstream the Lake Geneva (Figure 1). This basin (95,600 km² at Beaucaire station)
87 constitutes the main SPM input flowing into the Western Mediterranean Sea with a mean SPM
88 flux of 6.5 Mt year⁻¹ from 2000 to 2015 (Poulier *et al.*, 2019). This work focuses on flushing
89 operations conducted in June 2012 in three reservoirs located downstream of Lake Geneva in
90 Switzerland (Figure 1): Verbois, Chancy-Pougny, and Génissiat. These flushing operations are
91 described in Lepage et al. (2020). In brief, the water level of the three dams was lowered
92 following the drawdown flushing method (Fruchard and Camenen, 2012) in order to remove

93 stored sediments. The large-volume Génissiat reservoir located downstream of the two other
94 dams was flushed first (4-12 June 2012) in order to compensate for the deposition of the SPM
95 released from the Chancy-Pougny (9-16 June 2012) and Verbois dams (9-22 June 2012).
96 Discharge varied from $129 \text{ m}^3 \text{ s}^{-1}$ to $631 \text{ m}^3 \text{ s}^{-1}$ in the vicinity of Chancy-Pougny during the
97 flushing periods (Figure ESM1 in electronic supplementary materials). Discharge increased
98 from upstream to downstream and reached maximal values ($1600 \text{ m}^3 \text{ s}^{-1}$) at Jons (Station D in
99 Figure 1) on the 06/14, which correspond to discharges observed for biennial flood (Lepage et
100 al., 2020). SPM concentration reached 16.6 g L^{-1} near Génissiat during its flushing and the
101 highest SPM concentration was observed during the flushing of Verbois and Chancy-Pougny
102 with 48.6 g L^{-1} observed at Chancy-Pougny (Figure ESM1 in electronic supplementary
103 materials). The SPM concentrations decreased with distance and the maximum
104 concentrations observed at Jons was 0.9 g L^{-1} . It has to be noted that floods occurred in two
105 tributaries (Ain and Fier - Figure 1) with a limited impact on the transport of SPM (Launay,
106 2014; Lepage et al., 2020).

107 ***Sampling and samples***

108 To characterize the impact of the dam flushing operations on the concentrations of
109 HTO (water samples) and OBT (SPM samples), samples were collected at four stations (Figure
110 1, Table 1) with different sampling periods due to logistic constrain:

- 111 • Station A at Pougny, in the downstream vicinity of Chancy-Pougny and Verbois
112 dams. Samples were collected from the 06/09/2012 to the 06/20/2012 during
113 the flushing operations of these two dams.
- 114 • Station B at Seyssel, downstream Génissiat dam and during its flushing
115 operation with samples collected from the 06/04/2012 to the 06/10/2012.

- 116 • Station C at Creys-Malville in a monitoring station used to supply the regulatory
117 control of the releases from NPPs (IRSN, 2015) and used in this study for
118 temporal comparison. Sampling was conducted before, during and after the
119 flushing operations, from the 05/25/2012 to the 07/01/2012.
- 120 • Station D at Jons in a monitoring station (Masson *et al.*, 2018; Thollet *et al.*,
121 2018) located downstream a NPP (Figure 1) with samples collected for the main
122 period of flushing operations, from the 06/04/2012 to the 07/03/2012.

123

124 Two different sampling methods were used to collect water samples (Table 1).
125 Instantaneous water samples were obtained manually using a stainless-steel bucket (approx.
126 4 L) at stations A, B and D, and by an Automatic Water Sampler (AWS) at station C. The AWS
127 used for water sampling was a Bühler 4011 (HachLange, Germany) and set to collect 10 mL
128 every 65 minutes to constitute time integrated raw water samples (6 days) stored in glass
129 bottles. Samples were all stored in dark glass bottles at 4°C until analyses.

130 For OBT measurement, SPM samples were collected using Particle Trap (PT). These
131 samplers were built following the German Environmental Specimen Bank model (Masson *et*
132 *al.*, 2018; Schulze *et al.*, 2007). Water flows through the high-quality stainless steel box and its
133 velocity is reduced by two baffles. SPM settle in two sedimentation basins in the box. Samples
134 were collected every 1 to 4 days (see Table ESM1 in electronic supplementary materials). Due
135 to logistic constrain, the PT were set on the bottom of the river at Stations A, B and D while at
136 Station C it was approx. 50 cm below the surface. Prior to analysis, SPM samples were stored
137 in the dark at 4°C, deep-frozen, freeze-dried, and homogenized through a 2 mm stainless steel
138 sieve. Dried samples were then immediately sealed under soft vacuum in aluminized bags until
139 analyses in order to avoid the exchange of water molecules with the atmosphere.

140 **Grain-size distribution**

141 For the measure of volumetric grain size distribution, a representative aliquot of each
142 wet sample was taken before processing and was analyzed on a CILAS 1190 laser particle size
143 analyzer (Masson et al., 2018) according to the ISO 13320 standard method (AFNOR, 2009).
144 Clay (<1.95 µm), Silt (<63 µm) and Sand (<2000 µm) were estimated.

145 **Particulate Organic Carbon analysis**

146 The determination of Particulate Organic Carbon (POC) in SPM samples was performed
147 using a carbon analyzer (Thermo Electron, CHN Flash 2000) by INRA laboratory (Arras, France).
148 Decarbonation was completed using hydrochloric acid according to the NF ISO 10694 standard
149 method (AFNOR, 1995). The limit of quantification (LQ) was estimated to be 0.05 g kg⁻¹ and
150 analytical uncertainty varied between ~3% and ~6% (k=2), depending on the POC
151 concentration.

152 **Tritium analyses**

153 The concentrations of the two main forms of tritium (HTO and OBT) were investigated.
154 The HTO analyses were performed on 20ml of filtered water (< 0.2 µm) either directly filtered
155 in the field for punctual samples or in the laboratory for time-integrated ones sampled by
156 AWS. Filtered waters were analyzed by classical scintillation counting for HTO content (Tricarb
157 3180 TR/SL), by taking an aliquot of 10 mL and adding 10 mL of scintillation liquid (UltimaGold
158 LLT).

159 OBT analyses were conducted using the Helium-3 ingrowth method after placing the
160 sample in a vacuum (10⁻⁶ mbar) and storing it for 3 to 4 months (Cossonnet *et al.*, 2009). The
161 Helium-3 is a decay product of tritium—and its concentration is measured by mass
162 spectrometry (Jean-Baptiste *et al.*, 2010). OBT concentrations were converted in Becquerel

163 per liter of combustion water ($\text{Bq L}^{-1}_{\text{cw}}$) by using the percentage of hydrogen measured in each
164 sample by a CHNS elemental analyzer (Elementar, vario MICROcube).

165 For both methods, detection limit was around 0.6 Bq L^{-1} with a detection threshold of
166 1.2 Bq L^{-1} (Currie, 1968; Eyrolle et al., 2018). All the measured concentrations were corrected
167 for radioactive decay to the sampling date.

168 **Results**

169 ***Variation of HTO contents***

170 The concentrations of HTO measured during this study were similar at Stations A and
171 B (Figure 2; Table ESM1) with respectively a mean HTO concentration of 1.1 Bq L^{-1} (with
172 standard deviation $\text{sd} = 0.3 \text{ Bq L}^{-1}$) and 1.2 Bq L^{-1} ($\text{sd} = 0.2 \text{ Bq L}^{-1}$). At station C, the only value
173 observed above the detection limit ($0.8 \pm 0.7 \text{ Bq L}^{-1}$) was not significantly different to the two
174 upstream stations. The HTO concentration at this station remained very low as several values
175 were lower than the detection limit. For these three stations, no significant variation of HTO
176 contents were observed during the flushing operations. At station D, two significant increases
177 were observed during the flushing operation the 06/05/2012 and the 06/16/2012 with
178 respectively $13.1 \pm 1.0 \text{ Bq L}^{-1}$ and $11.8 \pm 1.0 \text{ Bq L}^{-1}$. The other concentrations measured at
179 station D were similar to the values observed at the other stations with 1.1 Bq L^{-1} ($\text{sd} = 0.3 \text{ Bq}$
180 L^{-1}).

181 ***OBT***

182 During the period studied, OBT contents ranged from $180 \pm 40 \text{ Bq L}^{-1}_{\text{cw}}$ to $11,700 \pm$
183 $2,300 \text{ Bq L}^{-1}_{\text{cw}}$ (Figure 3 - Table ESM2) with a mean value of $1,640 \text{ Bq L}^{-1}_{\text{cw}}$ ($\text{sd} = 2,600 \text{ Bq L}^{-1}_{\text{cw}}$).
184 The mean OBT concentration at stations A and B were similar with respectively $850 \text{ Bq L}^{-1}_{\text{cw}}$
185 ($\text{sd} = 320 \text{ Bq L}^{-1}_{\text{cw}}$) and $890 \text{ Bq L}^{-1}_{\text{cw}}$ ($\text{sd} = 330 \text{ Bq L}^{-1}_{\text{cw}}$) while significant variations of OBT were

186 observed at the two other stations. At station C, the first value measured was significantly
187 higher than the other with $11,700 \pm 2,300 \text{ Bq L}^{-1}_{\text{cw}}$ observed the 06/09/12, then decreased to
188 reach similar level than the upstream stations A and B. At station D, a high concentration of
189 OBT was observed 48h afterwards that of station C ($6,670 \pm 340 \text{ Bq L}^{-1}_{\text{cw}}$ the 06/11/12). The
190 other values measured during dam flushing operations (mean = $680 \text{ sd } 400 \text{ Bq L}^{-1}_{\text{cw}}$) were
191 similar to those of station A and B. Silt particles always constituted the major part of the SPM
192 whatever the station with proportions ranging from 35.8 to 94.2% (Table ESM2). Sand
193 particles were mostly observed at stations A and B, close to the studied dams. Those particles
194 were rapidly stored in the Upper Rhône River as the proportion of sand were very low at
195 Stations C and D. The POC concentration observed at Station A and C remained constant while
196 some variations were observed at the two other stations (Table ESM2). Maximal
197 concentration was observed at Station D with $36.0 \pm 1.8 \text{ mg kg}^{-1}$.

198

199 **Discussion**

200 Most of the HTO concentrations measured at the four stations were similar to those
201 observed from 2003 to 2015 by the Swiss Federal office of public health (OFSP, 2015) in water
202 samples collected near station A (1.03 Bq L^{-1} with $\text{sd} = 0.41 \text{ Bq L}^{-1}$) and not affected by NPP
203 releases. Furthermore, the concentrations remained in the range of values observed for the
204 natural background in waters of French pristine rivers (Ducros *et al.*, 2018). Although, the
205 increases observed at station D was strictly related to the releases of HTO by the NPP and not
206 related to the dam flushing operations. As mentioned in the introduction, NPPs are allowed
207 to release radionuclides into river systems conforming to liquid flow rate thresholds. The
208 sampling performed at station D for this study was conducted during short radionuclide

209 release operations with 12 events from 3 to 12 hours (Electricité De France, personal
210 communication). The absence of higher HTO concentrations in the other samples of station D
211 was due to the time lapse between the NPP's release operations and the samplings,
212 performed 10 hours after the end of the operations. The transit time between the NPP and
213 the sampling station has been validated by modeling using the hydrological model CASTEAUR
214 (Beaugelin-Seiller et al., 2002). The increase was only observed at station D as the NPP is
215 downstream the other stations (Figure 1). Overall, the values measured during this NPP's
216 operations were similar to the mean concentrations recorded during radionuclide release
217 operations at this NPP from 2011 to 2014 (12 Bq L^{-1}) (IRSN, 2015). Therefore, despite the input
218 of high quantity of water from the flushing operations and characterized by a lower level of
219 HTO than from the NPP releases, no significant effect of dilution was observed. In the Upper
220 Rhône River, dam flushing operations do not affect HTO concentrations in the water column
221 and, in the absence of NPP releases, these concentrations remain similar from upstream to
222 downstream. Thus, in contrast with certain trace metals remobilized during such events such
223 as arsenic (Bretier *et al.*, 2019; Monnin *et al.*, 2018), no significant transfer of tritium from
224 sediment remobilization to the dissolved phase was observed. Moreover, these results did not
225 show any significant contribution of tritium either from HTO potentially stored in the pore
226 waters of remobilized sediments, or from OBT associated to fine particles ($<0.45\mu\text{m}$) towards
227 waters.

228 Despite the high concentrations of OBT observed at stations C and D, all the
229 concentrations remained in the same range as those reported by Eyrolle *et al.*, (2018) (from
230 4 to $30,200 \text{ Bq L}^{-1}_{\text{cw}}$) and confirmed the high variability due to the presence of tritiated
231 technogenic particles in the Rhône River. In fact, OBT concentrations are generally expected
232 to be rather close to HTO concentrations in most other cases (Eyrolle-Boyer *et al.*, 2015). For

233 example, in the sediments of the Rhône's tributaries not affected by luminous paints,
234 background values were lower than $10 \text{ Bq L}^{-1}_{\text{cw}}$ (Eyrolle *et al.*, 2018). Since neither significant
235 temporal nor spatial trends were observed in OBT concentrations, we hypothesize that these
236 results can be explained by the heterogeneous distribution of technogenic tritium in
237 suspended or deposited sedimentary particles leading to large variations of tritium
238 concentrations within the samples even though collected in areas close to each other. Also,
239 this result is confirmed by the absence of relation between OBT and POC concentrations. In
240 the Rhône River, OBT is not only bound to organic matter of natural origin, but would very
241 likely be trapped inside fine polystyrene particles from technogenic tritium (Eyrolle *et al.*,
242 2018). Regarding grain size, any specific relation was observed but the highest level of OBT at
243 Jons ($6670 \text{ Bq L}^{-1}_{\text{cw}}$) was observed in a sample characterized by a high level of sand (42.2%)
244 (Table ESM2). This result highlights that these tritiated particles most probably come from the
245 sediment stored in the dams and flushed during the operations. It also confirms their
246 heterogeneously distribution as such increase of OBT concentration was not observed in
247 Stations A and B. Furthermore, with the evolution of technologies and the introduction of
248 guidelines for the protection of the environment (Morereau *et al.*, in prep.), OBT should no
249 longer be emitted at this level in the environment and its occurrence should be mainly related
250 to its long-time presence in the sediments of the Rhône River (Eyrolle *et al.*, 2018). The highest
251 concentrations observed below the dams might be related to the resuspension of old
252 contaminated sediments stored in the studied dams as observed for PAHs by Lepage *et al.*
253 (2020). The OBT is expected to be transported downstream and its concentration should
254 decrease from upstream to downstream in the following decades.
255

256 **Conclusion**

257 The consequences of dam flushing operations on tritium concentrations were
258 investigated in the Rhône River downstream Lake Geneva by characterizing HTO and OBT
259 concentrations respectively in filtered water and suspended particulate matter (SPM) samples
260 collected downstream three dams flushed in June 2012. Our results demonstrate that dam
261 flushing operations do not significantly affect tritium concentrations in the water column as
262 they remained similar to those previously recorded during normal flow conditions. Analyses
263 of OBT in the SPM demonstrate transient increases in concentration during dam flushing
264 operations. Those are most probably explained by the resuspension of fine tritiated particles
265 from watchmaking activities. As the increases were transient and not observed at all the
266 stations, no significant temporal nor spatial trend following dam flushing operations can be
267 drawn clearly. However, OBT is heterogeneously distributed in sediments of the Rhône River
268 and large amounts of this radionuclide are still stored in the Upper Rhône sediments. Extreme
269 events such as dam flushing operations can redistribute these storages to the downstream
270 part of the River. The radiotoxicity of free tritium (HTO) or organically bound tritium to
271 naturally occurring organic compounds (OBT) are low comparing to most other natural or
272 artificial radionuclides. Nevertheless, the specific radiotoxicity of organically bound tritium to
273 synthetic organic particles are unknown to our knowledge as well as their transfer rates
274 toward living organisms.

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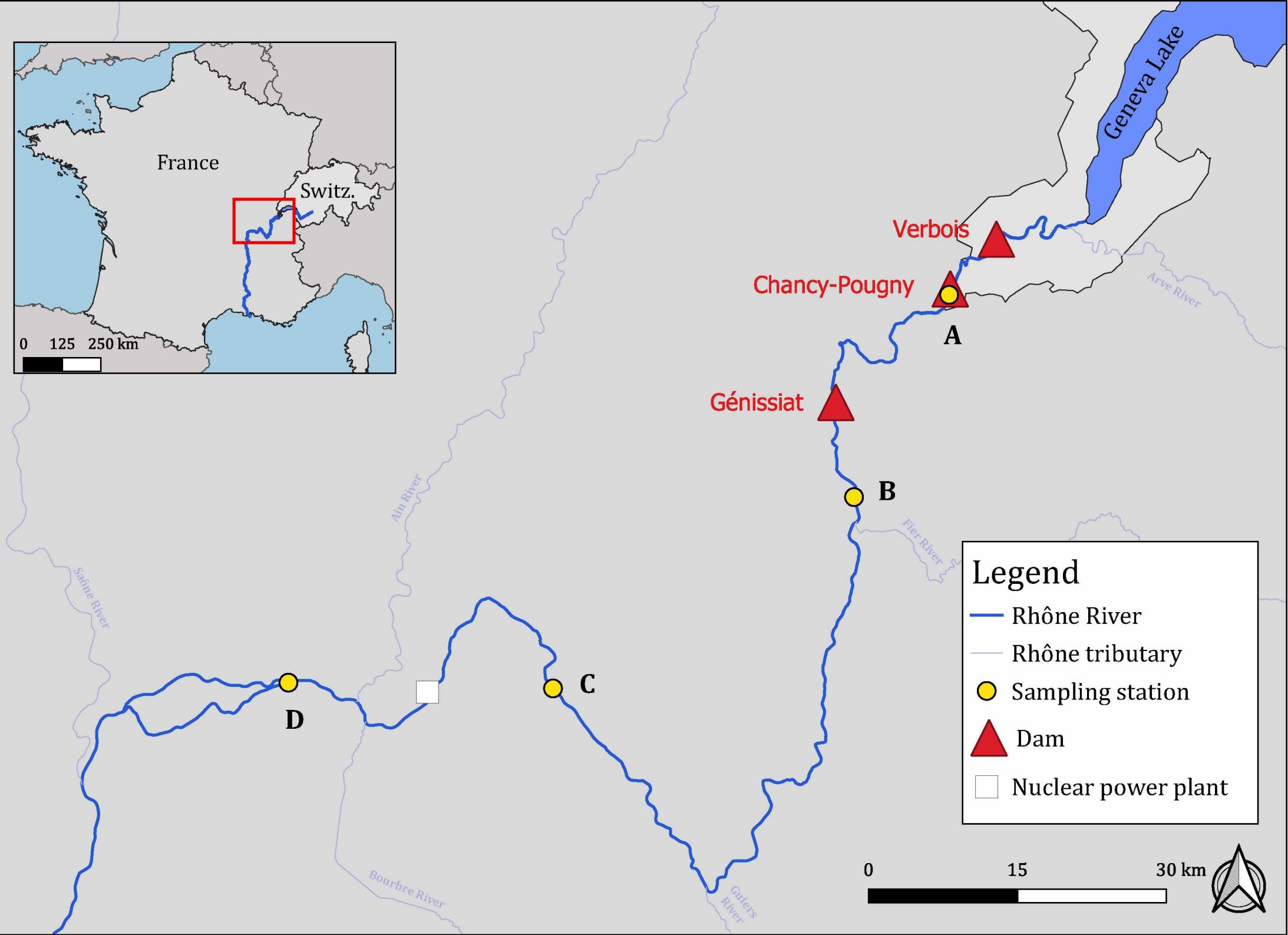
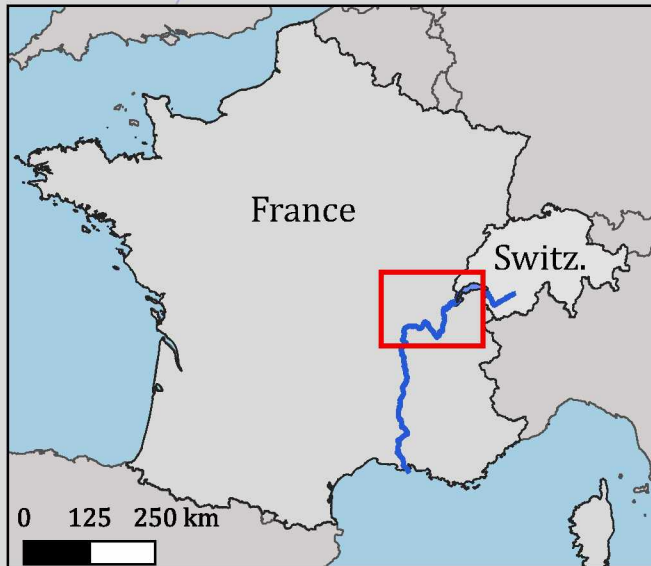
393 Ueda, S., Hasegawa, H., Kakiuchi, H., Ochiai, S., Akata, N., Hisamatsu, S., 2015. Nuclear
394 accident-derived ³H in river water of Fukushima Prefecture during 2011-2014. *J. Environ.*
395 *Radioact.* 146, 102–109. <https://doi.org/10.1016/j.jenvrad.2015.04.014>

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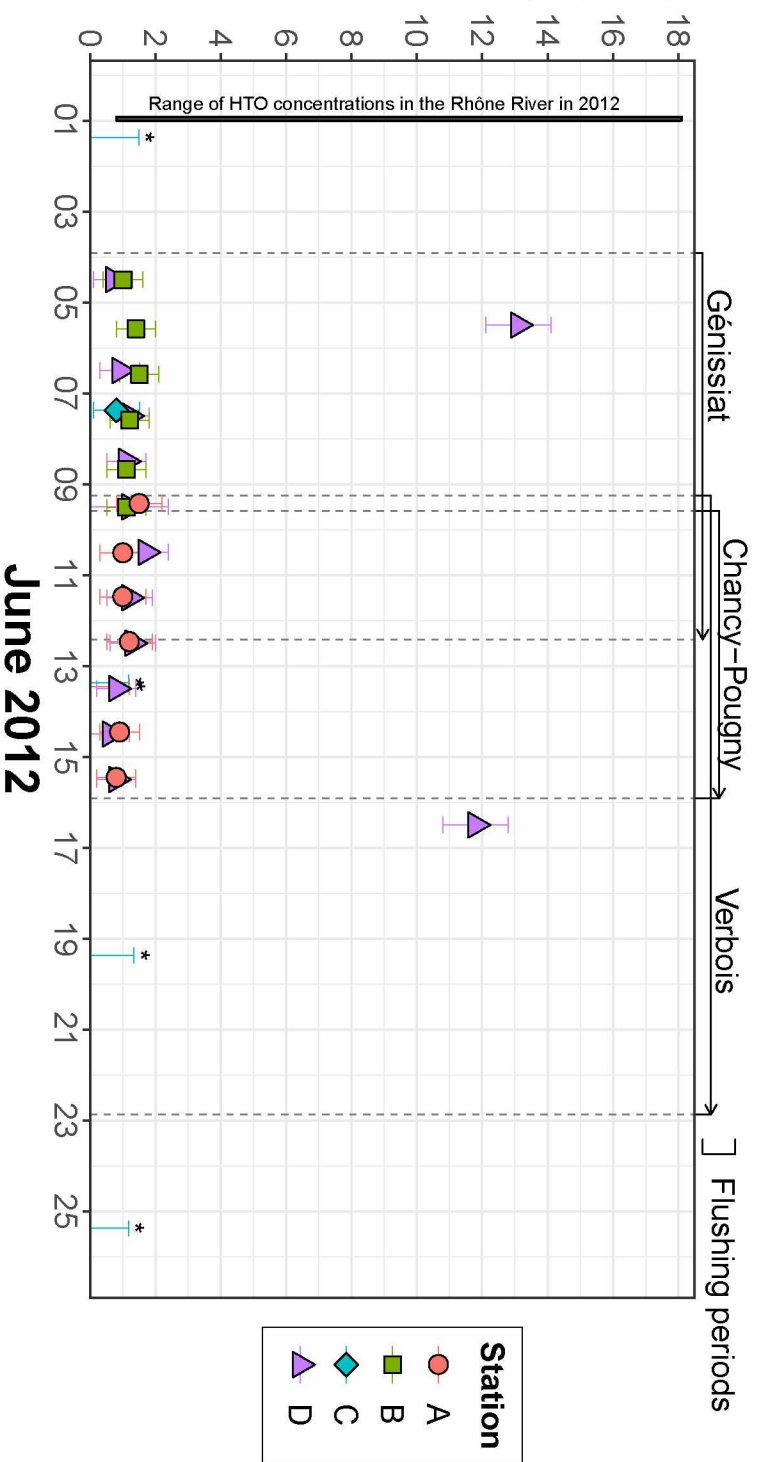
Figure 1 - Location of the studied dams, the nuclear power plant and the sampling stations in the Rhône River.

Figure 2 - Concentration of tritium in filtered waters (HTO in Bq L^{-1}) measured at the four stations during the flushing operations of Génissiat, Chancy-Pougny and Verbois dams and range of the concentrations observed on the water of the Rhône River in 2012 (IRSN, 2013). * samples with HTO concentration below the detection limit.

Figure 3 - Concentration of organically bound tritium (OBT in $\text{Bq L}^{-1}_{\text{cw}}$) measured in SPM collected at the four stations during the flushing operations of Génissiat, Chancy-Pougny and Verbois dams and range of the concentrations observed on sediment and SPM of the Rhône River in 2012 (Eyrolle *et al.*, (2018)).



HTO concentration (Bq.L⁻¹)



OBT concentration ($\text{Bq}\cdot\text{L}^{-1}_{\text{CW}}$)

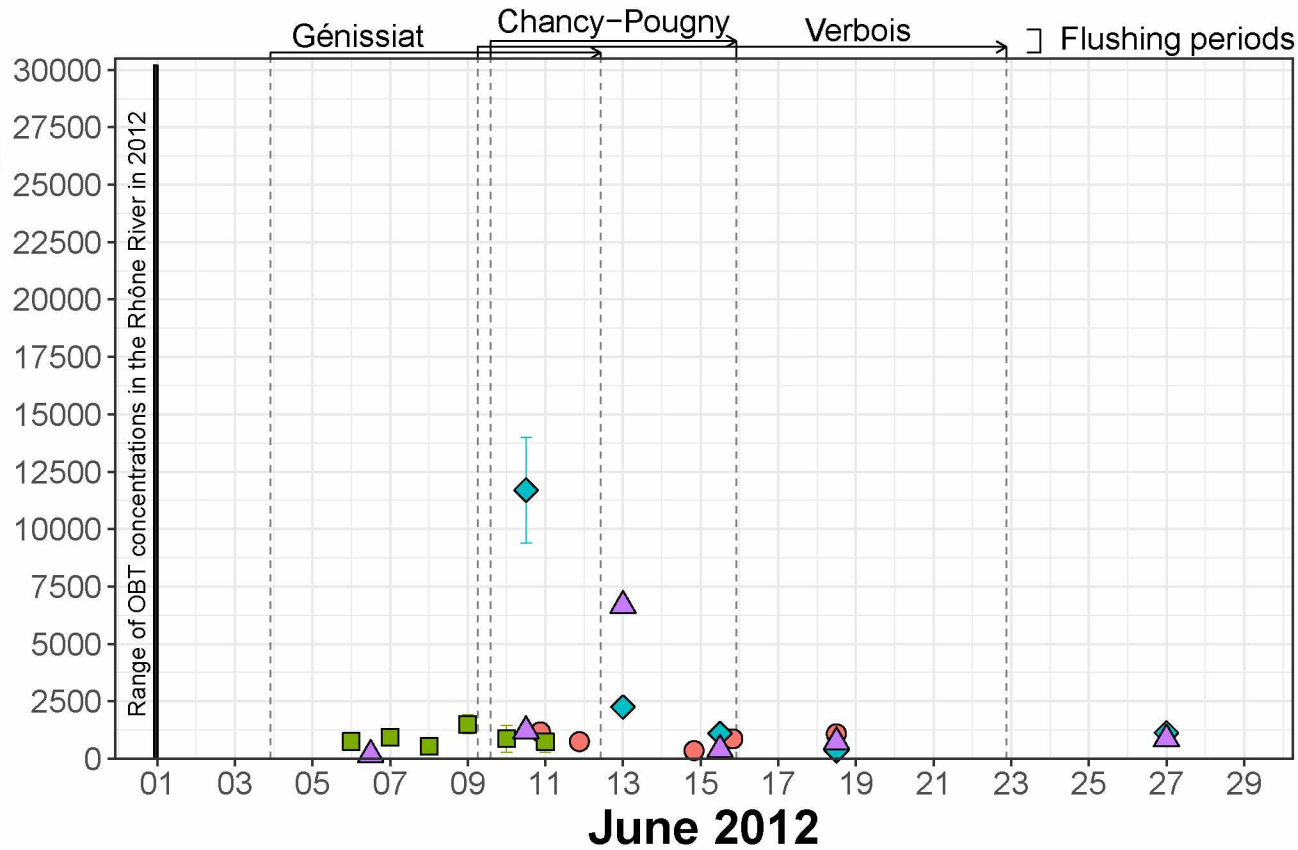


Table 1 - Number (n) of samples collected during the studied flushing operations for tritiated water (HTO) and organically bound tritium (OBT) and associated sampling method used. AWS = automatic water sampler, PT = particle trap.

Location	Latitude (WGS 1984)	Longitude (WGS 1984)	HTO	OBT
A	+46.1442	+5.9644	Manual (n=7)	PT (n=5)
B	+45.9642	+5.8310	Manual (n=6)	PT (n=6)
C	+45.80	+5.4322	AWS (n=6)	PT (n=5)
D	+5.0896	+45.8121	Manual (n=13)	PT (n=6)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Electronic supplementary materials

Figure ESM1 - Discharge and suspended particulate matters (SPM) concentration measured at the four stations during the flushing operations (Thollet et al., 2018).

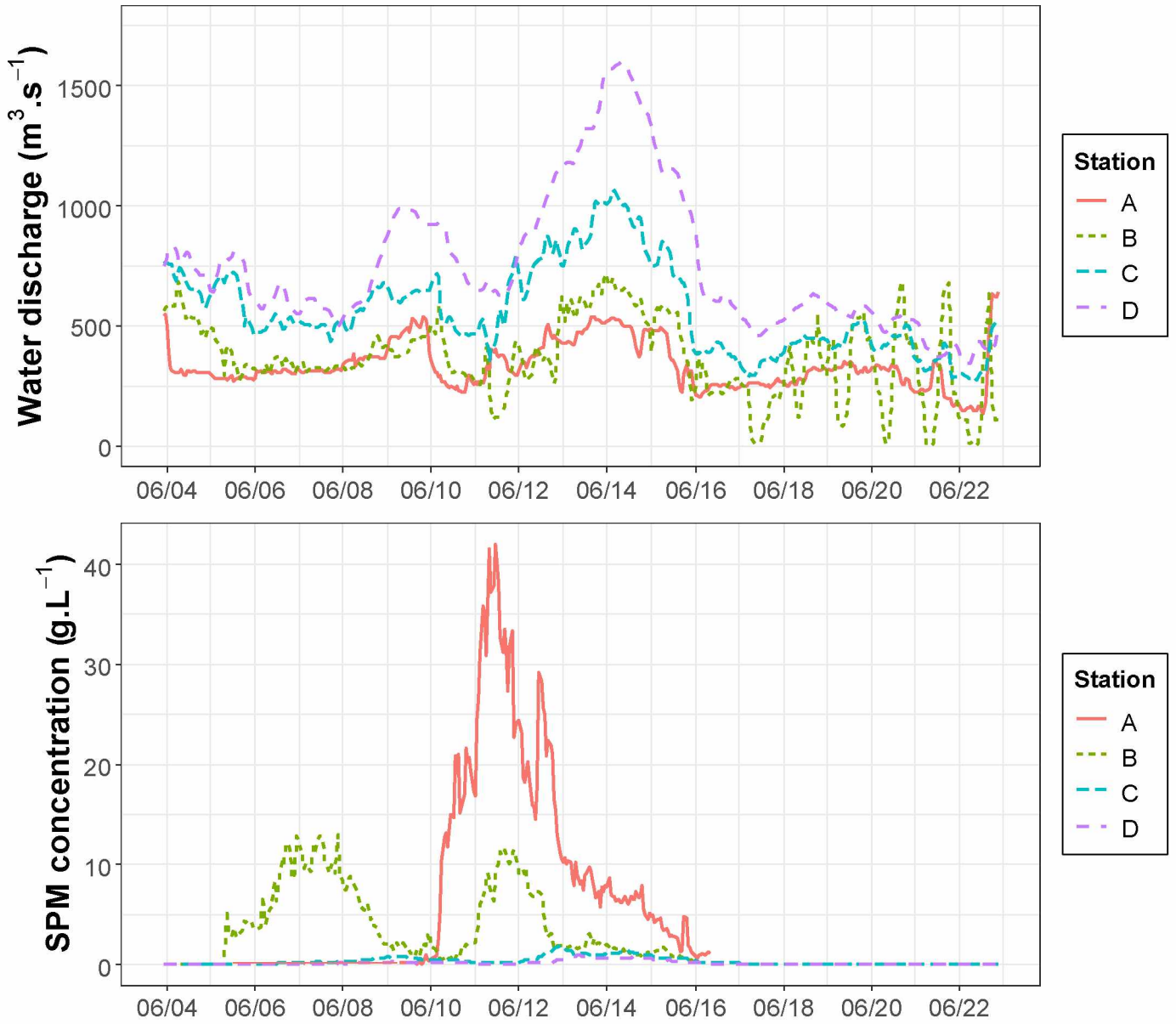


Table ESM1 - Tritiated water concentration in the water samples collected for this study. "<" indicate concentration under the detection limit.

Station	Sampling date	Concentration (Bq L ⁻¹)
A	06/09/2012 10:20	1.5 ± 0.7
A	06/10/2012 12:20	1.0 ± 0.7
A	06/11/2012 11:30	1.0 ± 0.7
A	06/12/2012 11:15	1.2 ± 0.7
A	06/13/2012 10:55	< 1.2
A	06/14/2012 11:00	0.9 ± 0.6
A	06/15/2012 11:00	0.8 ± 0.6
B	06/04/2012 12:05	1.0 ± 0.6
B	06/05/2012 14:00	1.4 ± 0.6
B	06/06/2012 14:00	1.5 ± 0.6
B	06/07/2012 14:15	1.2 ± 0.6
B	06/08/2012 16:15	1.1 ± 0.6
B	06/09/2012 12:15	1.1 ± 0.6
C	05/25/2012 09:00	< 1.4
C	06/01/2012 09:00	< 1.5
C	06/07/2012 09:00	0.8 ± 0.7
C	06/13/2012 09:00	< 1.2
C	06/19/2012 09:00	< 1.3
C	06/25/2012 09:00	< 1.2
D	06/04/2012 12:00	0.7 ± 0.6
D	06/05/2012 12:00	13.1 ± 1.0
D	06/06/2012 12:00	0.9 ± 0.6
D	06/07/2012 12:00	1.2 ± 0.6
D	06/08/2012 12:00	1.1 ± 0.6
D	06/09/2012 12:00	1.2 ± 1.2
D	06/10/2012 12:00	1.7 ± 0.7
D	06/11/2012 12:00	1.2 ± 0.7
D	06/12/2012 12:00	1.3 ± 0.7
D	06/13/2012 12:00	0.8 ± 0.6
D	06/14/2012 12:00	0.6 ± 0.6
D	06/15/2012 12:00	0.8 ± 0.6
D	06/16/2012 12:00	11.8 ± 1.0

Table ESM2 - Organically bound tritium concentrations, clay/silt/sand content and POC concentrations in the suspended particulate matters (SPM) samples collected by particles trap for this study. n.a.: not analyzed; ± analytical uncertainty.

Station	Sampling start	Sampling end	Concentration (Bq kg ⁻¹)	Concentration (Bq L ⁻¹ _{cw})	Clay (%)	Silt (%)	Sand (%)	POC (mg.kg ⁻¹)
A	06/10/2012 11:00	06/11/2012 07:00	16 ± 8	1180 ± 400	3.4	72.8	23.8	9.2 ± 0.5
A	06/11/2012 11:15	06/12/2012 07:00	7 ± 1	750 ± 40	2.5	50.4	47.1	9.8 ± 0.5
A	06/14/2012 08:00	06/15/2012 08:00	5 ± 1	360 ± 20	2.0	41.1	56.8	9.6 ± 0.5
A	06/15/2012 08:00	06/16/2012 08:00	8 ± 1	870 ± 40	n.a	n.a	n.a	n.a
A	06/16/2012 12:00	06/20/2012 11:59	15 ± 1	1090 ± 60	n.a	n.a	n.a	n.a
B	06/05/2012 12:00	06/06/2012 11:59	17 ± 1	750 ± 160	2.2	59.9	37.9	22.8 ± 0.9
B	06/06/2012 12:00	06/07/2012 11:59	12 ± 1	940 ± 330	2.0	53.1	44.9	18.8 ± 0.8
B	06/07/2012 12:00	06/08/2012 11:59	6 ± 1	540 ± 220	2.8	68.0	29.3	15.3 ± 0.7
B	06/08/2012 12:00	06/09/2012 11:59	24 ± 2	1500 ± 420	1.5	35.8	62.7	6.8 ± 0.4
B	06/09/2012 12:00	06/10/2012 11:59	6 ± 1	870 ± 580	1.6	42.7	55.7	12.1 ± 0.6
B	06/10/2012 12:00	06/11/2012 11:59	5 ± 1	730 ± 460	1.9	47.3	50.8	11.9 ± 0.6
C	06/09/2012 12:00	06/11/2012 11:59	279 ± 14	11700 ± 2300	7.1	92.7	0.2	15.3 ± 0.7
C	06/11/2012 12:00	06/14/2012 11:59	51 ± 3	2250 ± 120	4.4	94.2	1.3	11.8 ± 0.5
C	06/14/2012 12:00	06/16/2012 11:59	23 ± 1	1100 ± 60	5.2	93.2	1.7	11.3 ± 0.5
C	06/16/2012 12:00	06/20/2012 11:59	8 ± 1	340 ± 20	4.7	87.9	7.4	n.a
C	06/20/2012 12:00	07/03/2012 11:59	21 ± 2	1130 ± 60	n.a	n.a	n.a	n.a

D	06/05/2012 12:00	06/07/2012 11:59	4 ± 1	180 ± 40	4.8	83.9	11.4	15.8 ± 0.7
D	06/09/2012 12:00	06/11/2012 11:59	32 ± 2	1210 ± 210	4.7	93.2	2.1	17.1 ± 0.8
D	06/11/2012 12:00	06/14/2012 11:59	174 ± 9	6670 ± 340	3.2	54.6	42.2	8.1 ± 0.5
D	06/14/2012 12:00	06/16/2012 11:59	5 ± 1	400 ± 20	3.6	93.0	3.5	12.1 ± 0.6
D	06/16/2012 12:00	06/20/2012 11:59	10 ± 1	730 ± 40	5.6	92.5	1.9	n.a
D	06/20/2012 12:00	07/03/2012 11:59	20 ± 1	860 ± 40	4.9	93.0	2.0	36.0 ± 1.8