



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

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Manuscript Details

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Title	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.

- 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.	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).	
- Line 40: These forms?	OBT – corrected in the text	Part of OBT do not easily exchange with the surrounding water molecules and persist in the environment until organic compounds are biodegraded.
- Line 56: 0.6×10^9 . Is it suspended or precipitated in the bottom?	It is particles that were suspended but got stored by sedimentation.	
- Line 61-62: What is a difference between contaminated sediments and SPM?	See first comment for SPM and sediment definition. Sediments stored in the dam might be either contaminated or depleted so as the SPM.	
- Line 71: soil washout by rain?	Soil erosion. Corrected	[...] or finally progressively transferred due to soil erosion (Schürch et al., 2003).
- 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?	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.	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

- Line 118: For SPM sampling, is any water depth related to?	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.	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.
- Line 132: detection limit of HTO and OBT?	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.	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).
- Line 182: How much tritium released annually from the NPP?	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).	
- Line 224: What is the relationship between sediment and SPM?	Corrected, OBT is heterogeneously distributed in the sediments.	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.
- 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?	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.	
Reviewer 2		

<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>	

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".	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.	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.
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.	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).	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).
1. Change from unit of "Bq.L-1" to "Bq L-1" in manuscript. No period required.	Corrected for the whole manuscript.	
2. Line 45: Change from "coastal rivers" to "mountainous rivers".	Corrected	[...] 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) [...]
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.	Ranges of HTO and OBT concentrations were added to the figures 2 and 3.	
Reviewer 3		
- The graphical abstract looks inconsistent with the findings. Heterogeneous distribution of OBT is the key finding in my understanding. If so, the	Graphical abstract was improved	

heterogeneity should be illustrated in the graphical abstract.		
<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>

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

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

Introduction

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

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

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

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

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

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

Materials and Method

Dam location and description of the flushing operations

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

stored sediments. The large-volume Génissiat reservoir located downstream of the two other dams was flushed first (4-12 June 2012) in order to compensate for the deposition of the SPM released from the Chancy-Pougny (9-16 June 2012) and Verbois dams (9-22 June 2012). Discharge varied from 129 m³ s⁻¹ to 631 m³ 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 m³ 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).

Sampling and samples

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:

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

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

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

For OBT measurement, SPM samples were collected using Particle Trap (PT). These samplers were built following the German Environmental Specimen Bank model (Masson *et al.*, 2018; Schulze *et al.*, 2007). Water flows through the high-quality stainless steel box and its velocity is reduced by two baffles. SPM settle in two sedimentation basins in the box. Samples were collected every 1 to 4 days (see Table [ESMS1](#) in [electronic](#) supplementary materials). 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. Prior to analysis, SPM samples were stored in the dark at 4°C, deep-frozen, freeze-dried, and homogenized through a 2 mm stainless steel sieve. Dried samples were then immediately sealed under soft vacuum in

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

Grain-size distribution

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

Particulate Organic Carbon analysis

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

Tritium analyses

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

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

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

Results

Variation of HTO contents

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

OBT

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

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

Discussion

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

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

Despite the high concentrations of OBT observed at stations C and D, all the concentrations remained in the same range as those reported by Eyrolle *et al.*, (2018) (from 4 to 30,200 ~~Bq~~Bq L⁻¹_{cw}) and confirmed the high variability due to the presence of tritiated technogenic particles in the Rhône River. In fact, OBT concentrations are generally expected to be rather close to HTO concentrations in most other cases (Eyrolle-Boyer *et al.*, 2015). For example, in the sediments of the Rhône's tributaries not affected by luminous paints, background values were lower than 10 ~~Bq~~Bq L⁻¹_{cw} (Eyrolle *et al.*, 2018). Since neither significant temporal nor spatial trends were observed in OBT concentrations, we hypothesize that these results can be explained by the heterogeneous distribution of technogenic tritium in suspended or deposited sedimentary particles leading to large variations of tritium concentrations within the samples even though collected in areas close to each other. Also, this result is confirmed by the absence of relation between OBT and POC concentrations. In the Rhône River, OBT is not only bound to organic matter of natural origin, but would very likely be trapped inside fine polystyrene particles from technogenic tritium (Eyrolle *et al.*, 2018). Regarding grain size, any specific relation was observed but the highest level of OBT at Jons (6670 Bq L⁻¹_{cw}) was observed in a sample characterized by a high level of sand (42.2%) (Table ESM2). 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. Furthermore, with the evolution of technologies and the introduction of guidelines for the protection of the environment (Morereau *et al.*, in prep.), OBT should no longer be emitted at this level in the environment and its occurrence should be mainly related to its long-time presence in the sediments of the Rhône River (Eyrolle *et al.*, 2018). The highest concentrations observed below the dams might be related to the resuspension of old

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

Conclusion

The consequences of dam flushing operations on tritium concentrations were investigated in the Rhône River downstream Lake Geneva by characterizing the HTO and OBT concentrations respectively in filtered water and suspended particulate matter (SPM) samples collected downstream three dams flushed in June 2012. Our results demonstrate that dam flushing operations do not significantly affect tritium concentrations in the water column as they remained similar to those previously recorded during normal flow conditions. Analyses of OBT in the SPM demonstrated transient increases in concentration during the dam flushing operations. ~~This increase was~~ Those are most probably ~~linked explained by~~ the resuspension of fine tritiated particles from watchmaking activities. As the increases were transient and not observed at all the stations, ~~no significant temporal nor spatial trend following dam flushing operations can be drawn clearly trend could be linked to the dam flushing operations.~~ However, OBT is heterogeneously distributed in sediments of the Rhône River and SPM and a large amounts of ~~OBT this radionuclide are still might be currently~~ stored in the Upper Rhône ~~River sediments. Extreme events and could be redistributed following extreme events~~ such as dam flushing operations can redistribute these storages to the downstream part of the River. 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.

Acknowledgements

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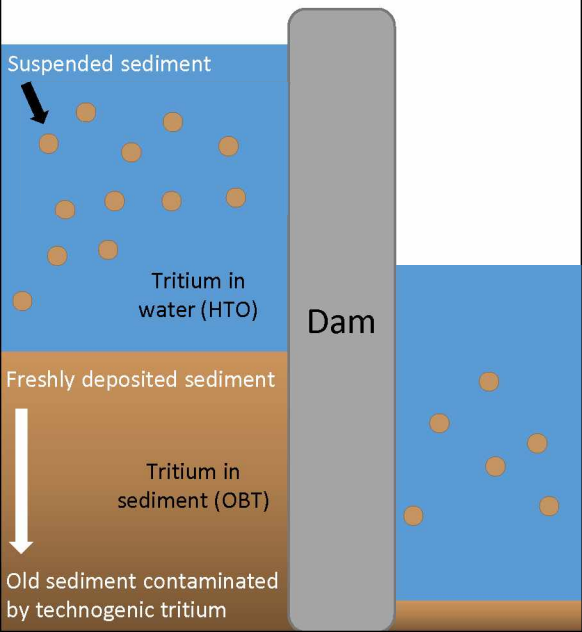
Highlights

- 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.

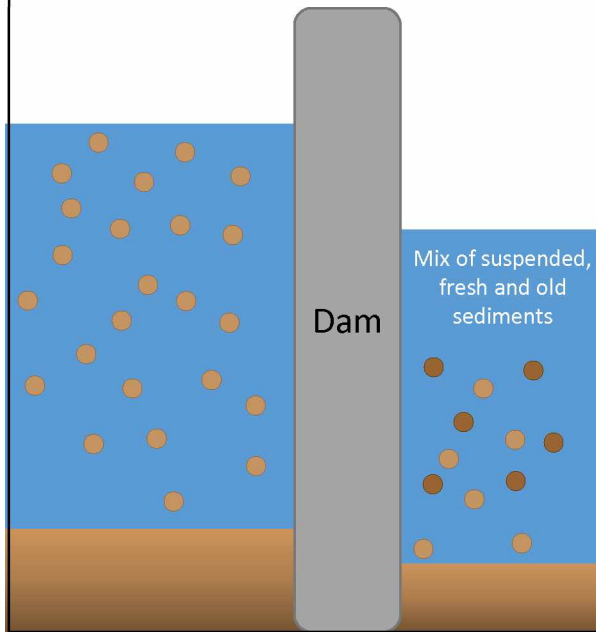
Abstract

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.

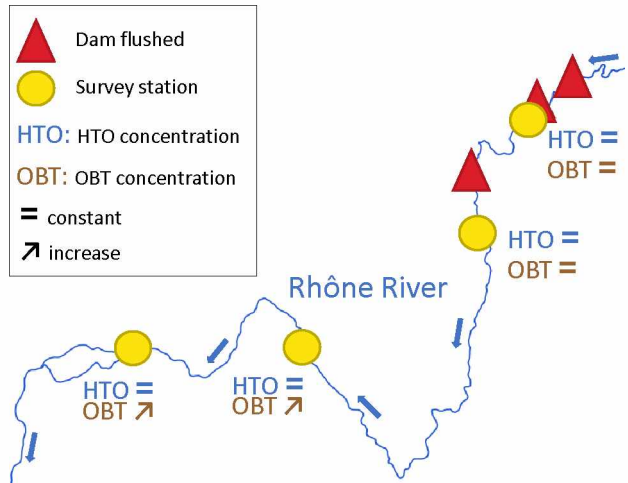
Before dam flushing operation



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

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

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

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

Introduction

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

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

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

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

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

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

Materials and Method

Dam location and description of the flushing operations

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

stored sediments. The large-volume Génissiat reservoir located downstream of the two other dams was flushed first (4-12 June 2012) in order to compensate for the deposition of the SPM released from the Chancy-Pougny (9-16 June 2012) and Verbois dams (9-22 June 2012). 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).

Sampling and samples

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:

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

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

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

For OBT measurement, SPM samples were collected using Particle Trap (PT). These samplers were built following the German Environmental Specimen Bank model (Masson *et al.*, 2018; Schulze *et al.*, 2007). Water flows through the high-quality stainless steel box and its velocity is reduced by two baffles. SPM settle in two sedimentation basins in the box. Samples were collected every 1 to 4 days (see Table ESM1 in electronic supplementary materials). 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. Prior to analysis, SPM samples were stored in the dark at 4°C, deep-frozen, freeze-dried, and homogenized through a 2 mm stainless steel sieve. Dried samples were then immediately sealed under soft vacuum in aluminized bags until analyses in order to avoid the exchange of water molecules with the atmosphere.

Grain-size distribution

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

Particulate Organic Carbon analysis

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

Tritium analyses

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

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

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

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

Results

Variation of HTO contents

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

OBT

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

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

Discussion

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

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

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

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

Conclusion

The consequences of dam flushing operations on tritium concentrations were investigated in the Rhône River downstream Lake Geneva by characterizing HTO and OBT concentrations respectively in filtered water and suspended particulate matter (SPM) samples collected downstream three dams flushed in June 2012. Our results demonstrate that dam flushing operations do not significantly affect tritium concentrations in the water column as they remained similar to those previously recorded during normal flow conditions. Analyses of OBT in the SPM demonstrate transient increases in concentration during dam flushing operations. Those are most probably explained by the resuspension of fine tritiated particles from watchmaking activities. As the increases were transient and not observed at all the stations, no significant temporal nor spatial trend following dam flushing operations can be drawn clearly. 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. Extreme events such as dam flushing operations can redistribute these storages to the downstream part of the River. 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.

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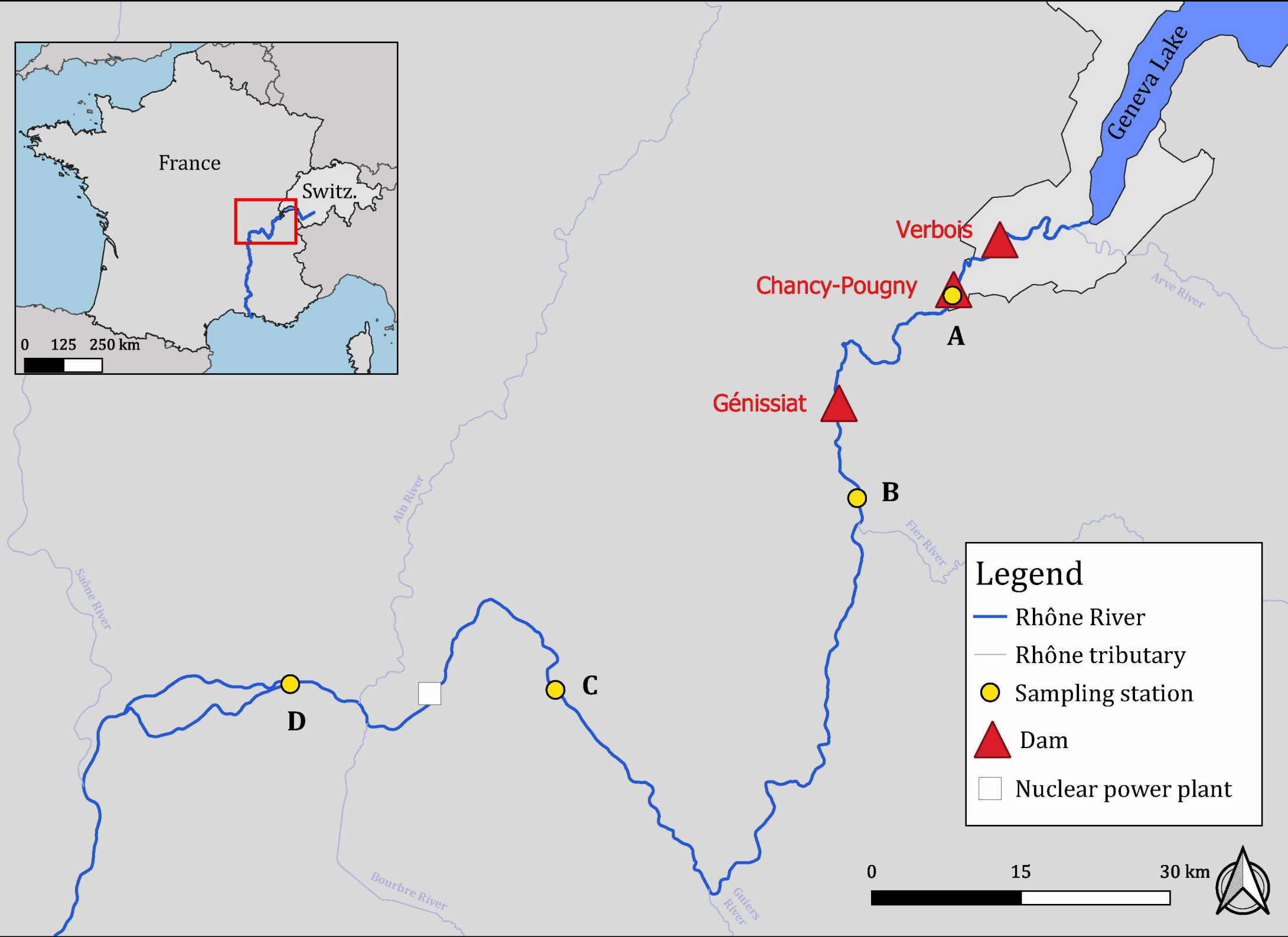
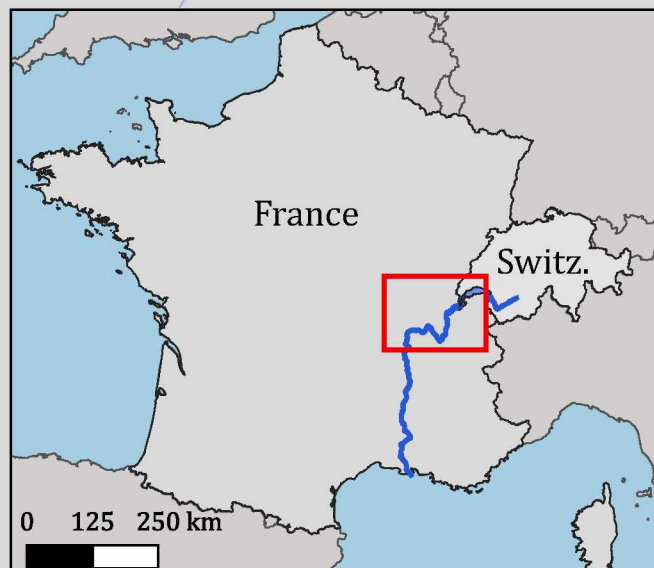
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Figure 1 – Location of the studied dams, the nuclear power plant and the sampling stations in the Rhône River.

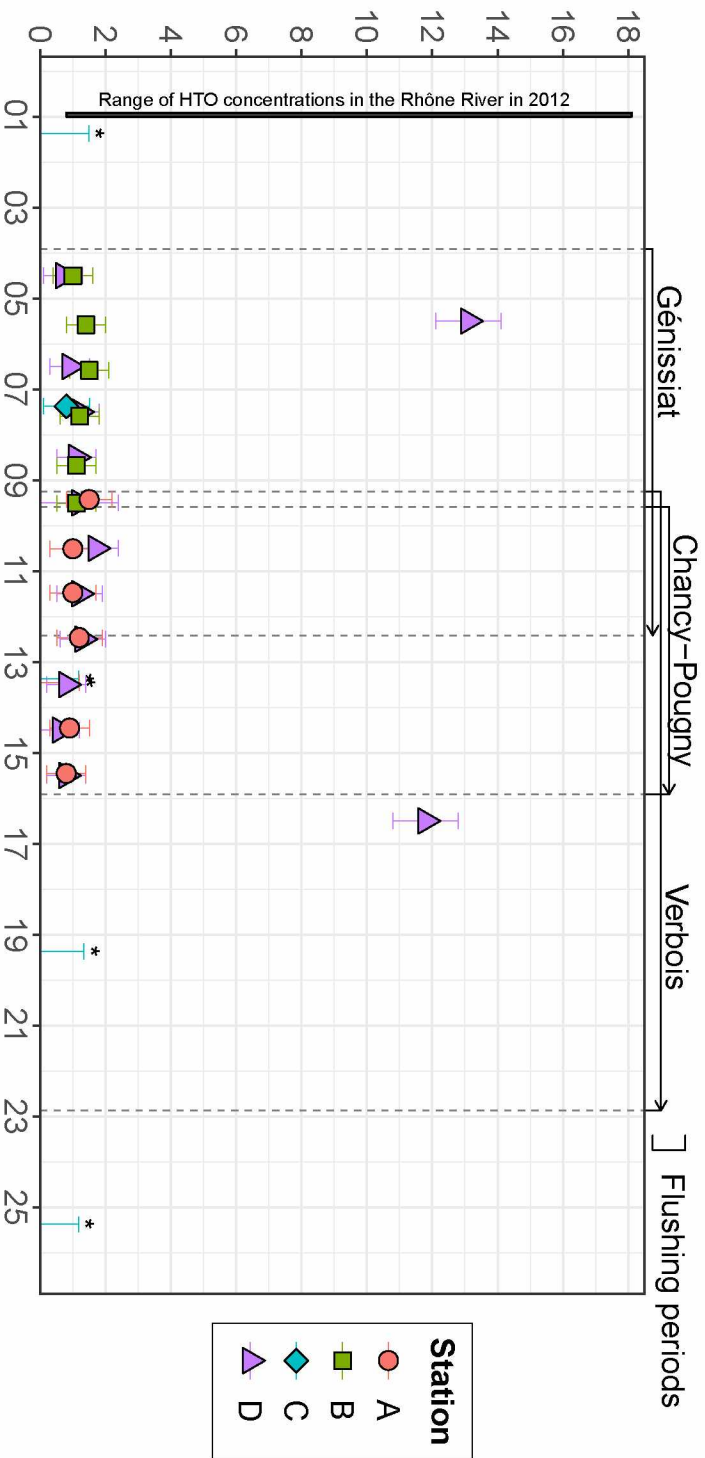
Figure 2 – Concentration of tritium in filtered waters (HTO in Bq L^{-1}) measured at the four stations during the flushing operations of Génissiat, Chancy-Pougny and Verbois dams and range of the concentrations observed on the water of the Rhône River in 2012 (IRSN, 2013). * samples with HTO concentration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

Figure 3 - Concentration of organically bound tritium (OBT in $\text{Bq L}_{\text{cw}}^{-1}$) 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)

June 2012



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

Range of OBT concentrations in the Rhône River in 2012

Génissiat

Chancy-Pougny

Verbois

Flushing periods

Station

A

B

C

D

June 2012

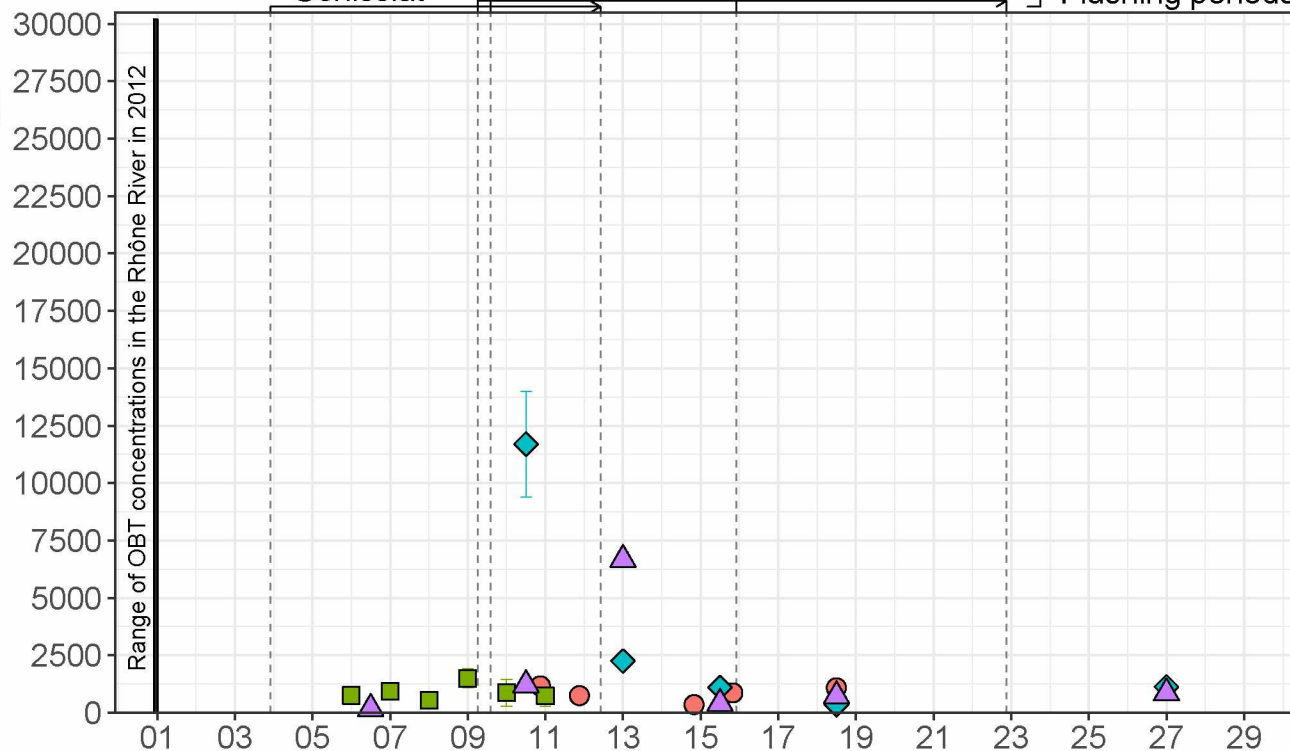


Table 1 - Number (n) of samples collected during the studied flushing operations for tritiated water (HTO) and organically bound tritium (OBT) and associated sampling method used. AWS = automatic water sampler, PT = particle trap.

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:

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

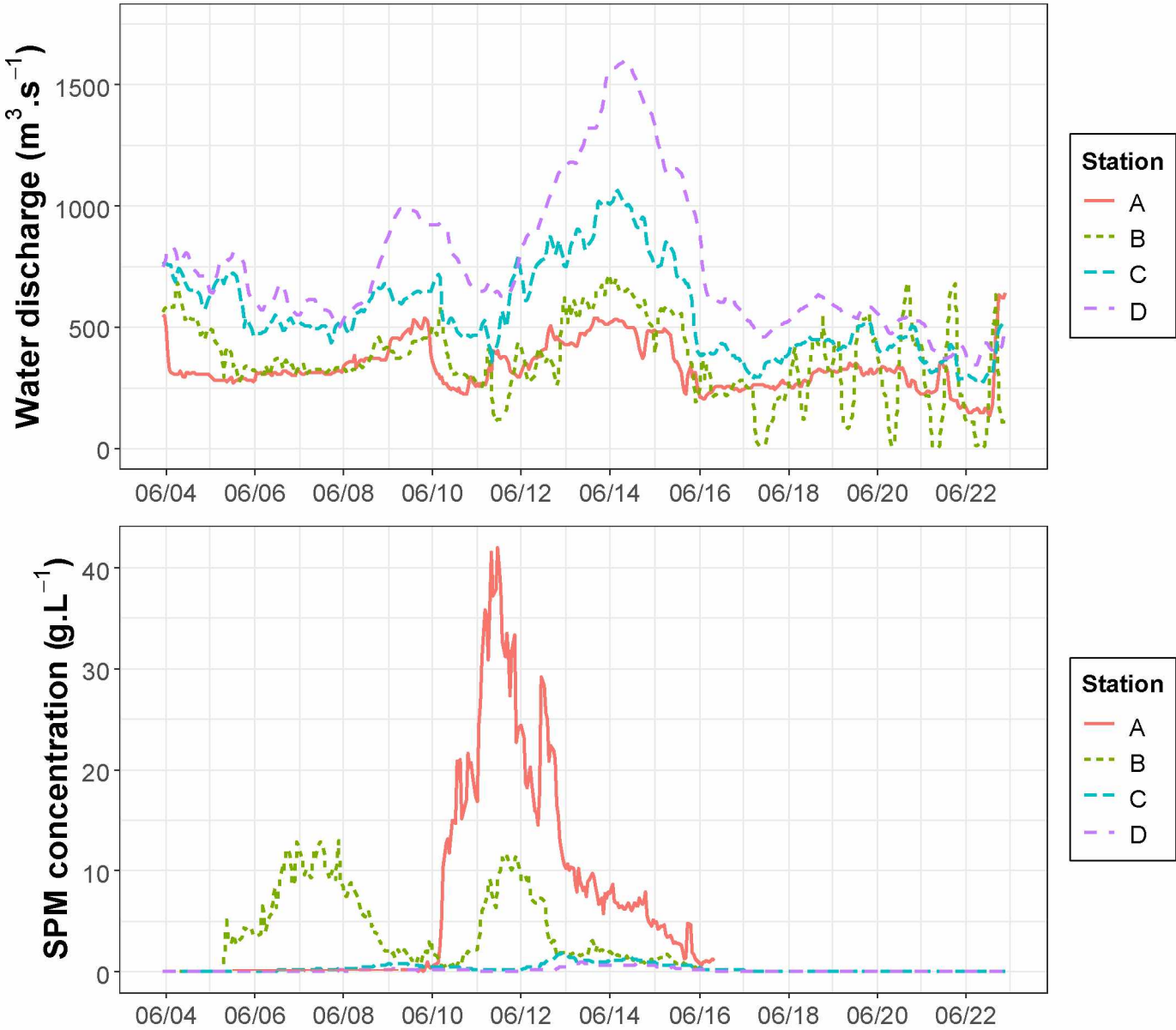


Table ESM1 - Tritiated water concentration in the water samples collected for this study. "<" indicate concentration under the detection limit.

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