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Trajectories of technogenic tritium in the Rhône River (France)

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Abstract

Tritium is a radioisotope of hydrogen with a half-life of 12.32 years and was used for its luminescent properties by the watchmaking industry from 1962 to the 2008. Tritiated luminescent salts were integrated in the paints applied on the index and dial of watches and clocks. French and Swiss watchmaking workshops used more than 28 000 TBq of tritium over this period of time and produced almost 350 million watches. Despite the end of tritiated salts use in watchmaking workshops in 1992 in France and 2008 in Switzerland, high level of organically bound tritium (OBT) are still observed in sediments of the Rhône River downstream the Lake Geneva. Contamination of the Rhône River by tritiated hot particles since 1962 up to nowadays remains poorly documented. In order to assess the long term behavior and fate of technogenic tritium in this river and its trajectories in the river system, two sediment cores were collected at the upstream (UC) and downstream (DC) part of the Rhône River in France and OBT contents were determined. For both sedimentary cores, maximum OBT contents were registered over the 1980s when tritium was intensively used by watchmaking industries. These residual OBT contents are 1 000 to 10 000 fold higher than current natural background levels in riverine sediments. The OBT contents progressively decreased since 1989 with close effective half-life in upstream and downstream area (5 ± 2 years). The OBT contents were lower in DC than in UC due to the dilution by uncontaminated sediments delivered by tributaries not affected by the watchmaking industries. Trajectories analysis indicates that the

resiliency of the Rhône River system in regards to this contamination would be reached in 14–70 years and in 14–28 years respectively for the upstream and downstream part of the river.

Keywords: Organically bound tritium; Watchmaking industry; Effective half-life; River system resiliency; Sediment core

1 Introduction

Tritium is the only radioactive isotope of hydrogen with a half-life of 12.32 years. This radionuclide is continually naturally produced in the environment, mostly through the absorption of neutrons from cosmic rays by nitrogen (^{14}N) atoms in the upper atmosphere. At the global scale the equilibrium content of tritium of natural origin is about 1 000 000 TBq (Eisenbud et al., 1979; Zerriffi, 1996), which corresponds to approximately 3.5 kg. In the environment, tritium is integrated in the hydrogen cycle and can be found in various forms such as tritiated hydrogen (HT), tritiated water molecule (HTO) or combined with naturally occurring organic compounds (organically bound tritium - OBT) (Eyrolle et al., 2018a). Tritium was artificially produced during the middle of the last century by atmospheric nuclear weapon testing, with two emission peaks in 1958 and 1962 (UNSCEAR, 1982). Those events enhanced at global scale the HTO concentrations in rainwater more than hundred times higher than natural levels (UNSCEAR, 2000). In France, OBT levels in non-nuclearized river sediments ($2.4 \pm 0.6 \text{ Bq L}^{-1}$) are currently almost similar to mean HTO contents recorded for rainwater ($1.6 \pm 0.4 \text{ Bq L}^{-1}$) and converge to HTO concentrations in river waters with almost balanced OBT/HTO ratios (Eyrolle-Boyer et al., 2015). Nevertheless, OBT/HTO ratio disequilibrium was recently observed in deep estuarine and riverine sediments highlighting tritium persistence in organic matter in aquatic systems (Croudace et al., 2012; Eyrolle et al., 2019). Given the fact that no specific technogenic tritium particle could be isolated in this study, the terminology “OBT” is considered as the total of the Non-Exchangeable OBT (NE-OBT) and the Tritiated Organic Molecules (TOM) (Kim et al., 2013).

Previous studies conducted in the Rhône River showed OBT contents in sediments and suspended matter from 10 to 10 000 times higher than HTO contents measured in rainwater over the same periods (Gontier and Siclet, 2011; Jean-Baptiste et al., 2007). It was the case for the northern tributaries of the Rhône River, mainly the Doubs and the Saône River, with OBT levels ranging from 10 to 50 000 Bq L^{-1} (Eyrolle et al., 2018a,b). These high levels of tritium have their origin in the release of technogenic tritium from the watchmaking industries in the environment (Ravi et al., 2002). In contrast, the southern tributaries (Durance, Ouvèze, Ardèche and Gardon Rivers) present OBT values close to values observed in rainwater ranging from 0.60 ± 0.04 to $2.19 \pm 0.11 \text{ Bq L}^{-1}$ (Eyrolle et al., 2018b).

The use of technogenic tritium in paint to make luminescent watch faces was prevalent in the watchmaking industry especially due to the ending of the use of radium in 1962–1963 when several national and international standards prohibited the use of radium, to protect watchmaking workers. Radium, one million times more radiotoxic than tritium, affected the health of numerous workers, mostly women, working in watchmaking workshops over almost five decades (Gunderman and Gonda, 2015). From 1962 to 2008 tritium was consequently widely used in watchmaking industries. Tritium was integrated to synthetic organic compounds such as polystyrenes and coated on zinc sulfide phosphor grains forming a luminescent powder (Ravi et al., 2002). French and Swiss watchmaking workshops used more than 28 000 TBq of tritium over this period of time and produced almost 350 million watches. However, with the evolution of luminescent technologies, societal concerns about the use of radioactive consumables and technical constraints of handling radioactive

products led to the progressive phasing out of tritium replaced by non-radioactive paints in the watchmaking industry (Murith et al., 2006). Thus, technogenic tritium was progressively stopped in France and Switzerland respectively in 1992 and 2008. Since 2004, most luminescent watches uses paints with non-radioactive luminescent pigments (Murith et al., 2006). Since 1985, campaigns were set up in Switzerland to collect watches containing tritium (OFSP, 2007). Between 1985 and 2004, 68 000 watch dials were collected, corresponding to a tritium amount of about 7 TBq. The radioactive waste was reconditioned by watchmaking companies and is stored currently in specific centers for 100 years (Murith et al., 2006). However, to our knowledge no collecting and reconditioning campaigns for watches with tritium luminescent dials were conducted by the watchmaking industry in France since the end of the tritium use.

Nowadays, despite the end of using tritium by the watchmaking industry, OBT contents observed in sediments all along the Rhône River unequivocally indicate a significant residual labelling originating from tritiated paint. Such OBT contamination most probably relates to fine solid particles originating either directly from paints or from the combustion of domestic wastes containing tritiated watches (Eyrolle et al., 2018a, 2018b; Jean-Baptiste et al., 2018; Murith et al., 2006). Finally, no clear relationship between tritium uses in watchmaking workshops and OBT contents in riverine sediment of the Rhône River has been proven.

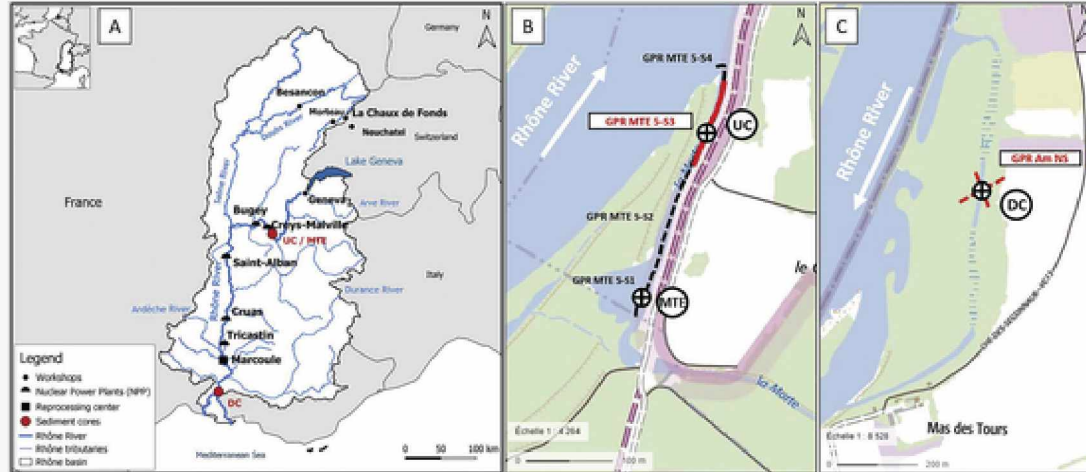
The present study aims (1) to review the history of tritium uses by the watchmaking industry at the Rhône River basin scale (France and Switzerland) in order to quantify the source terms and their evolution over the last decades and (2) to measure OBT contents in the Rhône River sediments over the same period of time in order to highlight the environmental trajectories of this contaminant in the river system. For this impact study, sedimentary coring was performed in the upstream and downstream parts of the Rhône River and OBT analyses were carried out along with several other parameters.

2 History of the watchmaking industry in the upper Rhône River and technogenic tritium uses

Historically the watchmaking industry is mainly located in the French-Swiss cross-border region (Moine, 2003). It started in 1530 with the opening of the first watchmaking center in Geneva (Switzerland – Fig. 1). It was followed later by workshops that opened progressively in the Jura Arc (France and Switzerland). In 1793, eighty Swiss watchmakers settled in Neuchâtel (Switzerland) and Swiss workshops opened along the Doubs River (Barbe and Lioger, 1999) in Besançon city (France) and continued on the outskirts of the town. In the 1900s, the largest part of watch manufacturing was in Switzerland (Neuchatel, Geneva and essentially La Chaux de Fond) but also in France (Morteau and mainly in Besançon) (Fig. 1). At this time, working from home was usual and small home-workshops were dispatched over the French-Swiss cross-border region. Since the 1960s Swiss watch manufacturers took over most of the French workshops consequently the main part of watch production came from Switzerland.

alt-text: Fig. 1

Fig. 1



A) Rhône basin in France and Switzerland with watchmaking workshops, coring sites and the reprocessing center of CEA Marcoule, B) UC and MTE GPR and coring site and C) DC GPR and coring site (maps B and C from www.geoportail.fr).

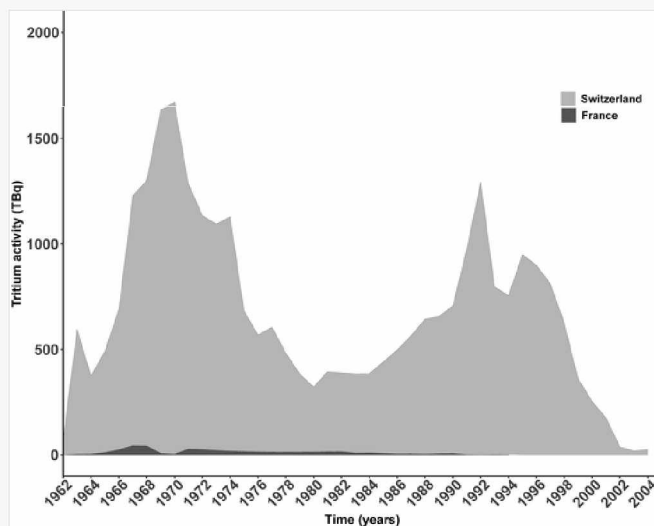
The use of radionuclides in the watchmaking industry started at the beginning of the 1900s after the discovery of the radium isolated for the first time in 1898 by Marie and Pierre Curie. This radionuclide with a half-life of 1600 years was characterized by X-ray emissions useful to combine with phosphorescent grains of zinc sulfide (ZnS) and produced radioluminescent matter (Murith et al., 2017). Herewith, radium-226 (^{226}Ra) was used for more than 50 years starting in the 1920s for its radioluminescent properties in watches all around the world (Murith et al., 2017). Unfortunately, radium known for its gamma emission has a high toxicity and many watchmaking workers were contaminated, because the workers applied the radium paint on needles and dial indices without any specific protection (Fry, 1998). Most of the workers were women selected because of their “skillful hands”. In addition to obtain greater precision they pointed their paintbrush with their lips, the direct radium ingestion caused adverse health effects. They were called “the Radium Girls” in the United States (Gunderman and Gonda, 2015). In 1930 many of them initiated proceedings against their company. An awareness of the radiological hazard of radium in the middle of the 1950s led to replace radium by tritium, considered far less toxic. The use of tritium started in France and Switzerland in 1962 and stopped in 1992 and 2008 respectively (Murith et al., 2017). The French Interministerial Commission has officialized this decision by authorizing only the use of tritium for the watchmaking industry in France. In addition, standards were set and updated several times to ensure the safety and security of using tritium in the industry like the International Standard ISO 3157 (ISO, 1975) and the French standard NF S86-305 (AFNOR, 1973). This latter was set up in September 1973 and updated two times, in June 1996 and in August 2014. In Switzerland, the distribution, importation, exportation and use of watches with luminescent paints in Switzerland were regulated by the article 129 of the Ordonnance sur la Radioprotection (OFSP, 1994). Nowadays, luminescent powder used in the watchmaking industry is devoid of radioactivity especially with the consumer's preference for non-radioactive consumables such as quartz or connected watches (Maury, 2015).

The inventory of tritium from the French-Swiss watchmaking industries is drawn up from various documentary archives of the French Institute of Radiation protection and Nuclear Safety (IRSN) and the Swiss Federal Office of Public health (OFSP). The total activity of tritium delivered to watchmaking workshop during the entire

period of its use was about 410 TBq in France (from 1962 to 1992), while in Switzerland, almost 28 400 TBq were delivered from 1962 to 2004 (Fig. 2), representing 98.6% of the total tritium delivered to French-Swiss workshops. No information about tritium delivered in workshops was available between 2004 and 2008. The major part of tritium was delivered to workshops in the Swiss city La Chaux-de-Fonds close to the French border where they specialized in the application of luminescent paints (Murith et al., 2006). Tritium was mainly delivered during two periods with a maximum activity of 2 TBq in 1969 and 1 TBq in 1995 (Fig. 2).

alt-text: Fig. 2

Fig. 2



Tritium activity (TBq) delivered in watchmaking workshops in France (Besancon) and Switzerland (mainly La Chaux de Fonds) from 1962 to 2004.

La Chaux de Fonds workshops (Fig. 1) constituted the main provider of tritiated pieces for the watches manufacturing in the workshops of the cities Morteau and Besancon in France and Neuchatel in Switzerland (Murith et al., 2006). The city La Chaux de Fonds has built incinerators for all kinds of waste including waste coming from the watchmaking industry further to a specific authorization. In addition the tritium waste cycle of La Chaux de Fonds is well controlled and traceable at least from 1988 to nowadays by yearly reports. Since 1991, tritiated waste with low activities from watchmaking industries are incinerated and the releases of tritium in liquid and atmospheric forms are controlled. In the case of tritium waste with high activity, a procedure of solidification in a metallic container is applied and containers are stored in a controlled area for 100 years (Murith et al., 2006). However, information on the tritium release before 1988 remains very sparse. Concerning France, to our knowledge no incinerator was functioning in Besancon and its periphery before the 1990s neither for domestic wastes nor for tritiated compounds. In addition, as employees might have worked also from home in the periphery of this city (Moine, 2003), it complicates the quantification of tritium residues diffused in the environment. In the absence of information it is suggested that some of the waste might have reached landfills without much control.

3 Methods and analyses

3.1 Studied sites and sediment cores sampling

The Rhône River is 812 km long from its source in Switzerland to its outlet in the Mediterranean Sea. It drains a catchment area of 97 800 km² and it is the most important river in France in terms of water discharge with an

annual average flow of $1700 \text{ m}^3 \text{ s}^{-1}$ at 60 km from the mouth. Its annual solid discharge ranges from 1.2 to 22.7 million tons per year between 1971 and 2016 (Copard et al., 2018; Pont et al., 2002; Poulhier et al., 2019; Sempere et al., 2000), and up to 80% of the total amount of discharge delivered to Mediterranean Sea occurs during floods episodes (Antonelli et al., 2004). The Rhône River is highly industrialized and characterized among other various industries by the presence of 21 hydropower plants, four nuclear power plants, and a spent fuel reprocessing center (Marcoule) in dismantlement since 1997. From the 19th century, several channels and dykes were set up to enhance the navigation and the trade (Provansal et al., 2014; Tena et al., 2020).

Two river sediment cores were collected in the upper part (upstream nuclear facilities) and the lower part (downstream all nuclear facilities) of the Rhône River in France to evaluate the temporal and spatial evolution of OBT concentration (Fig. 1). For this purpose, two sites were investigated from maps, aerial photographs, bibliographic study, field investigations and sampling. The aim was to determine specific areas which the sedimentary deposition was, as far as possible, continuous over the last decades allowing to establish the chronology of the aquatic environmental contamination from tritium used in the watchmaking industry. Prior to coring, geophysical analyses with a Ground Penetrating Radar (GPR) were conducted to obtain a representation of sedimentary deposition changes from the past to nowadays with a high vertical resolution (Bábek et al., 2008; Gu et al., 2019). In the case of the investigation of river sediments, electromagnetic techniques – by terrestrial GPR or Water Ground Penetrating Radar (WGPR) – are the most appropriated in terms of performance, feasibility and resolution (Huggenberger and Regli, 2006). Profiles obtained with GPR were helpful to understand the sedimentary filling of the upstream area and to select the most homogeneous coring location. The acquisition of the GPR profiles were carried out with the GSSI SIR 3000 system (Geophysical Survey System Inc., Salem, USA), operated with two shielded antennas at a central frequency of 200 MHz and 400 MHz, running in monostatic mode. The set is connected to a Trimble GPS. The data processing was performed using the GSSI Radan 7 software. This processing consisted in distance normalization, static time shift (to align direct ground wave arrival to 0 ns), background removal (to eliminate the high-amplitude direct ground wave), and Kirchhoff migration.

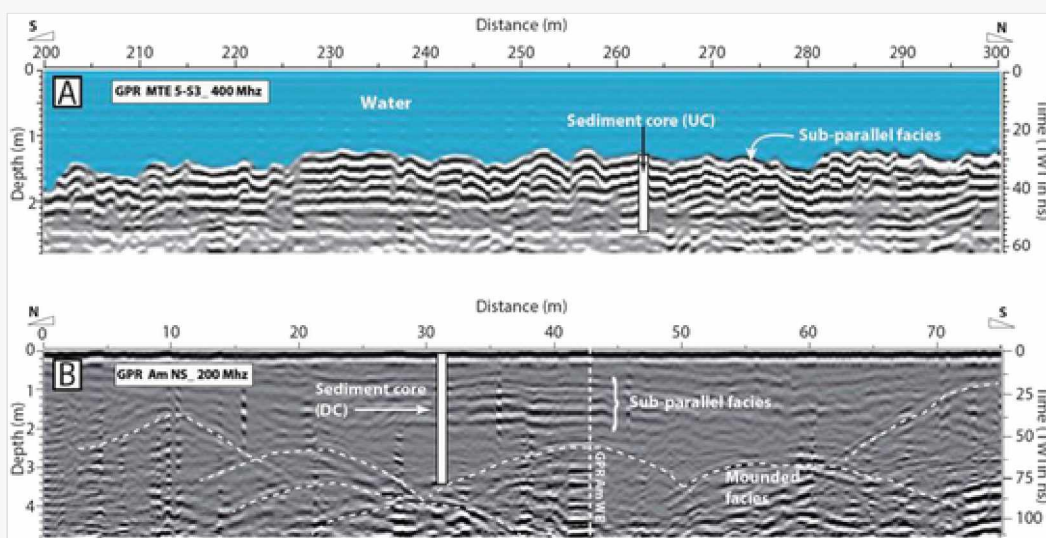
The upstream coring site (Groslée, France) was located 104 km downstream of the Lake Geneva in an area already cored in 2008 for polychlorinated biphenyl analyses (Desmet et al., 2012) and OBT concentrations (Eyrolle et al., 2018a,b). This sediment core is termed MTE for the remainder of this paper. This coring site was located on the right riverbank of the upper Rhône River and was connected to the Rhône River by its downstream end (Fig. 1B). The analyses carried out with GPR in this aquatic site allowed to determine a velocity of the electromagnetic wave of 0.075 m ns^{-1} by using the hyperbole method. This velocity value is in the same order of magnitude than the measurements results for sites with comparable conditions (Lin et al., 2009; O'Driscoll et al., 2010). The profile recorded with the GPR for this aquatic environment was carried out in the S–N direction and over a distance of 350 m (Fig. 1B). For the coring of this site, all the equipment was shipped on a flat-bottomed polyethylene boat (Lin et al., 2009; Mellett, 1995; Sebok et al., 2018). The upstream core (UC) was collected underwater in September 2018 (45.7034806 N, 5.555225 E) also from a flat-bottomed boat. An aquatic manual corer equipped with a transparent PVC tube (diameter 90 mm) was used to penetrate up to a depth of 1.5 m allowing an inspection of the sediment sampled. An apparent compaction of 31% was observed.

For the downstream site, to identify a continuous sedimentary deposition site turned out to be a challenging task on the one hand because of frequent landscaping of the riverbanks such as the construction of new dykes and on the other hand because of the high discharges measured in this part of the Rhône River. Furthermore, the aim was to core downstream all nuclear facilities and all major tributaries in order to obtain the most complete industrial testimonial of the last decades. A cartographic analysis was conducted to determine a representative

site of sediment deposition for which the anthropization has been limited for the past 100 years. Maps were compared and completed with aerial photographs allowing to retrace the evolution of riverbanks from 1930 to nowadays and to determine some areas potentially sustainable for the sampling. The site selected was located 60 km downstream the CEA Marcoule facility for spent fuel processing, recycling and radioactive waste management located along the Rhône River in the south of France. The sediment core was collected in a secondary channel on the left bank of the river (Fig. 1A–C). The latter was an active secondary channel where submersible embankments were implemented in the early 20th century. In the 1960s a transverse dyke was built in the middle of this channel, which resulted in an accumulation of sediments in the downstream part of the site. Since at least, the 1990s, the sedimentary filling disconnected the arm, allowing then sedimentary deposition only during flood periods. The aim was to precisely locate a coring location on an area of approximately 7000 m². Two GPR profile directions were selected: SW-NE (85 m) and N-S (75 m) (Fig. 1 C). A velocity of the electromagnetic wave of 0.086 m ns⁻¹ was determined from the hyperbole method and correlation with sedimentary cores that is comparable with those measured in the analogous alluvial deposits using the common midpoint method (Mumpy et al., 2007; Neal, 2004; Woodward et al., 2003). The downstream core (DC) was collected on 16 May 2017 (43.743833N, 4.626192E) with a Cobra TT percussion driller. Five cores (1 m long) have been collected in transparent PVC tubes (diameter, 90 mm) and combined to reconstitute a master core (3 m long). The presence of coarse components (several centimeters) at 3 m depth prevented to drilling at a deeper level. This coarser layer seemed to correspond to the mounded facies observed in the GPR profile (Fig. 3).

alt-text: Fig. 3

Fig. 3



Geophysical profiles obtained by GPR of A) upstream core (UC) and B) downstream core (DC).

3.2 Geochemical analysis

Micro-X-ray fluorescence core scanner (ITRAX, Cox Analytical Systems, Sweden) was applied for upstream and downstream sediment cores not only to characterize the deposition changes but also to optimize the slicing of the sediment cores by quantifying major elements (Croudace et al., 2006; Thomson et al., 2006) and investigating geochemical changes along the core. The idea was to carry out the most accurate slicing of each core to take into account the hydrodynamic evolution along the sedimentary deposition. A lithological layer-slice sampling was performed to take in account hydrological events registered into the sedimentary deposition with

43 and 23 layers slices respectively in DC and UC cores. All samples were freeze-dried, sieved at 2 mm and conditioned for analyses.

3.3 Total Organic Carbon, grain size analysis and zinc contents measurements

The Total Organic Carbon (TOC) stored in sediments was determined with a RockEval6 pyrolyzer (Vinci Technologies, France, see Lafargue et al., 1998 for further details). The grain size analysis was performed with a Malvern Panalytical particle size analyzer (Malvern Instruments Ltd., Malvern, UK) with a hydro SM small volume dispersion unit. Grain size classes were determined with clay (<2 μm), silt (2–63 μm) and sand (>63 μm) according to Blott and Pye (2001) classification. The D50 and D90 were calculated as the diameter for which respectively 50% and 90% of the particle distributions were lower. In sediment cores, the D90 is directly related to the intensity of flooding events (Dhivert et al., 2015). Concentrations of zinc were measured with an ICP-MS (Perkin-Elmer, Nexlon 300X) after an acid attack carried out for each sample of sediment to dissolve all the elements. The acid attack was with successively additions of HCl (34%), HNO₃ (67%), H₂O₂ (35%) and HF (47–51%). Solutions were diluted with ultrapure water Milli-Q (Merck).

3.4 Sediment core dating

Dry samples of sediment were conditioned in 17- or 60-mL boxing depending on the quantity of sediment available. The boxes were placed in vacuum sealed packages and stored during at least one month before measurement to ensure the secular equilibrium of the ²¹⁰Pb necessary to determine the concentration of ²¹⁰Pb_{xs} (²¹⁰Pb in excess, see below). Thereafter samples were analyzed with a gamma spectrometer for both sediment cores. A wide range of gamma emissions were detected with a germanium detector and used to assess the specific activity of ¹³⁷Cs and ²¹⁰Pb_{xs}. Those latter are widely used in order to date recent sediment deposits (100 last years) because their half-life allowed to cover several decades: 30.08 years for the ¹³⁷Cs and 22.20 years for the ²¹⁰Pb (Goldberg, 1963). Cesium-137 was adsorbed preferentially and almost irreversibly to clay and silt material (Francis and Brinkley, 1976). It is an anthropogenic radionuclide commonly used as time marker as it was mostly released in the environment during two specific events: atmospheric fallout from nuclear tests until 1963 (Ritchie and McHenry, 1990) and from the Chernobyl accident in 1986 (Petersen et al., 1990). As ¹³⁷Cs was also released in low quantities in rivers by Nuclear Power Plants (NPPs) via liquid effluents, the atmospheric markers of 1963 and 1986 might be diluted. In the specific case of the downstream part of the Rhône River, most of ¹³⁷Cs from 1964 to 1990 originated from the CEA Marcoule reprocessing spent fuel facility (Provansal et al., 2010) (Fig. 1). It is for this reason that a specific method of dating was used based on the estimation of the deposition of the official ¹³⁷Cs liquid releases (data from COGEMA by Charmasson (1998), Rolland (2006) and personal communication) associated with suspended matter. The calculation procedure to date the archive from ¹³⁷Cs activities released by Marcoule is briefly presented here but additional information is available in Supplementary Materials 1 (SM1). The model was developed considering two major characteristics: firstly, the Marcoule center is authorized to release liquid effluents only when the Rhône River discharge is between 400 and 4000 m³ s⁻¹ (Lambrechts et al., 1991). Then, as previously mentioned, the sediment core was collected in a specific area where sediment was mainly deposited during flood events. In light of these elements, the dating could not be carried out directly comparing ¹³⁷Cs releases with ¹³⁷Cs measured in the sediment core but considering the hydrodynamic conditions of the system. The net flow of suspended particulate matter with ¹³⁷Cs from Marcoule deposited in the DC location was modeled using hydrological model (Beaugelin-Seiller et al., 2002) and deposition equation (Abril, 2003). Then, the net flow modeled was smoothed with a process based on the wavelet analyzing and rebuilding signal and compared with the ¹³⁷Cs concentration measured in

the collected core (DC). Fifteen dates were modeled and the rest was deduced assuming a constant sedimentation rate between two dates modeled.

Lead-210 (^{210}Pb) is a natural radionuclide produced by ^{222}Rn decay. The ^{210}Pb is produced in sediments where it reaches a secular equilibrium with its parents (supported ^{210}Pb) and in the atmosphere (unsupported ^{210}Pb or $^{210}\text{Pb}_{\text{xs}}$). The $^{210}\text{Pb}_{\text{xs}}$ is currently used for dating lake sediments where inputs of ^{210}Pb are continuous (Appleby, 1998). Considering that the $^{210}\text{Pb}_{\text{xs}}$ flux was constant, the apparent sedimentary rate could be estimated from the linear regression of the naperian logarithm $\ln ^{210}\text{Pb}_{\text{xs}}$ versus depth (Goldberg, 1963).

3.5 Tritium analyses

The OBT concentrations were measured by the ^3He ingrowth method after placing the sample in a sealed vial under vacuum (10^{-9} mbar) and storing it during 3–4 months (Cossonnet et al., 2009). The measurement method is commonly used for samples containing few quantities of organic matter (%H < 2%) and consisted in the determination of ^3He produced by the decay of tritium contained in the sample. The ^3He measured is normalized to ambient atmospheric levels ($^3\text{He}/^4\text{He}$) (Clarke et al., 1976; Jean-Baptiste et al., 2010) and corrected to the radiogenic ^4He contained in the sample. The mass spectrometry analysis measures the $^3\text{He}/^4\text{He}$ and results are given in Bq kg^{-1} dry. In order to compare concentrations measured in samples containing various levels of organic matter, a commonly used conversion in Bq L^{-1} is carried out based on the content of hydrogen. The hydrogen amount in the samples is determined with a CHN analyzer (Elementar, Langensfeld, Germany). The conversion in Becquerel per liter of combustion water (Bq L^{-1}) is applied to determine the concentration of OBT contained in the carrier phase of tritium, i.e. water, in equivalent hydrogen and to compare values of OBT with environment HTO levels (Cossonnet et al., 2009; Eyrolle et al., 2018a). A correction of the radioactive decay based on the dating of the core (3.4) was applied in order to reconstitute the concentration of OBT initially deposited. In the following, all OBT data acquired from sedimentary cores analyses are corrected from radioactive decay and express in Bq L^{-1} . Results from OBT analyses (not corrected from radioactive decay) and expressed in Bq kg^{-1} are reported in supplementary materials.

3.6 Calculation of the effective half-life (EHL)

The effective half-life (EHL), constitutes a useful tool to assess decontamination kinetics within environmental compartments and resiliencies. It can be defined as the time needed to reach the half of initial concentration owing to various mechanisms including air or water mass dilution, sediment transfer, migration, degradation (Van Metre et al., 1998) and radioactive decay in the case of radionuclides (Gontier and Siclet, 2011; Eyrolle et al., 2020). This parameter was calculated from the slope (λ) of the exponential regression of the OBT concentration with time according to the following formula:

$$EHL_{(\text{year})} = \frac{\ln 2}{\lambda_{(\text{year}^{-1})}} \quad (1)$$

The EHL was used in this study to compare the temporal trend of OBT initially deposited in upstream and downstream sedimentary cores. They were calculated over the same period of time in order to allow comparison (i.e. from 1989 to 2008).

The resiliency or resilience was defined here as the ability of the river system to recover to pre-contamination state, i.e., to reach the geochemical background (Thoms et al., 2018).

4 Results

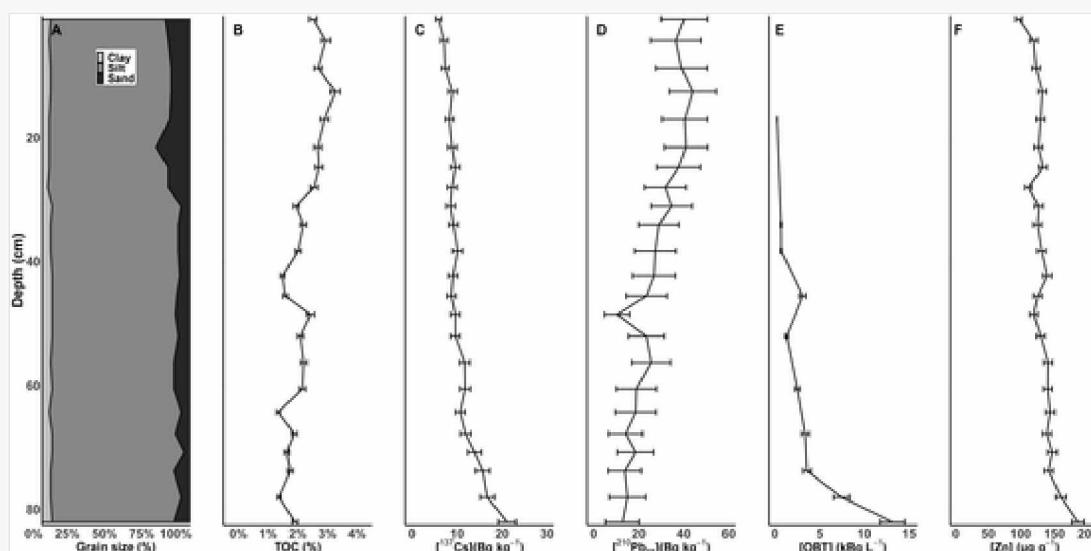
4.1 Results obtained for the upstream core (UC)

The GPR survey was carried out by boat navigating along the channel in the South – North direction (Figs. 1 B and 3 A). The GPR profiles showed a clear reflection of the sediment bottom at about 30 ns, which corresponded to a water depth of about 1.5 m. The GPR signal penetration in the bottom sediment was low (1.5 m), showing only a near-surface sediment facies between 30 and 50 ns of two-way travel time (TWT). The GPR profiles showed rather homogeneous sedimentary deposits with horizontal to subhorizontal reflectors. The coring zone was selected in a continuous fill with parallel reflectors.

The UC was characterized by a rather homogeneous sedimentary deposition as the grain size remained fairly stable with a major proportion of the fine fraction ($<62.5 \mu\text{m}$) represented by $83 \pm 4\%$ of silts and $6 \pm 1\%$ of clays (Fig. 4 A – Supplementary Material 2 - Table SM2). A slightly higher proportion of sand was observed in the first 28 cm (mean = $16 \pm 3\%$) than in deeper layers with an average of $8 \pm 2\%$. The maximum proportion of sand was observed at 21.5 cm depth (23%). In addition, the D50 values were about $18.2 \pm 2.0 \mu\text{m}$ between the top and 28 cm depth while it presented an average value of $14.1 \pm 1.5 \mu\text{m}$ from 28 cm depth to the bottom of UC (Table SM2). The D90 was about $76.9 \mu\text{m}$ from the top to 28 cm depth and equal to $43.0 \mu\text{m}$ between 28 cm depth and the bottom of UC. The maximum D90 value of $154 \mu\text{m}$ was observed at 25.5 cm depth (Table SM2).

alt-text: Fig. 4

Fig. 4



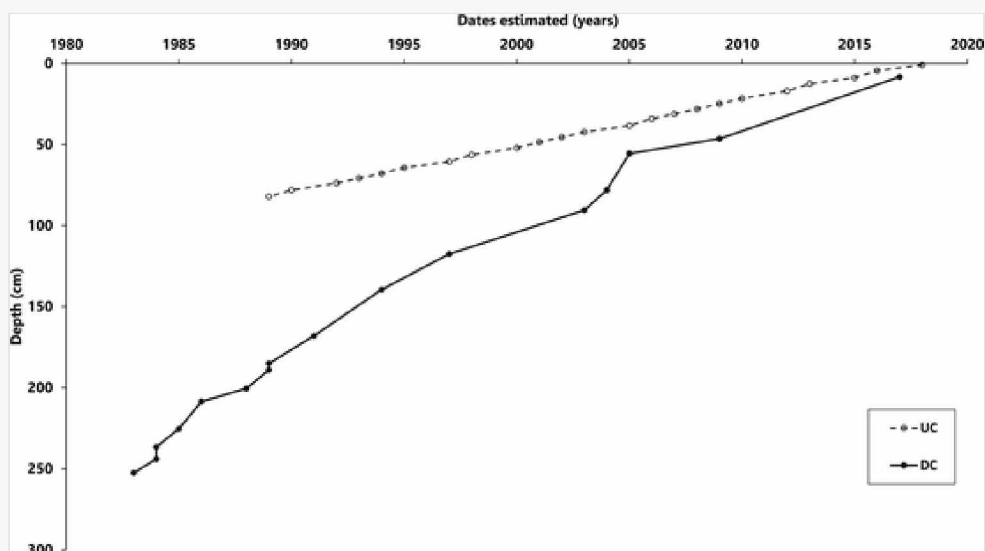
A) Grain size (%), B) Total Organic Carbon (TOC - %), C) concentration of ^{137}Cs (Bq kg⁻¹), D) concentration of $^{210}\text{Pb}_{\text{xs}}$ (Bq kg⁻¹), E) concentration of organically bound tritium (OBTT) initially deposited (kBq L⁻¹) and F) concentration of zinc ($\mu\text{g g}^{-1}$) in upstream core (UC).

The percentage of TOC in UC was on average $2.1 \pm 0.1\%$ (Fig. 4 B). It showed a discrete decreasing pattern from the top to the bottom with a maximum value of $2.9 \pm 0.2\%$ at 17 cm depth and a minimum value of $1.3 \pm 0.1\%$ at 64 cm depth (Table SM2).

The ^{137}Cs profile (Fig. 4 C) showed an increase from the top to the bottom, with respectively a minimum value of $5.9 \pm 0.7 \text{ Bq kg}^{-1}$ at 1 cm and a maximum value of $21.0 \pm 2.0 \text{ Bq kg}^{-1}$ at 82 cm depth. As the specific peak of ^{137}Cs from the Chernobyl fallout commonly used for dating was not clearly identified, the dating of UC core was performed by using the $^{210}\text{Pb}_{\text{xs}}$ method after the calculation of the sedimentation rate. This latter was 2.9 cm year^{-1} considering the compaction of 31%. The sedimentation rate allowed dating the sediment core to 1989 at the bottom. This observation was supported by the linear age-depth model (Fig. 5).

alt-text: Fig. 5

Fig. 5



Sedimentation accumulation rate of upstream core (UC - white dots) and downstream core (DC -black dots) determined by the dating method based on ^{137}Cs and ^{210}Pb concentrations for UC (Appleby, 2008; Appleby, 2008) and by the specific dating method from ^{137}Cs released by the spent fuel reprocessing center of Marcoule for DC.

OBT contents increased from the surface to the depth with a minimum value of $0.18 \pm 0.02 \text{ kBq L}^{-1}$ in 2012 (17 cm) and a maximum value of $12.9 \pm 1.4 \text{ kBq L}^{-1}$ in 1989 (82 cm) (Fig. 4 E). This increase pattern was rather regular over time with a small peak in 2002 (45.5 cm) with OBT concentration of $3.0 \pm 0.4 \text{ kBq L}^{-1}$.

Concentrations of zinc measured over the same period of time (1989–2018) were rising from $91.1 \mu\text{g g}^{-1}$ (2018–0.9 cm) to $178.9 \mu\text{g g}^{-1}$ (1989–82 cm) (Fig. 4 F). This trend showed a significant correlation with OBT concentrations with a p-value of 9.15×10^{-3} .

Over 1989–2008, which is the common period of time covered by the two upstream sedimentary archives of this study, the calculated EHLs were 4.7 ± 0.8 years for UC and 4.8 ± 1.1 years for MTE (Table 1) (see Table 2).

alt-text: Table 1

Table 1

i The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Effective half-life calculated in years for UC (Upstream Core), DC (Downstream Core) and MTE (Desmet et al., 2012) between

1989 and 2008.

Archive	Effective half-life (years)
UC	4.7 ± 0.8
DC	4.8 ± 1.7
MTE	4.8 ± 1.1
Tritium radioactive decay (years)	12.3

alt-text: Table 2

Table 2

i The table layout displayed in this section is not how it will appear in the final version. The representation below is solely for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Summary table of the use of tritium in the French-Swiss watchmaking industry.

Half-life ($T_{1/2}$) of the tritium	12.3 years
Physicochemical form of the tritium used in watchmaking industries	Integrated to polystyrenes and coated on zinc sulfide phosphor grains forming a luminescent powder then mixed with a binder and applied on watch patches (Ravi et al., 2002)
Period of use in Switzerland	1962–2008
Period of use in France	1962–1992
Total activity used in Swiss workshops (1962–2004)	28 400 TBq
Total activity used in French workshops (1962–1992)	410 TBq
Number of watches produced	350 millions
Number of watches collected in Switzerland between 1985 and 2004	68 000 (Murith et al., 2006 ; OFSP, 2007)
Activity per watch	About 100 MBq (max 185 MBq in France and 276 MBq in Switzerland) (AFNOR, 1973 ; Murith et al., 2006)
Tritium waste traceability available for treatment plant of La Chaux de Fond (Switzerland)	1988 – nowadays (annual reports from OFSP)

4.2 Results obtained for the downstream core (DC)

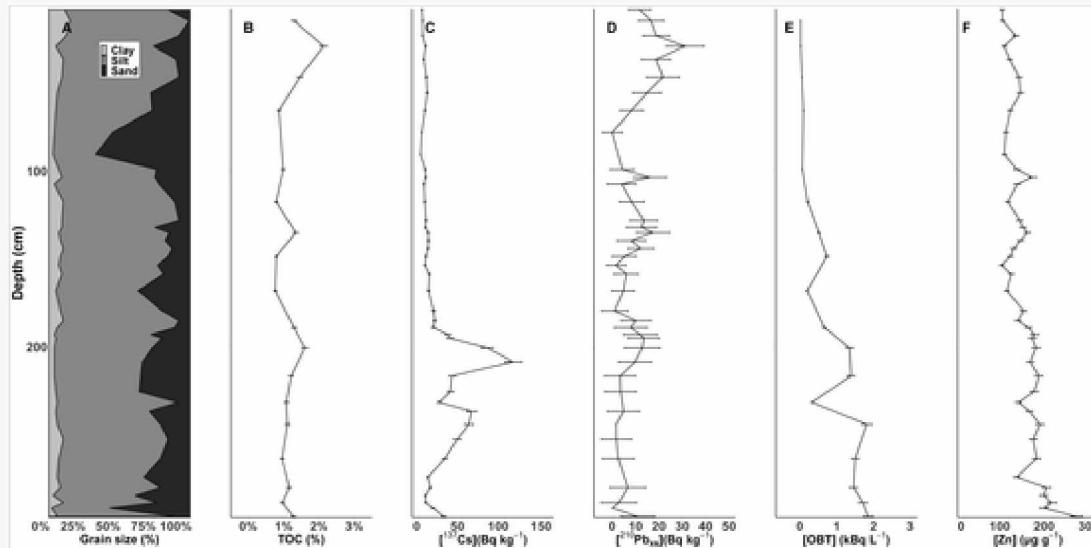
On the downstream site, a GPR north-south direction profile was carried out with a 200 MHz antenna (Figs. 1 C and 3 B). The GPR signal penetration in the sediments was deeper than for the UC, showing sediment structures

up to about 4.60 m. The profiles highlighted two distinct sedimentary units (radar facies). Horizontal to sub-horizontal reflectors were observed from the surface up to 3 m deep in some parts. These relatively homogeneous facies cover a more mounded facies, characterized by several hyperbolic reflections in the deepest part of the GPR profiles (Fig. 3 B). The downstream sediment core was collected in an area with sub-parallel facies according to the GPR analysis.

The sedimentary core was characterized by important variations of silt (from 30 to 85%) and sand amounts (from 1% to 67%) while the clay proportion ranged from 2 to 15% (Fig. 6 A). Despite those variations, DC was characterized by a dominant proportion of silts in almost the totality of the core representing $70 \pm 12\%$ as a mean value. The proportion of sand was larger than clay with on average $23 \pm 14\%$ and $7 \pm 3\%$, respectively (Fig. 6 A). The D50 ranged from $7.4 \mu\text{m}$ (14.5 cm) to $103.4 \mu\text{m}$ (90.5 cm) (SM2) and D90 varied between $28.3 \mu\text{m}$ (14.5 cm) to $433 \mu\text{m}$ (103.5 cm) (SM2).

alt-text: Fig. 6

Fig. 6



A) Grain size (%), B) Total Organic Carbon (TOC - %), C) concentration of ^{137}Cs (Bq kg^{-1}), D) concentration of $^{210}\text{Pb}_{\text{xs}}$ (Bq kg^{-1}), E) concentration of organically bound tritium (OBT) initially deposited (kBq L^{-1}) and F) concentration of zinc ($\mu\text{g g}^{-1}$) in downstream core (DC).

The TOC content was characterized by a slight decrease from the top to the bottom, with a mean value of $1.2 \pm 0.1\%$ (Fig. 6 B).

The ^{137}Cs profile (Fig. 6 C) was characterized by a significant positive inflection at 189 cm depth. Below the concentrations were significantly higher than above with respectively on average $36.6 \pm 3.4 \text{ Bq kg}^{-1}$ and $8.9 \pm 4.2 \text{ Bq kg}^{-1}$. Two peaks were observed at 208.5 cm and 236.5 cm depth with maximum values of $110.1 \pm 9.9 \text{ Bq kg}^{-1}$ and $61.7 \pm 5.6 \text{ Bq kg}^{-1}$ respectively. From 189 cm to the surface, the concentrations were low with a slight decrease concentrations from $18.6 \pm 3.1.8$ to $3.8 \pm 0.5 \text{ Bq kg}^{-1}$. The entire core and the revealed peaks were used for the dating using the mathematical model (SM1).

The sediment core DC covered a period of time from 1982 to 2017. The average sedimentation rate calculated from the ^{137}Cs dating for the entire core was about 7.8 cm year^{-1} . However, changes of sedimentation rate were observed around 55,5 cm depth (year 2005), 189 cm depth (year 1989), 208, 5 cm depth (year 1986) and 24 cm depth (year 1984) (Fig. 5). The $^{210}\text{Pb}_{\text{xs}}$ profile (Fig. 6 D) showed important variations with concentrations

ranging from $0.1 \pm 7.1 \text{ Bq kg}^{-1}$ to $31.1 \pm 8.1 \text{ Bq kg}^{-1}$ without significant decreasing trend preventing us from confirming the sedimentation rate.

The OBT concentrations in DC showed a consistent increase from the top to the bottom with a minimum value of $7 \times 10^{-3} \pm 3 \times 10^{-3} \text{ kBq L}^{-1}$ and a maximum value reaching $1.8 \pm 0.1 \text{ kBq L}^{-1}$. Several significant OBT peaks were observed in 1993 ($0.7 \pm 0.1 \text{ kBq L}^{-1}$), in 1985 ($1.4 \pm 0.9 \text{ kBq L}^{-1}$), in 1983 ($1.8 \pm 0.1 \text{ kBq L}^{-1}$) and in 1981 ($1.8 \pm 0.1 \text{ kBq L}^{-1}$).

Concentrations of zinc in DC increased with depth from $84.8 \mu\text{g g}^{-1}$ to $254.2 \mu\text{g g}^{-1}$ (Fig. 6 F). The trend with zinc was significantly correlated with OBT with a p-value of 1.44×10^{-6} .

The EHL calculated for the period of time 1989–2012 (i.e., the common period of time covered by the three sedimentary archives of this study) was 4.8 ± 1.7 years (Table 1).

5 Discussion

5.1 Temporal trends of OBT concentrations in the upper Rhône River sediments

In the upstream area of the Rhône River, the weak penetration of the GPR signal observed during the survey may be due to the high electrical conductivity of fine sediments (silty, clayed) which inhibit propagation of the electromagnetic waves (Lin et al., 2009). However, the GPR profiles showed a rather homogeneous sedimentary filling with horizontal to subhorizontal reflectors (Fig. 1 A). This sediment core was in fact mostly characterized by particles lower than $63 \mu\text{m}$ and the 1 m core retrieved in this zone (UC) confirmed the homogeneous deposition of the coring area (Fig. 3 A). The D50 supported those observations with a steady pattern of about $15.5 \pm 2.6 \mu\text{m}$ on average. The maximum value of D90 observed in 2010 (21.5 cm) was most probably related to the flood registered on the Rhône River in December 2010 with a discharge higher than $1000 \text{ m}^3 \text{ s}^{-1}$ during 3 days (the average discharge in Groslée station, located 1.6 km downstream the coring site, was about $463 \text{ m}^3 \text{ s}^{-1}$ between 1999 and 2019 – Thollet et al., 2018). The discrete decreasing of TOC between 2018 and 1989 could be related to the degradation of organic matter (Eyrolle et al., 2018b) (Fig. 4 B). Fresh matter such as tree leaves easily deposited during low discharge was observed in the first centimeters during the sampling suggesting that oldest tree leaves deposited during past floods are degraded nowadays. The continuous and regular pattern of ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ profiles confirmed a continuous sediment input and confirmed a constant sedimentation rate (Appleby et al., 2001) (Fig. 3 C).

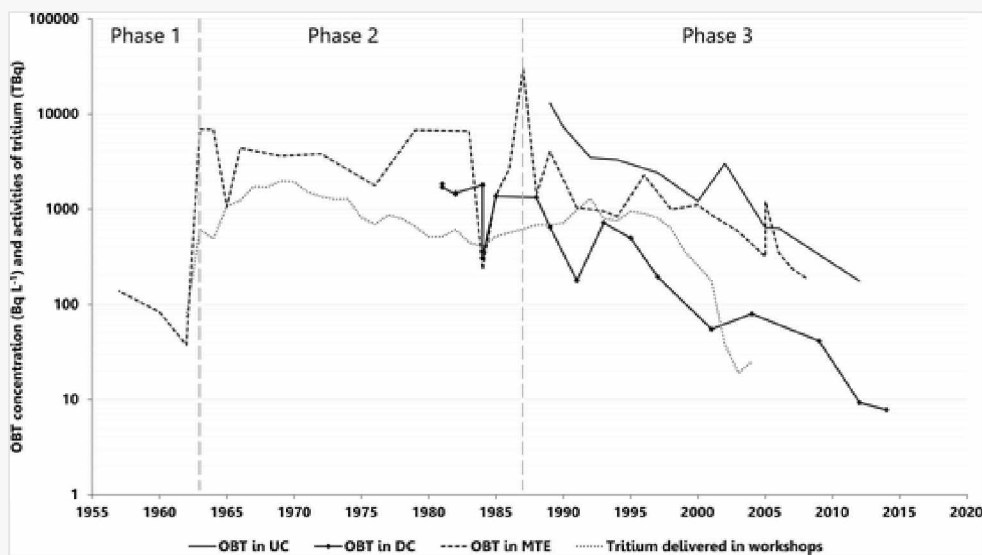
The OBT contents measured in UC were widely higher than levels commonly observed in French sediments (on average $2.4 \pm 0.6 \text{ Bq L}^{-1}$) with a minimum value of $0.18 \pm 0.02 \text{ kBq L}^{-1}$ in 2012 (17 cm) and a maximum value of $12.9 \pm 1.4 \text{ kBq L}^{-1}$ in 1989 (82 cm) (Fig. 4 E). This observation was in accordance with the levels measured in suspended matter and surface sediments in the upstream part of the Rhône catchment during the same period of time (1989–2018) from 0.54 ± 0.02 to $15.8 \pm 2.7 \text{ kBq L}^{-1}$ (Eyrolle et al., 2018b). Those high levels of OBT originated most probably from the city of Geneva and its watchmaking factories of the past.

In addition, OBT concentrations in UC were compared with those of the MTE core collected in 2008 at approximately 200 m at the North-East (Fig. 1). The MTE core covered a longer period of time with the oldest layer dated around 1960 (Desmet et al., 2012). The trend of OBT concentrations in both UC and MTE cores was very similar for the common period of time (1989–2008) but the most recent core (UC) was characterized by slightly higher values (Fig. 7). However, the maximum OBT content in UC ($12.3 \pm 1.4 \text{ kBq L}^{-1}$) did not reach the maximum value measured in 1989 in MTE core ($31.3 \pm 3.5 \text{ kBq L}^{-1}$). This maximum value could be explained either by the presence of an isolated highly tritiated particle (tiny tritiated polystyrene spherule) or by a

concentration of several particles due to releases by the watchmaking industry. The fact that only in one MTE sample a hot tritiated particle was observed and none was observed in UC samples shows clearly the heterogeneous dispersion of the contamination. This observation is supported by the distance between both cores and different sedimentation rates (2.9 cm year^{-1} for UC and 1.8 cm year^{-1} for MTE). Moreover, no peak was observed regarding the tritium deliveries to the workshops in 1989 (Fig. 2). In light of these observations, none of both hypothesis could be excluded. Nevertheless, the punctual high variations of OBT concentrations could be attributed to the heterogeneous dispersion of hot or/and numerous tritiated particles in the area. Despite those differences of OBT concentrations, the EHL of the two cores was close over the same period of time 1989–2008 (4.7 ± 0.8 years for UC and 4.8 ± 1.1 years for MTE) and as expected lower than the radioactive period (12.32 years). These results highlight the significant resiliency capacity of the Rhône River sediments in its upstream area regarding technogenic tritium particles (Table 1).

alt-text: Fig. 7

Fig. 7



OBT concentration in UC, DC and MTE from 1962 to 2017, total activity of tritium delivered in French-Swiss workshops. The vertical dotted lines correspond to virtual separations between phases of the tritium history.

5.2 Temporal trends of OBT concentrations in the lower Rhône River sediments

The GPR profile conducted in the downstream area of the Rhône River revealed mounded facies, typical for sandy to gravelly bottoms (Bábek et al., 2020), covered by horizontal facies (Figs. 1 C, 3 B and 6 A). Such radar facies were interpreted as the succession of an active functioning channel (with hydraulic dunes) followed by a filling phase (with finer sediments), which was later confirmed after coring. This pattern is typical for the disconnection reported in secondary channels of the Rhône River (Dépret et al., 2017). Indeed, the channel was artificially disconnected at its upstream end by the implementation of submersible embankments. The heterogeneous distribution of the particles sizes and the $^{210}\text{Pb}_{\text{xs}}$ concentrations in DC were mostly related to the flooding events that occurred during the last decades and their origins on the Rhône River (Poulier et al., 2019) (Fig. 6 A and D). River systems are characterized by variation of flow rate transporting particles with various size depending on hydrological conditions (Dhivert et al., 2015). The highest value of sand particle was observed in the slice dated in 2003 (90.5 cm) with 67% of sand and a D90 of $256 \mu\text{m}$, and was directly related to the Rhône River extreme flooding event in December of that year due to devastating winds and heavy rainfall (SM2). The flooding was characterized by an exceptional discharge of $11\,500 \text{ m}^3 \text{ s}^{-1}$ in Beaucaire expected to occur only

once every century (Antonelli et al., 2008). Owing to the variation of the discharge, the $^{210}\text{Pb}_{\text{xs}}$ profile (Fig. 6 D) showed high variations due to inconstant sedimentation rate over time (Fig. 5). Consequently, the lead method for dating could not be applied to confirm the dating conducted by modeling. Though, the ^{137}Cs , was commonly used for the dating of sedimentary deposition over the last decades due to its specific signal from global fallout (early 1960s) and from the Chernobyl accident (1986) (Appleby et al., 2001; Oldfield et al., 1995). In the case of the lower part of the Rhône River, the ^{137}Cs was essentially originating from the reprocessing spent fuel center of Marcoule and was identified as an interesting time marker owing to its well-known mostly irreversible labelling of the sediment by liquid releases (Charmasson, 2003; Eyrolle et al., 2008).

The decreasing trend of OBT concentration since the beginning of the 1980s was also previously observed in suspended matter and surface sediment in the downstream part of the Rhône River (Eyrolle et al., 2018b). In both cases, most OBT contents significantly exceeded current background levels and univocally highlighted the marking of sediment by technogenic tritium.

The drop of OBT contents in 1991 (168 cm) and in 1984 (231 cm) could also reflect the occurrence of flood events in southern tributaries, such as respectively the ones of the Durance River in April 1991 and the Ardèche River in November 1984. Most of the sediments transferred by the Lower Rhône River tributaries are free from technogenic tritium (Eyrolle et al., 2018b) and may significantly dilute OBT contents carried out from the upstream part of the Rhône River (Eyrolle-Boyer et al., 2015). In contrast, northern tributaries such as the Saône and Doubs Rivers, significantly labelled by technogenic tritium, can generate important inputs of technogenic tritium during flood events due to the remobilization of contaminated sediments accumulated in the past. These tributaries are characterized by OBT levels between 0.1 and 5 kBq L⁻¹ in suspended matter and surface sediment analyzed since the beginning of the 2000s (Eyrolle et al., 2018b), i.e. 2–1000 fold higher than OBT contents observed in the DC core over the same period of time. In the studied core, drastic increases of OBT contents might have been a direct result of the Saône or Doubs River floods which occurred from April to June in 1983, 1986 and March 1988.

Referring to the chronology of tritium uses by watchmaking industries in the Jura Arc area (Fig. 7, the dotted curve), an increasing trend took place during the same period of time between 1983 and 1988 supporting the likely relationship between tritium delivered to this industry and OBT measured in sediments. However, from 1988 to 1992 although the amount of tritium delivered to the watch manufacturers continued to increase, the OBT contents in DC decreased over the same period.

Apart from flood origins and from the evolution of technogenic source terms over decades, the huge variation of OBT contents among the sedimentary core is most probably explained by the heterogeneous distribution of technogenic tritiated hot particles in riverine sediments as recently proposed by Lepage et al. (2020), preventing a more precise interpretation of the causal links between the pressures exerted by watchmaking workshops releases and the responses observed in sediments of the Rhône River.

Finally, OBT contents registered in both upstream and downstream cores highlight that upstream of the Jura Arc, the upper Rhône River had a non-negligible role in the OBT input in Rhône sediments.

5.3 Comparison between upstream and downstream sedimentary archives

The sediment core collected downstream the Rhône River (DC) presented OBT contents generally lower than those measured in UC collected upstream all the nuclear facilities (5–50 fold lower) (Fig. 7). These results highlight that NPP's along the Rhône River did not induce any OBT concentration excess. Furthermore, the

OBT contents observed in the downstream site were lower than the OBT contents from the site upstream hence emphasizing the dilution by depleted sediments from non-contaminated tributaries. In fact, recent work of Poulrier et al. (2019) estimated that from 2000 to 2016 only $23 \pm 17\%$ of the sediment observed in the vicinity of the DC site came from upper catchment tributaries affected by technogenic tritium (Rhône River upstream the Isère tributary, including the Saône tributary).

Although technogenic tritium was bound with synthetic organic compounds, no significant correlation between TOC and OBT (Bq kg^{-1}) measured in sediment cores was observed, the Kendall correlation test had a p-value = 0.07 for UC and 0.9 for DC. These results suggest that the amounts of tritiated organic particles were lower than naturally occurring organic particles conveyed by soil erosion in the watershed and primary production in the river.

Because tritium was integrated to synthetic organic compounds and coated onto zinc sulfide to form the luminescent paint used by the watchmaking industries, zinc measurements were carried out in order to evaluate the metallic contamination associated with technogenic tritium. Zinc concentrations in UC and DC sedimentary cores were very similar with an average value of 127 ± 17.1 and $135 \pm 35.6 \mu\text{g g}^{-1}$ respectively (SM2). Zinc contents decreased over years from $159 \pm 7.9 \mu\text{g g}^{-1}$ in 1989 to $88.5 \pm 4.4 \mu\text{g g}^{-1}$ in 2017. These levels were close to those previously observed by Provansal et al. (2010); Ferrand et al. (2012) in sedimentary archives collected 1.5 km upstream the studied DC site.

The significant correlations between zinc and OBT in the studied sediment cores (p-value = 9.15×10^{-3} and 1.44×10^{-6} for UC and DC respectively) would suggest that the presence of tritiated particles are linked to a significant contamination in zinc of sediments transferred by the Rhône River over the years. Indeed, 67% of the grains used in tritiated paints contain zinc. In order to assess the contribution of this potential source of contamination in zinc for the Rhône sediments, the theoretical concentration of zinc from technogenic tritium compounds was estimated. The mass of zinc associated with the activity of technogenic tritium delivered to workshops was determined according to the manufacturing protocol of luminescent powder described by Ravi et al. (2002). Briefly, the tritium was bound with synthetic organic compounds like polystyrenes and coated on zinc sulfide phosphor grains with 67%/zinc, to form the luminescent powder. Then, it was mixed with a binder and formed luminescent paint applied on dials indices and needles (Ravi et al., 2002). As the zinc was the major constituent of the tritiated powder, the potential amount of zinc from watchmaking industry $[\text{Zn}]_{\text{th}}$ was calculated by using the following parameters:

- The mass of zinc contained in one gram of tritiated powder (0.67 g of zinc per gram of powder);
- The maximum activity of tritium associated to one gram of powder (2.22×10^{10} Bq (Bernard-Narbonne and Lachaussee, 1986));
- The concentration of tritium (OBT) measured in the sedimentary archive.

The calculation of the potential deposited zinc, $[\text{Zn}]_{\text{th}}$, in g.g^{-1} of sediment, from watchmaking workshops was performed as follows:

$$[\text{Zn}]_{\text{th}} = \frac{[\text{OBT}]_{\text{sample}}}{A_{\text{powder}}} \cdot [\text{Zn}]_{\text{powder}}$$

Where A_{powder} is the maximum activity of tritium in the watchmaking powder (2.2×10^{10} Bq g⁻¹ of powder), $[Zn]_{\text{powder}}$ is the mass of zinc, in g, contained in one gram of tritiated powder, i. e., luminescent powder and $[OBT]_{\text{sample}}$ is the concentration of OBT measured in the sedimentary archive in Bq g⁻¹ of sediment.

Based on these data, the theoretical zinc content due to the tritiated paints in UC was estimated from a minimum of 4.1×10^{-7} µg g⁻¹ at the top (2012) to a maximum of 2.1×10^{-5} µg g⁻¹ at the bottom (1989) (SM2). In the case of DC, the theoretical zinc content was ranged from 1.1×10^{-8} µg g⁻¹ in 2017 to 2.7×10^{-6} µg g⁻¹ in 1981 with an average value of $9.8 \times 10^{-7} \pm 9.1 \times 10^{-7}$ µg g⁻¹ (SM2). In light of these results, the hypothesis of a zinc contamination from the watchmaking industry has to be rejected. Indeed, theoretical zinc contents from watchmaking industries estimated from OBT contents in UC and DC cores were extremely low, i.e. values more than 10 000 times lower than Zn contents measured in the sedimentary cores (SM2). Furthermore, the decreasing trend observed for zinc contents over the last decades was observed as well for the major part of other metallic contaminants in the Rhône River over the same period of time (Ollivier et al., 2011; Radakovitch et al., 2008). To our knowledge, except zinc included as sulfide grains, there was no other trace metal associated with tritiated particles originating from the watchmaking industry. These results emphasize that the watchmaking industry did not significantly contribute to the enhancement of any trace metal contamination of the Rhône River sediments even though part of these contaminants are expected to be from anthropogenic origin (Radakovitch et al., 2008).

5.4 Trajectories of technogenic tritium in the Rhône River

The trajectories of technogenic tritium contamination in the Rhône River system can be interpreted over three major periods (Fig. 7):

During the 1960s, a dephasing gap of almost 4 years was observed between the increase of tritium theoretically released by watchmaking workshops and OBT contents measured in sediments of the river (Fig. 7 phase 1). The peak of OBT contents in MTE was registered in 1967 while the first peak of tritium delivered to workshops was in 1963. This time-lag between pressure and environmental response highlights the difficulty to directly correlate the amounts of tritium waste produced by the workshops to those released in the environment over this period of time. As previously mentioned, information regarding tritium releases in the environment were available only since 1988 (Murith et al., 2006, Table 2).

From the end of the 1960s to the end of the 1980s, tritium delivered to the workshops was almost constant with activities around 1 000 TBq per year. Over this same period of time technogenic tritium concentration in the sediment cores remained stable and were only characterized by depletion of OBT contents due to the occurrence of flooding events as explained previously (Fig. 7 phase 2). This observation reinforces the relationships between the releases of watchmaking industries and tritium uses. This specific period highlights the slow decrease of the OBT concentration in sediments of the Rhône River system regarding the continuous tritium releases into the environment caused by the regular use of tritium in the watchmaking industry.

From the end of the 1980s to present, a decreasing trend of OBT concentration in the sediment cores was observed even before the decrease of the use of tritium in the workshops (Fig. 7 phase 3). This dephasing could be explained by the retreatment processes of tritiated wastes which began around 1988 in Switzerland (Murith et al., 2006). Furthermore, it could be also related to the watch collection campaigns starting in 1985 (OFSP, 2007). These results prove the importance of regulatory pressures on the environmental response. The effective half-life (EHL) was calculated for each core on this third temporal phase in order to allow comparison (i.e. from 1989 to 2008). The three studied cores showed EHL not significantly different from each other (4.7 ± 0.8 , 4.8 ± 1.1 and 4.8 ± 1.7 years for UC, MTE and DC, respectively). Despite the fact that the extreme OBT value measured in

MTE previously mentioned ($31.4 \pm 3.6 \text{ kBq L}^{-1}$ in 1989) was more than twice as high as the maximum value measured in UC ($12.9 \pm 1.4 \text{ kBq L}^{-1}$), the EHLs calculated for UC and MTE were not significantly different (4.7 ± 0.8 and 4.8 ± 1.1 years respectively). These results indicate that the Rhône River would have a strong dilution capacity for technogenic tritium regardless of the distance between the source and the outlet of the contamination. The EHL allows to estimate the time necessary to reach current OBT background levels characterizing riverine sediments. In the upstream part of the Rhône River, current OBT contents in surface sediment and suspended matter range from 10 to 50 000 Bq L^{-1} (Eyrolle et al., 2018b). By considering these range of values and EHL calculated from UC, the actual OBT background contents of $2.4 \pm 0.6 \text{ Bq L}^{-1}$ (Eyrolle-Boyer et al., 2015) will be reached after 3 to 15 EHL, i.e. from 14 to 70 years in the upper part of the Rhône River, assuming that no major change either in climatic or anthropic pressures will take place. In the downstream part of the Rhône River, OBT measured in DC could be also compared with current reference level of OBT observed in French river sediments as considered for the upstream sediment core. Indeed, riverine sediments are slightly labelled by tritiated releases from NPPs as recently demonstrated by Eyrolle et al. (2019) because of their very low amounts of aquatic organic matter, most generally. According to the OBT level measured in DC (from $7.8 \pm 3.4 \times 10^{-3} \text{ kBq L}^{-1}$ to $1.8 \pm 0.3 \text{ kBq L}^{-1}$) the current background level could be reached after 3 to 6 EHLs, i.e. 14–28 years in the downstream part of the Rhône River. As expected, the time necessary to attain the OBT current referential level is significantly higher for the upstream than for the downstream part of the Rhône River. The higher the OBT concentrations, the longer the resiliency time.

6 Conclusions

This study investigated the contamination by technogenic tritium and its fate in the Rhône River from sediment cores analyses. Tritium was used to replace radium for luminescent paint in the watchmaking industry from the 1960s to the 2000s. Since 1992, 2008, French and Swiss workshops respectively, progressively phased out tritium for the benefit of non-radioactive luminescent paint. The accurate origin of technogenic tritium from workshops was difficult to determine essentially because of information gaps concerning use and releases of tritium by the watchmaking industries. Up to now, research conducted on French and Swiss watchmaking industries led to partial knowledge of the tritium used thanks to the traceable tritium delivery activities mainly to the La Chaux de Fonds and Besançon workshops. Most of the information and data available concerned the Jura Arc region, however the watchmaking history of the region downstream Geneva was almost totally unknown. This study provides a part of this history based on the analysis of sediment cores collected downstream Geneva allowing to retrace the past technogenic tritium contamination and to highlight the non-negligible part of industrial releases between Geneva and the upstream coring site since the beginning of the 1960s.

The upstream part of the Rhône River was significantly marked by nearly fifty years of the use of tritiated luminescent paint by watchmaking industries resulting not only in OBT concentrations far higher than the current background level but also with values higher than 10 kBq L^{-1} downstream of Lake Geneva while the current natural background in riverine sediments is close to 2 Bq L^{-1} . The downstream part of the Rhône River was also impacted by the watchmaking industry forming a receptacle for technogenic tritium transiting from both the Jura Arc and the downstream of Geneva. This impact occurred in a lesser extent with a maximum OBT value about 1 kBq L^{-1} due to the dilution by tributaries devoid of technogenic tritium. In both cases, maximum OBT contents were observed at the bottom of the sediment cores and the OBT content decreased over time without however reaching current natural background levels. The OBT measured in sediment cores was not only contemporaneous with the use of tritium in the watchmaking industry, it continued to be present after the end of the use of tritiated salts in workshops but with a decreasing trend. The effective half-life provided an evidence of the rapid resiliency of the Rhône River in regards with technogenic tritium contamination with an

apparent half-life three times shorter than the radioactive decay of the tritium. This was observed for both upstream and downstream sites revealing the high potential of the aquatic system to eliminate the contamination with the same kinetic regardless of the distance from the source of the contamination. The results demonstrate that actual OBT background level could be reached from 14 to 70 years and from 14 to 28 years in the upstream and downstream part of the River, respectively.

Tritium used in the watchmaking industry for more than fifty years in the French-Swiss workshops led to a long-lasting imprint of the Rhône River sediments.

Declaration of competing interest

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.

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Appendix A Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvrad.2020.106370>.

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Highlights

- History of tritium used in French and Swiss watchmaking workshops was reviewed.
- OBT was analyzed in sediment cores collected upstream and downstream the Rhône River.
- Reconstructed time series testimony anthropic pressures over three major periods of time.
- Maximum OBT contents were registered over the 1980 with higher levels upstream.
- Current background level would be reached in 14–70 years.

Appendix A Supplementary data

The following is the Supplementary data to this article:

[Multimedia Component 1](#)

Queries and Answers

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