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A brief history of origins and contents of Organically Bound Tritium (OBT) and ^{14}C in the sediments of the Rhône watershed

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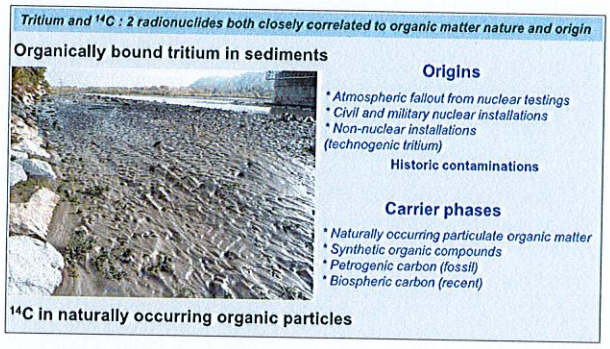
HIGHLIGHTS

- The sediments of the Rhône River and northern tributaries are labelled in OBT since decades.
- OBT is most likely carried by synthetic tritiated particles released by watchmaking workshops.
- In the Rhône watershed the particulate organic carbon displays various origins.
- Fossil and ancient organic carbon depleted in ^{14}C are drained by several alpine tributaries.
- Refractory organic particles probably modify the expected transfer of OBT and ^{14}C to the food chain.

GRAPHICAL ABSTRACT



ABSTRACT

Tritium (^{3}H) and Carbon-14 (^{14}C) are radionuclides of natural (cosmogenic) origin that have also been introduced into the environment by humans since the middle of the last century. They are therefore not compounds that have only recently been released into the environment and they do not pose a recognized health threat due to their low radiotoxicity. However, they hold an important place among current concerns because they are being discharged into the environment by the nuclear industry in large quantities compared to other radionuclides. Those both radionuclides partly integrate organic matter during metabolic processes (i.e., photosynthesis) leading to organically bound forms that can be found in sediments. Organically bound tritium (OBT) analyses carried out on the sediments of the Rhône and its tributaries indicate a significant and historical tritium labelling of sedimentary particles all along the Rhône river, as well as in several northern tributaries, in particular the Ognon and the Tille rivers (tributaries of the Saone), the Doubs River and the Loue River (a tributary of the Doubs) and the Arve river. The recorded levels (10 to over 20,000 Bq/L) are very likely to be related to the presence of synthetic tritiated particles (technogenic tritium), which were used in the past in watchmaking workshops. Although overall contamination levels decrease from north to south in the Rhône watershed and fade over time, particularly due to the radioactive decay of tritium, this contamination source of technogenic tritium in the Rhône watersheds is currently still not negligible. Carbon-14 analyses show that the Rhône sediments generally display ^{14}C levels close to the atmospheric reference values (231 $Bq \cdot kg^{-1}$ of C in 2015) or even lower in most of cases, and show sporadic and weak labelling near nuclear facilities. The low ^{14}C levels in the Rhône sediments are most likely related to the solid contributions from tributaries draining areas that are rich in fossil organic matter, and therefore devoid of ^{14}C. In the Rhône watershed, the presence in solid particles of tritium in a form

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organically bound to synthetic compounds and of petrogenic (fossil) organic carbon, can potentially alter the apparent assimilation rates to the food chain of these two radionuclid

1. Introduction

The environmental consequences of installing nuclear facilities along the banks of major rivers should be considered within the context of the mid-to long-term socio-economic development of these territories. Changes in environmental concerns, engineering techniques or political choices, sometimes taking place very rapidly, have been very marked during the nuclear era. These evolutions lead sometimes to a lack of precise and comprehensive information about the environmental consequences related to the various nuclear facilities commissioned since decades.

Like all major nuclearized rivers in France, the Rhône receives liquid discharges from the nuclear industry, where 5 Nuclear Power Plants (NPP's) are located on its banks (one of which being dismantled) (e.g. IRSN, 2011). There is also a spent nuclear fuel reprocessing center on the banks of this river, the Marcoule center, which has been in the process of being dismantled since 1997. The Rhône River has constituted, since the mid-1950s, the development cradle of nuclear energy in France, for both military and civilian purposes.

Organically bound Tritium (OBT) and Carbon-14 (^{14}C) are not compounds that have been recently introduced into the environment and they do not pose a recognized health threat given their low radiotoxicity (Le Guen, 2008; Le Guen et al., 2009). However, they hold an important place among current concerns because they are discharged into the environment by the nuclear industry in large quantities compared to other radionuclides (IRSN, 2011). They are part of the organic matter cycle thus accumulate in organic matter storage media, especially in the sediments of streams and rivers. In the vast majority of cases, most of the organic matter contained in river sediments is of allochthonous origin (e.g., Hedges et al., 1997) and does not come from in situ aquatic primary production (autochthonous), but rather is introduced through surface processes (weathering and erosion) in catchments. Thus the sources of these two radionuclides in rivers (natural/industrial, catchment erosion/liquid releases from nuclear industries) and their transfer dynamics cannot be directly identifiable since they partly depend on the origin and nature of the organic carrier phase.

Carbone-14 ($T_{1/2} = 5730$ years) and tritium ($T_{1/2} = 12.3$ years) have a low radiotoxicity (a dose factor 50 to 1000 times lower than that of ^{137}Cs, for example; Eyrolle-Boyer et al., 2014a, 2014b). They both have a naturally occurring cosmogenic source generated by the absorption of neutrons with different energies by nitrogen atoms at different levels in the atmosphere. Being mainly produced in the stratosphere, then they supply the troposphere, joining the major water and carbon cycles. These radioactive isotopes were also artificially introduced into the environment during atmospheric testing of nuclear weapons, and are discharged by the nuclear industry via gaseous and liquid effluents, in accordance with regulations. Surface nuclear tests carried out between 1945 and 1980 (with peak fallout in 1963) led to an increase in atmospheric tritium levels by three orders of magnitude (IAEA, 2004) and an increase in those of ^{14}C by around a factor of two (Levin and Heisshaimer, 2000).

At present, tritium and ^{14}C are the radionuclides that are discharged in the highest amounts by nuclear facilities in France, and in the downstream waters of the Rhône river where more than 80% of the unbound ^{3}H activity (HTO), and 50% of the ^{14}C, come from discharges by the nuclear industry (Eyrolle-Boyer et al., 2012; Eyrolle-Boyer et al., 2015a). These radionuclides remain present as trace elements in the environment, including in areas influenced by discharges from the nuclear industry (on the order of 10^{-6} to 10^{-9} ppm (mg/kg), that is to say, of a few tenths of a Bq to a few hundred Bq per liter or per kilogram of matter). The industrial component is, however, significantly observable on a regular basis in many environmental compartments (IRSN, 2011). Indeed, tritium and radiocarbon levels in samples collected in the Rhône river delta and along the French Mediterranean coastline, even very low, clearly show the influence of those radionuclide discharges carried by the Rhône plume along the Mediterranean coast (Jean-Baptiste et al., 2018).

Since several years, OBT and ^{14}C contents in sediments of the Rhône River and some of its tributaries were monitored in the frame of radiological surveys performed by IRSN. More recently additional data were acquired in the framework of the Rhône Sediment Observatory (OSR, which stands for *Observatoire des Sediments du Rhône*), in particular for numerous Rhône tributaries, in order to gain more knowledge of the concentration ranges, the origins and the behavior of these two radionuclides at the scale of the Rhône watershed. This paper presents the synthesis of these data after a review of the state of current knowledge on the behavior of tritium and ^{14}C in the environment.

2. Behavior of tritium and ^{14}C in the environment – a brief review

2.1. Specificity of tritium

Tritium can be found in gaseous form (TH or tritiated hydrogen), in HTO form (tritiated water molecule) or in combination with naturally-occurring organic molecules in an exchangeable (E-OBT or exchangeable bound organic tritium) or non-exchangeable way (NE-OBT or non-exchangeable bound organic tritium) (Eyrolle et al., 2018). The first form (E-OBT) involves weak carbon-hydrogen bonds, mainly hydrogen bonds. The second form (NE-OBT) basically corresponds to covalent bonds produced during metabolic reactions. OBT initially integrate organic matter cycle mainly during photosynthesis. It is generally accepted that E-OBT equilibrates very rapidly with tissue free-water tritium (TFWT), which is itself in equilibrium with water molecules in the surrounding medium (water or steam) (e.g., Brudenell et al., 1997). NE-OBT leads to remnant tritium within the organic matter, whose fate depends on the reaction kinetics, in particular the organic compound synthesis, degradation and recycling dynamics (Fig. 1). Thus, OBT levels higher than HTO concentrations have been frequently observed in terrestrial vegetation (Daillant et al., 2004; Jean-Baptiste et al., 2011; Kim and Korolevych, 2013) and aquatic vegetation (Fiévet et al., 2013; Eyrolle-Boyer et al., 2015a; Eyrolle et al., 2018). These observations confirm the results of the many experimental studies related to the formation and translocation of OBT in plants (Garland and Ameen, 1979; Guenot and Belot, 1984; Diabaté and Strack, 1997; Choi et al., 2002). OBT/HTO imbalances proving the persistence of tritium in organic matter have also been observed in soils (Kim et al., 2012; Thompson et al., 2015) and even river sediments collected beyond the area affected by discharges from nuclear facilities (Gontier and Siclet, 2011; Eyrolle-Boyer et al., 2015a). The persistence of tritium produced by the fallout from atmospheric nuclear weapons testing has led to significant imbalances in the OBT/HTO ratios. These ratios were of about 45 in the 1980s, and decreased gradually over time due, on the one hand, to the radioactive decay of tritium and, on the other hand, to the degradation and turnover of organic matter (Eyrolle-Boyer et al., 2015a). They can currently still reach values of about 15 in the sediments of rivers draining watersheds, where the fallout from atmospheric nuclear weapon testing was the most significant (Ducros, 2018). This last work also shows that in the organic horizons of undisturbed soils, the OBT/HTO ratios increase with the depth, i.e., in relation with the age of soil organic matter and its higher OBT content.

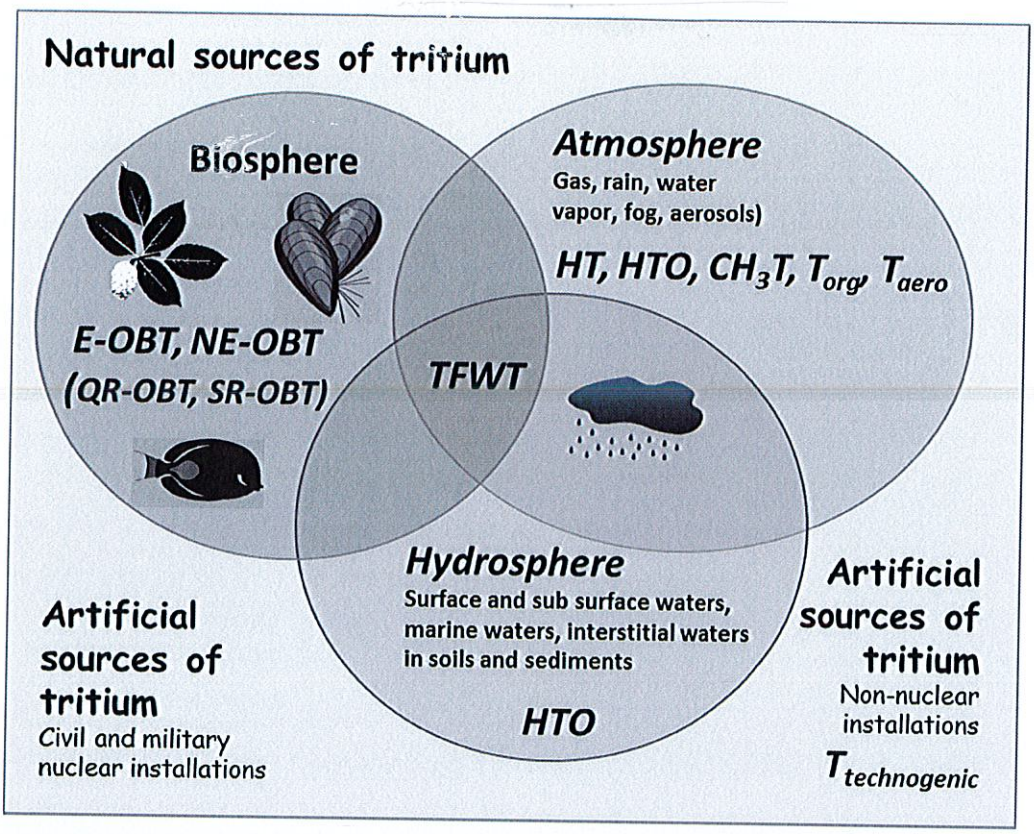

Fig. 1. Physico chemical forms of tritium in environment; HT (tritiated hydrogen), HTO (tritiated water), CH_3T (tritiated methane), T_{org} (tritiated organic gaz), T_{aero} (tritiated aerosols), E-OBT (exchangeable organically bound tritium), TFWT (tritium free water tissue), NE-OBT (non-exchangeable organically bound tritium), QR-OBT (quickly recyclable organically bound tritium), SR-OBT (slowly recyclable organically bound tritium), $T_{technogenic}$ (tritium from technogenic origin, i.e. from industrial processes using tritiated synthetic molecules or materials) (in Eyrolle et al., 2018).

The NE-OBT forms are the ones that will remain the longest in the biosphere depending on the dynamics of the organic matter biodegradation cycle, like ^{14}C. The persistence of tritium in the environment is however limited given its relatively short half-life. While the ^{14}C persistence within the terrestrial biomass is of the order of 40,000 years, it is of the order of 85 years for tritium (by considering 7 periods of radioactive decay leading to residual concentrations <1% of the initial ones).

In addition to tritium bio-integration in "natural" organic molecules, which conventionally characterize OBT, industrial processes that manipulate synthetic molecules and different materials can lead to the production of so-called "technogenic" tritium. These generally highly tritiated molecules or particles are produced either by pharmaceutical industries, as observed in the Bristol Channel and Cardiff Bay (UK) (McCubbin et al., 2001; Croudace et al., 2012), or by luminescent paint residues from watchmaking workshops, as found in the sedimentary archives of the upstream waters of the Rhône and in the surface sediments of rivers in the upper Rhône region (Krejci and Zeller, 1979; Jean-Baptiste et al., 2007; Gontier and Siclet, 2011; IRSN, 2012; Jean-Baptiste et al., 2018), or even by residues from luminescent safety lamp manufacturing plants (SRB factory Pembroke Technologies, Canada) (*Workshop on Current Uncertainties in Tritium Research*, 2016). In the case of these last two examples, it is currently expected that poorly biodegradable submicron tritiated particles, which are generally called "refractory", have been dispersed in the environment. Many luminescent objects containing tritium have been manufactured since the middle of the last century, especially in watchmaking. In most of the paints used, tritium was associated with zinc sulfides or polyester, for example. From the 1970s to the 2000s, tritium was used in watchmaking workshops to illuminate the paint applied to the hands and dials of watches and alarm clocks (Krejci and Zeller, 1979). French and Swiss watchmakers used nearly 22,000 TBq of tritium over more than 20 years (IRSN, 2017). The watch industry, both French and Swiss, is mainly located in the Rhône watershed and particularly in the part furthest upstream, the Doubs (tributary of the Saône). The watchmaking workshops were mostly located in three cities: Besançon and Morteau in France, and La Chaux-de-Fond in Switzerland.

The sources of technogenic tritium, probably multiple and diffuse, have not been precisely identified, nor has their temporal and spatial impact on environmental components. It should also be noted here that these forms potentially escape analysis when they are present in water due to the distillation of the samples (only water molecules and tritiated water molecules are extracted), and they are generally difficult to discern within solid matrices because of their high dilution with coarser particles. Finally, it may be important to emphasize that the assimilation of such particles by living organisms, their persistence, and their accumulation along the trophic chain have so far not been studied at all by the scientific community, in the particular case of tritium.

2.2. Specificity of ^{14}C

Since ^{14}C peak level in 1963 in the atmosphere subsequent to past nuclear tests, ^{14}C atmospheric levels gradually decrease mainly due to carbon redistribution within the atmosphere and through oceanic and continental pumping (Levin and Heisshaimer, 2000; Naegler and Levin, 2009). This decrease is disrupted by the fossil fuel emission containing depleted ^{14}C conducting to emphasize the decrease of $^{14}C/^{12}C$ ratio in the atmosphere (Sundquist, 1993; Soon et al., 1999; Levin and Heisshaimer, 2000; Roussel-Debet et al., 2006). In detail, Levin and

Heisshaimer (2000) reported that fossil gas emissions contributed in the 2000s to 50% of the reduction in the global atmospheric $^{14}CO_2$ levels. These works also indicate that, since the early 1990s, the biospheric organic compartment submitted to atmospheric fallout from nuclear tests redistributed the ^{14}C to the atmosphere (mineralization of biospheric organic matter enriched in ^{14}C), thus constituting an atmospheric ^{14}C source.

In rivers organic matter comes from various origins including autochthonous organic matter from aquatic primary production and allochthonous organic matter from the catchment (soils, sedimentary rocks) delivered to hydrosystems following subsequent surface processes. The former generally reflects ^{14}C levels close to those of the atmosphere however it can also be potentially labelled by liquid releases from nuclear industries. The latter can be divided into different origin as soil organic matter (with various ^{14}C concentrations) and fossil (petrogenic) organic matter (bearing dead carbon) (Cathalot et al., 2013; Copard et al., 2018). Carbon-14 levels in soil organic matter vary with its age then reflect characteristic ^{14}C levels of the atmosphere during photosynthesis. In river sediments, allochthonous organic matter is generally predominant since (i) its chemical and physical properties confer a higher recalcitrant character towards degradation referring to aquatic organic matter (e.g., Hedges et al., 1997) and (i) suspended load rapidly limit primary production in river systems (e.g., Meybeck, 2006) (Fig. 2).

Inorganic and organic carbon from sedimentary rocks are devoid of ^{14}C driving dilution of the ^{14}C biospheric concentrations. In this context, aquatic organic matter may not be in equilibrium with the atmosphere, depending on the fossil carbonate levels dissolved in water that may produce CO_2 depleted in ^{14}C. In addition, downstream nuclear power plants (NPP's), aquatic organic matter may be on the contrary enriched in ^{14}C when compared to atmospheric levels. The ^{14}C levels in soils and sediments, expressed in $Bq \cdot kg^{-1}C$, therefore depend, on the one hand, on the relative proportions of organic carbon and inorganic carbon (carbonates) and, on the other hand, when the carbonates have been removed from the sample, on the relative proportions of recent (biospheric) organic carbon and fossil (petrogenic) organic carbon.

3. Material and methods

3.1. Sampling methods

The sedimentary particles of the Rhône and its tributaries were collected either (i) by sampling surface sediments (2 first centimeters) accumulated on the beds of streams, (ii) by Time Integrated Suspended Sediment (TISS) samplers (Yoshimura et al., 2015), (iii) by collecting flood deposits on banks and (iv) by centrifugation of suspended sediments during floods. Even though these various sampling methods could lead to some heterogeneity bias mainly regarding grain size of sedimentary particles (Masson et al., 2018), we consider that these are lower than OBT and ^{14}C analytical uncertainties. The collected samples were refrigerated until lyophilization in the laboratory. Along the Rhône River, water samples were also taken at the sediment collection point to determine the unbound tritium (HTO) levels; i.e., the tritium present in dissolved form in the water (filtration at 0.22 μm). However, these samples were not collected systematically.

3.2. Analytical methods

HTO analyses were performed by the so-called "conventional" liquid scintillation counting (LSC) and by the "ALOKA" liquid scintillation counting method, making it possible to reduce the decision thresholds (and the detection limits) by a factor of approximately 10 (AFNOR, 2015). Indeed, while the decision threshold for the first method is 0.65 Bq/L (10 mL, 17 h counting) it reaches 0.15 Bq/L (70 mL, 24 h counting) for the second one (Table 1). These make it possible to obtain characteristic values of the sediment aqueous component.

OBT analyses are performed either by the combustion method (for the samples with the highest organic matter content) or by the ^{3}He ingrowth method after placing the sample in a vacuum (10^{-9} mbar) and after storage (for 3 to 4 months) (Jean-Baptiste et al., 2010). The first method consists in measuring by conventional liquid scintillation the ^{3}H concentrations in water collected after the combustion of the sample. The levels are then expressed in Bq per liter of combustion water (Bq/L)

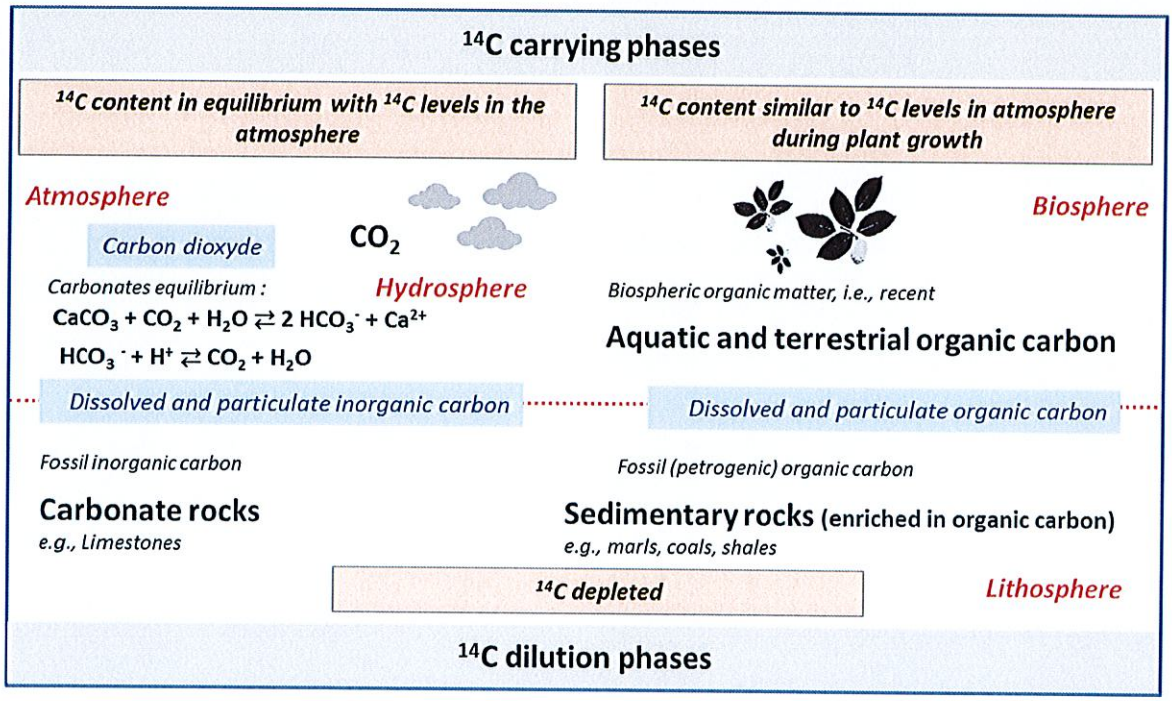

Fig. 2. Various carbon forms and origins in the environment and their expected ^{14}C contents.

Table 1
Decision threshold (SD) for the various analytical technics used for HTO and OBT measurement in the waters and solid compounds, respectively; SL: liquid scintillation, *: calculated by using %H contents.

HTO	SD (Bq/L)	Operating conditions
SL classical	0.65	10 mL, 17 h (counting)
SL ALOKA	0.15	70 mL, 24 h (counting)

OBT	SD ($Bq\ kg^{-1}_{dry}$)	SD (Bq/L)	Operating conditions
Combustion + SL	0.33*	0.65	20 g of dehydrated sample, 10 mL of combustive water, 1 000 min counting
^3He ingrowth	0.025	0.050*	100 g of dehydrated sample, 5 months of storage in devices under vacuum

(Table 1). The second, which is generally used when the samples contain little organic matter (%H < 2%), determines the ^3He levels produced by the decay of the ^3H contained in the sample after normalization of the values to ambient atmospheric levels ($^3He/^4He$) and correction of the radiogenic ^4He levels contained in the sample (gaseous inclusions). $^3He/^4He$ are measured by mass spectrometry (MS). The analysis results are expressed in $Bq\ kg^{-1}_{dry}$. The conversion to Bq/L requires the analysis of the sample hydrogen content. This last unit is necessary because it makes possible to address the carrier phase of tritium, that is to say, water, in hydrogen equivalent, thereby allowing the comparison of the OBT levels with the environment HTO levels. Whatever the OBT analysis method chosen, it is not possible at the moment to determine whether this OBT is linked to organic molecules of natural origin or to synthetic organic compounds.

Radiocarbon contents were analyzed using an accelerator mass spectrometer (LMC14 laboratory, Saclay, France). Sample preparation consisted of washing the sample (0.5 M HCl, 0.1 M NaOH) and then drying it under a vacuum to eliminate the carbonates. Samples were decarbonated in order to focus only on the organic counterpart. Decarbonated samples were then sealed in quartz tubes under a vacuum with an excess of CuO and silver wire. Tubes are introduced into a furnace at 835 °C for 5 h to convert the organic carbon into CO_2. The quartz tubes are then broken under a vacuum to release, dry, measure, and collect the CO_2. The graphite target is obtained with a direct catalytic reduction of the CO_2, using iron powder as a catalyst (Merck® for analysis reduced, 10 μm particles). The reduction reaction occurs at 600 °C with excess H_2 ($H_2/CO_2 = 2.5$) and is complete after 4–5 h. The iron-carbon powder is pressed into a flat pellet and stored under pure argon in a sealed tube. To reduce contamination from modern carbon or memory effects, all quartz and glass dishes are burned at 450 °C for at least 5 h. A turbo-molecular pump reaching 10^{-6} mbar is used to evacuate the vacuum lines. Measurements are performed using the Artemis facility: a 3 MV NEC Pelletron Accelerator coupled with a spectrometer dedicated to radiocarbon dating, measuring ^{12}C, ^{13}C and ^{14}C contents and counting the ^{14}C ions by isobaric discriminations. Analyses require 1 to 100 mg of dry sample (to obtain 1 mg of carbon). The specific ^{14}C activity is expressed as Becquerel of ^{14}C per kilogram of total organic carbon ($Bq \cdot kg^{-1}$ of C). The detection limit is 0.8 $Bq \cdot kg^{-1}$ of C and the uncertainty is 0.1% for modern samples ($k = 2$).

Data acquired within the framework of the OSR for the period from 2011 to 2012 are reported in Tables 2 and 3. These data set include the Rhône River (from upstream, Jons station, to downstream, Arles station (SORA)) and most of its tributaries.

4. Results and discussion

4.1. OBT levels and origin in the Rhône watershed

4.1.1. The Rhône River

In nuclearized rivers, where most of the tritium discharges from the NPP's take place (more than 90% of the tritium discharges from the NPP's are in liquid form, mainly because of the high dilution capacity of water compared to the atmosphere), the tritium environmental labelling is generally significant. On average more than 75% of the tritium present downstream from the NPP's comes from liquid discharges from the facilities. This proportion reaches 90% in the downstream part of the Rhône (Eyrolle-Boyer et al., 2015b); the spent fuel reprocessing center in Marcoule, which has been in the process of being dismantled since 1997, is currently discharging around 1000 times less tritium into the waters of the Rhône than all of the NPP's of the Rhône River together.

The persistence of tritium from atmospheric nuclear weapon tests and the natural production of cosmogenic tritium lead to an HTO background that is now <1 Bq/L in the river waters (Ducros et al., 2018). In comparison, the average HTO concentrations measured in recent years in water downstream from the NPP's range from 1 to 61 Bq/L in the Rhône and in the Alsace canal, and from 5 to 35 Bq/L in the Garonne, the Loire, the Vienne, the Meuse, the Moselle and the Seine Rivers (IRSN, 2017). These values are directly related to the discharges from NPP's, to the flow rate of the river and therefore to its capacity to dilute discharges, and, for sites located downstream from other sites, to a cumulative effect most generally. The tritium levels in the water of the nuclearized rivers thus increase or decrease from the upstream parts towards the downstream parts, depending on the successive discharges from the facilities and the efficiency of the tributaries in diluting the concentrations in transit. For the Rhône River, the general trend is a decrease of HTO concentrations towards downstream (Fig. 3). It is also evidenced by analyses performed on the dewatering water of the various matrices studied (surface sediments, mollusks, mosses, phanerogams,

Table 2
^{14}C contents in the sediments of the Rhône River and its tributaries (Bq/kgC).

^{14}C						
River	Sampling date	Latitude (°)	Longitude (°)	Concentration	Uncertainty	Unit
Gardon	11/21/2012	43.9510	4.5477	170,0	1.4	Bq per kg of C
Ain	01/11/2012	45.8369	5.2372	219.5	1.0	Bq per kg of C
Ardèche	12/18/2012	44.3025	4.5682	224.3	1.0	Bq per kg of C
Cèze	11/21/2012	44.1461	4.6875	193.5	2.0	Bq per kg of C
Durance	11/05/2011	43.6917	5.6527	118.8	1.0	Bq per kg of C
Durance	11/06/2011	43.6917	5.6527	40.3	0.7	Bq per kg of C
Durance	11/06/2011	43.6917	5.6527	40.8	0.7	Bq per kg of C
Durance	11/15/2012	43.7919	5.0475	190.3	1.4	Bq per kg of C
Bourbre	12/15/2011	45.7157	5.1594	186,0	1.0	Bq per kg of C
Grand Rhône	11/04/2011	43.6773	4.6187	226.5	1.7	Bq per kg of C
Grand Rhône	11/05/2011	43.6773	4.6187	142.7	1.0	Bq per kg of C
Grand Rhône	11/06/2011	43.6773	4.6187	150.3	1.4	Bq per kg of C
Grand Rhône	11/07/2011	43.6773	4.6187	144.5	1.4	Bq per kg of C
Grand Rhône	11/14/2011	43.6773	4.6187	293.8	2.0	Bq per kg of C
Grand Rhône	12/12/2011	43.6773	4.6187	317,0	2.0	Bq per kg of C
Saône	01/17/2012	45.7682	4.8130	204.2	1.0	Bq per kg of C

Table 3
OBT contents in the sediments of the Rhône River and its tributaries (Bq/L). Samples are analyzed either by the ^{3}He ingrowth method (^{3}He MS) or by classical liquid scintillation counting onto the water obtained after the combustion of the samples (LSC).

OBT						
River	Sampling date	Latitude (°)	Longitude (°)	Concentration	Uncertainty	Unit ^{3}He MS or LSC
Gardon	11/18/2011	43.9256	4.5748	1.65	0.09	Bq/L
Gardon	11/21/2012	43.9510	4.5477	1.99	0.17	Bq/L
Ain	01/10/2012	45.8369	5.2372	3.23	0.34	Bq/L
Ardèche	11/18/2011	44.2890	4.5921	1.34	0.07	Bq/L
Ardèche	12/18/2012	44.3025	4.5682	1.8	0.11	Bq/L
Aygues	12/09/2011	44.1485	4.7695	2.42	0.13	Bq/L
Cèze	11/18/2011	44.1460	4.6816	20.3	1.1	Bq/L
Cèze	11/21/2012	44.1461	4.6875	4.6	0.4	Bq/L
Durance	11/05/2011	43.6917	5.6527	1.5	0.5	Bq/L
Durance	11/06/2011	43.6917	5.6527	0.19	0.13	Bq/L
Durance	11/06/2011	43.6917	5.6527	0.68	0.11	Bq/L
Durance	11/18/2011	43.7919	5.0475	1.49	0.08	Bq/L
Durance	11/15/2012	43.7919	5.0475	0.8	0.21	Bq/L
Bourbre	12/15/2011	45.7157	5.1594	5.58	0.38	Bq/L
Grand Rhône	11/04/2011	43.6773	4.6187	16.7	0.9	Bq/L
Grand Rhône	11/05/2011	43.6773	4.6187	28.2	2.6	Bq/L
Grand Rhône	11/06/2011	43.6773	4.6187	5.01	0.26	Bq/L
Grand Rhône	11/07/2011	43.6773	4.6187	3.21	0.84	Bq/L
Grand Rhône	11/14/2011	43.6773	4.6187	18.1	0.9	Bq/L
Grand Rhône	12/12/2011	43.6773	4.6187	104	6	Bq/L
Ouvèze	12/09/2011	44.0416	4.9289	2.19	0.11	Bq/L
Saône	01/17/2012	45.7682	4.8130	123	13	Bq/L
Rhône	02/28/2011	43.9615	4.8486	137	7	Bq/L
Rhône	02/28/2011	43.9872	4.8543	67.3	3.4	Bq/L
Rhône	02/28/2011	43.9872	4.8543	125	7	Bq/L
Rhône	02/28/2011	43.9900	4.8498	55.8	2.8	Bq/L
Rhône	02/28/2011	43.9900	4.8498	72.5	3.7	Bq/L
Rhône	02/28/2011	43.9900	4.8498	97.4	4.9	Bq/L

fishes) (IRSN, 2014b). The OBT levels within these same matrices also follow these trends, and in general are not significantly different from the concentrations recorded in open waters, with the exception of the Rhône. For this river, previous work has already shown that suspended solids and sediments have OBT levels 10 to 10,000 times higher than the free or bound tritium levels recorded in the other matrices and decreasing from the upstream parts towards the downstream parts. These high OBT concentrations are associated to the releases of the watchmaking industry developed close to the Swiss border (Jean-Baptiste et al., 2007; Gontier and Siclet, 2011; IRSN, 2014b, 2017; Eyrolle et al., 2018; Jean-Baptiste et al., 2018).

The data set acquired within the framework of the OSR confirms that the sediments have OBT levels 10 to 10,000 times higher than the HTO levels in the rain collected at Thonon-les-Bains (the atmospheric reference), and this along the entire course from the downstream waters of Lake Geneva to Arles (SORA station). These levels are also higher than the HTO concentrations in the river water (Fig. 3). This was observed over the entire period during which OBT measurements were made, i.e., over the last 35 years, which shows a significant historical tritium anthropization of the river along its entire course. Although HTO in waters can be attributed to liquid discharges from nuclear facilities (Eyrolle-Boyer et al., 2015a), such sediment labelling cannot be fully explained by these discharges because high OBT concentrations, leading to significant disequilibrium of OBT/HTO ratios, are observed from the upstream of the first NPP's indicating an additional source term directly associated to sedimentary particles.

Over the observation period, OBT/HTO imbalances were greater in sediments collected from upstream areas compared to similar matrices taken further downstream. Over the years, imbalances appear to be declining more quickly upstream than downstream from the system. The effective periods were estimated for the most upstream and the most downstream area of this river. The effective period is the time after which half of the initial contamination has disappeared from a medium by transfer, dilution, degradation, or also by radioactive decay in the case of radionuclides. Despite the heterogeneity of the data sets, the calculations made seem to indicate that the effective period calculated upstream (5.54 years) would be shorter than that calculated downstream (7.06 years). These results tend to comfort that, in the absence of an uncertainty assessment for these results, the OBT contamination sources in the sedimentary compartment originate upstream from the Rhône. These contamination sources have decreased in recent decades, but currently still remain significant. Indeed, in the upstream Rhône, surface sediments with OBT levels greater than 10,000 Bq/L, such as those observed at the beginning of the 1980s, are still currently sporadically recorded (IRSN, 2017).

In the particular case of the Rhône, tritium is most probably not only bound to organic matter of natural origin, but rather would very likely be trapped inside fine polystyrene particles from technogenic tritium residues (luminescent paints) used in the watchmaking workshops located on the upper Rhône watersheds (Jean-Baptiste et al., 2007; Gontier and Siclet, 2011; IRSN, 2012, 2017; Eyrolle et al., 2018; Jean-Baptiste et al., 2018).

4.1.2. The Rhône River tributaries

OBT analyses were carried out on the surface sediments of the various tributaries of the Rhône, mainly between 2009 and 2015, partly as part of the OSR programs, as well as being carried out in Lake Geneva in Geneva, in 1986 and in 2009 (Station 46.23215; 6.16581) (Figs. 4 and 5).

Fig. 4 shows that the surface sediments of the northern tributaries of the Rhône, mainly the Doubs and the Saône Rivers, have high OBT levels (between 10 and 50,000 Bq/L), as recorded in the sedimentary particles of the Rhône. The Arve, the Isère, the Guiers, the Ognon rivers and the Tille river (a tributary of the Saône River), and the Loue river (a tributary of the Doubs river) also have sediments enriched in OBT compared to atmospheric reference values (Thonon-les-Bains rain), with OBT levels ranging between 2 and 90 Bq/L. This labelling seems to be historic since it was recorded in the late 1980s and early 2000s in some tributaries. It may be interesting to note that the surface sediments of Lake Geneva are also marked with tritium (512 ± 31 Bq/L in 1986 to 214 ± 11 Bq/L in 2009).

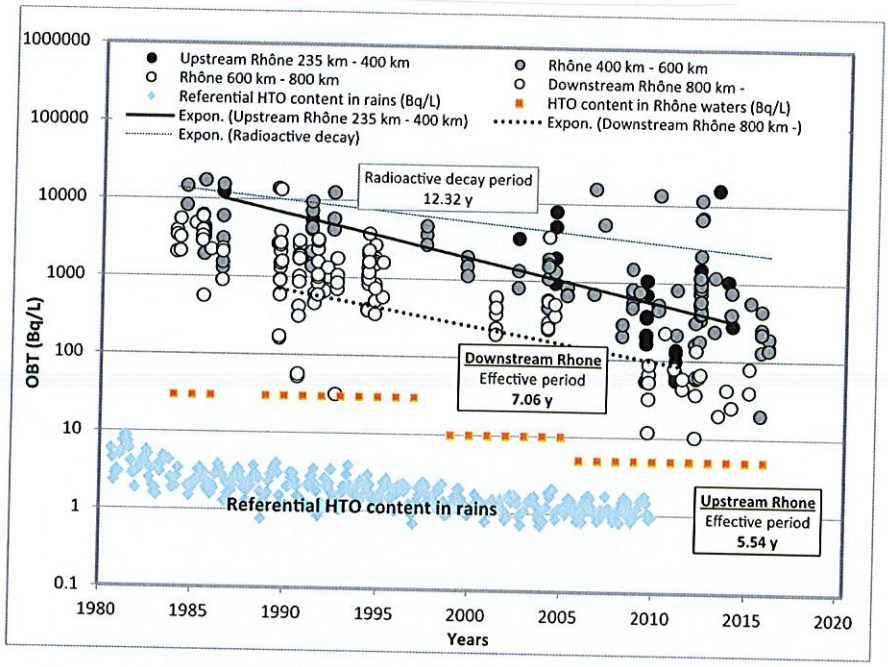

Fig. 3. Organically bound tritium concentrations (OBT), in Bq/L, in sediments of the Rhône river over the last 35 years. In black the upstream Rhône river, between 235 and 400 km from its source (Genève to Bregnier-Cordon), in dark grey the Rhône River between 400 and 600 km from its source (Bregnier-Cordon to Sablons), in grey the Rhône River between 600 and 800 km from its source (Sablons to Arles), and in white the Rhône River downstream 800 km from its source (Downstream Arles); HTO concentrations (in Bq/L) in the Rhône River waters, in orange, are mean values; in blue, referential HTO concentrations (Bq/L) in rains collected at Thonon les bains (IAEA Wiser Data base, Global Network of Isotopes in Precipitation). Expon. expresses the decreasing exponential relationships of OBT concentrations with time from which effective periods are determined.

About the Ognon, the Tille, the Loue and the Arve rivers, OBT levels certainly reflect that contributions of tritium organically bound to synthetic residues have marked sediments of these tributary, most likely in connection with the watchmaking workshops located in the upper Rhône area and in Switzerland.

About the Guiers, the Isère, the Aygues, and the Ain rivers, the measured levels are lower than those recorded in the Rhône river and could also be due to the persistence, in the organic matter of the sediments from the catchments, of fallout from atmospheric nuclear weapon testing (Gontier and Siclet, 2011; Eyrolle-Boyer et al., 2015b; Eyrolle

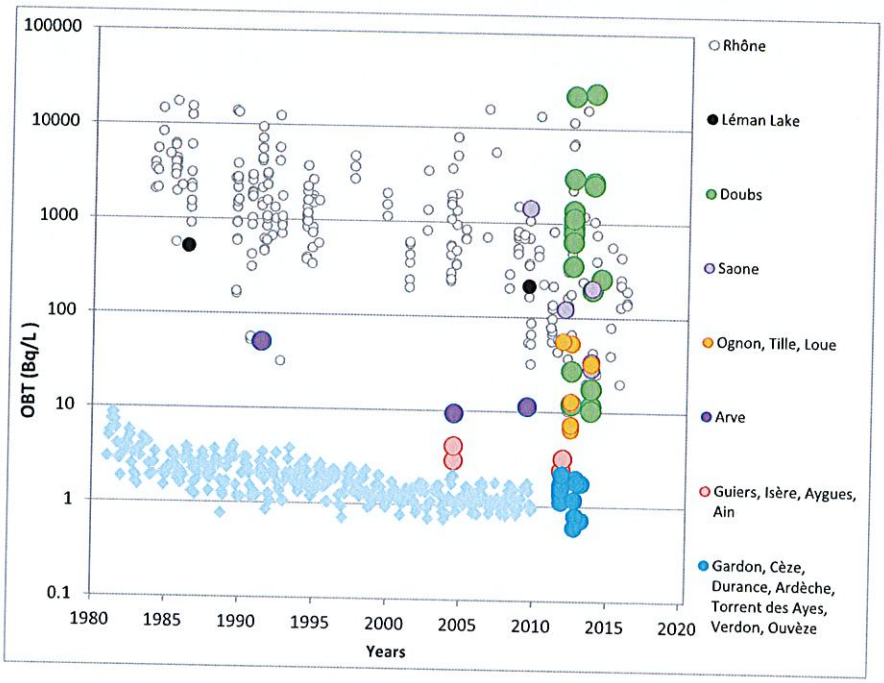

Fig. 4. Organically bound tritium concentrations (OBT), in Bq/L, in sediments of the Rhône River over the last 35 years, white points, and in various Rhône tributaries or in the Leman Lake. In blue, referential HTO concentrations (Bq/L) in rains collected at Thonon les Bains (IAEA Wiser Data base, Global Network of Isotopes in Precipitation).

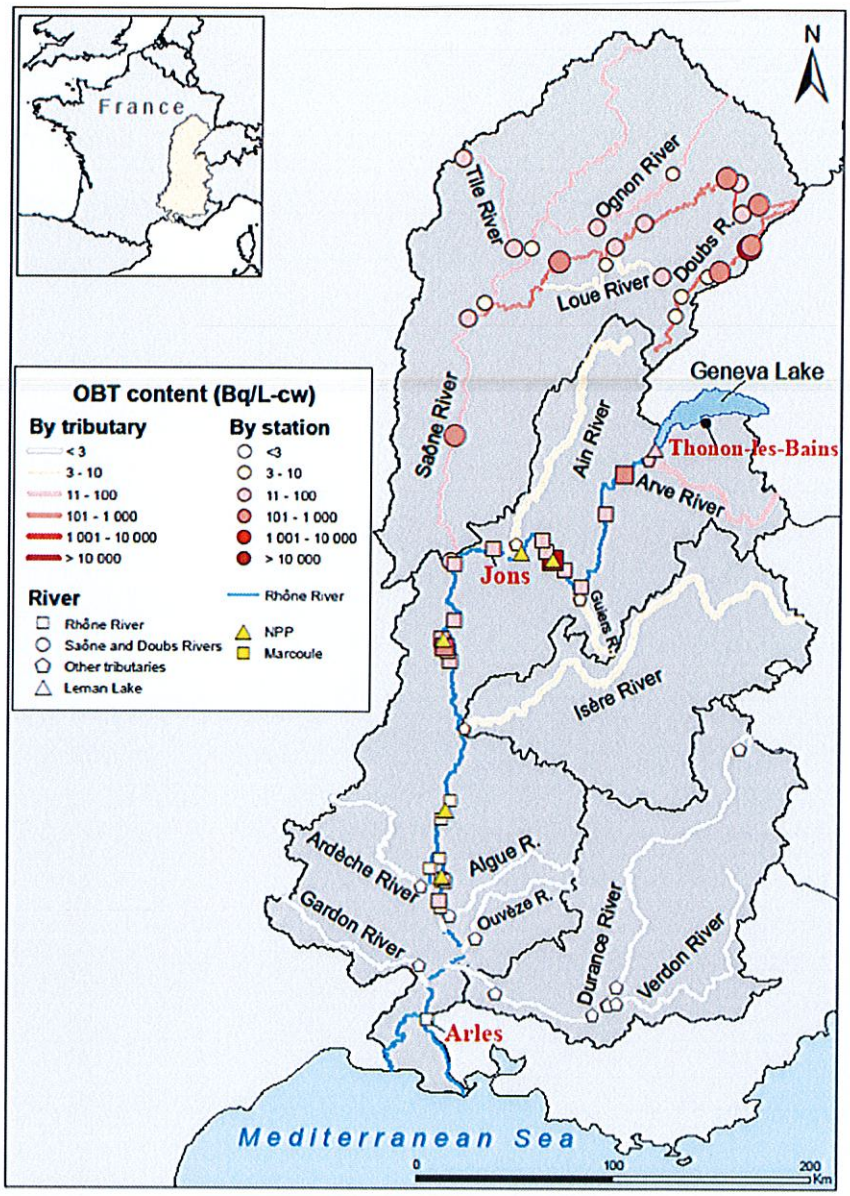

Fig. 5. OBT levels (Bq/L) in sediments of the Rhône watershed over the last 10 years (2007–2017). Data acquired most usually near tributary confluences with the Rhône River are generalized to the whole tributary watershed.

et al., 2018; Ducros, 2018). In particular for the Isère river, it is expected that OBT labelling in sediments could be linked to tritium discharges from the Institut Laue-Langevin (ILL) in Grenoble (ASN, 2010). Discrimination between these different sources is not possible from the data currently available.

Finally, for the southern tributaries studied, the Gardon, the Cèze, the Durance rivers, the Torrent des Ayes and the Verdon river (tributaries of the Durance river), the Ardèche and the Ouvèze rivers, the OBT levels (between 0.60 ± 0.04 Bq/L and 2.19 ± 0.11 Bq/L) are close to the HTO concentrations in the reference rainfall. These systems thus do not exhibit any additional significant tritium anthropogenic labelling in connection with discharges of synthetic tritiated compounds.

4.1.3. Summary

The analysis of all of the data obtained makes it possible to represent the OBT labelling of the surface sediments at the scale of the Rhône watershed (Fig. 5). Tritium discharges in the sub-watersheds of the upper Rhône, linked to the use of luminescent paints used in watchmaking since the middle of the last century, probably led to the significant labelling of the sediments of many tributaries, as well as to the labelling of the entire course of the Rhône. Although the overall contamination levels decrease from north to south of the Rhône watershed and fade over time, particularly due to the radioactive decay of tritium, the technogenic tritium contamination source in the Rhône watersheds seems to currently still be non-negligible. An inventory of watchmaking workshops located in the watershed, knowledge of their operating period and of their residue treatment methods (discharges, incineration), and the labelling of the biomass and soils of the watersheds concerned would confirm the technogenic origin and assess the persistence of this tritium contamination source for the river. It is important to emphasize here that the transfer of these tritiated particles to the trophic chain is currently not known even if there is no radiotoxicity issue.

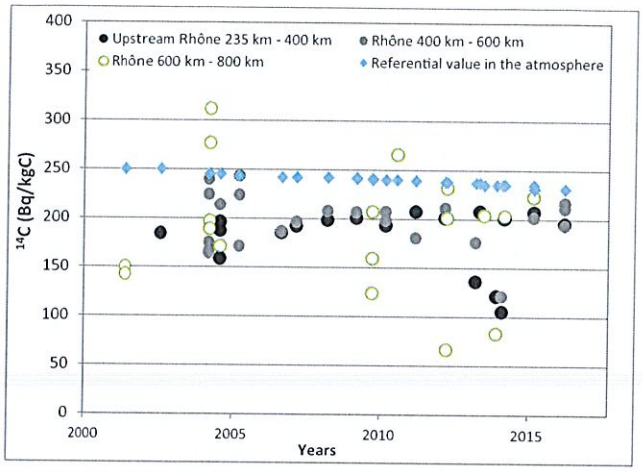

Fig. 6. ^{14}C contents, in Bq/kgC, in sedimentary particles of the Rhône River over the last 15 years. In black the upstream Rhône river, between 235 and 400 km from its source (Genève to Bregnier-Cordon), in dark grey the Rhône River between 400 and 600 km from its source (Bregnier-Cordon to Sablons), in white the Rhône River between 600 and 800 km from its source (Sablons to Arles), in blue, referential atmospheric ^{14}C contents (Bq/kgC) (Roussel-Debet et al., 2006).

4.2. Levels and origin of ^{14}C in the Rhône watershed

4.2.1. The Rhône River

Unlike tritium, most of the ^{14}C discharges from the NPP's are atmospheric (93%, IRSN, 2014a). In terrestrial environments, the ^{14}C labelling near these nuclear facilities is generally very weak with a relative increase in ^{14}C of around 3 Bq·kg^{-1} of C (Roussel-Debet et al., 2006). The work by Eyrolle-Boyer et al. (2012, 2015b) indicates that downstream from the Rhône, one of the most nuclearized rivers in France, the proportions of ^{14}C of industrial origin in suspended matter in transit would be of the order of 30 to 50%.

Our results for surface sediments and suspended matter from the Rhône River are presented in Fig. 6. These data are compared to the atmospheric reference system (Roussel-Debet et al., 2006). The results indicate that the ^{14}C levels in these matrices are generally lower than the atmospheric reference values (231 ± 3 Bq·kg^{-1} of C in 2015), with the exception of 3 samples collected in 2004 between the area downstream from the Cruas NPP's and the area upstream of the Tricastin site, and in 2011 in the Caderousse dam downstream from the Marcoule complex. These data show that the ^{14}C levels in the organic matter of the sediments from the course of the Rhône have a wide range of variation, between 67 ± 1 and 312 ± 3 Bq·kg^{-1} of C, without significant spatial and temporal trends. Although levels higher than the atmospheric reference indicate ^{14}C contributions from the liquid discharges of the Rhône nuclear facilities, lower values indicate a dilution of the sedimentary particles in transit in the river by particulate organic matter containing no ^{14}C or depleted in ^{14}C (aged biospheric organic matter), imported by the tributaries. Indeed, the presence of outcrops of sedimentary rocks enriched in organic carbon, such as (i) black marl (locally named Terres Noires), locally constituting highly erodible surfaces (i.e., badlands, Nadal-Romero et al., 2011), (ii) black shales, and (iii) coal mines in the catchments, export fossil organic matter devoid of ^{14}C to the rivers, through surface processes. Depleted ^{14}C organic matter in sediments could also reflect the contribution of organic compounds from the pre-nuclear tests period of time (McGee et al., 2004). The dilution rates obviously depend on the fossil and aged biospheric organic matter fluxes from tributaries. Their contribution is related to the intensity and variability of erosion rates partly governed by the hydro-climatology and geomorphology contexts as seen for the Durance catchment (Copard et al., 2018).

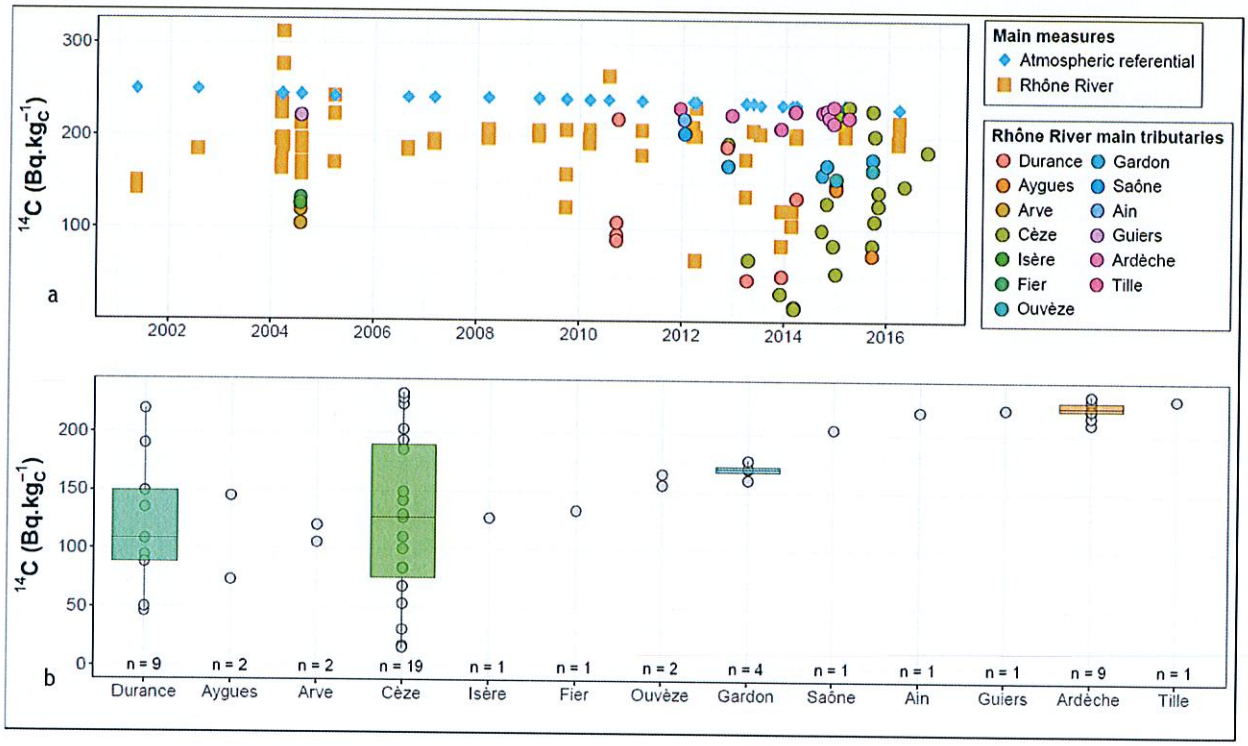

Fig. 7. a, ^{14}C contents, in Bq/kgC, in sedimentary particles of the Rhône River over the last 15 years (2002–2017), in orange, and various Rhône tributaries. In blue, referential ^{14}C contents in the atmosphere in Bq/kgC (Roussel-Debet et al., 2006); b, statistical distribution of ^{14}C contents in the various Rhône tributaries.

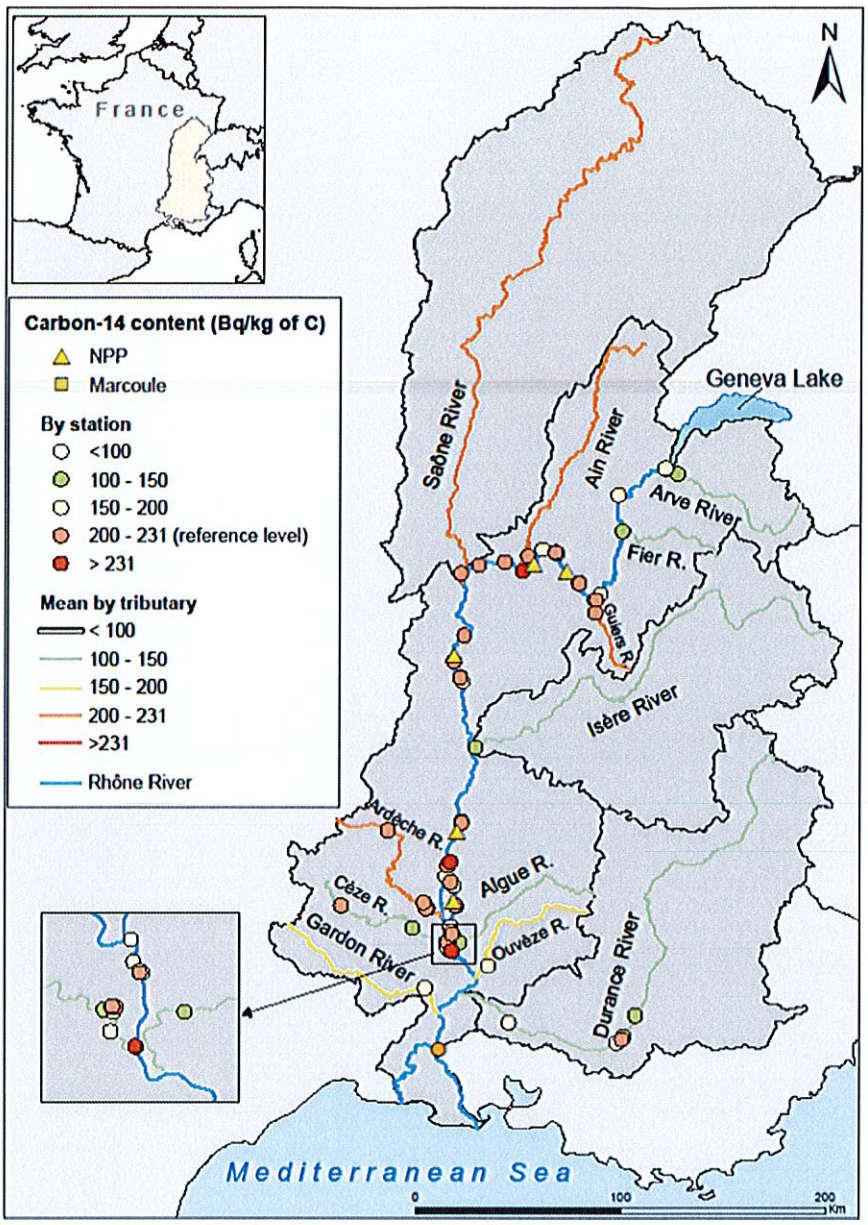

Fig. 8. ^{14}C contents (Bq/kgC) in sediments of the Rhône watershed over the last 10 years (2007–2017). Data acquired most usually near tributary confluences with the Rhône River are generalized to the whole tributary watershed.

4.2.2. The tributaries of the Rhône

The ^{14}C levels in the Rhône tributaries are extremely variable and range from atmospheric reference values (231 ± 3 Bq·kg^{-1} of C in 2015) to <16 ± 1 Bq·kg^{-1} of C, as observed in sedimentary particles collected in 2013 in the Cèze (Figs. 7 and 8). The data obtained show that although the ^{14}C levels in the sediments are close to the atmospheric reference values in the Saone (204 ± 1 Bq·kg^{-1} of C, n = 1), the Ain (219 ± 1 Bq·kg^{-1} of C, n = 1), the Guiers (222 ± 3 Bq·kg^{-1} of C, n = 1), the Ardèche (224 ± 7 Bq·kg^{-1} of C, n = 9), and the Tille (213 ± 2 Bq·kg^{-1} of C, n = 1) rivers, the other tributaries have lower concentrations; in particular, in decreasing order, the Gardon (170 ± 6 Bq·kg^{-1} of C, n = 4), the Ouvèze (161 ± 7 Bq·kg^{-1} of C, n = 2), the Fier (133 ± 1 Bq·kg^{-1} of C, n = 1), the Durance (127 ± 60 Bq·kg^{-1} of C, n = 9), the Isère (127 ± 3 Bq·kg^{-1} of C, n = 1), the Cèze (125 ± 71 Bq·kg^{-1} of C, n = 19), the Arve (113 ± 10 Bq·kg^{-1} of C, n = 2), the Aygues (109 ± 51 Bq·kg^{-1} of C, n = 2) rivers. The number of data obtained per tributary is not homogeneous (Fig. 7) so it does not provide the intrinsic variability of the ^{14}C levels for most of tributaries with the exception of the Cèze, the Durance and the Ardèche rivers. For the Ardèche river ^{14}C levels do not reveal a large variability contrary to the Cèze and the Durance rivers.

The lowest values recorded for the Durance, Aygues, Arve, Cèze, Fier and Isère rivers most likely show fossil organic carbon contributions devoid of ^{14}C without the opportunity to know exactly these contributions with the exception of the Durance River (Copard et al., 2018). These could also reflect the contribution of aged biospheric organic matter photosynthesized prior to the nuclear testing era (<1950). These depleted ^{14}C inputs are probably involved in the internal variability of ^{14}C levels in sediments as observed for the Cèze and the Durance rivers contrary to the Ardèche River. The most relevant hypothesis would be that aged or fossil organic matter inputs depend on the hydroclimatic dynamics (e.g. heavy precipitations, Cevennol episodes) as their

outcrops are heterogeneously spatially distributed in the catchment. For these two catchments, it is realistic to consider that fossil organic matter (e.g., Carboniferous coal fields for the Cèze catchment and Terres Noires for the Durance one) would be the main contributors to ^{14}C dilution processes, contrary to aged biospheric organic matter for which its preservation in these catchments would be not promoted by the geomorphological context (i.e. high erosion rate).

4.2.3. Summary

Our data provide the spatial distribution of the ^{14}C labelling at the scale of the Rhône catchment (Fig. 8). Substantially higher levels than the atmospheric reference values sporadically point out the liquid discharges from the nuclear facilities. Above all, the measurements carried out in the tributaries confirm that these may be the cause of a significant dilution of the ^{14}C levels of the particles in transit in the Rhône River by contributions of ancient particulate organic matter, depleted or devoid of ^{14}C. The dilution capacity depends both on the ^{14}C concentration of suspended particles conveyed by the river and on the importance of the solid export to the Rhône River. The Durance and the Isère rivers, which contribute to the most of suspended sediment load for the Rhône River (Zebracki et al., 2014; Mahrez et al., 2016) and episodically the Cèze rivers during the Cevennes events, must display a strong dilution capacity. In this context, the huge variability of ^{14}C contents in sediments at the scale of the Rhône catchment, may limit any precise estimation of the ^{14}C labelling by NPPs.

In addition, aged (fossil or biospheric) particulate organic matter is most likely refractory compared to the recent organic matter since these materials were previously subjected to a significant degradation and cannot be easily assimilated by aquatic organisms. By this way, the presence of this refractory material could involve, in some parts of the Rhône River, disequilibrium between ^{14}C levels measured in living organisms (e.g. fishes), which preferentially assimilate biospheric (more labile) carbon, and ^{14}C levels in sedimentary or suspended particles.

5. Conclusions

Artificial OBT and Carbon-14 (^{14}C) were introduced since several decades into the environment in France. Both radionuclides have low to very low radiotoxicity but they hold an important place among environmental concerns because they constitute most of the radionuclide discharges by the nuclear industry (in terms of percentage of activity discharged). In addition, the evolution of the Nuclear Power Plant park and of the fuel management methods, the development of the new facilities producing tritium (i.e. ITER project) suggest increasing discharges in a foreseeable future.

Measurements performed on sedimentary particles in the Rhône watershed confirm a recurring labelling in OBT of sediments of the Rhône River as well as numerous of its tributaries. The origin of this labelling is most likely related to the watchmaking workshops, using tritiated luminescent paints, settled in the upper Rhône since the middle of the last century.

Our results show that the Rhône sediments display ^{14}C levels close to atmospheric reference values (231 ± 3 Bq·kg^{-1}) of C in 2015 or even lower in most of cases. Only substantially higher levels sporadically reflect the contribution of liquid discharges from the nuclear facilities. The low ^{14}C levels in the Rhône sediments, reflecting a dilution process, are related to the solid contributions from tributaries (most alpine rivers: Arve, Isère, Durance, Fier, Aygues, and Cevennol river: Cèze). Two ^{14}C depleted phases were considered: sedimentary rocks bearing fossil organic matter, and therefore devoid of ^{14}C, and aged soils with organic matter photosynthesized prior the nuclear tests (<1950). In Durance catchment, these geological surfaces correspond to some marly badlands and probably to coal fields for the Cèze.

This work highlights the difficulty to assess ^{14}C reference values within aquatic ecosystems. In particular for the sediments classically used to assess the specific labelling from the NPPs. Speciation of the ^{14}C within organic matter, by focusing only on recent organic matter and by excluding fossil and aged organic matter, would be a real improvement to significantly assess these estimates. Another option would be to systematically determine the proportion of fossil carbon (i.e. the ratio fossil organic carbon/total organic carbon) within the samples.

In the Rhône, the presence of tritium in a form that is organically bound to synthetic compounds (technogenic tritium) as fossil organic carbon is expected to modify the assimilation rates of tritium and ^{14}C to the food chain. Synthetic compounds and fossil carbon are poorly biodegradable. The pathways and assimilation rates of these two components to aquatic organisms are expected to differ from those classically associated with forms organically bound to naturally occurring organic matter (for tritium), and from those associated with biospheric organic carbon (for ^{14}C), raising potential consequences on effective assimilation rates by the food chain. A more detailed analysis of these organic compounds, particularly those present in the Rhône watershed, would improve the understanding of the tritium and ^{14}C transfer processes in the various abiotic and biological environmental components and the estimate of nuclear environmental labelling in worldwide rivers.

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