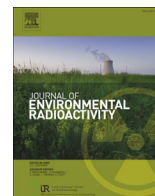


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## Tritium and $^{14}\text{C}$ background levels in pristine aquatic systems and their potential sources of variability

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### ABSTRACT

Tritium and  $^{14}\text{C}$  are currently the two main radionuclides discharged by nuclear industry. Tritium integrates into and closely follows the water cycle and, as shown recently the carbon cycle, as does  $^{14}\text{C}$  (Eyrolle-Boyer et al., 2014a, b). As a result, these two elements persist in both terrestrial and aquatic environments according to the recycling rates of organic matter. Although on average the organically bound tritium (OBT) activity of sediments in pristine rivers does not significantly differ today (2007–2012) from the mean tritiated water (HTO) content on record for rainwater ( $2.4 \pm 0.6$  Bq/L and  $1.6 \pm 0.4$  Bq/L, respectively), regional differences are expected depending on the biomass inventories affected by atmospheric global fallout from nuclear testing and the recycling rate of organic matter within watersheds. The results obtained between 2007 and 2012 for  $^{14}\text{C}$  show that the levels varied between  $94.5 \pm 1.5$  and  $234 \pm 2.7$  Bq/kg of C for the sediments in French rivers and across a slightly higher range of  $199 \pm 1.3$  to  $238 \pm 3.1$  Bq/kg of C for fish. This variation is most probably due to preferential uptake of some organic carbon compounds by fish restraining  $^{14}\text{C}$  dilution with refractory organic carbon and/or with old carbonates both depleted in  $^{14}\text{C}$ . Overall, most of these ranges of values are below the mean baseline value for the terrestrial environment ( $232.0 \pm 1.8$  Bq/kg of C in 2012, Roussel-Debet, 2014a) in relation to dilution by the carbonates and/or fossil organic carbon present in aquatic systems. This emphasises yet again the value of establishing regional baseline value ranges for these two radionuclides in order to account for palaeoclimatic and lithological variations. Besides, our results obtained from sedimentary archive investigation have confirmed the delayed contamination of aquatic sediments by tritium from the past nuclear tests atmospheric fallout, as recently demonstrated from data chronicles (Eyrolle-Boyer et al., 2014a,b). Thus Sedimentary archives can be successfully used to reconstruct past  $^{14}\text{C}$  and OBT levels. Additionally, sediment repositories potentially represent significant storages of OBT that may account for in case of further remobilisation. We finally show that floods can significantly affect the OBT and  $^{14}\text{C}$  levels within suspended particles or sediments depending on the origin of particles reinforcing the need to acquire baseline value range at a regional scale.

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### 1. Introduction

Tritium ( $T_{1/2} = 12.3$  years) and  $^{14}\text{C}$  ( $T_{1/2} = 5730$  years) both have a naturally occurring cosmogenic source that is generated by the absorption of neutrons of different energies by nitrogen atoms at

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various levels of the atmosphere. These radioactive isotopes were also artificially introduced into the environment during past nuclear testing and are still legally discharged by the nuclear industry in liquid and gaseous effluents. Surface nuclear tests conducted between 1945 and 1980 increased atmospheric tritium levels by three orders of magnitude (UNSCEAR, 2000) and those of  $^{14}\text{C}$  by a factor of around two (Levin and Hesshaimer, 2000).

Tritium and  $^{14}\text{C}$  are currently the two main radionuclides discharged by France's nuclear facilities (Gontier and Siclet, 2011). For

example, more than 80% of the unbound  $^3\text{H}$  activity present in the downstream waters of the Rhône River is believed to come from discharges from the nuclear industry (Eyrolle-Boyer et al., 2013).

Unlike most trace elements for which transfers within the environmental compartments are governed by balances at their interfaces (Kd, transfer coefficient), tritium and  $^{14}\text{C}$  integrate into and closely follow the water and carbon cycles. As a result,  $^{14}\text{C}$  and tritium are present in organic and inorganic form, as is the case with stable carbon and hydrogen.

The organic forms of tritium and  $^{14}\text{C}$  produced during photosynthesis persist in living or detritic organic matter in both terrestrial and aquatic environments according to the growth and degradation process of the plant matter (biomass). Although tritiated water (HTO) and the inorganic forms of  $^{14}\text{C}$  (associated with carbonates and hydrogen carbonates) follow the dynamics of water mass, the organic forms – in particular NE-OBT (non-exchangeable organically bound tritium) and  $^{14}\text{C}$  integrated with living or detritic organic matter – are highly dependent on the biological cycles (Eyrolle-Boyer et al., 2014a,b).

Inorganic and organic compounds depend from one each others as abiotic and biological compartments are straight linked together. The inorganic forms contribute to the formation of plant mass during photosynthesis. These producers are eaten by primary consumers (members of fauna and microfauna), which themselves are eaten by upper-level predators, such as herbivorous, omnivorous and carnivorous fishes in the case of aquatic ecosystems. This is how these two radionuclides are ubiquitously present in the various abiotic and biological environmental components.

In order to be able to constrain the results of radiological assessments of the environmental impact of nuclear energy, it is essential to know the characteristic values of the baseline levels (geochemical backgrounds) of HTO, OBT and  $^{14}\text{C}$  in both terrestrial and aquatic environments. This paper presents data sets obtained over the last decades in pristine French rivers where such background values can be acquired. These values are discussed in a historical and regional context to emphasize the variability factors. Additionally we present original data acquired on a sedimentary archive collected in a pristine area in the north eastern France that reinforce our data chronicles. Finally we present results obtained during a flood event at the lower course of nuclearised large river in order to underline the role of particle origins on OBT and  $^{14}\text{C}$  activity levels.

## 2. Updating of current knowledge on tritium and $^{14}\text{C}$ behaviour in the environment

Tritium ( $^3\text{H}$ ) is a radioisotope of hydrogen. By emitting a low-energy  $\beta$ -particle, it decays into stable helium-3 (He-3), with a radioactive half-life of 12.32 years. The behaviour of this radioactive isotope in the environment has been widely studied since the 1950s, both through laboratory experiments and, more recently, through field observations (e.g., Kirchmann et al., 1979; Belot, 1986; McCubbin et al., 2001; Kim et al., 2012; Fievet et al., 2013; Baglan et al., 2013; Jean-Baptiste and Fourné, 2013). Because it is an isotope of hydrogen, tritium has all the chemical properties of hydrogen. These properties determine its state and environmental fate as a component of the water molecule and a component of the organic molecules. As a result,  $^3\text{H}$  is present in the environment mainly in the form of tritiated water (HTO) or incorporated into plant or animal organic matter (organically bound tritium, or OBT). The activity of tritium can be expressed in Bq/L of water in all environmental components, be they rainwater, surface water (rivers, lakes), ground water, seawater or water extracted from organic matter (plants and animals). Water extracted by calcination after freeze-drying of biological matrices corresponds to tissue

water (easily exchangeable with water bound, weak hydrogen bonds) and to atoms of hydrogen extracted from the organic structures of the matrices (non-exchangeable with bound water). The former is conventionally defined as exchangeable organically bound tritium (E-OBT) and the latter is conventionally defined as non-exchangeable organically bound tritium (NE-OBT). For example, in terrestrial environments, E-OBT is the form that will be exchanged during evapotranspiration. NE-OBT is initially generated during photosynthesis and persists in the environment by following the biodegradation cycle of organic matter, as is the case with  $^{14}\text{C}$ . Today, it is analytically impossible to reproducibly measure these two species in the various environmental matrices (ASN, 2011). Lastly, tritium can be observed in more detail in a form associated with synthetic organic molecules (e.g., paint residues) known as technogenic tritium (Croudace et al., 2012). The organic matter present in the suspended or settled particles of continental aquatic systems (waterways, rivers and lakes) is brought in from watersheds by erosion and runoff of degradation products contained in the soils (allogenic matter) and the primary production developed in situ (autogenic matter). Tritium bound to allogenic organic matter comes from the degradation of the terrestrial biomass. This species thus provides a picture of the historical contamination levels of the terrestrial biomass. Provided the age of this organic matter and/or its recycling period within the watershed is known, it is possible to reconstruct past levels and vice versa. On the other hand, tritium bound to autogenic organic matter is in balance with the HTO of the waterway during its growth.

The allogenic organic matter within rivers transfers contamination from the terrestrial environment. Thus it is inert with regard to the uptake of HTO present in river freshwaters (detritic matter). By contrast, autogenic organic matter integrates the HTO in waterways besides that released in liquid effluents discharged from nuclear facilities. This is a rather theoretical scheme as allogenic OM (Organic Matter) will be colonized once in the water by aquatic organisms (microbes, invertebrates) which will contain autogenic OM, so the distinction is expected to become moot. Indeed, the two pools of organic matter (allogenic/autogenic) coexist in aquatic systems in varying proportions depending on their intrinsic typology and characteristics. This explains why waterways and rivers are primarily subject to inputs of organic matter from watersheds whereas canals and lakes generally have higher proportions of autogenic matter. Contamination of organic suspended particles and sediments in surface aquatic systems results from both the allogenic/autogenic ratio and the contamination level of these two pools of organic matter. Contaminated autochthonous compounds produced, for example, in rivers downstream of liquid radioactive releases, are expected to be largely and rapidly diluted by the allogenic non-contaminated organic compounds from the watershed (if not contaminated by recent or past atmospheric inputs), whether in the flow of suspended particles or in settled particles (sediments). The proportion of autogenic carbon is highly limited in most rivers. It generally decreases from upstream to downstream mainly because of the increase in the concentration of suspended particles.

Inversely, within watersheds affected by several decades of atmospheric releases, contaminated allogenic organic compounds progressively transfer tritium and  $^{14}\text{C}$  contamination to rivers depending on the biomass degradation rate. The most persistent species (lignin, cellulosic compounds, refractory organic matter in soils, clay–humic complexes, etc.) will be degraded long after their contamination and their impact on rivers will persist for long time as recently demonstrated (Eyrolle-Boyer et al., 2014a,b).

According to this schema, efficient transfer of contaminated organic compounds by tritium and/or  $^{14}\text{C}$  to living species is

expected to largely depend on preferential consumption of either of these two main organic sources when contamination differently affects, or has differentially affected, the terrestrial and aquatic components.

Inorganic  $^{14}\text{C}$  is closely associated with the geochemistry of carbonates while organic  $^{14}\text{C}$  is closely associated with the cycle of living matter. It is this second property that has made it a geochronometer of choice for decades. The increase in atmospheric  $\text{CO}_2$  levels over the 20th century, linked with the increasing use of fossil fuels, which have no  $^{14}\text{C}$ , led to a global decrease of the  $^{14}\text{C}/\text{C}$  ratio in the atmosphere (Sundquist, 1993; Soon et al., 1999; Roussel-Debet et al., 2006). Fossil organic matter or alteration of limestone watersheds may also lead to a decrease in this ratio at different scales of time and space. There is abundant data on the behaviour of carbon in terrestrial environments. This is due in particular to work conducted in the past several years as part of research on greenhouse gases, such as carbon dioxide, for which the sources and sinks are studied in particular. In continental aquatic environments, there are fewer such data and the specific behaviour of carbon in aquatic systems makes this data even more difficult to interpret (Roussel-Debet, 2014a). As is the case with tritium, it can be expected that transfers to organisms living in aquatic environments depend highly on the source of the organic compounds (allogenic/autogenic) and the contamination levels in these different pools.

### 3. Methods and analyses

#### 3.1. Samplings

As part of a radioecological survey and environmental monitoring, HTO, OBT and  $^{14}\text{C}$  analyses were performed on surface sediments collected over the past decades from rivers in mainland France at points located far from the influence of the nuclear industry. Sampling stations are described in details in Eyrolle-Boyer et al. (2014a,b). Additionally a 37.5 cm depth sediment core was sampled in June 2011 from a shallow artificial lake created in the OPE area (Meuse, North-East France; <http://www.andra.fr/ope>) in 1978. This sedimentary archive was split into 5 cm sections from the surface down. The strata were freeze dried then packed in the same way as the surface sediments. Lastly, suspended particles were collected along the lower course of the River Rhone (south east France) at the SORA observatory station and the Durance tributary during a flood event that occurred in November 2011. These particles, contained in several liters of water, were allowed to settle then transferred into large volume containers. Samples for HTO analysis in river water were performed on 50 mL water samples filtered during collection and stored in dark glass bottles at 4 °C until analysis. The  $^{14}\text{C}$  and OBT concentrations (without discrimination between E-OBT and NE-OBT forms) were measured in the sediments and suspended particles after freeze drying of the samples as described by Cossonnet et al. (2009).

#### 3.2. Tritium and $^{14}\text{C}$ analyses

In situ filtered waters and the water recovered in the condensates were analysed for its HTO content by taking 10 mL of this fraction and adding 10 mL of scintillation liquid (liquid scintillation counting). The dehydrated fraction (15–40 g) was burnt in a special tubular furnace with oxygen in the presence of a catalyst. Hydrogen and tritium (OBT) were trapped at the outlet of the furnace. Recovered combustion water was adjusted to pH 7 and distilled, and tritium was measured by scintillation counting, as for HTO. OBT activity was expressed in Bq/L of combustion water (CW). The detection limit is 0.7 Bq L<sup>-1</sup> and the uncertainty is 0.1% ( $k = 2$ ).

$^{14}\text{C}$  was analysed by accelerator mass spectrometry. Sampling preparation consisted of washing the sample (0.5 M HCl, 0.1 M NaOH) then drying it under vacuum. Organic samples are 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 in order to transform the organic matter into  $\text{CO}_2$ . The quartz tubes are then broken under vacuum to release, dry, measure, and collect  $\text{CO}_2$ . The graphite target is obtained by direct catalytic reduction of the  $\text{CO}_2$ , using Fe powder as the catalyst. The reduction reaction occurs at 600 °C with excess  $\text{H}_2$  ( $\text{H}_2/\text{CO}_2 = 2.5$ ) 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<sup>-6</sup> mbar is used to evacuate the vacuum lines. Measurements are performed using the Artemis facility: a 3 MV NEC Pelletron Accelerator coupled to a spectrometer which is dedicated to radiocarbon dating and to measure  $^{12}\text{C}$ ,  $^{13}\text{C}$  and  $^{14}\text{C}$  currents and count the  $^{14}\text{C}$  ions by isobaric discriminations. Analyses require 1–100 mg of dry sample in order to obtain  $\geq 1$  mg of carbon. The specific  $^{14}\text{C}$  activity is expressed as becquerels of  $^{14}\text{C}$  per kilogramme of total carbon (Bq/kg of C). The detection limit is 0.8 Bq/kg of C and the uncertainty is 0.1% for modern samples ( $k = 2$ ).

#### 3.3. Gamma spectrometry analyses for sedimentary archive dating

Freeze-dried samples were sieved through a 2 mm mesh and placed into sealed 60 mL plastic containers for gamma-emitter radionuclide analyses as described in Ferrand et al., 2012.  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  are widely used for dating recent sediment deposits (less than 100 years) because of their half-lives of 22.3 and 30.2 years, respectively (Walling and He, 1997; Piégay et al., 2008). Dating using  $^{210}\text{Pb}_{\text{xs}}$  is commonly employed for lake sediments where inputs of  $^{210}\text{Pb}$ -bearing particles are continuous (Appleby et al., 1988). Excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) activities were calculated by subtracting the  $^{226}\text{Ra}$  activities, estimated by the  $^{214}\text{Pb}$  activities measured by gamma counting, from the total  $^{210}\text{Pb}$  activities. Measurements were made at least two months after packing of the samples to allow the secular equilibrium to be established between  $^{226}\text{Ra}$  and its granddaughter  $^{214}\text{Pb}$ .

$^{137}\text{Cs}$  is an anthropogenically derived radionuclide that first widely entered the environment from 1954 following atmospheric nuclear testings. The maximum atmospheric global fallout was registered in 1963. At a more regional scale, atmospheric fallout also rose to a maximum following the Chernobyl accident in 1986. In well preserved sedimentary profiles, the maximum depth of  $^{137}\text{Cs}$  penetration is assumed to correspond to the year 1954 and the maximum levels of  $^{137}\text{Cs}$  are attributed to 1963 and 1986 fallout pulse inputs which provide temporal markers.

## 4. Results and discussion

#### 4.1. HTO and OBT background levels in pristine rivers

Before the nuclear age,  $^3\text{H}$  activity values in rainwater were of the order of 0.1–0.6 Bq/L (UNSCEAR, 2000). Massive amounts of  $^3\text{H}$  were produced by atmospheric testing of nuclear weapons. UNSCEAR assessments (2000) indicate that nearly 600 kg (1.86 10<sup>8</sup> TBq) were introduced during surface nuclear tests whereas the global inventory of naturally occurring tritium is approx. 2.65 kg (9.6 10<sup>5</sup> TBq). The tritium produced during these atmospheric tests can be measured in its HTO and OBT forms. In continental compartments beyond the reach of local industry (non influenced zones), the free form (HTO) is in balance with current atmospheric activities in terrestrial environments (balance with

water in the atmosphere) and aquatic environments (balance with water in waterways) as shown by Fig. 1. More than 500 Bq/L of tritium was measured in rainwater at the French towns of Thonon-lès-Bains and Vienne in the 1960s, the activity concentration dropped to less than 10 Bq/L by the late 1970s. It has been below 2 Bq/L since the late 1990s. The seasonality in tritium activities is a far well known mechanism here observed from the monthly data extracted from the IAEA data base. These specific results were previously discussed in details in Eyrolle-Boyer et al., 2013. During the period of 2007–2010, the mean value we calculated based on the IAEA data base (IAEA/WMO, 2012) for the rainwater collected at Thonon-lès-Bains is  $1.6 \pm 0.4$  Bq/L. The values obtained for HTO in French river freshwaters beyond the reach of industrial discharges (upper end of the watershed or aquatic systems not affected by radiation) across the same period are not significantly different from the levels observed in rainwater ( $1.4 \pm 0.4$  Bq/L). These levels are similar to those observed in terrestrial environments in tree leaves and foodstuffs collected in French non-influenced zones from 2007 to 2012,  $1.4 \pm 1.2$  Bq/L (Roussel-Debet, 2014a).

In terrestrial environments, the OBT activity measured in the biological samples (terrestrial mosses, tree leaves) or abiotic samples (soils) containing living or detritic organic matter accounts for the mean atmospheric activity of tritium across the period of plant growth. This period lasts, for example, for approximately two months for salads, the previous spring for tree leaves, and several years for tree wood (Fuma and Inoue, 1995) and lichens (Daillant et al., 2004). Inventories of organically bound tritium thus form and persist according to the recycling rates of the terrestrial biomass, as recently modelled by Eyrolle-Boyer et al., 2014a,b. OBT analyses in tree leaves and terrestrial foodstuffs collected in French non-influenced zones from 2007 to 2012 had a mean value of  $1.4 \pm 1.2$  Bq/L CW (combustion water), which is close to the mean value for HTO concentrations observed in rainwater or river waters. However, it is likely that the OBT baseline values in perennial plant matrices are greater than these values on account of the uptake of tritium at levels representative of the ambient levels of previous years. Currently, the OBT levels in the various matrices of the aquatic environments, in particular sediments, overall seem to approach the HTO concentrations of the waterways (Fig. 1). Substantially higher values are expected at a regional scale of observation, particularly based on the tritium inventories in place within the biomass of the watershed and the rate of transfer of these inventories to the waterways. Indeed, the OBT levels within the aquatic systems depend on the tritium inventories in the organic matter of the soils and biomass of the watersheds, the recycling

rates of the organic matter, the transfer rates of the organic matter to the waterways (allochthonous organic inputs), and the dilution rates of the allochthonous organic matter with the organic matter produced within the waterways (autochthonous organic matter). When the autochthonous organic matter is produced, its OBT levels are indeed in balance with the HTO levels in the atmosphere or the water of the waterway when it is produced.

Currently, the mean OBT concentration of the sediments in French rivers is  $2.4 \pm 0.6$  Bq/L CW (2007–2012 average,  $n = 31$ ). This is not significantly different from the mean HTO content on record for rainwater for the same period ( $1.6 \pm 0.4$  Bq/L). However, regional variability has not yet been established.

On the global scale, significantly different levels of these values are expected particularly based on climatic differences responsible for variability in the quality and recycling rates of the terrestrial biomass. Thus, arid environments and cold continental environments are most probably the systems that most retain current and historical atmospheric contamination by tritium.

#### 4.2. $^{14}\text{C}$ background levels in pristine rivers

$^{14}\text{C}$  is a low-energy pure beta emitter with a half-life of  $5730 \pm 40$  years. It is produced naturally by cosmic-ray action upon nitrogen at a rate of approximately 1.54 PBq/year for an inventory estimated at 12 750 PBq. Its mass abundance is extremely low compared to that of the stable isotopes of carbon; carbon-12 has a natural abundance of 98.9% and  $^{13}\text{C}$  has a natural abundance of 1.1%. Approximately 213 PBq of  $^{14}\text{C}$  were released across the planet during atmospheric nuclear tests conducted from the 1950s to the 1980s. In addition, approximately 2.8 PBq of  $^{14}\text{C}$  were released by nuclear facilities between 1950 and 1997 (UNSCEAR, 2000). Most of the  $^{14}\text{C}$  present in the atmosphere was produced by atmospheric testing of nuclear weapons. The atmospheric specific activity of  $^{14}\text{C}$  rose to more than 400 Bq/kg of C when the fallout peaked before falling after the cessation of atmospheric testing and the increase in the proportions of atmospheric  $\text{CO}_2$  from the growing use of fossil fuels, which have no  $^{14}\text{C}$ , since the advent of the second industrial revolution in Europe.

In terrestrial environments, the overall assumption (relatively well corroborated by the observations) is that the specific activity expressed as Bq/kg of C is in balance in the environmental components and particularly with that of atmospheric  $\text{CO}_2$ . In 1999, the specific activity in the terrestrial environment was  $255 \pm 7$  Bq/kg of C. In 2011, it was estimated at  $232 \pm 2$  Bq/kg of C

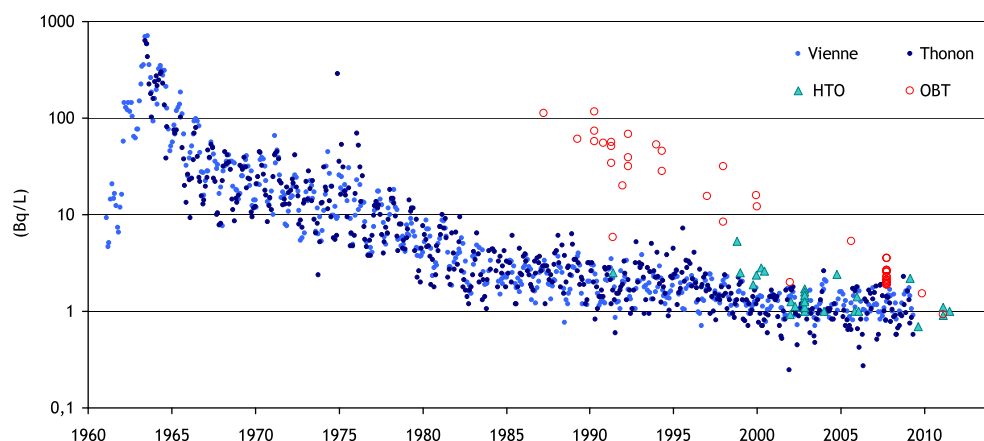


Fig. 1.  $^3\text{H}$  activities in rainwater at Thonon-lès-Bains and Vienne (monthly sampling) and in freshwaters (HTO) (24 samplings) and surface sediments (OBT) (37 samplings) in various French rivers not affected by known anthropogenic sources of tritium; HTO and OBT were detected systematically when investigated.

(Roussel-Debet, 2014b) and was close to the atmospheric specific activity before the first atmospheric tests ( $226 \pm 1$  Bq/kg of C).

Unlike in terrestrial environments, the  $^{14}\text{C}$  in freshwater ecosystems is not in balance with atmospheric  $\text{CO}_2$  on account of its dilution, particularly with the carbonates of old sedimentary rocks. The specific activity beyond the reach of local industry in this environment is therefore lower and varies depending on the content of old carbonates or the presence of fossil organic carbon, as observed in Alpine watersheds (Graz et al., 2011). In France, the data acquired within the continental aquatic systems beyond the reach of industrial sources indicate that the  $^{14}\text{C}$  levels within the matrices studied, i.e., sediments, aquatic plants, filtered water (carbonates) and fish, are significantly lower than the baseline values established for the terrestrial and atmospheric compartment (Fig. 2). The data recorded between 2007 and 2012 show that the levels for all the matrices combined span a relatively broad range of  $94.5 \pm 1.5$  to  $273.3 \pm 2.5$  Bq/kg of C. The lowest values were observed for sediments ( $94.5 \pm 1.5$  to  $234 \pm 3$  Bq/kg of C, with an average of  $186 \pm 21$  Bq/kg of C). The highest levels were recorded for fish ( $199 \pm 1.3$  to  $238 \pm 3.1$  Bq/kg of C). The average value for this matrix ( $219 \pm 9$  Bq/kg of C) was significantly lower than the mean baseline value for the terrestrial environment ( $232.0 \pm 1.8$  Bq/kg of C in 2012). Activities in fishes vary among a large range of values. We think this is mainly due to the various fish species that were investigated among years and rivers depending on available species when samplings occurred for monitoring purposes. We consider further on that fishes reflect the  $^{14}\text{C}$  levels of naturally occurring organic compounds they preferentially consume. These may probably exclude refractory organic compounds (fossil carbon) and inorganic compounds (in particular old carbonates depleted in  $^{14}\text{C}$ ). There are numerous sedimentary basins in France that include 'old' carbonates and fossil carbon (Alps and Cevennes mountains, Loire basin). Nevertheless our data set doesn't allow us to a more focussed investigation. This reinforces the role played by regional heterogeneity on  $^{14}\text{C}$  levels in aquatic systems in particular concerning fishes. These results highlight that dilution by carbonates and/or fossil organic carbon may significantly influence the  $^{14}\text{C}$  activities of the freshwater environments. They also highlight the value of establishing ranges of regional values that take into account palaeoclimatic and lithological heterogeneities. The data obtained for fish indicate that the levels reported over the past 15 years decreased proportionally with the baseline levels of the terrestrial and atmospheric compartment despite significant

dispersion of the distribution of the data ( $n = 28$ ,  $R^2 = 0.21$ ). The relationship established thus makes it possible to assess the  $^{14}\text{C}$  levels expected within this matrix for the coming years (Fig. 2).

#### 4.3. OBT and $^{14}\text{C}$ background levels over the last decades reconstructed from sedimentary archives

Apart from the previous data set and in order to reinforce the medium-term change in the  $^{14}\text{C}$  and OBT background values in continental aquatic environments, a 37.5 cm depth sediment core was collected in June 2011 from a small artificial lake created at Bure in 1978. This area extends beyond the reach of nuclear discharges. The  $^{137}\text{Cs}$  and  $^{210}\text{Pb}_{\text{xs}}$  levels were determined in the various strata of the profile in order to assess the continuity of sediment accretion and the age of the various strata studied. The results indicate relatively constant sedimentation rates, as emphasised by the  $^{210}\text{Pb}_{\text{xs}}$  activity profile (Fig. 3). The average apparent sedimentation rate established from the  $^{210}\text{Pb}_{\text{xs}}$  activities is of the order of 1.2 cm/year. These results indicate that the base of the profile corresponds to the year 1978 and confirms the system creation date. The  $^{137}\text{Cs}$  peak between a depth of 25 and 30 cm may be associated with the atmospheric fallout from the Chernobyl accident and consolidates the age assessment of the various sedimentary strata. The system studied is therefore a continuous, conservative sedimentary record of the flows of solid particles from 1978 to 2011 and is characteristic of an environment beyond the reach of radioactive industrial discharges.

The  $^{14}\text{C}$  levels along the sedimentary profile vary from  $93.7 \pm 1.5$  Bq/kg of C at depth to  $219 \pm 2.1$  Bq/kg of C at surface level. They are significantly lower than the levels reported for the terrestrial environment during this same period (Fig. 3). The results show that the  $^{14}\text{C}$  levels in this system are most probably influenced by inputs of carbonates characteristic of the Bure sedimentary basin. However, the decrease in the  $^{14}\text{C}$  activities with depth within a system of constant accretion cannot be fully explained by these inputs. It may be related to a loss of organic carbon through methane and carbon dioxide emission associated with diagenetic processes (Billett et al., 2007; Garnett et al., 2013a,b). However, the data acquired to date does not make it possible to go any further in the interpretation of these original results.

The OBT levels increase from  $1.25 \pm 0.07$  Bq/L CW to  $1.91 \pm 0.10$  Bq/L CW with depth and demonstrate tritium levels in the organic matter introduced by runoff (allogenic organic matter)

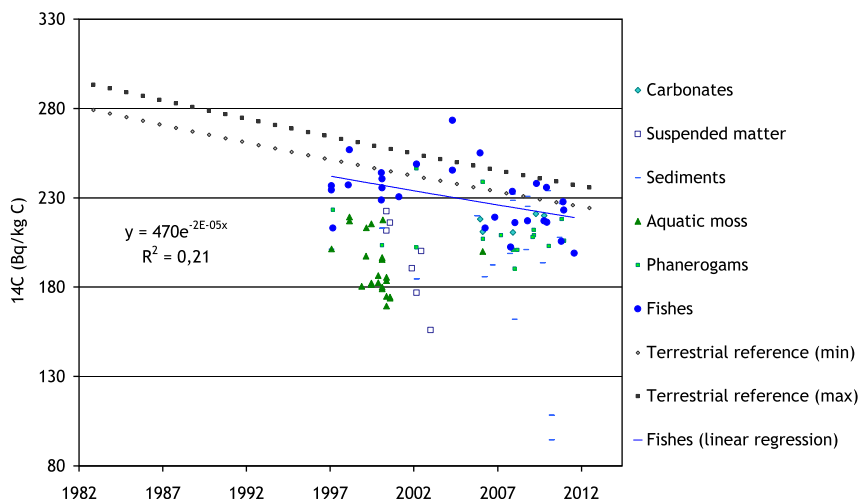
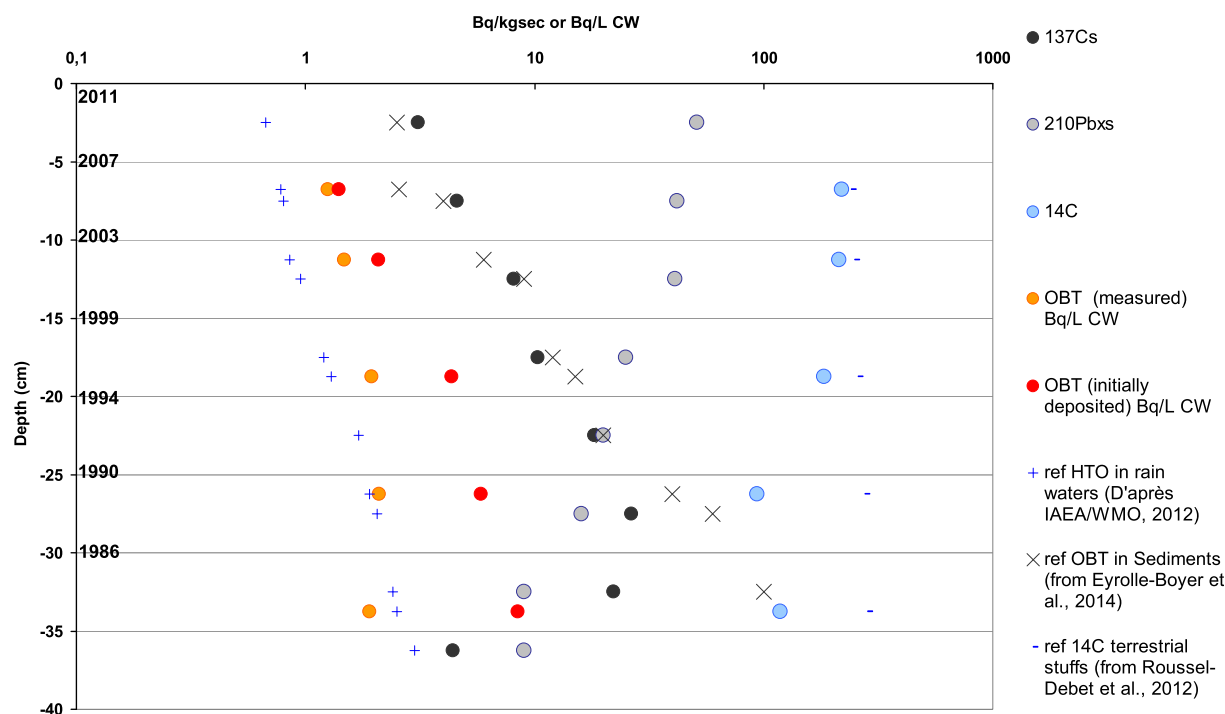


Fig. 2.  $^{14}\text{C}$  activities in Bq/kg C within the different matrices of the continental aquatic environment (carbonates, suspended matter, sediments, aquatic mosses, phanerogams and fishes) and comparison with the minimum and maximum terrestrial background values from Roussel-Debet et al., 2006.



**Fig. 3.**  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}_{\text{xs}}$ ,  $^{14}\text{C}$  and OBT contents in Bq/kg<sub>dry</sub>, Bq/kg C or Bq/L CW (combustion water) in the successive sedimentary strata of a 37 cm depth sediment core collected in a pristine lake (Bure area, North-east France). Referential values associated with the estimated age of the various strata are reported for rain waters, river sediments and terrestrial stuffs for comparison.

or produced within the system (autogenic material) over the past 30 years. The OBT levels in the organic matter of the sediments at the time of their deposition were estimated using the OBT levels measured and by taking into account the radioactive half-life of tritium (12.3 years) (Fig. 3, red dots). Although the results obtained do not cover the entire period of atmospheric contamination by tritium from past atmospheric tests (before 1963 to present day), they seem to make it possible to approximately reconstruct the historic background levels within this environment over the past three decades. Our results show that historic OBT background levels are between the ranges of values recorded for rainwater and those recently reported for river sediments (Eyrolle-Boyer et al., 2014a,b). Furthermore, knowing the characteristic tritium levels in rainwater and river sediments for a given year, the relationship (1) makes it possible to assess the rates of the allochthonous matter within the system studied. Our results show that they vary here between 8 and 35%. Therefore, and as expected, most of the organic carbon in the pond is primarily autogenic.

$$X(\%) = (\text{OBT}_y - \text{HTO}_{\text{ry}}) / (\text{OBT}_{\text{sy}} - \text{HTO}_{\text{ry}}) \times 100 \quad (1)$$

Where  $X$  is the rate of allochthonous matter (in %);  $\text{OBT}_y$  is the tritium content measured within the sedimentary layer of year  $y$  (in Bq/L CW);  $\text{HTO}_{\text{ry}}$  is the tritium content in rainwater recorded during year  $y$  (in Bq/L); and  $\text{OBT}_{\text{sy}}$  is the OBT level characteristic of year  $y$  (in Bq/L CW) (according to Eyrolle-Boyer et al., 2014a,b).

Our work therefore highlights that the sedimentary archives make it possible to provide a relatively good explanation of the  $^{14}\text{C}$  and OBT baseline values that characterise *a posteriori* the continental aquatic systems. We do not exclude that the  $^{14}\text{C}$  and OBT levels recorded in these archives may be affected by diagenetic processes leading to underestimation of their contents. However, our results are, to our knowledge, the first ones that allow us to access to past OBT levels from sedimentary archives and to

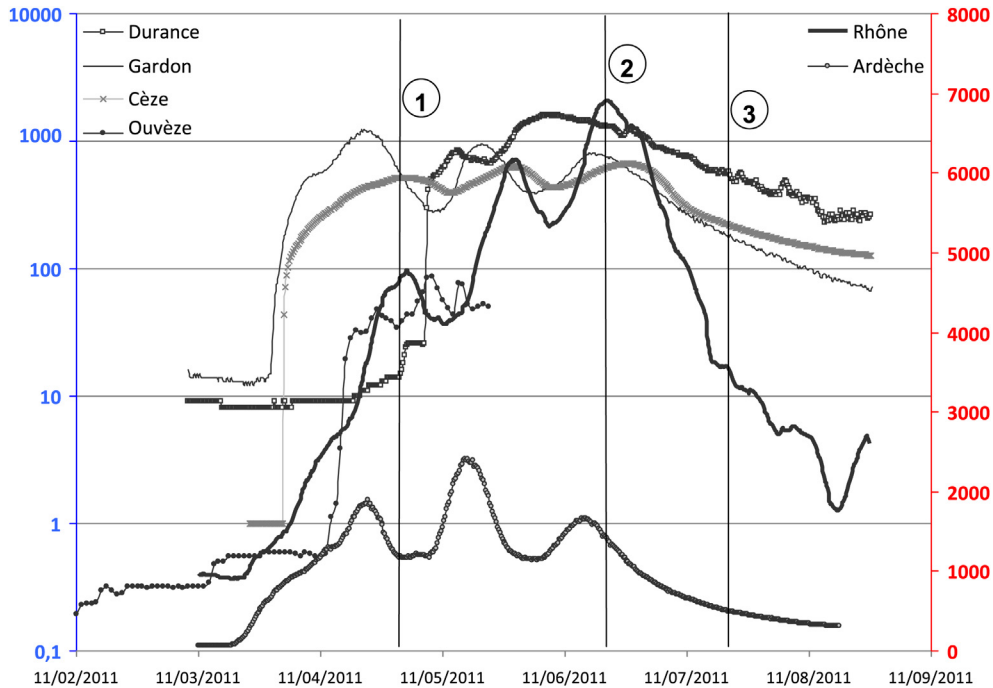
demonstrate the delayed transfer of OBT by the allochthonous suspended matter from soils to aquatic systems.

#### 4.4. Consequence of flood events on OBT and $^{14}\text{C}$ activities in rivers: case of the downstream part of the Rhône River

Floods events largely affect sedimentary storages in aquatic systems by generating sediment remobilisation from the upper stream and the various loading tributaries. Flood events are then expected to considerably modify the OBT and  $^{14}\text{C}$  levels at the various points of a watershed depending on the origin of particles. In this frame we studied the role of a flood event on OBT and  $^{14}\text{C}$  levels at the lower course of a large nuclearized river.

The Rhône is one of the rivers in the world with the most of nuclear facilities. Various nuclear industries have been discharging low-level radioactive liquid releases into its waters since the middle of the 20th century. For the past two decades it has been monitored for gamma emitters by the SORA station located along its lower course downstream of its last tributary and upstream of the seawater influence even during severe low water flows (Eyrolle et al., 2012). The  $^{14}\text{C}$  and OBT activities were measured on samples of suspended particulate matter (SPM) collected during the flood event of November 2011 along the downstream part of the Rhône from the SORA station in order to assess the effect of flooding on the activity levels of these two radionuclides. The flood hydrograph is shown Fig. 4. This flood was started on 4th November 2011 by waters from the southern tributaries of the right bank of the Rhône (tributaries from the Cévennes mountains). On 5th November 2011, it was fuelled by waters from the Durance, its southern tributary along its left bank (subalpine tributary).

The results obtained during this event highlight the significant dilution of the specific activities of these two radionuclides, starting on 6th November 2011, related to the inputs of particles from the watersheds of the Ardèche and Durance rivers (Fig. 5). The

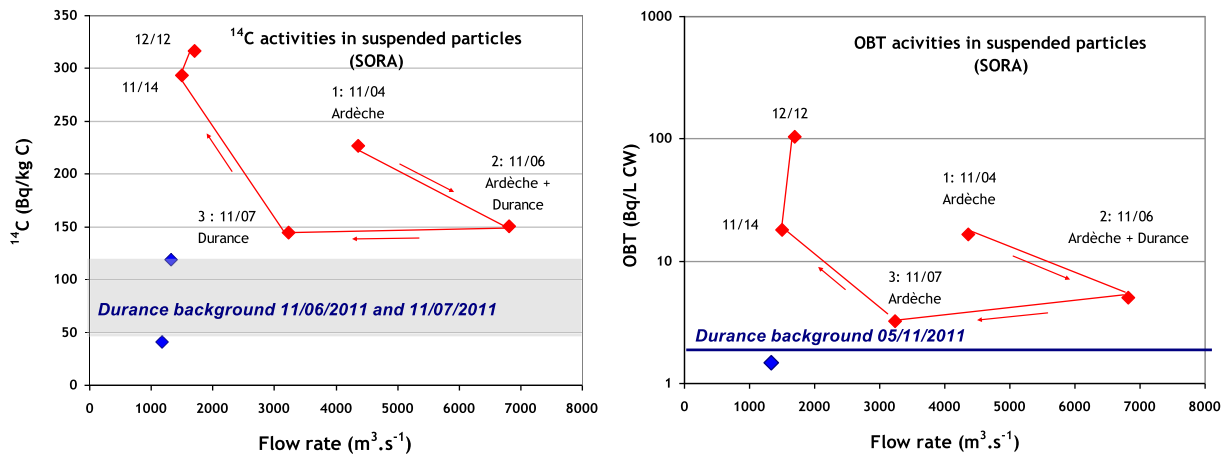


**Fig. 4.** Contributions of the Rhône River's southern tributaries during the flood event of November 2011. Flow rates for the Durance, Gardon, Cèze and Ouvèze tributaries refer to the scale on the left while those registered for the Ardèche tributary and the downstream part of the Rhône River refer to the scale on the right. The circled numbers indicate the dates when the samples were collected during the event. These sampling numbers are also used within the Fig. 5.

clockwise hysteresis loop shows dilution of the activities by related sources made up of the various contributing tributaries. Although we did not have any data prior to the event that would have allowed us to understand and refer to the initial state of the system, the results obtained during the flood show a decrease in the  $^{14}\text{C}$  and OBT activities within the suspended matter in the downstream section of the Rhône River concomitant with the inputs from the Ardèche and then secondly from the Durance. Indeed, the levels observed in the waters of the downstream part of the Rhône on 6th and 7th November 2011 approach the  $^{14}\text{C}$  levels measured in the Durance on 5th and 6th November 2011 ( $41 \pm 1$  and  $119 \pm 1$  Bq/kg of C, respectively) and the OBT levels ( $1.5 \pm 0.5$  Bq/L) measured in the same river on 5th November 2011. No measurements were taken for the Ardèche River. After the flooding subsided on 7th

November 2011, the  $^{14}\text{C}$  and OBT in the system returned to higher levels characteristic of the suspended matter in the downstream part of the Rhône during hydrologically calm periods. The activity levels recorded on 14th November and 12th December are between  $294 \pm 2$  and  $317 \pm 2$  Bq/kg of C for  $^{14}\text{C}$  and between  $18 \pm 1$  and  $104 \pm 6$  Bq/L for OBT. These levels are as much as eight times and seventy times higher than those observed during the flood event studied. This directly reflects the liquid releases from the nuclear industries that are allowed for moderated flow rate range.

These results indicate that inputs of solid particles by some of the Rhône's southern tributaries (the Ardèche and the Durance) lead to significant dilution of the tritium and  $^{14}\text{C}$  carried by SPM in the water of the river's lower course. The same is probably true for all of the Rhône's other tributaries, although resuspension of



**Fig. 5.** Changes in the  $^{14}\text{C}$  (left) and OBT levels (right) during the flood event of November 2011. The background levels measured in the SPM in the Durance River are shown by the blue points and the grey zone. Numbers before dates refer to those defined in Fig. 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

tritium/ $^{14}\text{C}$  sediment inventories affected by the liquid releases of nuclear facilities along the river during flood events is not ruled out. The contribution of these inventories to the flows of  $^{14}\text{C}$  and OBT measured along the lower course of the river is expected to be higher for the tributaries that are likely to affect larger forebays, i.e., for ocean-derived flooding or generalised flooding.

Our results tend to highlight that the OBT and  $^{14}\text{C}$  levels within the suspended particles or sediments downstream of liquid discharge points of nuclear facilities are strongly affected by inputs from tributaries, and thus by hydrology, the origin of previous floods and flood chronologies. These parameters are therefore to be taken into consideration to explain the ranges of variability of the  $^{14}\text{C}$  and OBT activities in the sediments downstream of the liquid discharge points of nuclear facilities and to establish relevant background values.

## 5. Conclusions

Tritium and  $^{14}\text{C}$  are currently the two main radionuclides discharged by industry and particularly by heavy-water reactors (i.e., CANDU reactors). Tritium widely integrates into the water cycle and follows the water mass dynamics but it may equally integrate the carbon cycle for long term, as is the case with  $^{14}\text{C}$  as shown recently by Eyrolle-Boyer et al. (2014a,b). As a result, these two elements persist in both terrestrial and aquatic environments according to the recycling rates of organic matter.

Currently, the mean OBT concentration in the sediments of French rivers is not significantly different from the mean HTO concentration on record for rainwater ( $2.4 \pm 0.6$  Bq/L and  $1.6 \pm 0.4$  Bq/L, respectively). However, regional differences are expected depending on the biomass inventories affected by the global fallout and the recycling rates of the organic matter in the various affected watersheds.

Unlike in the terrestrial environment, the  $^{14}\text{C}$  in freshwater ecosystems is not in balance with atmospheric  $\text{CO}_2$  on account of its dilution, particularly with the carbonates of old sedimentary rocks. The results obtained between 2007 and 2012 for  $^{14}\text{C}$  show that the levels vary between  $95 \pm 2$  and  $234 \pm 3$  Bq/kg of C for the sediments in French rivers and across a slightly higher range of  $199 \pm 1$  to  $238 \pm 3$  Bq/kg of C for fishes. We think that this disparity is probably due to preferential uptake of organic carbon by organisms within the total carbon pool. Overall these values ranges are below the mean background value for the terrestrial environment ( $232 \pm 2$  Bq/kg of C in 2012) mainly due to dilution by carbonates and/or fossil refractory organic carbon transiting through the aquatic systems. These last observations made for  $^{14}\text{C}$  reinforce the value of establishing ranges of regional values, here in order to account for palaeoclimatic and lithological heterogeneity.

This study of a sedimentary record from a pristine lake has made it possible to show that this type of archive can be used to particularly well reconstruct past  $^{14}\text{C}$  and OBT levels despite diagenetic processes that can lead to potential dilution of activities with depth. To our knowledge, this type of investigation on sedimentary archives for these two radionuclides is completely novel. In addition, our work on the sedimentary archives showed that, provided the tritium levels characteristic of rainwater and river sediments are known for a given year, it is possible to assess the proportions of allochthonous/autochthonous organic matter within the system being studied within the various strata. This approach probably provides a new tool to assess the organic matter quality and origin in continental and coastal water systems.

Lastly, our results tend to highlight that the OBT and  $^{14}\text{C}$  levels within the suspended particles or sediments downstream of liquid discharges of nuclear facilities are strongly affected by inputs from pristine tributaries, and thus by hydrology, the origin of floods and

event chronologies. These parameters are therefore to be taken into consideration to explain the ranges of variability of the  $^{14}\text{C}$  and OBT activities in the sediments downstream of liquid discharge points of nuclear facilities and to establish relevant background values.

The work presented in this paper illustrates that the background values for tritium and  $^{14}\text{C}$  within aquatic systems can vary greatly depending on a number of parameters that include the origin, age and quality of the organic matter. The downstream effects of tritium and  $^{14}\text{C}$  discharges from nuclear facilities therefore seem to be highly conditioned by inputs from upstream tributaries, which lead to more or less significant dilution of activity levels, and local primary production which is in balance with the activity levels of the river waters at the time of its production.

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