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ABSTRACT

The Rhone River is one of the most nuclearized river in the world. Radionuclide concentrations in water and suspended sediments transferred to the marine environment were intensively monitored in this river over the last decades (2002–2018). Over this period of time, more than 12 and 25 time integrating samples were collected each year in filtered waters and suspended sediments, respectively, and analyzed for their radionuclide contents at ultra-trace levels by using top performance analytical tools. While more than 60% of plutonium, americium, cesium, cobalt, silver, beryllium and actinium radioisotopes are carried by sedimentary particles, sodium, tritium, antimony and strontium are mainly exported as dissolved species (>90%) due to their low affinity with particles. Most natural radionuclides contents show low seasonal variation. No significant trends are observed over the last two decades for these elements, even for ^{40}K widely used in fertilizers after the middle of the last century, indicating that the basin has currently converged towards geochemical equilibrium for all of them. In contrast, the concentrations of numerous anthropogenic radionuclides originating from nuclear industries significantly declined since the beginning of the 2000s. Assuming no change of the current anthropic and climatic pressures over the next decades, apparent periods, i.e. the time required for a reduction by half the concentrations in the downstream part of the Rhône River, would be close to 6 years for most artificial radionuclides, except for tritium and other artificial radionuclides conveyed to the river by soil leaching and erosion (^{90}Sr, ^{241}Am, plutonium isotopes) which would be far longer. Referring to regional referential backgrounds, only few anthropogenic radionuclides specifically produced by nuclear industries are still detectable at the downstream part of the Rhone River and excess contents of tritium, ^{238}Pu and ^{241}Am are observed in filtered waters.

1. Introduction

Numerous organic or inorganic contaminants and chemical parameters were monitored for decades in many river systems all over the world. Time series acquired most generally constitute useful tools to assess environmental impact from anthropic pressures exerted over time, address pollutant trajectories and forecast modelling (e.g., Meybeck et al., 2008; Molle and Wester, 2009; Duan et al., 2018; Ghashghaie et al., 2018). Since the middle of the last century when nuclear industries have developed, contents of naturally occurring and anthropogenic radionuclides are widely investigated within the various environmental compartments around the world due to the radiotoxicity of these elements. Radionuclides display a large range of physico-chemical properties and cannot be always directly compared to the behavior and fate of their homologous stable element (Gil-Díaz et al., 2020). Time series from high frequency monitoring of radionuclides are regularly reported in the literature for river systems (e.g., Palms et al., 2007; Eyrolle et al., 2008; Maringer et al., 2009;) or marine environments (e.g., Thompson, 1988; Topçuoğlu et al., 2010; Buesseler et al., 2017), giving precious data sets for environmental impact and resiliency assessment of hydro systems faced to these contaminant family.

The Rhone River is one of the most nuclearized rivers in the world, with four Nuclear Power Plants (Bugey, Saint-Alban, Cruas and Tricastin) and a spent fuel reprocessing center (Marcoule) that has undergone dismantlement since 1997. These installations use the Rhone River waters for cooling the reactor and diluting liquid effluents with low levels of radioactivity that they produce and discharge in regards of the regulations.

The river is also the receptacle of erosion products from the soils of a watershed covering nearly a fifth of the surface area of continental France. Such eroded products contain both radionuclides of natural origin as well as radionuclides of anthropogenic origin due to their remanence in soils since the atmospheric fallout of nuclear tests and the Chernobyl accident (Leroux, 2007; Eyrolle et al., 2012; Zebracki et al., 2013b).

The Rhone River is a considerable water resource at the inter-regional scale, notably for irrigation and drinking water supplies. Lastly, it is one of the major rivers flowing into the Mediterranean Sea and exports the major part of freshwater and sediment fluxes provided by continental surfaces in this marine environment (Ludwig et al., 2009; Panagiotopoulos et al., 2012).

For almost two decades, the SORA monitoring station (Rhone Observatory Station at Arles), located at the downstream part of the Rhone River, collected water and suspended sediments to determine the concentrations of numerous gamma, beta and alpha emitting radionuclides. Thanks to samples of large volumes of water and high performance metrology capable of analyses at very low levels, SORA allows the detection of a multitude of anthropogenic radionuclides now present at trace levels, notably in filtered waters (Antonelli, 2017).

The aim of this article is to (1) make known the current levels of natural and anthropogenic radionuclides in waters at the downstream part of the Rhone River, (2) describe the trajectories of these trace elements, i.e. temporal trends over the studied period and (3) contrast these data with data sets acquired from surrounding coastal rivers preserved from industrial nuclear discharges in order to estimate excess contents and environmental impact.

2. Method Summary

2.1 Samples and samplings

2.1.1 Monitoring station on the lower course of the Rhone River (SORA)

Suspended sediments (SS) and filtered water (FW) samples were collected according to a protocol described by Masson et al. (2004). Briefly, outside flood periods, a composite sample (7000 L) resulting from samples (13.5 L) taken every 80 minutes is collected over a period of about one month. During flood periods (discharges over 3 000 m^3/s), the composite sample is produced using 5 L samples taken every 60 minutes over 24 hours and directly filtered onto 0.5 µmMilligard® cellulose acetate cartridges. The filter clogging is continuously monitored, so that the filtration is stopped when 50% of clogging was achieved or after 8 h. Radionuclide analyses are performed on the particulate fraction and on the dissolved fraction (fraction less than 0.5 µm). Additionally, a Time integrated sediment sampler (TISS) continuously collected SS for 1 month for organically bound tritium (OBT) analyses and a time integrated water sampler, preserving water samples from atmospheric exchanges, collected few milliliters per 80 minutes for tritium (HTO) analyses after a subsampling of 50 mL filtered with 0.22 µm glass fiber filters.

2.1.2 Regional referential backgrounds: Orb and Hérault rivers

The SS and FW samples were collected each two years between 2011 and 2017 in the non-nuclearized coastal rivers Orb (Cessenon-sur-Orb) and Hérault (Aspiran) in order to acquire regional environmental references (Figure 1). Water samples are directly filtered onto 0.5 µmMilligard® cellulose acetate cartridges. The filter clogging is

continuously monitored, so that the filtration is stopped when 50% of clogging was achieved or after 8 h. Radionuclide analyses are performed on the particulate fraction and on the dissolved fraction (fraction less than 0.5 µm). For tritium analyses 70 mL water samples were filtered in situ using a syringe equipped with a 0.22 µm glass fiber filter, placed in a preconditioned amber glass flask and stored at 4°C until analyses.

2.2 Radionuclide analyses

2.2.1. Gamma emitters

For gamma spectrometry analyses SS samples were ashed and FW samples were slowly evaporated (40°C) to dryness. All the samples were put into tightly closed plastic boxes for gamma counting (20–60 g) using low-background and high resolution Germanium Hyper pure detectors at the IRSN/LMRE laboratory in Orsay (Bouisset and Calmet, 1997). For each sample, up to 25 gamma emitting radionuclides (both natural and anthropogenic) were determined. Efficiency calibrations were constructed using gamma-ray sources in a 1.15 g/cm^3 density solid resin–water equivalent matrix. Activity results were corrected for true coincidence summing and self-absorption effects (Lefèvre et al., 2003). Measured activities, expressed in Bq/kg dry weight or Bq/L, are decay-corrected to the date of sampling. The activity uncertainty was estimated as the combination of calibration uncertainties, counting statistics, and summing and self-absorption correction uncertainties.

2.2.2. Alpha emitters

When available sample amount was sufficient (i.e., 50–200 g of dry matter), analyses of plutonium isotopes (238Pu and 239 + 240Pu) and other transuranium elements (^{241}Am, ^{244}Cm) were performed by alpha spectrometry at IRSN/LMRE (Goutelard et al., 1998; Lansard et al., 2007). In brief, ashed samples were leached with nitric acid, co-precipitated and purified using exchange resins before electro-deposition, and then counted on low background PIPS® detectors for up to 14 days. The detection limit for the analytical procedure was 1 mBq for both ^{238}Pu and $^{239+240}$Pu.

2.2.3. ^{90}Sr analyses

In brief, samples were ashed and leached with hydrochloric acid. Strontium was separated through oxalate precipitation. Impurities were removed with hydroxide precipitation then another oxalate precipitation following

by Eichrom Sr-resin for separation of strontium. Equilibrium reached with yttrium. Then Y-90 was measured as yttrium oxalate by gas proportional counter. Yield was measured with Sr-85 tracer by gamma spectrometry (NF ISO 18589-5, 2009).

2.2.4. HTO and OBT analyses

HTO analyses were performed by the so-called conventional liquid scintillation counting (LSC) (AFNOR, 2015). The decision is 0.65 Bq/L (10 mL, 17 h counting). OBT analyses were performed 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). This method is generally used when the samples contain little organic matter (%H<2%), determines the ^{3}He levels produced by the decay of the ^{3}H contained in the sample after normalization of the values to ambient atmospheric levels ($^{3}He/^{4}He$) and correction of the radiogenic ^{4}He levels contained in the sample (gaseous inclusions). $^{3}He/^{4}He$ are measured by mass spectrometry (MS). The analysis results are expressed in Bq/kg_{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.

3. Origin of radionuclides in the Rhone River

3.1. Naturally occurring radionuclides

Natural radioactivity is mainly due to primordial telluric radionuclides from ^{238}U, ^{232}Th families and ^{40}K. The ^{238}U and ^{232}Th families comprise 14 and 10 daughter nuclides, respectively including ^{234}Th and ^{234m}Pa for the former, and ^{228}Ac for the latter. These mother radionuclides present on earth since their origin have very long radioactive half-lives (4.5 billion years for ^{238}U, 14 billion years for ^{232}Th). In rivers, most of radionuclides from this natural origin originate from the drainage of soils in the watershed even though their use over the nuclear fuel cycling for military and industrial purpose can be expected to modify their natural contents and trajectories at local or regional scales. Naturally occurring radionuclides are also produced continuously in the atmosphere under the action of cosmic radiation. Radionuclides involved in these latter processes are for example ^{3}H, ^{14}C, ^{7}Be and ^{22}Na. These cosmogenic radionuclides are deposited on soil surfaces by rains and finally converged to river systems by drainage of the watershed soils (Le Roux, 2007; Zebracki et al., 2013a, 2013b; Eyrolle-Boyer et al., 2014c).

Geological and climatic diversity, as observed at the regional scale, leads to a considerable spatial variability of the contents of natural radionuclides in soils and river systems (Le Roux, 2007). Additionally, due to their specific physicochemical properties, radionuclides from natural origin are liable to be enriched or depleted in various environmental compartments leading to disequilibrium from initial sources. Those results in natural radioactivity being strongly dependent on geological and environmental conditions, whether in the soils, sediments or river waters.

The ^{40}K and families of ^{238}U and ^{232}Th contribute the most to the natural radioactivity of rivers, most generally in close proportions, whether in the dissolved or particulate phases (Eyrolle et al., 2008).

3.2. Anthropogenic radionuclides

Anthropogenic radionuclides were initially introduced in the environment at the beginning of the last century through the use of their luminescent properties (radium, tritium) in watchmaking workshops. Various radionuclides were then introduced from the middle of the 20th century by the military and industrial uses of nuclear energy.

Anthropogenic radionuclides currently conveyed by the Rhone River have several origins:

- Atmospheric fallout from nuclear tests carried out between 1945 and 1980 and that from the Chernobyl accident. Although most of the short-lived and medium-lived radionuclides (i.e., $T_{1/2} < 5$ years) originating from these fallouts have disappeared from the environment due to their radioactive decay, residual contents in ^{137}Cs, ^{90}Sr and in transuranium elements (^{238}Pu, $^{239+240}Pu$, ^{241}Am) were registered in the soils of the Rhone basin (Perkins and Thomas, 1980; Duffa, 2001; IRSN, 2013). These residual radionuclides are progressively transferred to the river systems as dissolved species and/or associated with solid particles by soil leaching and erosion processes.

- Liquid discharges from nuclear industries located along the Rhone River carried out according to regulations: the spent nuclear fuel reprocessing plant of Marcoule (under dismantlement since 1997), the Nuclear Power Plants (NPP) of Bugey, Saint-Alban, Cruas and Tricastin and, to a lesser extent, the sites of Pierrelatte and Creys-Malville NPP's which is being dismantled. The center of Marcoule still contributes today to significant industrial discharges of radionuclides into the Rhone River waters (Antonelli; 2008b; Eyrolle et al., 2012a; Eyrolle et

al., 2012b; Eyrolle-Boyer et al., 2015a). Tritium is currently the preponderant radionuclide released in waters by nuclear facilities in France. At the downstream part of Rhone River, more than 95% of tritium and around 50% of ^{14}C originate nowadays from the liquid discharges from the nuclear industry (Eyrolle et al., 2013; Eyrolle-Boyer et al., 2015a).

- Hospital discharges. Several diagnostic and care units using radioactive sources are installed along the Rhone River and several of its tributaries. The radionuclides used are generally short-lived (e.g. ^{131}I, $T_{1/2}$=8 days) and quickly disappear from the environment.

- Liquid discharges from installations located on tributaries of the Rhone River, such as the AREVA plant and the Research Institute of Grenoble both on the Isère River and the Cadarache Center on the Durance River.

- Tritiated residues from watchmaking workshops installed on the watershed of the upper Rhone since the middle of the 20th century (e.g., Krejci and Zeller, 1979; Jean-Baptiste et al, 2007). These compounds discharged into the environment are most probably in the form of refractory sub-micrometric particles (polystyrene) even though they have never been characterized precisely. As a consequence, relatively high contents of organically bound tritium (OBT) are observed along the whole length of the river (Eyrolle et al., 2018; Jean-Baptiste et al, 2019). The use of tritium in watchmaking has decreased from the 1970s in Switzerland, and it has been forbidden in France since 1990 and in Switzerland since 2007 (Morereau et al., in prep).

4. Results and discussion

4.1. Solid/solution partitioning of radionuclides in waters of the downstream part of the Rhone River

In river waters, most stable and radioactive trace elements are distributed among the dissolved and particulate phases. These distributions depend upon various parameters including the chemical properties of the element, the nature and concentration of suspended sedimentary particles, the physicochemical characteristics of river waters such as pH and ionic strength. It is most generally assessed by apparent distribution coefficient (Kd, in L/kg), expressing the partition of the element between the two phases (Abril et Fraga, 1996). The greater the propensity of the radionuclide to be fixed onto particles, the higher the Kd value. Conversely, the more the element remain in

177 solution, the lower it is. Table 1 shows, in decreasing order, the mean and standard deviations of the Kd values of
178 the main radionuclides quantified over the 2002-2018 period for the downstream part of the Rhone River. These
179 Kd values are in good accordance with the IAEA Kd distributions for all the anthropogenic radionuclides: ^{241}Am,
180 ^{60}Co, ^{54}Mn, ^{137}Cs, ^{239,238}Pu, ^{90}Sr and ^{244}Cm. For naturally occurring radionuclides, the accordance is correct for ^{7}Be,
181 ^{226,228}Ra, ^{234,238}U, ^{40}K and ^{228}Th but not for ^{234}Pa, ^{232,230,234}Th and ^{125}Sb for which the Kd values in the downstream
182 part of the Rhone River are one order of magnitude lower than the 5th percentile of the IAEA Kd distributions.

183 Amounts of radionuclides transferred by suspended sediments, ASS in %, are related to Kd and SS content owing
184 the following theoretical relationship :

185 $$ASS = 100*Kd*SSC / (1 + Kd*SSC)$$

186 with Kd in L/kg, and SSC, the suspended sediment content, in kg/L.

187 The ASS were calculated for the various radionuclides based on mean Kd values determined over the 2002-2018
188 period and the mean SSC of the downstream part of the Rhône River which is 50 mg/L during this same period.
189 Figure 2 shows that more than 60% of plutonium, americium, cesium, cobalt, silver, beryllium and actinium
190 deliveries towards the marine environment are associated with solid particles due to the strong affinity of these
191 elements with SS (high Kd values). In contrast, sodium, tritium, antimony and strontium are mainly exported as
192 dissolved species (>90%) due to their low affinity with particles (low Kd values). ASS calculated in this study with
193 the mean values of Kd and SSC are very close to ASS reported in Antonelli, 2017 which were estimated from the
194 yearly monitoring of SS content, flow rate and radionuclide concentration in dissolved and solid phases (Figure 3).
195 These results highlight the relevance of both Kd values determined at the downstream Rhone River and
196 dissolved/solid exports quantified from monitoring.

197 4.2 Radionuclide contents in suspended sediments and trajectories

198 4.2.1. Naturally occurring radionuclides

199 ^{40}K, ^{7}Be and daughter elements from ^{238}U and ^{232}Th chains, such as ^{234m}Pa and ^{228}Ac, contribute for the greater part
200 of radioactivity of natural origin of suspended sediments transported by the Rhone River as generally observed in
201 most of environmental media (Le Roux, 2007, Eyrolle et al., 2008, Laubenstein and Magaldi, 2008; Eyrolle et al.,

202 2012a,b). It is not expected that concentrations of radionuclides of natural origin change over time at human scale
203 and measures performed since the 2000s have shown the relative stability of concentrations over this timescale
204 (Figure 4). However, intra-annual variations of the concentrations of various radionuclides from telluric origin, such
205 as ^{228}Ac and ^{40}K, should be emphasized. For these elements, time series concentrations indicate minimal
206 radionuclide contents during spring and maximal values during autumn. These observations are most probably
207 explained by the nature and origin of the minerals transferring these elements according to Rhone River's
208 hydrology characterized by contrasting geo climatic water mass supplies among the year at basin scale (Pardé,
209 1925; Pont, 1997; Ottlé et al., 2001). Moreover, in the case of ^{40}K, the utilization of potassium-based fertilizers can
210 disturb natural concentrations and their seasonal variations. At the beginning of the 1990s, excess contents in ^{40}K
211 were recorded in the suspended matter of most French hydrosystems (Figure 5). These contents have decreased
212 since this period in most watersheds as reported in Grosbois et al. (2016). Our data indicate that ^{40}K contents in
213 suspended sediments at the downstream part of the Rhone River are stable since almost two decades (2002-2018)
214 with a mean value of 477±97 Bq/kg, which is about half ^{40}K contents registered in the middle of the 2000s for the
215 Loire River draining important sedimentary basin surfaces. These results underline that anthropic pressures
216 associated with potassium-based fertilizer uses would have declined towards geochemical backgrounds for the
217 Rhone River suggesting resiliency recovery for this radionuclide. Nevertheless, observations on longer time scale
218 are needed to confirm this trajectory.

219 The ^{7}Be is a short-lived radionuclide of cosmogenic origin that disappears relatively quickly from the environment
220 due to its short radioactive decay ($T_{1/2}$=53 days). The ^{7}Be contents vary over a wide range of values in comparison
221 with other naturally occurring radionuclides. Its contents strongly depend on both the age of the river water
222 masses and precipitation amounts in the watershed. High ^{7}Be contents would point to recent contribution of
223 rainwaters and rapid transfer of waters and particles from the watershed surfaces towards the river. During flood
224 events, particles are most generally depleted in ^{7}Be due the contribution of older materials that no longer contain
225 ^{7}Be through remobilization of bed sediments or deep soil erosion. The ^{7}Be therefore contribute more sporadically
226 than the other naturally occurring radionuclides to the natural radioactivity of suspended sediments in transit in
227 the river.

4.2.2. Anthropogenic radionuclides

Radioactive discharges from nuclear industries performed under regulation are not continuous. Anthropogenic radionuclide contents obviously depend on the fluctuation of radioactive discharges from nuclear industries when these latter constitute the major source term. Furthermore, rising flow rates and suspended sediment concentration most generally lead to the decrease of anthropogenic radionuclides contents owing to dilution with the sediments delivered by tributaries (Eyrolle et al., 2012). This trend has been widely reported for trace metals and is suggested to be due to a higher contribution of coarse materials and/or to the erosion of less polluted sediments (e.g., Schleichert 1975; Bradley and Lewin 1982; Dawson and Macklin 1998).

Concentrations in anthropogenic radionuclides are significantly lower than those of natural radionuclides, by one or two orders of magnitude (Figure 4). The radionuclides of anthropogenic origin detected in 2018 in the suspended sediments of the downstream part of the Rhone River are, by decreasing order of contents, ^{137}Cs, ^{60}Co, ^{241}Am, ^{90}Sr, OBT, $^{239+240}$Pu, ^{238}Pu and ^{244}Cm. Among these radionuclides, only ^{60}Co and ^{244}Cm originate only from nuclear industries. The other ones are also contributed by soil erosion of the watersheds submitted to atmospheric fallout from past nuclear tests and the Chernobyl accident. The ^{58}Co is no more detected since 2012 in suspended sediments, likewise ^{110m}Ag and ^{54}Mn since 2014. In 2018, as in previous years, ^{137}Cs is the preponderant radionuclide of anthropogenic origin in suspended sediments with contents ranging from 4.1±0.6 to 43.9±1.1 Bq/kg$_{dry}$, i.e. values close to those recorded during previous years. The ^{60}Co, detected in 2018 in 100% of the samples, also remains a preponderant anthropogenic radionuclide in the suspended sediments transiting in the lower part of the Rhone River. Its concentration, ranging from 0.7±0.2 to 12.4±1.6 Bq/kg$_{dry}$ in 2018, are significantly lower than those of ^{137}Cs, on average by a factor of 4 over the period 2002-2018 (Figure 6). Time series indicate very close reductions of contents for these two radionuclides since the beginning of the 2000s (Figure 6). This observation could point to a same predominant origin, and would indicate that most ^{137}Cs continues today to originate from nuclear industries; contribution from watershed erosion being secondary as observed at the beginning of the 2010s (Eyrolle et al., 2014a).

Effective (or apparent) periods (EP), i.e. the time required for a reduction by half of radionuclide contents in environmental media, can be assessed from time series by considering exponential type decreasing over a given period of time, following the theoretical relationship:

$$SSR = a*\exp^{(Ln2/EP)*t}$$

with SSR, the content of radionuclides in suspended sediments, in Bq/kg_{dry}, a, the initial content at t=0, t the time, in day, and EP the effective period, in day.

The EP includes both radioactive decay and natural dilution/dispersion processes and are useful tools to assess both dilution processes in environmental compartments and predict temporal trends of pollution levels. Exponential type relationships obtained for ^{137}Cs and ^{60}Co over 2002-2018 are reported in Figure 6. Calculated EP are both close to 6 years which is as expected shorter than radioactive decay periods of ^{137}Cs ($T_{1/2}$=30.1y) and ^{60}Co ($T_{1/2}$=5.2y). These results would reflect the reduction of anthropic pressure (reduction of industrial radioactive discharges) as well as the efficiency of the Rhone River system to dilute and remove particle reactive contaminants.

The ^{90}Sr contents are almost stable since the two last decades, varying from 0.25±0.08 Bq/kg_{dry} to 1.8±0.3 Bq/kg_{dry}. The transuranium elements ($^{239+240}Pu$, ^{238}Pu, ^{244}Cm and ^{241}Am) are most generally detected at very low levels in suspended sediments following radiochemical extraction and purification steps. In 2018, their contents ranged from 0.27±0.04 to 7.7±0.1 Bq/kg_{dry} for ^{241}Am, from 0.09±0.02 to 0.33±0.04 Bq/kg_{dry} for $^{239+240}Pu$, from 0.011±0.002 to 0.07±0.01 Bq/kg_{dry} for ^{238}Pu, and from 0.003±0.0001 to 0.09±0.02 Bq/kg_{dry} for ^{244}Cm. Each of these ranges extends over several orders of magnitude and no significant temporal trend can be pointed out among the two last decades. These results suggest long resiliency periods for the river system regarding these latter elements whatever are their origins assuming no change of the current climatic and anthropic pressures.

The $^{238}Pu/^{239+240}Pu$ activity ratio (AR) is a useful tool to discriminate the origins of plutonium isotopes among industrial discharges and soil erosion. Figure 7 shows that industrial releases still contribute today to a significant marking of suspended sediments in this part of the river. Indeed, AR measured in 2018, ranging from 0.024±0.002 to 0.136±0.008, are in most of cases significantly higher than AR characterizing atmospheric fallout, i.e. eroded products form the soils (0.03; Hirose and Povinec, 2015). Calculations resulting from AR mixing equations (Rolland,

2006) indicate that about 40% of the $^{239+240}$Pu and 80% of ^{238}Pu measured in 2018 in the suspended sediments would come from industrial releases. In the 1990s, these proportions were both close to 100%. Part of these amounts can obviously originate from contaminated sediment remobilization from sedimentary reservoirs. These results reinforce that without any modification of the current climatic and anthropic pressures the resiliency of the Rhone River face to plutonium industrial inputs from the spent fuel reprocessing plant will be long (> 50 years).

Since 2008, OBT analyses are performed on suspended sediments collected at SORA. OBT contents directly depend on organic matter contents and vary over a wide range of values, from 0.05±0.01 to 5.34±0.27 Bq/kg_{dry}, i.e. values close to ^{90}Sr contents for example. OBT contents in suspended sediments expressed in Bq/L of combustive water (Bq/L_{cw}) allow considering the carrying organic phase only (Eyrolle et al., 2018). Between 2008 and 2018, OBT concentrations varied over a wide range, from 3.21±0.84 to 141±7 Bq/L_{cw}. These levels are far higher than referential values recorded in sediments of non-industrialized rivers, i.e. river systems preserved from liquid releases of nuclear installations, i.e. 2.4±0.6 Bq/L (Eyrolle-Boyer et al., 2015b; Ducros et al., 2017). These are also most generally higher than free tritium contents (HTO) in the Rhône river waters (varying from 1.0±0.7 to 61.5±2.7 Bq/L) (Figure 8). Such gap between HTO and OBT contents, reaching in some cases one order of magnitude, univocally testify additional non-nuclear sources of tritium in the River. These additional sources associated with watchmaking workshops installed on the watersheds of the Upper Rhone in the middle of the last century were already widely related in the literature (Jean-Baptiste et al, 2007; Jean-Baptiste et al, 2019; Eyrolle et al., 2018). No clear trend can be drawn for OBT contents in suspended sediments from the data set acquired over the 2008-2018 period in this part of the River, due to both the high variability of OBT contents and the short period of time available.

Since the beginning of the 90's when society started to act for environmental protection and limitation of anthropic pressures, the contents of numerous pollutants, including trace metals, persistent organic substances and radionuclides from the nuclear industry, significantly decreased in various environmental compartments (e.g. Desmet el al., 2012; Ferrand et al., 2012; Grosbois et al., 2012). Resiliency of the Rhone River face to anthropogenic radionuclides would depend on several parameters such as their radioactive decay period, their propensity to fix onto particles, their origin and the capacity of the river system to export sediments.

4.3. Radionuclide contents in filtered waters and trajectories

4.3.1. Naturally occurring radionuclides

As observed for suspended sediments, ^{40}K and the different affiliated elements of the chains of ^{238}U and ^{232}Th, such as ^{234m}Pa and ^{228}Ac, make up the major part of the radioactivity of natural origin in filtered waters (<0.45µm) of the Rhone River (Figure 4). The ^{40}K contents in the filtered waters show low seasonal variations, with minima in summer (0.04±0.02 Bq/L) and maxima in winter (0.06±0.02 Bq/L). This seasonal variability, nonetheless out of phase by about 3 months with that of suspended sediments, most probably reflects natural processes such as soil leaching and water mass cycling and dilution.

The ^{7}Be is present in significantly lower and more variable concentrations than those of telluric origin. The ^{7}Be is mainly associated with particles as testified by its high Kd value (Table 1). As previously described, ^{7}Be contents in waters depends to a great extent on the age of the masses of water in transit and of the occurrence of precipitations on the watershed. Thus, depending on climatic forcing, ^{7}Be contents may extend over more than two orders of magnitude as previously reported for suspended sediments.

Sodium is widely present in the environment mainly as highly mobile dissolved species. The ^{22}Na ($T_{1/2}$=2.6y) is a comosmogenic radionuclide which is not detected in suspended sediments. Its contents in filtered waters are constant over years, without any significant seasonal variation, and are about one order or magnitude below those of other radionuclides of natural origin (Figure 4).

As underlined for suspended sediments, concentrations in radionuclides of natural origin in filtered water are generally stable in time, at the inter-annual scale.

4.3.2. Anthropogenic radionuclides

With the exception of tritium (^{3}H), concentrations in anthropogenic radionuclides are significantly lower than those of natural radionuclides, most of them by several orders of magnitude (Figure 4). Tritium, of which 95% is of anthropic origin in the Rhone River (Eyrolle et al., 2013; Eyrolle-Boyer et al., 2015a), is the preponderant radionuclide in filtered waters of the river since decades. Over 2006-2018, tritium contents in time integrated water samples (one month) ranged at least one order of magnitude, from 1.0±0.7 Bq/L to 61.5±2.7 Bq/L, with a

mean value of 6.0±5.4 Bq/L. Daily samplings performed in 2013, from mid of January to the end of April, underline the amplitude of intra-monthly variabilities of tritium contents due to the non-continuous liquid discharges from nuclear industries (ranging from 1.0±0.7 Bq/L to 21.5±2.3 Bq/L).

Besides tritium, $^{90}Sr > ^{137}Cs > ^{60}Co$ show the highest concentrations. The ^{90}Sr contents in filtered waters are mainly due to the low Kd value of this element (550±90 L/kg). The ^{90}Sr contents were almost stable over the studied period, ranging from 0.60±0.1 10^{-3} Bq/L to 0.73±0.03 10^{-2} Bq/L over 2002-2018 (mean value 0.002±0.001 Bq/L).

In 2018, ^{137}Cs and ^{60}Co contents ranged from 0.055±0.008 10^{-3} Bq/L to 0.28±0.03 10^{-3} Bq/L and from 0.017±0.004 10^{-3} Bq/L to 0.037±0.018 10^{-3} Bq/L, respectively. Since the beginning of the 2000s, contents of these latter radionuclides have decreased by around a factor of 4 as closely recorded for suspended sediments.

The ^{58}Co, $^{124,125}Sb$ and ^{131}I were not detected in any of the filtered water samples since 2012. The $^{239+240}Pu$, ^{238}Pu, ^{241}Am and ^{244}Cm contents are between one and more than three orders of magnitude below the range of contents observed for ^{90}Sr, ^{137}Cs and ^{60}Co. They do not show any significant decrease over the monitoring period (2004-2018), except for ^{238}Pu whose contents would decrease by one order of magnitude over this period. For this latter radionuclide, EP assessment based on this time series appears to be quite similar to those calculated for ^{137}Cs and ^{60}Co either for suspended sediments or filtered waters, i.e. 6 years. This reinforce that all these anthropogenic radionuclides originate from a predominant single source, i.e. industrial releases.

4.4. Comparison to regional referential backgrounds

Excess contents due to anthropic pressures can be addressed by using referential background values. Works related to enrichment factors or geo-accumulation index characterization referring to referential backgrounds are widely reported in the literature for many contaminants (e.g. Salomons W. and Forstner, 1984; Global Investigation of Pollution in the Marine Environment, 1999; Feng et al., 2011; Ferrand et al., 2012; Barbieri, 2016). As for many other trace elements, e.g. trace metals, referential backgrounds for naturally occurring or artificially produced radionuclides are expected to vary over a wide range of values at the regional scale (Leroux, 2007; Eyrolle et al., 2008). Among many environmental parameters that can be involved in such variability soil type in the catchment, soil erosion and the amount of atmospheric fallout from past nuclear tests and the Chernobyl accident

would be the predominant ones (Zebracki et al., 2013a,b). Finally referential background values, i.e. addressing pre-anthropic pressure levels, are needed for environmental resiliency assessment.

The Hérault and Orb coastal rivers (Figure 1) were used as regional referential systems in order to assess the impact of anthropic pressures exerted by nuclear industries located along the Rhone valley on suspended sediments and filtered waters transported at the lower part of the Rhone River.

Our results show that mean contents of natural radionuclides from telluric origin (^{238}Ac, ^{234}Pa, ^{40}K) recorded in suspended sediments from Orb and Hérault rivers are close to those characterizing the Rhone River even though inter-annual variation, expressed by standard deviation (SD), can be observed (Table 2). The ^{7}Be contents in the suspended sediments of Orb and Hérault rivers show high inter-annual variabilities (SD>50%) nevertheless falling within the ranges of variation registered for the Rhone River.

Naturally occurring radionuclide contents in river systems strongly depend on hydrology, in particular the origin of water and sediment deliveries from the soils in the catchments and on the quality of materials transported (Leroux, 2007). Our results show that at the studied regional scale, although including contrasting watersheds spreading over Alps, Cevennes or Pyrenees mountainous areas, all these parameters do not significantly influence mean natural radionuclide contents.

These results suggest that for naturally occurring radionuclides, geochemical heterogeneity would most generally dominate anthropic pressures associated to nuclear fuel cycle exploitation in the Rhone valley. These results do not exclude that excess contents of these radionuclides could be reached at more local scales.

For anthropogenic radionuclides expected in regional rivers (^{137}Cs, ^{90}Sr and transuranium elements ^{238}Pu, $^{239+240}$Pu, ^{241}Am) the contents observed in the Hérault River were similar to those measured in the lower part of the Rhone River. However for most of these radionuclides, contents recorded in the Orb River were higher than those found in the Rhone River. For example, the concentrations in $^{239+240}$Pu measured between 2011 and 2017 in the suspended sediments of the Orb River were between 2 and 10 times higher than the concentrations in $^{239+240}$Pu recorded in the lower part of the Rhone. Similar differences between the Orb and the lower part of the Rhone were also observed for ^{90}Sr. For these latter elements, the differences in concentrations at this regional scale can be explained either by the relative magnitude of the initial atmospheric deposits resulting from nuclear tests

and/or the Chernobyl accident or by contrasting erosion rates of the soils of the watersheds (Renaud et al., 2004). Part of the watershed of the Orb drains the massif of the Montagne Noire, an area of known remanence of atmospheric fallout from nuclear testings (Leroux, 2007).

These results suggest that for anthropogenic radionuclides deposited by atmospheric fallout from past nuclear tests and the Chernobyl accident, geo-climatic heterogeneity at the studied regional scale would currently dominate anthropic pressures associated to nuclear fuel cycle exploitation in the Rhone valley.

As expected OBT contents in the sediments of Orb and Hérault rivers (<0.1 Bq/kg_{dry}; < 1 Bq/L_{cw}) are much lower than those observed in the downstream part of the Rhone River (0.5±0.4 Bq/kg_{dry}; 30±18 Bq/L_{cw}) testifying the significant impact of the watchmaking industries on this river system, as previously described.

In filtered waters, similar conclusions as those highlighted for suspended sediments can be drawn for naturally occurring radionuclides. Natural radionuclides from telluric origin (^{238}Ac, ^{234}Pa, ^{40}K) and ^{7}Be recorded in filtered waters from the Rhone River show close contents to those characterizing Orb and Hérault rivers. These results underline that at the lower part of the Rhone River there is no significant impact onto the water resource quality due to the use of natural radionuclides of U/Th chains, involved in the nuclear fuel cycle.

For ^{137}Cs, ^{90}Sr and transuranium elements (^{238}Pu, $^{239+240}$Pu, ^{241}Am), all the contents are close to referential values except for ^{238}Pu and ^{241}Am which are at least one order of magnitude higher in the downstream part of the Rhone River waters. These gaps which were not observed for suspended sediments most probably testify the direct impact of nuclear industry releases onto the water resource.

All other radionuclides specifically released by the nuclear industries located along the Rhone valley, i.e., ^{60}Co, ^{54}Mn, ^{110m}Ag, were obviously not detected neither in sediments nor filtered waters of referential river systems.

Finally, tritium contents in the Rhone River waters are significantly higher by more than one order of magnitude than in the Orb and Hérault Rivers, underlying the significant impact from nuclear industries in the Rhone River.

5. Conclusions

The SORA station has been performing continuous sampling of large water volumes at the downstream part of the Rhone River for almost twenty years, in order to monitor the contents of natural and anthropogenic radionuclides

405 at trace levels. Most plutonium, americium, cesium, cobalt, silver, beryllium and actinium deliveries towards the
406 marine environment (>60%) are associated with solid particles due to the strong affinity of these elements with
407 suspended sediments (high Kd values). In contrast, sodium, tritium, antimony and strontium isotopes are mainly
408 exported as dissolved species (>90%) due to their low affinity with particles (low Kd values).

409 Naturally occurring radionuclides are the most abundant in suspended sediments while in filtered waters tritium
410 contents are at least two order of magnitude higher than those of all other radionuclides.

411 The concentrations of the naturally occurring are almost constant at a multi-year scale, despite the fact that an
412 intra-annual variability is often observed for several of these elements most probably in relation to the river's
413 hydrology.

414 The ^{40}K contents seem to have decreased towards geochemical backgrounds in the lower Rhone River suggesting
415 that anthropic pressures from potassium-based fertilizer uses in the Rhone basin have obviously declined and that
416 resiliency of the river is reached for this radionuclide.

417 Time series also point to a significant reduction of the concentrations of most of the anthropogenic radionuclides
418 over the two last decades, except for tritium, organically bound tritium, ^{90}Sr and transuranium elements suggesting
419 slow resiliency of the river system for these latter elements considering no change in climatic and anthropic
420 pressures.

421 Finally, radionuclide contents in suspended sediments exported at the downstream part of the Rhone River are
422 very close to regional referential backgrounds, except for organically bound tritium which originate from
423 watchmaking workshops located in upper Rhone watersheds. The contents of most of the anthropogenic
424 radionuclides specifically released by industries are now at ultra-trace levels and often below the limit of detection
425 even though high performance analytical procedures are used. In filtered waters only tritium, ^{241}Am and ^{238}Pu
426 significantly testify nowadays the anthropic pressures from the nuclear industries.

427 Nowadays, anthropic pressures from exploitation of the nuclear fuel in the Rhone River during more than seventy
428 years are still distinguishable in suspended sediments and filtered waters at the lower course of the river.
429 Nevertheless, current contents of radionuclides would suggest that the resiliency of the river regarding this
430 pollutant family is going on.

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References

Abril, J.M., Fraga, E. (1996) Some physical and chemical features of the variability of Kd distribution coefficient for radionuclides. J. Environ.Radioact. 30-3, 253–270.

AFNOR NF EN ISO 9698 (2015) Qualité de l'eau - Détermination de l'activité volumique du tritium – Méthode par comptage des scintillations en milieu liquide. AFNOR.

Antonelli C. (2017) Rapport d'exploitation. Station SORA – Année 2017. RT/PSE-ENV/SEREN/2017-00027.

Barbieri M. (2016) The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination, J Geol Geophys 2016, 5, 1.

Boyer, P., Wells, C., Howard B. (2018) Extended Kd distributions for freshwater environment. Journal of Environmental Radioactivity, 192, pp. 128-142.

Bradley SB, Lewin J (1982) Transport of heavy metals on suspended sediments under high flow conditions in a mineralised region of Wales. Environ Pollut Ser B 4, 257–267.

Duan W, He B, Chen Y, Zou S, Wang Y, Nover D, et al. (2018) Identification of long-term trends and seasonality in high-frequency water quality data from the Yangtze River basin, China, PLoS ONE 13(2), e0188889. doi: 10.1371/journal.pone.0188889. eCollection 2018.

Dawson J, Macklin MG (1998) Speciation of heavy metals on suspended sediment under high flow conditions in the River Aire,West Yorkshire, UK. Hydrol Process 12, 1483–1494.

Desmet, M., Mourier, B., Mahler, B.J., Van Metre, P.C., Roux, G., Persat, H., Lefèvre, I., Peretti, A., Chapron, E., Simonneau, A., Miège, C., Babut, M. (2012) Spatial and temporal trends in PCBs in sediment along the lower Rhône River, France. Sci. Total Environ. 433, 189–197.

460 Ducros L., Eyrolle F., Della Vedova C., Charmasson S., LeBlanc M., Mayer A., Babic M., Antonelli C., Mourier D.,
461 Giner F. (2017) Tritium in river waters from French Mediterranean catchments: background levels and variability,
462 Science of the Total environment, 612, 672-682.
463 Duffa C. (2001) – Répartition du plutonium et de l'américium dans l'environnement terrestre de la basse vallée du
464 Rhône. Thèse de doctorat, Université Aix-Marseille III. 179 p.
465 Eyrolle F., Charmasson S. (2001) Distribution of organic carbon, selected stable elements and artificial
466 radionuclides among dissolved, colloidal and particulate phases in the Rhône River (France): Preliminary results
467 Journal of Environmental Radioactivity, 55-2, 145-155.
468 Eyrolle F., Charmasson S. (2004) Importance of colloids in the transport within the dissolved phase (<450 nm) of
469 anthropogenic radionuclides from the Rhône river towards the Gulf of Lions (Mediterranean Sea). Journal of
470 Environmental Radioactivity, 72-3, 273-286.
471 Eyrolle F., Gontier G., Claval D., Antonelli C., (2008) Radioactivity levels in major French rivers: summary of
472 monitoring chronicles acquired over the past thirty years and current status. Journal of Environmental Monitoring,
473 10, 800-811.
474 Eyrolle F., Radakovitch O., Raimbault P., Antonelli C., Ferrand E., Raccasi G., Aubert D., Gurriaran R. (2012) Long
475 term survey of suspended particles and associated natural and artificial radionuclides transport in the Rhône River.
476 Journal of Soils and Sediments, 12, 1479-1495.
477 Eyrolle-Boyer F., Renaud P., Le Doré F., Tournieux D., Claval D., Blanchet J. F., Antonelli C., Zebracki M., Cossonnet
478 C., Boulet B., Cagnat X., De Vismes A., Guriaran R. (2014a) Radiological characteristics of water transport channels
479 Example of Rhone Languedoc Roussillon regional network, Radioprotection, 49, 2, 123-134.
480 Eyrolle-Boyer F., Renaud P., Claval D., Tournieux D., Le Doré F., Blanchet J. F., Loyen J., Antonelli C., Cossonnet C.,
481 Cagnat X. (2014b) Radiological quality Assessment of the Rhône River filtered waters at its lower course in the
482 framework of water production for human consumption with historical and regional perspectives,
483 Radioprotection, 49, 3, 183-193.
484 Eyrolle-Boyer F., Boyer P., Claval D., Charmasson S., Cossonnet C. (2014c) Apparent enrichment of organically
485 bound tritium in rivers explained by the heritage of our past, Journal of Environmental Radioactivity, 136, 162-168.
486 Eyrolle-Boyer F., Antonelli C., Renaud Ph., Tournieux D. (2015a) Origins and trend of radionuclides within the
487 Rhône River over the last decades, Radioprotection, 50, 1, 27-34.
488 Eyrolle-Boyer F., Thébault H., Claval D., Calmon P., Zebracki M., Cossonnet C. (2015b) Tritium and ^{14}C background
489 levels in pristine aquatic systems and their potential sources of variability, Journal of Environmental Radioactivity,
490 139, 24-32.
491 Eyrolle F., Lepage H., Copard Y., Ducros L., Claval D., Saey L., Cossonnet C., Giner F., Mourier D., (2018) A brief
492 history of origins and contents of Organically Bound Tritium (OBT) and 14C in the sediments of the Rhône
493 watershed, STOTEN, 643, 40-51.

494 Feng H, Jiang H, Gao W, Weinstein MP, Zhang Q, et al. (2011) Metal contamination in sediments of the western
495 Bohai Bay and adjacent estuaries, China. J Environ Manag 92, 1185-1197.
496 Ferrand E., Eyrolle F., Radakovitch O., Provansal M., Dufour S., Vella C., Raccasi G. and Gurriaran R. (2012)
497 Historical levels of heavy metals and artificial radionuclides reconstructed from overbank sediment records in
498 lower Rhône River (South - East France), Geochemica and Cosmochimica Acta, special Issue on Environmental
499 Records of Anthropogenic Impacts, 82, 163-182.
500 Global Investigation of Pollution in the Marine Environment (1999) Guidance on Assessment of Sediment Quality.
501 IOCeUNEPeIMO.
502 Ferrand E., Eyrolle F., Radakovitch O., Provansal M., Dufour S., Vella C., Raccasi G. and Gurriaran R., 2012, Historical
503 levels of heavy metals and artificial radionuclides reconstructed from overbank sediment records in Lower part of
504 the Rhone River (South - East France), Geochemica and Cosmochimica Acta, special Issue on Environmental
505 Records of Anthropogenic Impacts, 82, 163-182.
506 Filella M., Belzile N., Chen Y.W. (2002) - Antimony in the environment: a review focused on natural waters. I.
507 Occurrence, Earth Science Review, 57, 125-176.
508 Ghashghaie M., Ostad-Ali-Askari K., Eslamian S., Singh P.V. (2018) Application of Time Series Modeling to Study
509 River Water Quality, American Journal of Engineering and Applied Sciences, DOI: 10.3844/ajeassp.2018.574.585.
510 Gil-Díaz T., Schäfer J., Keller V., Eiche E., Dutruch L., Möβner C., Lenz M., Eyrolle F. (2020) Tellurium and selenium
511 sorption kinetics and solid fractionation under contrasting estuarine salinity and turbidity conditions, Chemical
512 Geology, 532, 119370.
513 Grosbois C., Meybeck M., Lestel L., Moatar F., Lefèvre I. (2012) Severe and contrasted polymetallic contamination
514 patterns (1900–2009) in the Loire River sediments (France), Science of the Total Environment, 435-436, 290-305.
515 Grosbois C., A. Coynel, F. Eyrolle-Boyer, C. Lemarchand, C. Mouneyrac, L. Poirier (2016) Micropolluants
516 métalliques, organiques et radionucléides : depuis les eaux et sédiments vers le biote La radioactivité des eaux de
517 la Loire, Chapitre 8, dans Moatar, F., Dupond N. 2016. La Loire fluviale et estuarienne: un milieu en évolution.
518 2016. Ed. Quae, ISBN: 978-2-7592-2401-2; ISSN: 1777-4624.
519 Hirose K., Povinec P. (2015) Sources of plutonium in the atmosphere and stratosphere-troposphere mixing,
520 Scientific Reports, DOI: 10.1038/srep15707.
521 IAEA (2012) Environmental Modelling for radiation Safety (EMRAS). A summary report of the results of the EMRAS
522 Programme (2003-2007). Vol. 1678 (IAEA-TECDOC, 2012).
523 IRSN (2013) Constat radiologique Vallée du Rhône. Rapport final relatif au milieu Aquatique, Rapport PRP-
524 ENV/SESURE/2013-37.
525 Jean-Baptiste Ph., Baumier D., Clavel B. (2007) The distribution of tritium in the terrestrial and aquatic
526 environments of the Crey-Malville nuclear power plant (2002-2005), Journal of Environmental Radioactivity, 94, 2,
527 107-118.

528 Jean-Baptiste, P. et al. (2019) Organically bound tritium (OBT) and carbon-14 accumulation in the sediments off the
529 mouth of the Rhône river. Environ. Earth Sci. 78(3), 78.
530 Krejci, K., Zeller, A. (1979) Tritium pollution in the Swiss luminous compound industry. In: Behaviour of Tritium in
531 the Environment, IAEA Proceedings Series, IAEA-SM-232/11, Vienna, pp. 65-77.
532 Laubenstein M., Magaldi D. (2008)Natural radioactivity of some red Mediterranean soils. Catena, 76, 22-26.
533 Le Roux G. (2007) Radionucléides naturels en France. Approche géochimique de la variabilité des radionucléides
534 naturels d'origine tellurique (40K et chaînes U-Th) dans les sols et sédiments fluviaux, Rapport IRSN/DEI/SESURE
535 2007-42.
536 Ludwig W., Dumont E., Meybeck M., Heussner S. (2009) River discharges of water and nutrients to the
537 Mediterranean and Black Sea: Major S.drivers for ecosystem changes during past and future decades? Progress in
538 Oceanography, 80, 199-217.
539 Maringer F. G., Hrachowitz V., Baumgartner M., Weilner A., Seidel S. C. (2009) Long-term monitoring of the
540 Danube river-Sampling techniques, radionuclide metrology and radioecological assessment. Applied radiation and
541 isotopes : including data, instrumentation and methods for use in agriculture, industry and medicine. 67. 894-900.
542 Masson O., Eyrolle F., Antonelli C., Boullier V. (2004) Station observatoire « Rhône aval »-Réseau OPERA-Bilan
543 2001-2003, rapport IRSN/DEI/SESURE/LERCM-2004-05.
544 Meybeck M., Lestel L., Carré C., Bouleau G., Garnier J., Mouchel J. M. (2018) Trajectories of River Chemical
545 Quality Issues over the Longue Durée: The Seine River (1900s-2010), Environmental Science and Pollution
546 Research, Springer Verlag, 25 (24), 23468-23484.
547 Molle F. , Wester P. (2009) River Basin Trajectories: Societies, Environments and Development, Edited by François
548 Molle and Philippus Wester.
549 Morereau A., Lepage H., Claval D., Cossonnet C., Mourier B., Winiarski T., Ambrosi J. P., Eyrolle F., Technogenic
550 tritium contamination from watchmaking industry and its fate in sediment cores of the Rhône River (France), in
551 prep.
552 NF ISO 18589-5 May 2009 Measurements of radioactivity in the environment - Soil - Part 5 : measurement of
553 strontium 90.
554 Ottlé, C., Etchevers, P., Golaz, et al. (2001) Hydro-meteorological modelling of the Rhône Basin: general
555 presentation and objectives. Phys. Chem. Earth, (B) 26 (5–6), 443–453.
556 Palms J., Patrick R., Kreeger D., Harris C. (2007) 25-y study of radionuclide monitoring with terrestrial and aquatic
557 biomonitors, Health Phys., 92(3):219-25.
558 Panagiotopoulos C., Sempéré R., Para J., Raimbault P., Rabouille C., Charrière B. (2012) The composition and flux
559 of particulate and dissolved carbohydrates from the Rhone River into the Mediterranean Sea. Biogeosciences, 9,
560 1827–1844.
561 Pardé M. (1925) Le régime du Rhône. Etude hydrologique. Thesis, University of Grenoble, France, 887 pp.

562 Perkins R. W., Thomas C. W. (1980) Worldwide Fallout, p. 53-82 *in* W. C. Hanson editor. "Transuranic elements in
563 the environment", U.S. DOE, USA.
564 Pont D. (1997) Les débits solides du Rhône à proximité de son embouchure: données récentes (1994-1995). Revue
565 de Geographie de Lyon 72-1, 23–43.
566 Renaud P., Métivier J.M., Castellier J.M., Pourcelot L., Louvat D. (2004) Cartographie des dépôts de ^{137}Cs en mai
567 1986 sur l'ensemble du territoire français métropolitain, Radioprotection, 39(1), 23-38.
568 Rolland B. (2006) Transfert des radionucléides artificiels par voie fluviale : conséquences sur les stocks
569 sédimentaires rhodaniens et les exports vers la Méditerranée. Thèse, Université Paul Cézanne d'Aix-Marseille,
570 243p.
571 Salomons W. and Forstner U. (1984) Metals in the Hydrocycle. Sinpringer, Berlin.
572 Schleichert U. (1975) Annual variation of the heavy metal contents of suspended sediments in the Rhine River at
573 Koblenz. Dtsch Gewässerkd Mitt 19, 150–157.
574 Thompson T.M. (1988) Environmental monitoring for radionuclides in marine ecosystems; Are species other than
575 man protected adequately? J. Environ. Radioactivity 7, 275-283.
576 Topçuoğlu S. , Ergül H.A., Belivermiş M., Kılıç O. (2010) Monitoring of radionuclide concentrations in marine algae, mussel
577 and sediment samples from the Turkish marine environment during the period of 2001-2009 J. Black Sea/Mediterranean
578 Environment Vol. 16(3): 285-293.
579 Zebracki M., Eyrolle F., Cagnat X., Antonelli C., De Vismes-Ott A., Boullier V. (2013a) Characterization of naturally
580 occurring radionuclides in the Lower part of the Rhone River waters (France), preliminary results from suspended
581 sediments monitoring, Water Resources Management VII, WIT Transactions on Ecology and the Environment, 171,
582 235-245.
583 Zebracki M., Eyrolle-Boyer F., De Vismes-Ott A., Antonelli C., Xavier Cagna X., Boullier V. (2013b) Radionuclide
584 contents in suspended sediments in relation to the flood types in the Lower part of the Rhone River, Procedia
585 Earth and Planetary Science, 7, 936-939.
586 Buesseler K., Dai M., Aoyama M., Benitez-Nelson C., Charmasson S., Higley K., Maderich V., Masqué P., Morris P.J.,
587 Oughton D., Smith J.N. (2017) Fukushima Daiichi–Derived Radionuclides in the Ocean: Transport, Fate, and
588 Impacts, Annual Review of Marine Science, 9, 173-203.
589

Radionuclides in waters and suspended sediments in the Rhone River (France) - Current contents, anthropic pressures and trajectories

Figures and tables

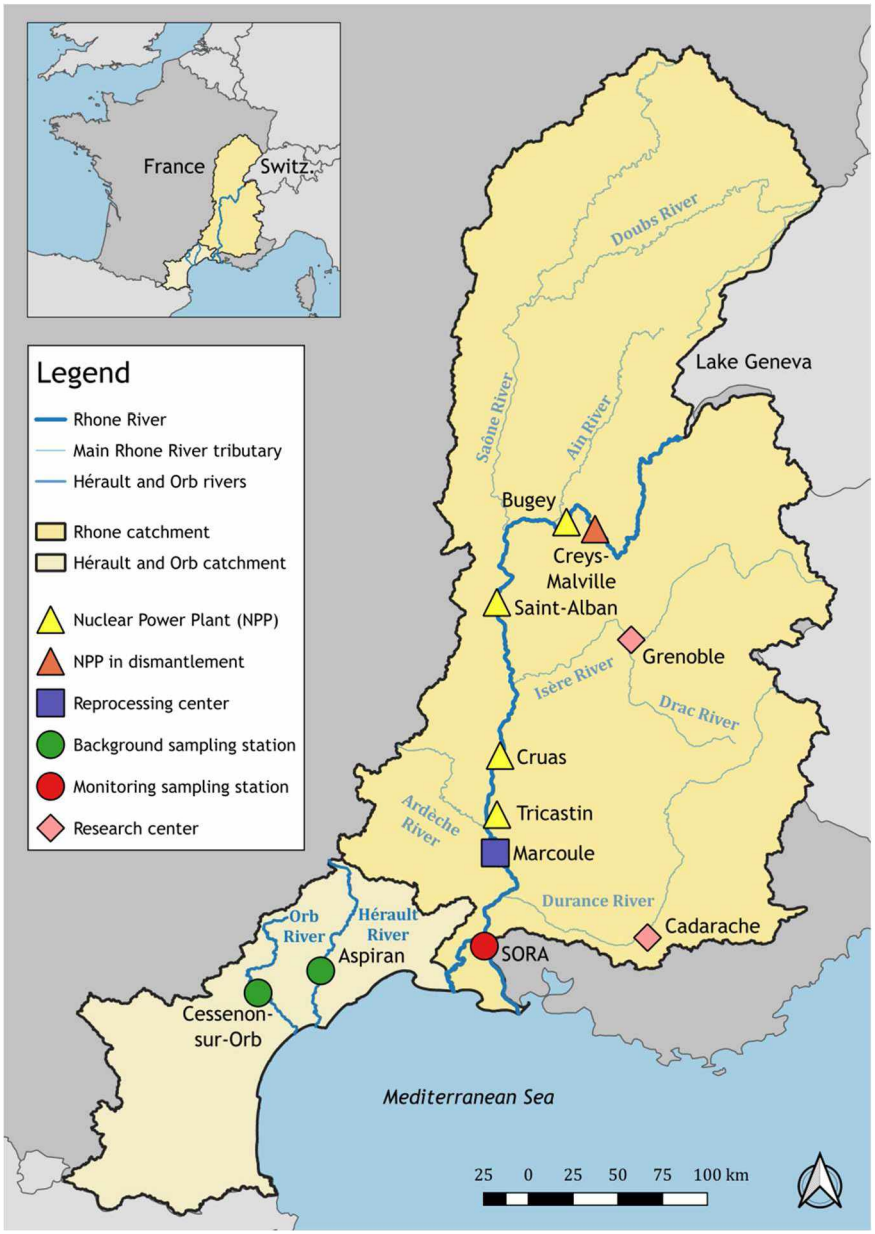


Figure 1: Sampling stations on the Rhone, Orb and Hérault rivers and location of nuclear installations.

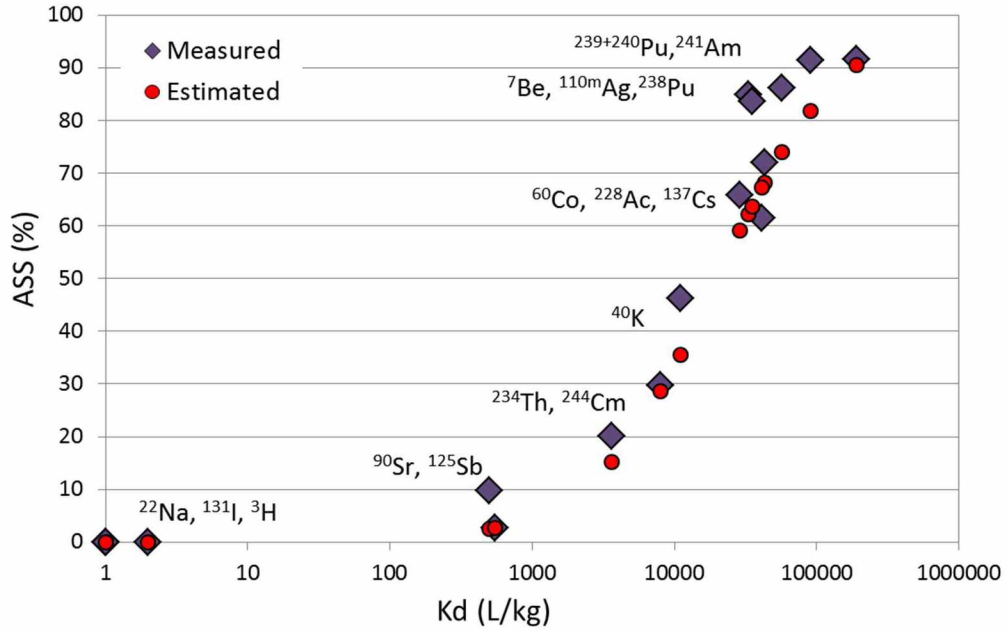
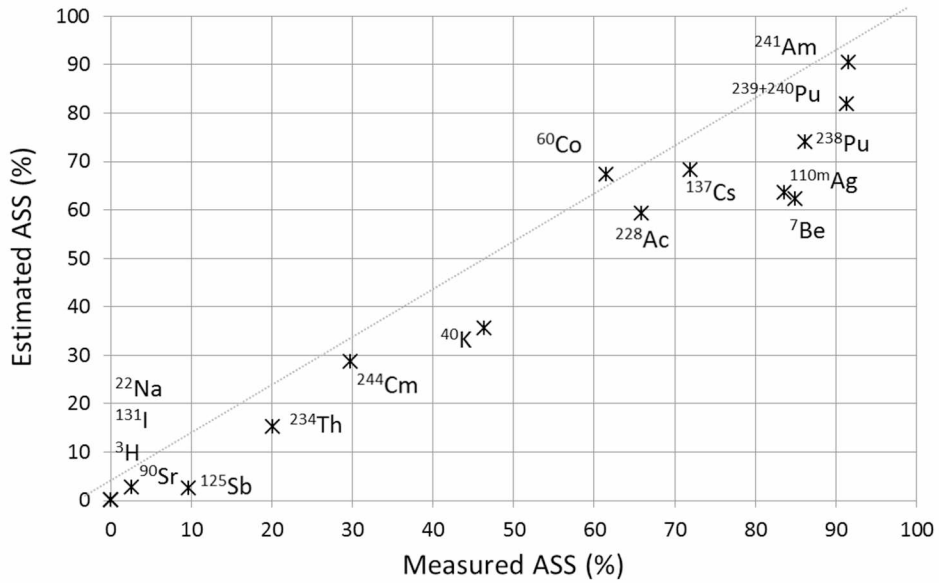


Figure 2: Measured* and estimated amounts of radionuclides exported by suspended sediments (ASS, in %) related to their apparent distribution coefficient** (Kd, in L/kg); * from Antonelli (2017): data set acquired in 2016 at the SORA monitoring sampling station (Rhone River).** From data set acquired from 2002-2018 at the SORA monitoring sampling station (Rhone River).



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18 Figure 3: Amounts of radionuclides exported by suspended sediments (ASS, in %): calculations from mean apparent distribution
19 coefficient (Kd, in L/kg) and mean suspended matters content (50 mg/L) - Estimated ASS *vs* direct measurements from Antonelli 2017 -
20 Measured ASS.

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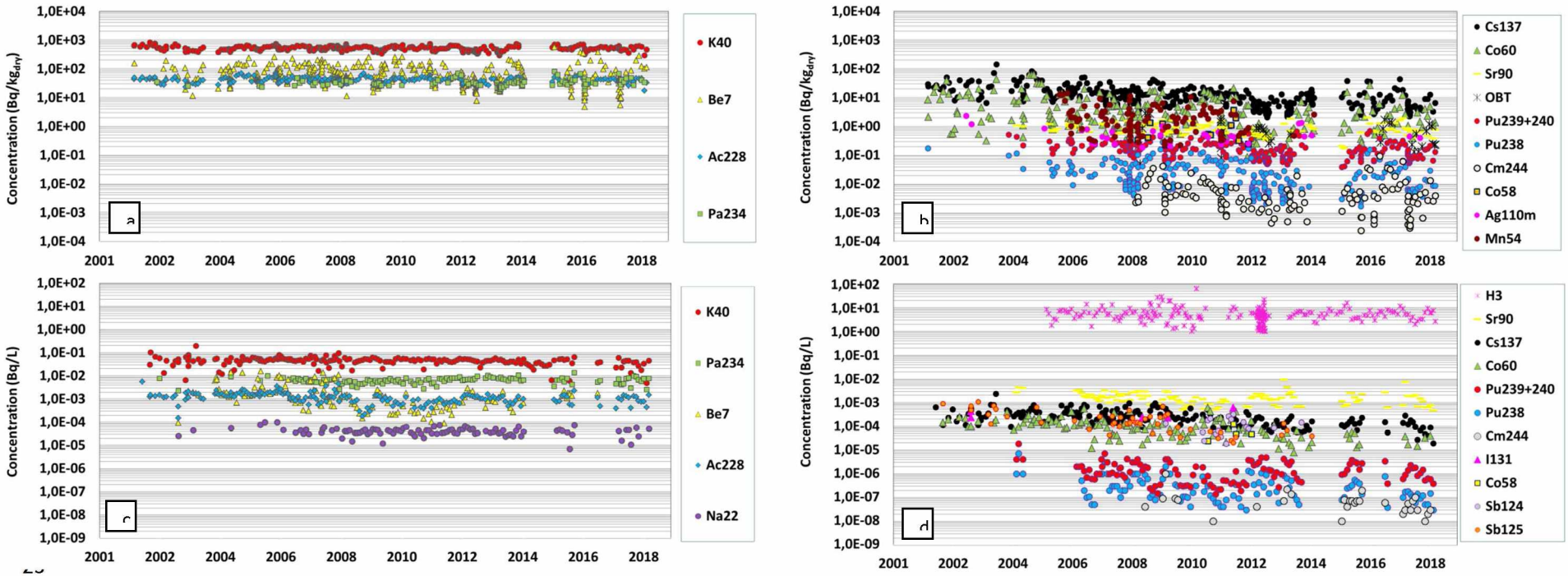

Figure 4: Time series of radionuclide contents in suspended sediments (a, b), in Bk/kg$_{dry}$ and filtered waters (c, d), in Bq/L measured at the SORA monitoring sampling station (Rhone River) over 2002-2018 ; Naturally occurring radionuclide contents in a, c and artificial radionuclide contents in b,d.

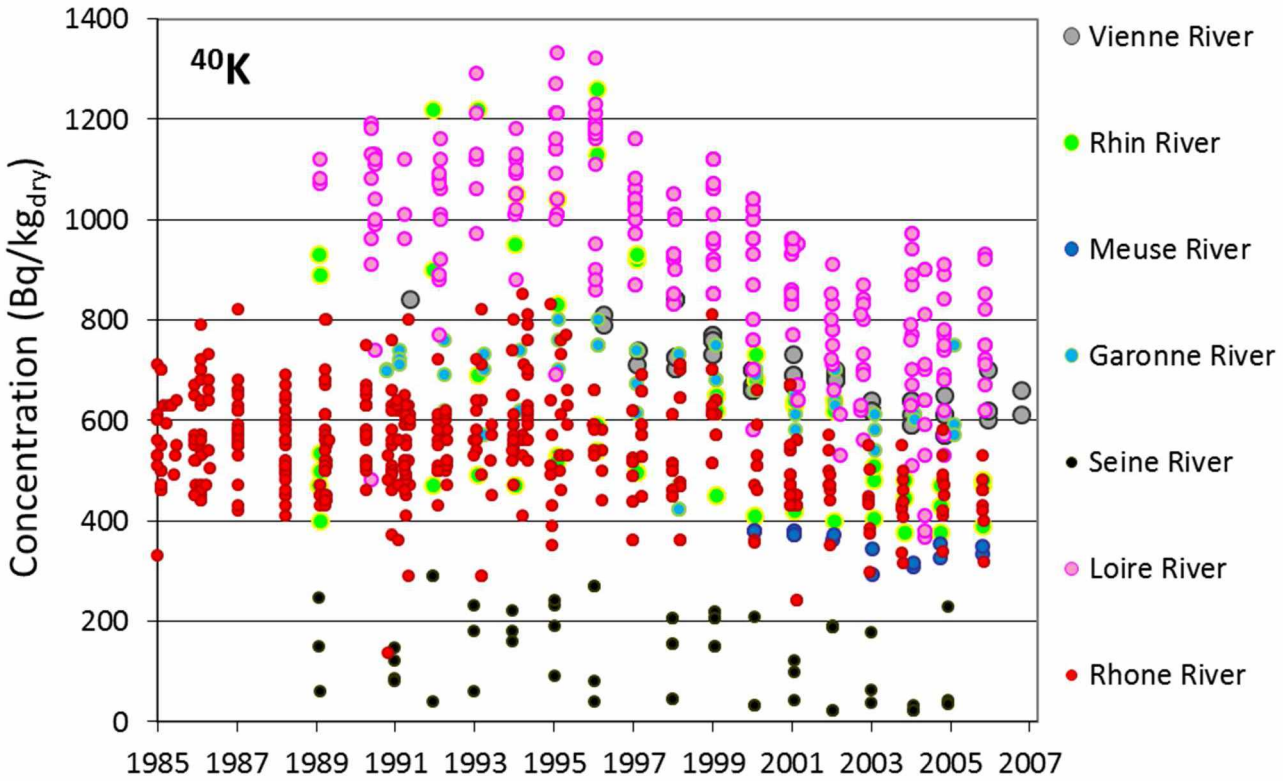

Figure 5: Time series of ^{40}K contents in the suspended sediments of French large rivers (according to Eyrolle-Boyer, 2016).

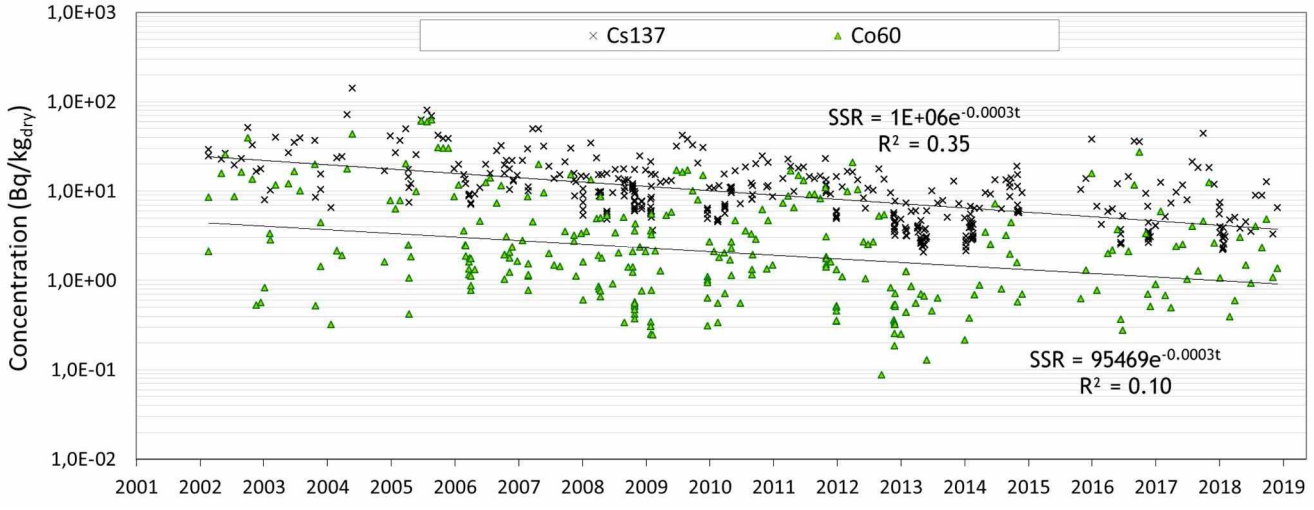

Figure 6: Trends of ^{137}Cs and ^{60}Co contents in suspended sediments; SORA monitoring sampling station (2002-2018), Rhone River (France).

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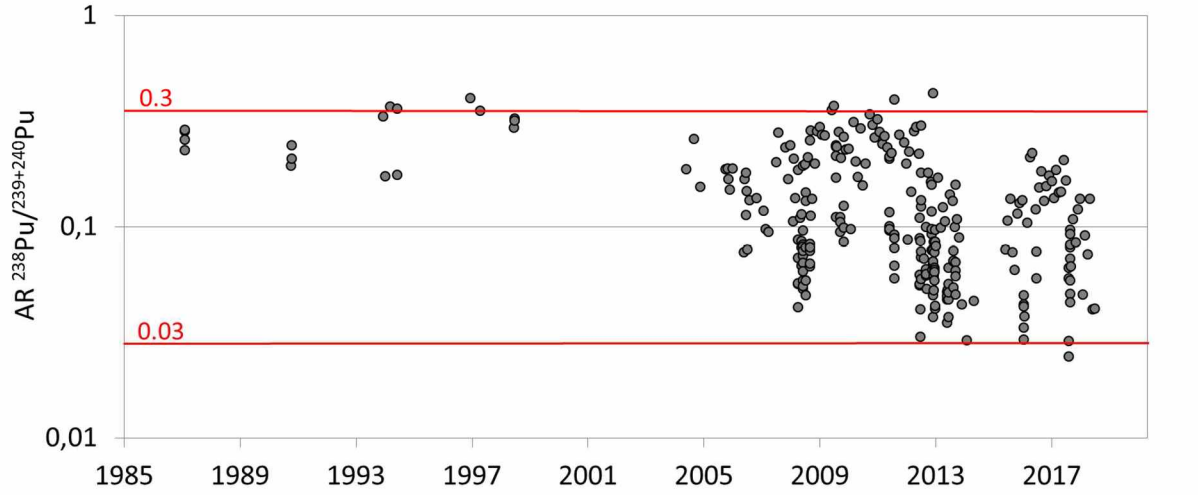

Figure 7: Time series of $^{238}Pu/^{239+240}Pu$ activity ratios (AR) in the suspended sediments collected in the lower Rhone River between 1987 and 2018 (SORA station from 2004 to 2018). The red lines correspond to theoretical AR values for discharges from the Marcoule spent fuel reprocessing plant (AR=0.3) and for the soils of the watershed (AR=0.03).

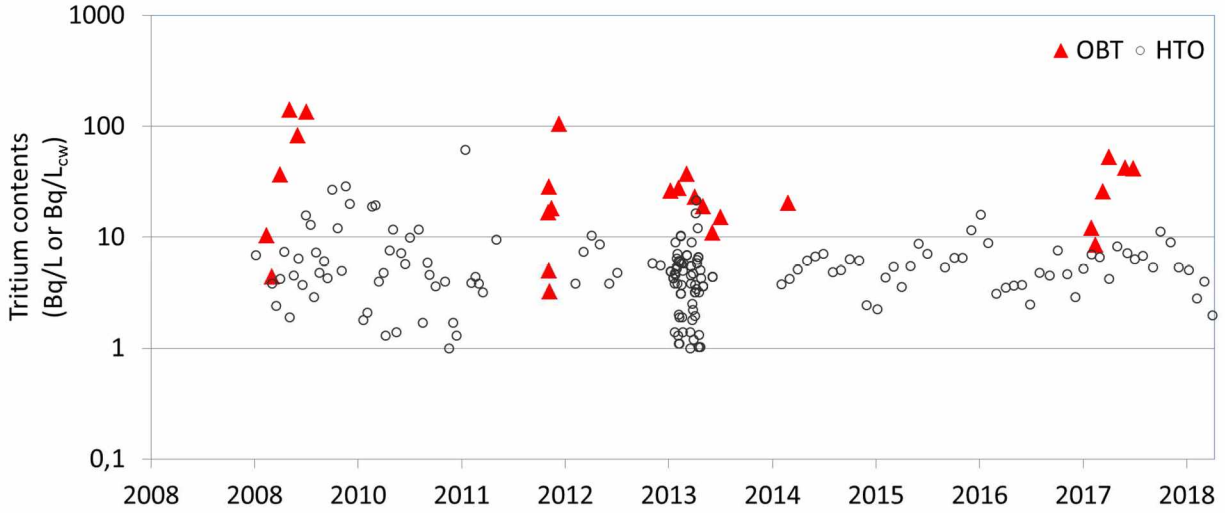

Figure 8: Time series of organically bound tritium contents (OBT, in Bq/L_{cw}) and of free tritium contents (HTO, in Bq/L).

Table 1 - Mean apparent distribution coefficient, Kd in L/kg_{dry} in the lower Rhone River; SORA station (2002-2018) and *IAEA Referential Kd distributions (Boyer et al., 2018).

Kd (L/kg)	Downstream Rhone River	IAEA Referential Kd Distributions*		
		GM	5%	95%
Américium 241	191 000 ± 7 000 (n=211)	7.94E+04	3.90E+03	1.62E+06
Plutonium 239,240	90 000 ± 11 000 (n=92)	1.47E+05	1.94E+03	1.11E+07
Plutonium 238	57 000 ± 7 000 (n=82)	1.47E+05	1.94E+03	1.11E+07
Plomb 210	53 000 ± 1 200 (n=204)	2.63E+05	6.66E+04	1.04E+06
Césium 137	43 000 ± 11 000 (n=218)	1.35E+05	2.64E+04	6.69E+05
Cobalt 60	41 000 ± 11 000 (n=76)	4.43E+04	1.00E+04	1.96E+05
Thorium 228	37 000 ± 7 000 (n=182)	1.52E+05	2.64E+04	8.76E+05
Argent 110m	35 000 ± 5 000 (n=38)	4.85E+05		
Béryllium 7	33 000 ± 11 000 (n=183)	3.87E+04	8.06E+03	1.85E+05
Actinium 228	29 000 ± 8 000 (n=222)			
Manganese 54	23 000 ± 1000 (n=104)	7.21E+04	1.09E+04	4.76E+05
Potassium 40	11 000 ± 2 000 (n=225)	1.93E+03	5.66E+02	6.95E+03
Curium 244	8 000 ± 1 000 (n=46)	3.26E+04	8.96E+03	1.18E+05
Protactinium 234	6 100 ± 1 600 (n=222)	1.21E+05	4.73E+04	3.11E+05
Thorium 232	5 000 ± 900 (n=132)	1.52E+05	2.64E+04	8.76E+05
Thorium 230	3 700 ± 800 (n=66)	1.52E+05	2.64E+04	8.76E+05
Thorium 234	3 600 ± 1 000 (n=206)	1.52E+05	2.64E+04	8.76E+05
Radium 226	1 700 ± 300 (n=195)	5.21E+03	9.79E+02	2.77E+04
Radium 228	1 600 ± 300 (n=105)	5.21E+03	9.79E+02	2.77E+04
Uranium 234	1 400 ± 300 (n=35)	1.19E+04	6.94E+02	2.04E+05
Uranium 238	1 400 ± 300 (n=195)	1.19E+04	6.94E+02	2.04E+05
Antimoine 125	500 ± 100 (n=93)	8.14E+03	1.65E+03	4.01E+04
Strontium 90	550 ± 90 (n=104)	2.96E+03	3.31E+02	2.65E+04
Iode 131	<1	3.32E+03	2.06E+03	5.36E+03
Sodium 22	<1	1.53E+03	8.01E+02	2.92E+03

Table 2: Mean contents of main naturally occurring and artificial radionuclides in suspended sediments and filtered waters of the Hérault and Orb coastal rivers (2011-201) and at the downstream part of the Rhone River (2018); In bold, excess contents referring to referential regional backgrounds; nd: not determined; * in Bq/L_{cw}; SD : Standard Deviation.

	Referential Regional Background (2011-2018)								Nuclearized River (2018)			
	Hérault River				Orb River				Lower Rhone River			
	SS (Bq/kg_{dry})		Filtered water (Bq/L)		SS (Bq/kg_{dry})		Filtered water (Bq/L)		SS (Bq/kg_{dry})		Filtered water (Bq/L)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
H3	nd		0.7	0.1			0.2	0.1	nd		**7**	**2**
OBT	0.05	0.03	nd	-	0.07	0.04	nd	-	**0.5**	**0.4**	nd	-
OBT*	0.7	0.4	nd	-	0.9	0.5	nd	-	**30**	**18**	nd	-
K40	656	50	0.04	0.01	618	23	0.04	0.01	510	81	0.04	0.01
Be7	62	33	0.002	0.001	81	25	0.004	0.001	61	33	0.002	0.001
Pa234	47	11	0.02	0.01	46	9	0.006	0.002	43	14	0.006	0.003
Ac228	45	8	0.003	0.001	42	5	0.001	0.001	41	6	0.001	0.001
Cs137	6	1	0.0001	0.0001	20	4	0.0001	0.0001	10	4	0.0002	0.0001
Sr90	0.5	0.1	0.002	0.001	2,5	0.5	0.002	0.001	0.6	0.1	0.003	0.001
Na22	nd		0.00003	0.00001	-	-	0.00003	0.00001	nd	-	0.00004	0.00001
Pu239+240	0.08	0.03	0.0000007	0.0000001	0,7	0.1	0.0000011	0.0000005	0.2	0.1	0.0000012	0.0000008
Pu238	0.003	0.001	< 0.0000001	-	0.03	0.01	< 0.0000001	-	0.03	0.02	**0.0000003**	**0.0000001**
Am241	0.05	0.01	<0.00000001	-	0.29	0.05	0.00000008	0.00000001	0.1	0.1	**0.0000002**	**0.0000001**

Kd (L/kg)	Downstream Rhone River	IAEA Referential Kd Distributions*		
		IAEA - GM	IAEA - 5%	IAEA - 95%
Américium 241	191 000 ± 7 000 (n=211)	7,94E+04	3,90E+03	1,62E+06
Plutonium 239,240	90 000 ± 11 000 (n=92)	1,47E+05	1,94E+03	1,11E+07
Plutonium 238	57 000 ± 7 000 (n=82)	1,47E+05	1,94E+03	1,11E+07
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Thorium 228	37 000 ± 7 000 (n=182)	1,52E+05	2,64E+04	8,76E+05
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Sodium 22	<1	1,53E+03	8,01E+02	2,92E+03

	Referential Regional Background (2011-2018)						
	Hérault River				Orb River		
	SS (Bq/kg_{dry})		Filtered water (Bq/L)		SS (Bq/kg_{dry})		Filtered water
	Mean	SD	Mean	SD	Mean	SD	Mean
H3	nd		0.7	0.1			0.2
OBT	0.05	0.03	nd	-	0.07	0.04	nd
OBT*	0.7	0.4	nd	-	0.9	0.5	nd
K40	656	50	0.04	0.01	618	23	0.04
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Cs137	6	1	0.0001	0.0001	20	4	0.0001
Sr90	0.5	0.1	0.002	0.001	2,5	0.5	0.002
Na22	nd		0.00003	0.00001	-	-	0.00003
Pu239+240	0.08	0.03	0.0000007	0.0000001	0,7	0.1	0.0000011
Pu238	0.003	0.001	< 0.0000001	-	0.03	0.01	< 0.0000001
Am241	0.05	0.01	<0.00000001	-	0.29	0.05	0.00000008

Radionuclides in waters and suspended sediments in the Rhone River (France) - Current contents, anthropic pressures and trajectories

GRAPHICAL ABSTRACT