

# Organically bound tritium (OBT) and carbon-14 accumulation in the sediments off the mouth of the Rhône river

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1	Organically Bound Tritium (OBT) and Carbon-14 accumulation in the
2	sediments off the mouth of the Rhône river
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16	
17	Abstract
18	
19	We have studied the recent history of Organically Bound Tritium (OBT) and
20	carbon-14 in suspended organic matter carried by the Rhône from the analysis of two
21	cores collected in the sedimentary cone off the river mouth. Measured OBT and
22	carbon-14 concentrations highlight characteristic anthropogenic traces in the
23	suspended matter of the Rhône, with a peak of tritium and carbon-14 commencing at
24	the start of the 1970's and extending over some thirty years. In spite of the influence
25	of the atmospheric nuclear tests of the 1950's and 1960's and of the discharges of
26	carbon-14 by the nuclear industries located along the Rhône, carbon-14 levels are

27	low due to the diluting effect of a refractory carbon component very low in carbon-14
28	present in the coastal sediments. Organically bound tritium (OBT) levels are well
29	above the modern background created by the global imprint of bomb-tritium. Detailed
30	study of the impact of the various contribution to the tritium peak indicates that these
31	traces are mostly the result of the sediments in the Rhône being contaminated by
32	past tritium releases by the watchmaking industry in the upper Rhône.
33	

- *Keywords*: Rhône prodelta; tritium; carbon-14; radioactive contamination;
  watchmaking industry

## 37 **1. Introduction**

38

The Rhône valley and the french nuclear-based industry share a long common 39 history that started in the 1950s and 1960s with the commissioning of several major 40 nuclear facilities dedicated to the production and reprocessing of plutonium and 41 tritium. Today, the Rhône valley has the highest density of nuclear activities in 42 Europe (Fig. 1), comprising two major nuclear sites (Marcoule and Tricastin) housing 43 44 civilian and military activities and four nuclear power plants (Bugey, Saint-Alban, Cruas, Tricastin) with a total of 14 reactors (to which Crey-Malville should be added; 45 this reactor was decommissioned in 1997). Over this period, a repository of artificial 46 radionuclides has built up in the sediments delivered to the Mediterranean Sea and 47 deposited in the sedimentary prism (Rhône prodelta) off the mouth of Rhône river. 48 These sediments enable us to reconstruct the history of the inputs to the river of 49 some radionuclides, including <sup>60</sup>Co, <sup>137</sup>Cs, <sup>238</sup>Pu, <sup>239,240</sup>Pu (Charmasson et al., 1998; 50 51 Charmasson, 2003 ; Lansard et al., 2007). This paper presents a study of the vertical 52 distribution of organically bound tritium (OBT) and carbon-14 in two sediment cores taken from the Rhone prodelta. The aim of the study was to obtain the first historical 53 record of these two radionuclides in the suspended matter of the Rhône and to 54 evaluate the extent of anthropogenic tritium and carbon-14 accumulation in the 55 Rhône prodelta. Throughout the text, tritium levels are expressed in Tritium Units 56 (TU), 1 TU corresponding to a T/H ratio of 10<sup>-18</sup>. The unit used for carbon-14 is the 57 58 pmC (% modern Carbon): with this unit, the pre-industrial specific activity for carbon-14 (226 Bg/kgC) corresponds to 100 pmC (Mook and van der Plicht, 1999). 59

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#### 61 **2. Background**

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63 The Rhône (812 km long) is one of the main rivers in Europe. It rises in the Swiss Alps at an altitude of 2,200 m and ends in the Camargue delta before flowing into the 64 65 Gulf of Lyon, a large continental shelf located in the northwestern Mediterranean Sea. It is the largest river flowing into the western Mediterranean basin, both in terms 66 of water and particulate matter, accounting for 80% of the solid riverine inputs to the 67 Gulf of Lions (Monaco et al., 1990). At the mouth of the Rhône the particulate matter 68 69 settles quickly and creates a sedimentary prism. Its proximal fan, as the extension to the Rhône's land-based channel, is marked by a slight slope. The prodelta itself 70 71 starts with a clean break to the slope and extends to a depth of 60 m. It is 72 characterised by the highest rates of sedimentation in the Gulf of Lion, reaching up to between 0.2 and 0.5 m yr<sup>-1</sup> (Charmasson et al., 1998). The distal fan, below a depth 73 74 of 60 m, corresponds to a second break in the slope and is characterised by less 75 energetic hydrodynamics that favour finer particles settling with sedimentation rates 76 no greater than a few millimetres per year (Radakovitch et al., 1999). This 77 sedimentary complex captures a large proportion of the pollutants carried by the 78 Rhône.

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# **3.** Origin of carbon-14 and tritium in the organic matter of Rhône sediments

The origin of the particulate organic matter in the Rhône is 90% non-native (allochthonous), in other words due to the leaching of the catchment areas (Lansard et al., 2009; Hamelin-Vivien et al., 2010). The remaining 10% corresponds to the autochtonous organic matter, that is the organic matter photosynthesised by plants in the river itself. As a consequence, the carbon-14 and tritium tagging of organic suspended matter in the Rhône has two origins: the export of organic residues from

catchment areas, influenced by the tritium (HTO) and carbon-14 atmospheric
contents, and organic matter formed in-situ, influenced by the tritium and carbon-14
content of the Rhône waters.

90 3.1. Natural sources

Tritium (<sup>3</sup>H) and carbon-14 (<sup>14</sup>C) are produced naturally in the atmosphere by the 91 92 effect of cosmic radiation principally on nitrogen. Tritium enters into the water cycle in the form of a molecule of tritiated water (HTO), then spreads into the biosphere as 93 94 Tissus Free Water Tritium (TFWT) and organically bound tritium (OBT) - Eyrolle et al., (2018). The natural T/H ratio for surface waters is in the range 10<sup>-18</sup> - 10<sup>-17</sup>, i.e. 1 95 96 to 10 TU (Cauquoin et al., 2015). In the same way, carbon-14 is oxidised to form a molecule of carbon dioxide (<sup>14</sup>CO<sub>2</sub>) that enters the natural cycle of organic carbon 97 98 (photosynthesis) and inorganic carbon.

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100 3.2. Global human-made inputs

101 Substantial amounts of tritium and carbon-14 were released into the environment by the atmospheric nuclear tests of the 1950's and 1960's. When the test ban treaty 102 103 came into force in 1963, the atmospheric content of carbon-14 had reached 200 pmC, i.e. twice the natural level (Nydal and Lövseth, 1996) and that of tritium 2,000 104 105 ΤU in the northern hemisphere (IAEA water isotopes database at 106 https://nucleus.iaea.org /wiser/gnip.php). Because carbon and hydrogen in the biosphere equilibrates isotopically with the atmosphere, this global tritium and 107 108 carbon-14 imprint of the atmospheric nuclear tests is recorded in vegetation, and 109 therefore, in the organic matter deposited in particulate form in the Rhône and along the Mediterranean coast, associated with the leaching of organic material in the soil. 110

111

## 112 3.3. Tritium and carbon-14 of local industrial origin

113 3.3.1 Local gaseous discharges of carbon-14 and tritium (HTO)

114 Atmospheric discharges of tritium (HTO) influencing the Rhône catchment are 115 mainly due to the nuclear activities of the Marcoule site, operated by the French Atomic Energy Commission (CEA) and the AREVA company, and of the CEA-Valduc 116 117 military site (Fig. 2); gaseous tritium discharges from the nuclear power stations 118 currently make up less than 1% of the total (and hence even less in the past). These atmospheric discharges of tritium produce substantial local traces in the land 119 120 environment. The data available for the Marcoule site indicates levels of tritium (OBT) 121 in the organic matter of plants up to 20,000 TU for the most exposed zones (Rousset-Debet, 2012). Measurements taken for lichens in Valduc (Daillant et al., 122 123 2001) indicate maximum values on the order of 80,000 TU for the most exposed 124 lichens. Since the origin of the particulate organic matter in the Rhône is 90% nonnative (allochthonous), in other words due to the leaching of the catchment areas 125 (Lansard et al., 2009; Hamelin-Vivien et al., 2010), the leaching of tritiated organic 126 127 material in soil may therefore have a significant effect on organic tritium in suspended 128 matter and sediments.

With respect to airborne discharges of carbon-14, only recent data are available, because previously carbon-14 releases were not recorded separately from other beta/gamma emitters. Anyway, the traces in the land environment due to discharges into the atmosphere of carbon-14 are low due to a net predominance (80%) of discharges in the form of methane (Le Guen and Siclet, 2009) that cannot be absorbed by vegetation. Nevertheless, a slight increase is noted in the local land vegetation on the order of 5% to 15% (Roussel-Debet, 2012).

136

# 137 3.3.2 Direct liquid discharges of carbon-14 and tritium (HTO) into the Rhône

The two major contributors to liquid discharges of tritium (in the form of HTO) into the Rhône river are the Marcoule nuclear site and the nuclear power plants (Jean-Baptiste et al., 2018). In the past, Marcoule releases were predominant, but today releases are mainly due to the nuclear power plants (Fig. 3). Unfortunately, as noted above for carbon-14 airborne discharges, only recent data for liquid discharges of carbon-14 are available, because previously carbon-14 releases were not recorded separately from other beta/gamma emitters.

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146 3.3.3 Indirect liquid discharges of tritium (HTO) into the Rhône

147 CEA-Valduc is located in Bourgogne to the north-east of Dijon. The local 148 hydrology connects it to the Rhône via the Tille and the Saône. Although its tritium 149 discharges are in gaseous form only (mostly HTO), when a large amount of tritium (in 150 the form of HTO) are released into the atmosphere, it produces significant local 151 traces in the river network (Guétat et al., 2013). In the absence of dedicated studies, 152 the extent of the tritium contamination of the rivers around Marcoule and Valduc are 153 not known precisely. For several decades CEA-Valduc was the largest emitter of 154 tritium in the atmosphere in France. Based on the data of Guétat et al. (2013), the 155 proportion of tritium from gaseous discharges carried away by the local river network 156 can be estimated at around 2% (Jean-Baptiste et al., 2018). Here, we assume that 157 this figure also applies to Marcoule.

158

159 3.3.4 Tritium (OBT) discharges into the upper Rhône from the watchmaking industry

Substantial quantities of tritium (as a substitute for radium) were used between 160 1960 and 1990 by the watchmaking industry (Krejci and Zeller, 1979). Several 161 production units for fluorescent paints based on tritiated polystyrene supplied 162 163 numerous watchmaking workshops, principally in Switzerland but also, to a lesser 164 extent, in eastern France. This use of tritiated organic material is linked with the 165 significant traces found in sediments and suspended matter of the Rhône (Gontier and Siclet, 2011; Jean-Baptiste et al., 2018), although we cannot say if these are due 166 167 to past direct deposits into the Rhône or indirect deposits via the catchment areas. 168 These traces are at their highest in the upper Rhône, upstream of Creys Malville, the 169 northernmost nuclear power station on the Rhône, with current values in sediments between 10<sup>5</sup> - 10<sup>6</sup> TU (Jean-Baptiste et al., 2007) but are observed all along the river 170 (Fig. 4). This situation is only found in the Rhône - no such tritium contamination of 171 172 the sediments is observed for the other major French rivers where nuclear power stations are also in operation (Gontier and Siclet, 2011). 173

174

#### 175 **4. Methods**

176

177 KBROUS and KB-06 cores were analysed to determine the amounts of tritium 178 (OBT) and carbon-14 in the sedimentary organic matter. The sediment cores were taken with a Kullenberg corer in November 2001 during the REMORA 2 campaign of 179 the French Institute of Radioprotection and Nuclear Safety (IRSN). The KBROUS 180 181 core was extracted close to the mouth of the Rhône (43°18.30'N, 4°51.01'E) where 182 the sedimentation rates are the highest, thus ensuring a good temporal resolution, 183 while KB-06 (43°18.02'N, 4°52.62'E) was taken further offshore (Fig. 1 inset). The 184 cores were kept in cold storage and then cut into 10 cm sections. The sediment

samples were then lyophilised during 48 hours to ensure a complete removal of the
water, passed through a 2 mm sieve, ground up, then packaged in sealed plastic
bags.

The amount of tritium was determined by mass spectrometry using the <sup>3</sup>He 188 189 regrowth method (Clarke et al., 1976), with a detection limit below 0.1 TU. The dried sediment powder (typically 150 g) was transferred into a 100 mL low helium 190 diffusivity Corning 1724 glass bulb. To minimise <sup>3</sup>He blank, the bulbs were previously 191 192 baked in a flow of argon at 600°C for 24 hours to remove the helium dissolved in the 193 glass. All manipulations were undertaken in a glove-box flushed with argon to 194 minimize contamination by ambient air moisture. The bulbs were attached to a high vacuum line and evacuated down to  $<10^{-5}$  Torr, they were then flame-sealed. After 195 sealing, the samples were stored at -20°C to further minimise helium diffusion 196 197 through glass (Jean-Baptiste et al., 1989). After a period of storage of typically 100-150 days, the bulbs were connected to the inlet line of a mass spectrometer for <sup>3</sup>He 198 199 analysis. The instrument is a MAP 215-50 noble gas mass spectrometer equipped with a stainless steel low blank inlet system ( ${}^{3}$ He blank<  $3x10^{-20}$  mol). The analysis 200 201 protocol is described in detail by Jean-Baptiste et al. (2010).

The carbon-14 activities were measured by Accelerator Mass Spectrometry (AMS) at the LMC14-ARTEMIS facility (Saclay). The sediment samples were decarbonated (HCI 0.5N) and rinsed with de-ionised water before being dried at 60°C in a drying oven at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE). The samples were then introduced into quartz tubes in the presence of 500 mg of copper oxide and a silver thread. They were then heated to 835°C for 6 hours in order to transform the organic material into CO<sub>2</sub> (Hatté et al., 2003).

Accuracies on tritium and carbon-14 measurements are given in the tables of results.

In addition, following Gauthier and Hatté (2008), a few milligrams of sediment were used to measure the stable organic carbon isotope composition ( $\delta^{13}$ C). The measurements were carried out by EA-IRMS in continuous flow coupling an elementary analyser (Fisons Instrument NA 1500 Element Analyser) to a mass spectrometer (Thermo-Finigan Delta + XP Isotope-Ratio Mass Spectrometer). The  $\delta^{13}$ C is expressed in ‰ with respect to the standard PDB (Pee Dee Belemnite), with precision of ±0.08 ‰.

218

#### 219 **5. Results**

220

#### 5.1 OBT and carbon-14 vertical profiles

The vertical profiles of organically bound tritium (OBT) and carbon-14 are shown in Fig. 5 (see also Table 1 and 2). From the base to the top, the vertical profile of OBT in the KBROUS core displays an increase up to an initial peak at 390 cm depth, followed by two other peaks at 280 and 240 cm. The upper part of the core (230 cm to 0 cm) shows a decrease in tritium content. A peak of OBT is also present in the KB-06 core, with a maximum much nearer to the surface (30 - 40 cm deep) due to the lower sedimentation rate in this area.

The vertical profiles of carbon-14 present similar variations but the difference between the peaks and the baseline is much lower than for tritium. The carbon-14 activities are low (the majority are lower than 100 pmC) due to the diluting effect of an ancient refractory carbon component very low in carbon-14 (~ 0 pmC) present in

233 the coastal sediments held in suspension (Cathalot et al., 2013). Taking 100 pmC as 234 a reference for pre-industrial carbon-14, the baseline values for KB-06 (37 pmC) correspond to 37%-63% mixture of modern organic matter and ancient refractory 235 236 carbon. Using this mixing ratio, the peak value of 79.98 pmC recorded in the KB-06 core corresponds to a modern organic matter maximum of 216 pmC. This value is 237 close to the carbon-14 bomb-peak value of 200 pmC (Nydal and Lövseth, 1996). 238 239 Hence it does appear that a significant contribution from the carbon-14 bomb-peak 240 may have been captured in this sedimentary record.

 $\delta^{13}C$  of organic carbon is reported in Tables 1 and 2. Values range between -241 25.11‰ and -26.70‰ for KB-06 and between -25.11‰ and -27.31‰ for KBROUS. 242  $\delta^{13}$ C values within KB-06 are slightly greater than those of KBROUS, consistent with 243 the location of the core where there is more influence of marine conditions (see 244 below). The two cores display, from the base to the top, a similar and regular 245 decrease in the carbon isotopic composition, in good agreement with observations 246 for recent sediments and soils (Bentaleb and Fontugne, 1996): this 1% - 1.5% 247 decrease in  $\delta^{13}C$  values has to be related to the Suess effect and the atmospheric 248 input of CO<sub>2</sub> with a low <sup>13</sup>C/<sup>12</sup>C ratio resulting from the combustion of fossil fuel since 249 250 the beginning of the industrial period (Friedly et al., 1986; Trundiger et al., 1999).

The cores received organic carbon from two sources: terrestrial suspended matter from the Rhône and marine phytoplankton from the Mediterranean. In most sedimentary environment marine planktonic organic carbon is isotopically heavier than that of the carbon delivered to the ocean from terrestrial environments. Solution of the mixing equation  $\delta^{13}C = F_t \times \delta^{13}C_t + F_m \times \delta^{13}C_m$  (with  $F_m + F_t = 1$ ) provides a simple method for estimating the proportions of the two types of organic matter present in a given sample (Calder and Parker, 1968; Fontugne and Duplessy, 1986;

Fontugne and Jouanneau, 1987). In this equation,  $F_t$  and  $F_m$  are the fractions of terrestrial and marine organic matter, and  $\delta^{13}C_t$  and  $\delta^{13}C_m$  are the isotopic composition of the terrestrial and marine organic carbon sources, respectively. Following Fontugne and Calvert (1992) and Fontugne et al. (1989), we use  $\delta^{13}C$ values of -21‰ and -27‰ for the marine and terrestrial end-members, respectively. The calculation shows that the terrestrial fraction varies between 75% and 85% for KB-06 and between 85% and 90% for KBROUS.

265

266 5.2 Core timelines

The discharge of solid matter from the Rhône to the sea is characterised by large 267 seasonal and interannual variations; overall, on the order of 2 to 8 million tons per 268 year (Mt.yr<sup>-1</sup>), but it can reach up to 26.5 Mt.yr<sup>-1</sup> (Pont et al., 2002). The high 269 270 discharge episodes, responsible for about 80% of the total amount delivered to the coast (Antonelli et al., 2004; Roussiez et al., 2005), occur during floods. Due to the 271 impulsive nature of the discharge of solid matter, but also to the resuspension of 272 273 surface sediments by storms (Aloisi et al., 1982), the core samples do not reflect a 274 continuous sedimentation process. In addition, other processes such as bioturbation 275 and biological uptake add further complexity to the establisment of a reliable 276 chronology. Therefore, it is beyond the scope of the present study to produce a detailed chronology on which conclusions could be based. Nevertheless, it is very 277 278 important to place the measured vertical profiles on a time scale to calculate decaycorrected OBT concentrations in each core and thus to obtain OBT levels at the time 279 of deposition. In the following, we use the <sup>239,240</sup>Pu and <sup>241</sup>Am concentration 280 measurements in the cores along with historical discharges of <sup>239,240</sup>Pu by the 281 282 Marcoule site to infer a simplified chronology for each core assuming an average

sedimentation rate, as proposed by Lansard (2004). The main interest of these
radionuclides is that, apart from the small imprint by the bomb-tests fallouts, they
have a unique source in the Rhône river (the Marcoule site); the start of the releases,
in the mid-1970's, thus constitutes a convenient tie-point.

287

### 288 5.2.1 KBROUS core

The vertical distribution of <sup>239,240</sup>Pu in the KBROUS core is reported by Lansard et 289 290 al., 2007. The primary source of plutonium measured in the sediments near the Rhône mouth originates from the liquid effluents released by the Marcoule 291 292 reprocessing plant. The chronology of these discharges is available from Eyrolle et al., 2004. The visual comparison of the <sup>239,240</sup>Pu profile with the history of plutonium 293 liquid discharges from the Marcoule site allows us to estimate a mean sedimentation 294 295 rate of 0.186 m.yr<sup>-1</sup> (Fig. 6). This average sediment accumulation rate is in good agreement with that determined by Lansard (2004) who concludes, based on the 296 historical release of <sup>239,240</sup>Pu from Marcoule, that the average sedimentation rate for 297 KBROUS over the last forty years is of the order of 0.17 m.yr-1 298

299

### 300 5.2.2 KB-06 core

In the KB-06 core the vertical distribution of <sup>241</sup>Am, an other artificial radionuclide released along with plutonium by Marcoule military activities, was measured by IRSN (unpublished results). The history of <sup>241</sup>Am discharges from the Marcoule site can be reconstructed from that of <sup>239,240</sup>Pu (Eyrolle et al., 2004) using the good correlation between <sup>239,240</sup>Pu and <sup>241</sup>Am observed in the KBROUS core (Fig. 7) and assuming that, since both radionuclides have the same strong affinity for solid particles, the

 $^{241}$ Am/ $^{239,240}$ Pu ratio is not significantly modified between the liquid releases and the deposition in the sediment. From the visual comparison of the  $^{241}$ Am profile with the history of  $^{241}$ Am liquid discharges (Fig. 8), we deduce a mean sedimentation rate of 0.025 m.yr<sup>-1</sup>.

311

## 312 5.3. Time-evolution of the OBT record

313 Figure 9 displays the time-evolution of the tritium (OBT) content of the organic 314 matter in the KB-06 and KBROUS cores. For each core, the time scale used is that determined in Section 5.2. The tritium concentrations have been decay-corrected so 315 316 the OBT content is that of suspended organic matter at the date of deposition. In both 317 cores, tritium concentrations start to increase in the early 1970's and decrease after 1990. The chronological agreement between the two OBT profiles of Figure 9 shows 318 319 that our strategy of using average sedimentation rates gives coherent results in spite 320 of its oversimplification. For the KBROUS core (Fig. 9 black solid line), the higher resolution relative to KB-06 allows us to distinguish two peaks, a first one reaching up 321 to 40,000 TU and a second one with values up to 30,000 TU. For 1986-1987, Gontier 322 323 et al. (1992) reported a tritium (OBT) value of 26,160 TU in surface sediments (0-3 324 cm) at the mouth of the Rhône. This is fully consistent with the tritium concentrations 325 recorded in the KBROUS core (see Fig. 9). Later on, tritium levels decrease strongly, in agreement with tritium (OBT) measured in suspended matter at Arles in 2010-2011 326 327 (Jean-Baptiste et al., 2018).

The tritium maximum measured in the KB-06 core, 20,000 TU (black dotted line Fig. 9), is lower than that of the KBROUS core. This decrease in tritium as distance from the mouth increases, has already been noted by Gontier et al. (1992). It can be explained by the fact that the size distribution of river suspended matter is shifted

towards larger particles compared to marine suspended matter (Eisma et al., 1991; Reynolds et al., 2010). Because of this, river particles tend to settle preferentially close to the river mouth. Therefore, sediments closer to the river mouth are proportionally richer in organic matter of riverine origin (i.e., with a greater tritium content) than sediments further offshore.

337

# **6.** Attributing OBT levels in organic matter to the various known sources

339 6.1 Tritium from atmospheric nuclear tests

The OBT for the land-based organic material due to atmospheric nuclear tests is of the same magnitude as that for rain. The mean annual tritium content for rain peaks towards 2,000 TU in 1963 at the latitude of France. This figure is far lower than the maximum values recorded for the KBROUS core (~ 40,000 TU). This clearly indicates that atmospheric nuclear tests are not the main cause of the peak in tritium recorded in the Rhône prodelta.

346

347 6.2 Liquid tritium discharges

348 The OBT content of the organic matter at the surface of the KBROUS core (corresponding to year 2001) was  $1855 \pm 200$  TU for a total annual liquid discharge 349 of 200.8 TBg (Fig. 3). With the mean flow rate of the Rhône being 1700 m<sup>3</sup> s<sup>-1</sup>, this 350 discharge corresponds to an elevation of the tritium content of the river water of 351 31.4 TU. In comparison, on the Loire river (mean flow rate = 850 m<sup>3</sup> s<sup>-1</sup>), where four 352 353 nuclear electricity production sites are in operation with total annual liquid tritium 354 discharges of about 150 TBg (EDF, 2007), the OBT level in sediments downstream 355 of the nuclear plants in 2003 was only 55 TU (Gontier and Siclet, 2011), in spite of a

356 higher mean elevation of the tritium content of the river water (47 TU). The maximum of the liquid discharge of tritium (HTO) to the Rhône reaches ~1000 TBq (Fig. 3), 357 358 corresponding to an additional tritium content of the river waters of 156 TU. Scaled to 359 the Loire river data, a tritium level in the organic matter on the order of 183 TU should be expected. This value is far from the maximum values (40,000 TU) recorded in the 360 361 KBROUS core. These comparisons with the Loire river data clearly indicate that the 362 liquid tritium discharges cannot be held responsible for the high values of tritium 363 recorded in the Rhône prodelta. This fact is corroborated by the close examination of 364 the data which reveals that, whereas the tritium discharges start to increase again 365 after 1998 (with an increase by 70% between 1998 and 2010 - Fig. 3), the tritium 366 content of sediments decreases continuously (Fig. 9), thus indicating that the two 367 records are not correlated.

368

369 6.3 Gaseous tritium discharges

370 We have seen (Section 3.3.1) that gaseous tritium (HTO) discharged into the 371 atmosphere later appears in the land-based environment. The two largest emitters of tritium into the atmosphere are the CEA-Valduc and Marcoule sites. Environmental 372 data gathered around these sites (Section 3.3.1) show that these releases have a 373 374 very significant effect on the local land vegetation. However, the global influence at the scale of the Rhône watershed, and therefore on the organic matter transferred to 375 376 the river, remains to be quantified. In the study into the influence of tritium gaseous 377 discharges on the environment around the Bruyère-le-Châtel nuclear site operated 378 by CEA, Baglan et al. (2011) demonstrated that the tritium content in the land-based 379 organic material decreases with distance following an exponential rule described by 380 the formula:

381 
$$(T/H) = (T/H)^{0} + (T/H)^{max} \exp(-r/r_{0})$$
 (1)

where r is the distance, (T/H)<sup>max</sup> is the value in the immediate environment of the 382 source of the discharge (corresponding to r=0) and  $(T/H)^0$  is the value from 383 background noise. Baglan et al. (2011) suggest a value for r<sub>0</sub> equal to 0.8 km. 384 Applied to the data obtained around Marcoule in 2008-2011 by Roussel-Debet 385 386 (2012), it is noted that this value is satisfactory for the local environment, but 387 minimises the influence of discharges beyond a few kilometres (Fig. 10). The data for Marcoule is better described using a linear combination of two exponentials, one as 388 389 near-field with an r<sub>0</sub> of 0.8 km and a second with an r'<sub>0</sub> equal to 8 km which increases 390 the distance influenced by the discharge to 60-80 km:

391 
$$(T/H) = (T/H)^{0} + (T/H)^{max} [exp(-r/r_0) + 0.1 exp(-r/r'_0)]$$
 (2)

with  $(T/H)^{max} = 30,000$  TU. Over the same period 2008-2011, the mean value for gaseous tritium discharge from Marcoule was  $D^{T} = 302$  TBq.yr<sup>-1</sup>.

The mean value for year n of the tritium added to the land vegetation by the gaseous tritium releases  $D_n^T$  can therefore be written :

396 
$$(T/H)_n = A^{-1} (T/H)_n^{max} \int_0^{\infty} [exp(-r/r_0) + 0.1 exp(-r/r'_0)] 2\pi r dr$$
 (3)

where A is the total surface area of the Rhône watershed (A ~100000 km<sup>2</sup>). Since formula (3) implies that  $(T/H)_n^{max}$  is proportional to the annual discharge  $D_{n}^T$ , (T/H)<sub>n</sub><sup>max</sup> can be expressed as  $(T/H)_n^{max} = \alpha D_{n}^T$ , with  $\alpha = 30,000/302$  by reference to the situation around Marcoule in 2008-2011.

### 401 Solving the integral in formula (3) leads to :

402 
$$(T/H)_n = 2\pi A^{-1} \alpha D_n^T \times [r_0^2 + 0.1 r_0^2]$$
 (4)

Finally, the mean tritium content of land vegetation for the whole Rhône catchment under the influence of the gaseous discharges from both Marcoule and Valduc for the year n can be expressed as :

$$(T/H)_n^{\text{total}} = (T/H)_n^0 + (T/H)_n^{\text{Marcoule}} + (T/H)_n^{\text{Valduc}}$$
(5)

407 The peak value for the tritium gaseous discharges by Marcoule and Valduc occurred around 1974 with 8600 TBg and 38800 Tbg respectively (Fig. 2). This 408 corresponds to  $(T/H)_{1974}^{Marcoule} = 378 \text{ TU}$  and  $(T/H)_{1974}^{Valduc} = 1704 \text{ TU}$ . Taking 409 (T/H)<sup>0</sup><sub>1974</sub> = 100 TU (IAEA database at <u>https://nucleus.iaea.org /wiser/gnip.php</u>), the 410 mean tritium content for the land vegetation of the whole Rhône catchment under the 411 412 influence of the discharges of Marcoule and Valduc at their historical peak of 1974 413 amounts to 2182 TU. This value represents about 5% of the tritium peak value recorded in the KBROUS core. Moreover, this estimate is probably an upper limit for 414 415 the following reasons:

416 - The function describing the decreasing influence of the discharge with the417 distance was deliberately chosen as an envelope curve.

The integration over 360° is certainly an overestimation as the wind rose has a
very pronounced directional element: at the Marcoule site for example, the wind
(Mistral) blows from the north more than half of the time.

421 - A substantial proportion of the gaseous discharges from Valduc enters the River
422 Seine basin.

The calculation does not take into account the smoothing effect caused by the
fact that the residence time of the organic matter in the land vegetation is greater
than one year.

This probable overestimation by formula (5) is consistent with the fact that, in the case of Valduc, the comparison of the tritium contents of the sediments in the Rhône

downstream of Le Bugey power station and upstream of Saint Alban power station 428 429 (Gontier and Siclet, 2011) reveals no anomaly associated with the confluence of the Saône (see Fig. 1). With regard to Marcoule, the tritium contents measured in the 430 431 sediments of the Rhône at the level of Tricastin power station (Gontier and Siclet, 2011) are similar to those measured in the prodelta. As Tricastin is to the north of the 432 Marcoule site and therefore little influenced by its discharges (Roussel-Debet, 2012), 433 this again suggests, as with the case of Valduc, that the imprint of gaseous 434 435 discharges from Marcoule in the sediments is masked by a much larger signal. This 436 inevitably points to the legacy of the past use of tritiated luminous paints by the 437 watchmaking industry in the upper Rhône area.

As already pointed out in Section 3.3.4, the tritium anomaly in the upstream 438 sediments of the Rhône, attributed to the watchmaking industry, is still very 439 pronounced, with maximum values in the range 10<sup>5</sup> to 10<sup>6</sup> TU between 2002-2005 440 441 near to the Swiss border (Jean-Baptiste et al., 2007). This shows that there is still a 442 considerable amount of tritium stored in the upstream Rhône sediments. This 443 quantity of stored sediment, whose tritium-contaminated particulate matter moves from upstream to downstream particularly when the dams are flushed (every three 444 years from the 1970s until 2003), has a very high T/H ratio. Due to its scale, this 445 446 contamination of the Rhône sediments seems capable by itself of explaining what 447 lies behind the peak in tritium recorded in the prodelta sediments, masking all other sources of tritium. 448

449

# 450 **7. Conclusion**

451 Tritium (OBT) and carbon-14 levels in suspended organic matter carried by the 452 Rhône over the period 1970-2001 were obtained based on the study of two sediment

453 cores collected in the sedimentary cone off the river mouth. The main conclusions of454 the present work are as follows:

455 - Measured tritium and carbon-14 concentrations display a peak commencing at
456 the start of the 1970s and extending over some thirty years.

- The source of the carbon-14 peak is difficult to establish due to the fact that carbon-14 releases by the nuclear industry are unknown (until recently, carbon-14 releases were not recorded separately from other beta/gamma emitters). However, it appears that a significant contribution from the carbon-14 bomb-peak may have been captured in the sedimentary record. Anyway, carbon-14 levels remain low (below the modern carbon-14 natural value of 100 pmC) because of the diluting effect of a refractory carbon component very low in carbon-14 present in the coastal sediments.

- Organically bound tritium levels are more pronounced, with maximum values up
to 40,000 TU (i.e., 20 times the tritium peak of the atmospheric nuclear tests of the
1950's and early 1960's).

467 - Detailed study of the impact of the various contributions to the OBT seen in the 468 sedimentary record strongly suggests that these high tritium levels cannot be 469 explained neither by the bomb-peak nor by the releases of the nuclear industry but are the result of the sediments in the Rhône being contaminated from upstream to 470 471 downstream by the past utilisation of tritiated luminous paints by the watchmaking 472 industry. This contamination is at its highest in the upper Rhône, upstream of Creys Malville, the northernmost nuclear power station on the Rhône. Its influence, which is 473 474 well documented all along the river, masks all other sources of tritium and seems capable by itself of explaining what lies behind the peak in tritium recorded in the 475 476 prodelta sediments.

477

#### 478 **References**

Aloisi J.C., Cambon J.P., Carbonne J., Cauwet G., Millot C., Monaco A. and Pauc H.
(1982) Origin and role of the bottom nepheloid layer in the transfer of particles
into the marine environment. Application to the Gulf of Lions. Oceanologica Acta
5 (4), 481-491.

Antonelli C., Provansal M. and Vella C. (2004) Recent morphological channel
changes in a deltaic environment. The case of the Rhone River, France.
Geomorphology 57, 385–402.

Baglan, N., Alanic, G., Le Meignen, R., Pointurier, F. (2011) A follow-up of the
decrease of non-exchangeable organically bound tritium levels in the
surroundings of a nuclear research center. J. Environ. Radioact. 102, 695-702.

- Bentaleb I., Fontugne M. (1996) Anthropogenic CO<sub>2</sub> invasion of the surface Ocean:
  its influence on the organic carbon isotope composition of phytoplankton.
  C.R.Acad. Sci., Paris, Ser. IIa, 322, 743-748.
- 492 Calder, J. A. and Parker, P. L. (1968) Stable carbon isotope ratio as indices of 493 petrochemical pollution of aquatic systems. Environ. Sci. Technol., 2, 535-539.

494 Cathalot, C., Rabouille, C., Tisnérat-Laborde, N., Toussaint, F., Kerhervé, P., 495 Buscail, R., Loftis, K., Sun, M.Y., Tronczynski, J., Azoury, S., Lansard, B., 496 Treignier, C., Pastor, L., Tesi, T. (2013) The fate of river organic carbon in 497 coastal areas: A study in the Rhône river delta using multiple isotopic ( $\delta^{13}$ C, 498  $\Delta^{14}$ C) and organic tracers. Geochimica et Cosmochimica Acta 118, 33-55.

Cauquoin, A., Jean-Baptiste, P., Risi, C., Fourré, E., Stenni, B., Landais, A. (2015)
 The global distribution of natural tritium in precipitation simulated with an

Atmospheric General Circulation Model and comparison with observations. Earth
Planet. Sci. Lett. 427, 160-170.

- 503 Charmasson S. (2003) <sup>137</sup>Cs inventory in sediment near the Rhone mouth: role 504 played by different sources. Oceanologica Acta 26, 435–441.
- Charmasson S., Bouisset P., Radakovitch O., Pruchon A.S., Arnaud M. (1998) Long core profiles of <sup>137</sup>Cs, <sup>134</sup>Cs, <sup>60</sup>Co and <sup>210</sup>Pb in sediment near the Rhone River
   (Northwestern Mediterranean Sea). Estuaries 21, 367–378.
- 508 Clarke, W.B., Jenkins, W.J., Top, Z. (1976) Determination of tritium by mass 509 spectrometry measurement of <sup>3</sup>He<sup>+</sup>. Int. J. Appl. Radiat. Isot. 27, 515 - 522.
- 510 Daillant, O., Pigrée, G., Gueidan, C., Jacquiot, L. (2001) Recherche de tritium
  511 organiquement lié dans les lichens des environs de Valduc. Rapport de
  512 l'Observatoire Mycologique pour la Structure d'Echange et d'Information sur
  513 Valduc (SEIVA), Observatoire Mycologique, F-71250 Mazille.
- 514 EDF (Electricité de France) (2007) Nucléaire & Environnement 2007 Report, 36pp.
- Eisma, D., Bernard, P., Cadée, G.C., Ittekkott, V., Kalf, J., Laane, R., Martin, J.M.,
  Mook, W.G., Van Put, A., Schuhmacher, T. (1991) Suspended-matter particle
  size in some west-european estuaries : Part I : particle size distribution.
  Netherlands Journal of Sea Res. 28, 193-214.
- 519 Eyrolle F., Charmasson S., Louvat D. (2004) Plutonium isotopes in the lower 520 reaches of the River Rhone over the period 1945–2000: fluxes towards the 521 Mediterranean Sea and sedimentary inventories. J. Environ. Radioact. 72, 273– 522 286.

- 523 Eyrolle-Boyer, F., Boyer, P., Claval, D., Charmasson, S. (2014) Apparent enrichment
  524 of organically bound tritium in rivers explained by the heritage of our past. J.
  525 Environ. Radioact. 136, 162-168.
- Eyrolle, F., Ducros, L., Le Dizès, S., Beaugelin-Seiller, K., Charmasson, S., Boyer,
  P., Cossonnet, C. (2018) An updated review on tritium in the environment. J.
  Environ. Radioact. 181, 128-137.
- 529 Fontugne M. and Jouanneau J.M. (1987) Modulation of the particulate organic 530 carbon flux to the ocean by a macrotidal estuary: organic carbon isotopes 531 evidence from the Gironde system. Estuarine Coastal Shelf Sci. 24, 377-387.
- Fontugne M., Paterne M., Calvert S.E., Murat A., Guichard F., Arnold M. (1989)
  Adriatic deep warer formation during the Holocene. Implication for the reoxygenation of the deep eastern Mediterranean Sea. Paleoceanography 4, 199206.
- 536 Fontugne M. and Calvert S.E. (1992) Late Pleistocene variability of the carbon 537 isotopic composition of organic matter in the eastern Mediterranean: monitor of 538 changes in carbon sources and atmospheric CO<sub>2</sub> concentrations. 539 Paleoceanography 7, 1-20.
- Friedly H., Lötscher H., Oeschger, H., Siegenthaler U., Stauffer, B. (1986) Ice core
  record of the <sup>13</sup>C/<sup>12</sup>C ratio of the atmospheric CO<sub>2</sub> in the two past centuries.
  Nature 324, 237-238.
- Gauthier C. and Hatté, C. (2008) Effects of handling, storage and chemical
  treatments on <sup>13</sup>C values of continental sediments. Geochem. Geophys.
  Geosyst., 9(8), Q08011, doi:10.1029/2008GC001967.

Gontier, G., Grenz, C., Calmet, D., Sacher, M. (1992) The contribution of Mytilus sp.
in radionuclide transfer between water comlumn and sediments in the estuarine
and delta systems of the Rhône River. Estuarine Coastal Shelf Sci. 34, 593-601.

Gontier, G. and Siclet, ,F. (2011) Organic tritium in freshwater ecosystems: long-term
trends in the environment of French nuclear power plants. Radioprotection 46,
457-491.

Guétat, P., Le Goff, P., Boyer, C., Duda, J.M. (2013) Apports de la surveillance du
centre CEA-Valduc sur la connaissance des transferts de l'eau tritiée
atmosphérique dans les différents compartiments de l'environnement.
Radioprotection 48, 367-389.

Harmelin-Vivien, M., Dierking, J., Banaru, D., Fontaine, M.F., Arlhac, D. (2010)
Seasonal variation in stable C and N isotope ratios of the Rhone River inputs to
the Mediterranean Sea (2004–2005). Biogeochemistry 100, 139-150.

559 Hatté, C., Poupeau, J.J., Tatman, J.F., Paterne, M. (2003) Development of an 560 automated system for preparation of organic samples. Radiocarbon 45, 421-430.

- Jean-Baptiste, P., Andrié, C., Lelu, M. (1989) The diffusion of helium through glass.
  Glass Technol. 30, 228–230.
- Jean-Baptiste, P., Baumier, D., Fourré, E., Dapoigny, A., Clavel, B. (2007) The
  distribution of tritium in the terrestrial and aquatic environments of the CreysMalville nuclear power plant (2002-2005). J. Environ. Radioact. 94, 107-118.
- Jean-Baptiste, P., Fourré, E., Dapoigny, A., Baumier, D., Baglan, N., Alanic, G.
   (2010) <sup>3</sup>He mass spectrometry for very low-level measurement of organic tritium
   in environmental samples. J. Environ. Radioact. 101, 185-190.

Jean-Baptiste, P., Fontugne, M., Fourré, E., Marang, L., Antonelli, C., Charmasson,
S., Siclet, F. (2018) Tritium and radiocarbon levels in the Rhône river delta and
along the French Mediterranean coastline. J. Environ. Radioact. 187, 53-64.

572 Krejci, K. and Zeller, A. (1979) Tritium pollution in the Swiss luminous compound 573 industry. In: Behaviour of tritium in the Environment. IAEA Proceedings series 574 STI/PUB/498, 65-77.

Lansard B., Charmasson, S., Gascó, C., Antón, M.P., Grenz, C., Arnaud, M. (2007)
Spatial and temporal variations of plutonium isotopes (<sup>238</sup>Pu and <sup>239,240</sup>Pu) in
sediments off the Rhone River mouth (NW Mediterranean). Sci. Total Environ.
376, 215–227.

- Lansard, B. (2004) Distribution et remobilisation du Plutonium dans les sédiments du
  prodelta du Rhône (Méditerranée Nord-Occidentale). PhD thesis, Université de la
  Méditerranée Aix-Marseille II, pp.279.
- Lansard, B., Rabouille, C., Denis, L., Grenz, C. (2009) Benthic remineralization at the
  land-ocean interface: A case study of the Rhône River (NW Mediterranean Sea).
  Estuarine Coastal Shelf Sci. 81, 544-554.
- Le Guen, B., Siclet, F. (2009) Impact du carbone-14 autour des centrales nucléaires
   EDF. Radioprotection 44, 495-504.

587 Monaco, A., Courp, T., Heussner, S., Carbonne, J., Fowler, S.W., Deniaux, B. (1990)

- Seasonality and composition of particulate fluxes during ECOMARGE-I, western
  Gulf of Lions. Cont. Shelf Res. 10, 959-987.
- 590 Mook, W.G. and van der Plicht, J. (1999) Reporting C-14 activities and 591 concentrations. Radiocarbon 41, 227-239.

Nydal, R. and Lövseth, K. (1996) Carbon-14 Measurements in Atmospheric CO<sub>2</sub> from
Northern and Southern Hemisphere Sites, 1962-1993. ORNL/CDIAC-93, NDP057. Carbon Dioxide Information Analysis Center, Oak Ridge National
Laboratory, Oak Ridge, Tennessee. 67 pp. doi: 10.3334/CDIAC/atg.ndp057

- Pont, D., Simonnet, J.P., Walter, A.V. (2002) Medium-term changes in suspended
  sediment delivery to the ocean: Consequences of catchment heterogeneity and
  river management (Rhone River, France). Estuarine Coastal Shelf Sci. 54 (1), 118.
- Radakovitch O., Charmasson S., Arnaud M. and Bouisset P. (1999) <sup>210</sup>Pb and
   caesium accumulation in the Rhône delta sediment. Estuarine Coastal Shelf Sci.
   48, 77-99.
- Reynolds, R.A., Stramski, D., Wright, V.M., Wozniak, S.B. (2010) Measurements and
  characterisation of particle size distributions in coastal waters. J. Geophys. Res.
  115, C08024, doi: 10.1029/2009JC005930.
- Roussel-Debet, S. (2012) Constat radiologique Vallée du Rhône. Rapport final relatif
   au milieu terrestre. Rapport IRSN PRP-ENV/SESURE/2012-06.
- Roussiez V., Aloisi J. C., Monaco A. and Ludwig W. (2005) Early muddy deposits
  along the Gulf of Lions shoreline: a key for a better understanding of land-to-sea
  transfer of sediments and associated pollutant fluxes. Mar. Geol. 222, 345–358.
- Trundinger C.M., Enting I.G., Francey R.J., Etheridge D.M., Rayner P.J. (1999) Long-term variability in the global carbon cycle inferred from a high-precision  $CO_2$  and  $\delta^{13}C$  ice-core record. Tellus B 51, 233–248.

#### 614 **Figure captions**

Figure 1: Location of main nuclear activities in the Rhône catchment: power stations (in red) operated by Electricité de France (EDF) and nuclear facilities (in blue) operated by the French Atomic Energy Commission (CEA) and the AREVA company. Inset: location of the KBROUS and KB-06 cores taken in November 2001.

Figure 2: Tritium (HTO) airborne releases (Jean-Baptiste et al., 2018). Dotted curve:
Marcoule releases. Solid curve: cumulative releases from Marcoule and Valduc.

Figure 3: Tritium liquid releases (Jean-Baptiste et al., 2018). Dotted curve: Marcoule releases. Solid black curve: cumulative releases from Marcoule and EDF nuclear power stations. Blue curve: cumulative releases from Marcoule, EDF nuclear power stations and indirect inputs to the Rhône by the contamination of the hydrographic network by tritium airborne releases (see Section 3.3.3).

Figure 4: Spatial distribution of the tritium (OBT) content of sediments along the
Rhône in 2004-2005 (Gontier & Siclet, 2011).

Figure 5: Profiles of organically bound tritium (OBT) (in black) and carbon-14 (in blue)
in the organic matter of (a) the KB-06 and (b) the KBROUS sediment core samples
collected in 2001 at the mouth of the Rhône.

Figure 6: Comparison between the history of <sup>239,240</sup>Pu discharges from the Marcoule
site (Eyrolle et al., 2004) and the vertical distribution of <sup>239,240</sup>Pu in the KBROUS core
(Lansard et al., 2007) for a constant sedimentation rate of 0.186 m.yr<sup>-1</sup>.

Figure 7: Correlation between <sup>239,240</sup>Pu and <sup>241</sup>Am (in Bq.kg<sup>-1</sup> of dry sediment) for the
KBROUS core (<sup>241</sup>Am data are from the Institute of Radioprotection and Nuclear
Safety - IRSN).

Figure 8: Comparison between the history of  $^{241}$ Am discharges from the Marcoule site and the vertical distribution of  $^{241}$ Am in the KB-06 core for a constant sedimentation rate of 0.025 m.yr<sup>-1</sup> ( $^{241}$ Am data are from IRSN).

Figure 9: Time-evolution of the tritium content of the organic matter (OBT) in the KBROUS (solid black curve) and KB-06 (dotted black curve) cores. Red rectangle: OBT in a surface sediment (0-3 cm) from the mouth of the Rhône in 1986-1987 by Gontier et al., 1992; Red crosses: tritium content of suspended matter at Arles in 2010-2011 (Jean-Baptiste et al., 2018).

- 645 Figure 10: Organically bound tritium (OBT) for land vegetation in the environment
- around Marcoule with the distance to the source of tritium discharges into the
- atmosphere (Roussel-Debet, 2012). The black curve represents the exponential
- 648 decrease proposed by Baglan et al. (2011) to explain the data around the CEA site of
- 649 Bruyère-le-Châtel. The red curve is the one adopted for this study (see Section 6.3).

# 650 **Table captions**

- Table 1: Tritium, carbon-14 and  $\delta^{13}$ C measurements in the KBROUS sediment core.
- <sup>652</sup> <sup>241</sup>Am and <sup>239,240</sup>Pu data (in Bq.kg<sup>-1</sup> of dry sediment) are from the IRSN database and
- 653 Lansard et al. (2007), respectively.
- 654
- Table 2: Tritium, carbon-14 and  $\delta^{13}$ C measurements in the KB-06 sediment core.
- <sup>656</sup> <sup>241</sup>Am data (in Bq.kg<sup>-1</sup> of dry sediment) are from the IRSN database.

Depth	<sup>14</sup> C		δ <sup>13</sup> C	OBT (TU)		·U)	Year	OBT (TU)			<sup>241</sup> Am			<sup>239,240</sup> Pu		
(cm)	(pmC)		(‰)				(18.6 cm.yr <sup>-1</sup> )	decay-corrected		rrected	(Bq.kg <sup>-1</sup> )		g <sup>-1</sup> )	(Bq.kg <sup>-1</sup> )		g <sup>-1</sup> )
0-10	76,65 ±	0,25	-26,30	1093	±	118	2001,59	1855	±	200	<0,7			0,256	6 ± 0,012	
10-20	67,06 ±	0,34	-26,27	640	±	90	2001,05	1120	±	157	0,58	±	0,25			
20-30	74,79 ±	0,27	-26,29	2296	±	250	2000,52	4141	±	451	<0,8			0,356	±	0,016
30-40	82,37 ± 0,30 -26,45 2565 ± 329		1999,98	4769	±	612	<1,2									
40-50	75,08 ±	0,24	-26,45	1400	±	147	1999,44	2682	±	282	<1,1			0,357	±	0,014
50-60	65,88 ±	0,25	-25,82	2088	±	302	1998,90	4123	±	596	<0,7					
60-70	67,31 ±	0,32	-26,44	1906	±	194	1998,37	3879	±	395	<1,0			0,308	±	0,015
70-80	69,33 ±	0,25	-26,17	1797	±	211	1997,83	3771	±	443	0,64	±	0,22	0,393	±	0,013
80-90	79,93 ±	0,25	-26,49	2469	±	279	1997,29	5340	±	603	1,16	±	0,27	0,770	±	0,025
90-100	81,37 ±	0,29	-26,41	2428	±	338	1996,75	5413	±	753	1,04	±	0,26			
100-110	72,49 ±	0,24	-26,35	2508	±	315	1996,21	5762	±	724	<1,1			0,841	±	0,023
110-120	68,97 ±	0,23	-26,31	2299	±	395	1995,68	5445	±	936	<1,2					-
120-130	83,40 ±	0,57	-26,41	2435	±	294	1995,14	5944	±	718	1,04	±	0,26	1,247	±	0,035
130-140	76,45 ±	0,25	-26,21	1829	±	254	1994,60	4601	±	639	0,54	±	0,26			
140-150	77,26 ±	0,29	-26,13	2289	±	222	1994,06	5935	±	575	0,66	±	0,28	0,616	±	0,018
150-160	70,46 ±	0,22	-26,07	1664	±	162	1993,53	4448	±	433	<1,2			0,340	±	0,012
160-170	91,53 ±	0,42	-26,42	2727	±	258	1992,99	7512	±	710	1,27	±	0,27	1,665	±	0,047
170-180	79,95 ±	0,25	-26,35	3136	$ _{\pm} $	362	1992,45	8904	±	1029	1,21	±	0,3	1,225	±	0,032
180-190	87,16 ±	0,64	-27,31	3131	±	311	1991,91	9162	±	911	2.8	±	0,4	2,768	±	0,069
190-200	84.57 ±	0.36	-26.51	3148	±	327	1991,38	9497	±	986	2.5	±	0.4	2,142	±	0,051
200-210	80.63 ±	0.34	-25,96	3663	$ _{\pm} $	389	1990.84	11388	±	1208	4.7	±	0.5	3,895	±	0,097
210-220	73.60 ±	0.32	-26.02	4164	$ _{\pm} $	749	1990.30	13342	+	2402	5.0	$ _{\pm}$	0.5	-,		-,
220-230	77.23 ±	0.27	-25,99	4298	$ _{\pm} $	519	1989.76	14195	±	1714	5.1	±	0.5	3.983	±	0.115
230-240	84.34 ±	0.30	-26.07	8720	±	1191	1989.23	29684	±	4054	7.2	±	0.6	,		,
240-250	76.53 ±	0.42	-26,11	4589	$ _{\pm} $	506	1988.69	16101	±	1774	5.9	±	0.6	4.770	±	0.127
250-260	74,46 ±	0,29	-26,34	6163	$ _{\pm} $	895	1988,15	22289	±	3236	5,7	±	0,5	,		,
260-270	118.30 ±	0.34	-26.08	5226	$\left  \pm \right $	616	1987.61	19482	±	2295	7.3	$\pm$	0.6	5.631	±	0.248
270-280	95.35 ±	0.34	-25.68	7708	$ _{\pm} $	851	1987.08	29615	±	3269	9.0	±	0.7	,		,
280-290	60,43 ±	0,25	,	6038	±	600	1986,54	23913	±	2377	9,4	±	0,7	5,974	±	0,258
290-300	67.62 ±	0.22	-26.15	3856	$\left  \pm \right $	426	1986.00	15741	±	1738	6.2	±	0.6	3.394	±	0.088
300-310	57.51 ±	0.23	-26.09	2540	±	311	1985,46	10687	±	1308	1.22	±	0.3	1,090	±	0,056
310-320	77.04 ±	0.28	-26,13	3877	$ _{\pm} $	385	1984.92	16813	±	1669	4.4	±	0.5	2.896	±	0.072
320-330	79.82 ±	0.25	-26.79	2842	$ _{\pm} $	328	1984.39	12700	±	1466	4.5	±	0.5	3.071	±	0.140
330-340	69.29 ±	0.26	-25.66	3112	±	352	1983.85	14338	±	1623	2.5	±	0.4	,		,
340-350	,	,	-25.83	3721	$ _{\pm} $	447	1983.31	17668	±	2122	3.1	±	0.4	2.838	±	0.137
350-360	66.61 ±	0.27	-25.86	3621	±	448	1982.77	17720	±	2191	2.6	±	0.4	,		,
360-370	62.76 ±	0.30	-25.89	3660	$\left  \pm \right $	450	1982.24	18461	±	2270	2.7	±	0.4	3.696	±	0.177
370-380	63.08 ±	0.22	-25.82	3598	$\left  \frac{1}{2} \right $	440	1981.70	18708	±	2289	2.13	$ _{\pm}$	0.29	-,	-	-,
380-390	64 27 +	0.22	-25 60	7524	$\left  \begin{array}{c} - \\ + \end{array} \right $	848	1981 16	40318	+	4544	24	+	0.4	2,499	+	0.122
390-400	62 85 +	0.27	-25 71	2965	$\left  \begin{array}{c} - \\ + \end{array} \right $	317	1980.62	16377	+	1751	31	+	0.4	_,		-, -==
400-410	64 80 +	0.45	-25.92	4419	$\left  \begin{array}{c} - \\ + \end{array} \right $	493	1980.09	25156	+	2807	2 55	+	0.32	1 504	+	0.082
410-420		0,10	-25.86	2909	$\left  \begin{array}{c} - \\ + \end{array} \right $	329	1979 55	17067	+	1931	1 22	+	0.27	.,	- 0,002	
420-430	49 09 +	0 19	-25 47	3311	$\left  \begin{array}{c} - \\ + \end{array} \right $	340	1979.01	20027	+	2056	0.87	+	0.3	1 057	± 0.048	
430-440	59 79 +	0.21	-25.69	2595	-	335	1978 47	16178	_	2087	<0.7	-	5,5	.,	-  -, -, -, -, -, -, -, -, -, -, -, -, -,	
440-450	59.95 +	0.23	-25.95	2000	÷	250	1977 94	13483	_+	1606	<1.3			1 067	± 0.050	
450-460	58 60 +	0.34	-25 11	2465	<del>`</del>	337	1977 40	16324	_	2234	<1 4			.,	-	2,000
460-470	49.97 +	0.24	-25.96	2721	÷	309	1976 86	15161	$ _{+}^{\perp} $	2109	<1 1			0.630	_	0 029
470-473		0,21	_0,00	1888	$\left \frac{1}{2}\right $	272	1976.51	13145	$\left  \frac{1}{2} \right $	1892	<1.1			0,550	$ _{\pm}^{-} $	0,026

Depth	oth <sup>14</sup> C			δ <sup>13</sup> C	OBT (TU)			Year	OBT (TU)			<sup>241</sup> Am		
(cm)	(cm) (pmC)			(‰)				(2.5 cm.yr <sup>-1</sup> )	decay-corrected			(Bq.kg⁻¹)		
0-10	59,61	ŧ	0,22	-26,33	1212	±	153	1999,86	2269	ŧ	287			
10-20	61,76	±	0,25	-26,70	2020	±	279	1995,86	4734	±	653			
20-30	79,98	±	0,30	-26,32	1921	±	237	1991,86	5640	±	695	0,71	±	0,27
30-40	74,44	±	0,25	-26,58	4272	±	505	1987,86	15703	±	1857	3,70	±	0,40
40-50	77,70	±	0,26	-26,19	3583	±	485	1983,86	16497	±	2233	4,40	±	0,50
50-60	62,98	±	0,24	-26,32	3380	±	424	1979,86	19489	±	2446	1,69	±	0,21
60-70	53,77	±	0,24	-25,97	2201	±	288	1975,86	15897	±	2083	1,16	±	0,29
70-80	41,62	±	0,20	-25,82	397	±	58	1971,86	3592	±	522	0,68	±	0,16
80-90	36,65	±	0,20	-26,46	24	±	9	1967,86	276	±	102	0,52	±	0,23
90-100	41,14	±	0,19	-25,59	19	±	7	1963,86	262	±	102			
100-110	34,99	±	0,18	-25,11	-			1959,86	-					
110-120	39,60	±	0,19	-25,51	-			1955,86	-					



















