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► To cite this version:

Anaëlle Magre, Beatrice Boulet, Anne de Vismes Ott, Olivier Evrard, Laurent Pourcelot. Identification of the origin of radiocesium released into the environment in areas remote from nuclear accident and military test sites using the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature. *Environmental Pollution*, 2023, 329, pp.121606. 10.1016/j.envpol.2023.121606 . cea-04076669

HAL Id: cea-04076669

<https://cea.hal.science/cea-04076669v1>

Submitted on 21 Apr 2023

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1 Identification of the origin of radiocesium released into
2 the environment in areas remote from nuclear accident
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4 signature

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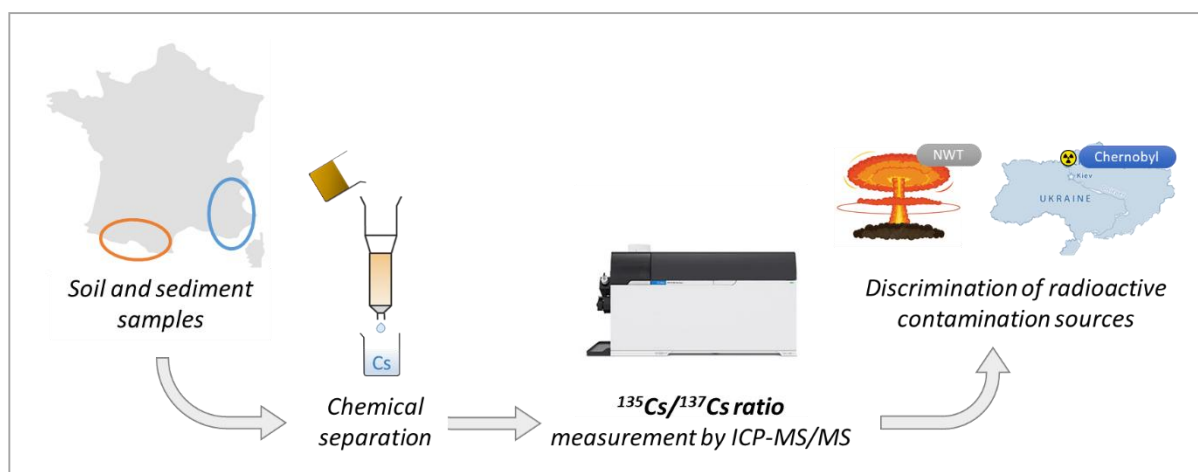
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14

15 Abstract

16 The isotopic signature of radionuclides provides a powerful tool for discriminating radioactive
17 contamination sources and estimating their respective contributions in the environment. In this
18 context, the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio has been tested as a very promising isotopic ratio that had not been
19 explored yet in many countries around the world including France. To quantify the levels of
20 radioactivity found in the environment, a new method combining a thorough radiochemical
21 treatment of the sample and an efficient measurement by ICP-MS/MS has been recently developed.
22 This method was successfully applied, for the first time, to soil and sediment samples collected in
23 France in two mountainous regions preferentially impacted either by global fallout from nuclear
24 weapons testing (*i.e.*, the Pyrenees) or by the Chernobyl accident (*i.e.*, the Southern Alps). The
25 $^{135}\text{Cs}/^{137}\text{Cs}$ ratios measured on twenty-one samples ranged from 0.66 ± 0.04 and 4.29 ± 0.21 (decay-
26 corrected to January 1st, 2022) corresponding to the characteristic signatures of the fallout from
27 Chernobyl and global fallout associated with the nuclear weapons testing, respectively. Moreover,
28 large variations of both the ^{137}Cs mass activity and the studied isotopic ratio recorded by most
29 samples from the southern Alps suggest varying proportions of these two ^{137}Cs sources. For these
30 samples, the contribution of each source was estimated using this new tracer ($^{135}\text{Cs}/^{137}\text{Cs}$) and
31 compared with the mixing contribution given by activity ratio: $^{239+240}\text{Pu}/^{137}\text{Cs}$. This work has
32 successfully demonstrated the applicability of the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature to nuclear forensic
33 studies and could be extended to better evaluate the environmental impact of nuclear facilities
34 (*i.e.*, NPP, waste reprocessing).



35 Keywords

36 Environmental monitoring, radioactive contamination, isotopic signatures, ICP-MS/MS

37 Introduction

38 Since the 1950s, nuclear activities have been undertaken to develop medical, industrial,
39 energy or military applications¹. These activities resulted in radioactive releases of about
40 8.1×10^{20} Bq^{2,3}. Radiocesium isotopes including ^{134}Cs ($T_{1/2} = 2.1$ y), ^{135}Cs ($T_{1/2} = 2.3 \cdot 10^6$ y) and ^{137}Cs
41 ($T_{1/2} = 30.2$ y) rank among the radionuclides that were released in highest quantities^{4,5}. With more
42 than 1.4×10^8 Bq dispersed into the environment and its relatively long half-life, ^{137}Cs is considered
43 as the main source of long-term artificial radiation to the public⁴⁻⁸. Its monitoring in the
44 environment is therefore of major interest to evaluate the risks incurred by the population and
45 ecosystems⁹⁻¹². It is therefore essential to be able to identify unambiguously the origin of
46 radioactive contamination and to anticipate their potential impacts. Three main radioactive
47 contamination sources of ^{137}Cs are distinguished in the environment, even if the proportion of each
48 varies from an environmental sample to another. Thus ^{137}Cs may result from nuclear weapons
49 testing (NWT), nuclear power plant accidents (Chernobyl in 1986 and Fukushima in 2011) and
50 authorized discharges from nuclear facilities^{2,13-15}.

51 ^{137}Cs is easily measured by gamma-ray spectrometry^{7,16,17}. However, due to its potential
52 supply from contrasted sources and its accumulation in the environment for several decades, its
53 measurement alone does not allow to identify the origin of this contamination. To discriminate it,
54 a method has been proposed based on the occurrence of contrasted isotopic signatures between
55 the different radiocesium sources¹⁸⁻²⁰. The isotopic ratios are commonly employed to understand
56 the mechanisms of release, transport, or redistribution of radionuclides in the environment.
57 Knowledge of radionuclide signatures is also of major interest for characterizing the radiological
58 background to assess the specific contribution of potential future contamination events. In this
59 context, several ratios have been employed to identify and characterize ^{137}Cs sources in the
60 environment such as the $^{239+240}\text{Pu}/^{137}\text{Cs}$ activity ratio²¹⁻²⁶. Nevertheless, the hypothesis of
61 fractionation of two elements (Pu and Cs) with different bio-geochemical properties could not be
62 excluded. As an alternative, the radiocesium isotopic signature was also used for many years by
63 directly measuring the $^{134}\text{Cs}/^{137}\text{Cs}$ ratio by gamma-ray spectrometry^{15,17,27-30}. However, the use of
64 this ratio is limited to a period of maximum ten years following the release due to the relatively
65 short half-life of ^{134}Cs , a radionuclide that is no longer detectable in areas lowly affected by
66 Fukushima fallout^{12,31,32}. In this context, an alternative was recently proposed by analyzing the much
67 longer-lived ^{135}Cs ($T_{1/2} = 2.3 \cdot 10^6$ y). The discriminating power of the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio was
68 demonstrated in several studies, which aims at identifying nuclear contamination sources and for

69 improving our understanding of the dispersion patterns of anthropogenic radionuclides^{1,20,32–34}.
70 The characteristic $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios reported in the literature for fallout from the NWT, the
71 Chernobyl accident and the Fukushima accident were 3.70 ± 0.68 ^{32,35}, 0.66 ± 0.03 ^{1,20,32,36,37} and
72 0.45 ± 0.02 ^{12,33,36,38} (decay-corrected to January 1st, 2022), respectively. Nevertheless, it is
73 noteworthy that very few data were reported for the NWT.

74 Despite the potential usefulness of the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio, few data are available in
75 environmental samples collected away from exclusion zones and former nuclear testing areas, due
76 to several analytical challenges associated with the ^{135}Cs quantification^{39,40}. Its measurement was
77 previously extremely difficult, if not impossible, by the use of radiometric methods because of the
78 ^{135}Cs low-beta emissions (β^- , E_{max} 268.9 keV)^{33,41}. The most suitable measurement technique for ^{135}Cs
79 is therefore mass spectrometry⁴² such as ICP-MS/MS, first commercialized in 2013 by Agilent,
80 requiring a specific sample treatment^{12,32,43}. However, in the environment and in zones that were
81 not exposed to accidental or military radionuclide releases, only a low amount of radiocesium is
82 available, while much higher levels of several elements causing spectral interferences at m/z 135
83 and 137 (^{135}Ba , ^{137}Ba , $^{95}\text{Mo}^{40}\text{Ar}$, $^{97}\text{Mo}^{40}\text{Ar}$, $^{119}\text{Sn}^{16}\text{O}$, $^{121}\text{Sb}^{16}\text{O}$) are found⁴⁴. To overcome these
84 difficulties, a high Cs-selective radiochemistry procedure must be applied to a large quantity of
85 sample (resulting in complex chemistry) and it must be combined with an efficient mass
86 spectrometry measurement to remove any trace of interferences before the quantification of the
87 $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio^{12,32,36,37}.

88 The goal of the current research was therefore to investigate the applicability of the
89 $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature for identifying contrasted ^{137}Cs sources and estimating their
90 respective contributions to radiocesium found in environmental samples collected in an area
91 remote from nuclear accident and test sites (*i.e.*, mainland France). To achieve this objective, twenty-
92 one soil or sediment samples (matrices known to strongly absorb ^{137}Cs by clay minerals) were
93 collected in two main regions preferentially impacted by either fallout from atmospheric nuclear
94 weapons tests, the Chernobyl accident or both sources^{21,23}. Indeed, ^{137}Cs deposited in France soon
95 after the releases from the Fukushima accident is considered to be negligible in comparison with
96 ^{137}Cs from Chernobyl accident (500 to more than 1000 lower levels)⁴⁵. The $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio
97 were then quantified by ICP-MS/MS after extracting and purifying the cesium from the solid matrix
98 according to the method recently proposed by Magré et al. (2022)⁴³.
99 The data obtained on the soils and sediments samples taken in France were then used to estimate
100 the contribution of each source by comparing the original $^{135}\text{Cs}/^{137}\text{Cs}$ ratios determined in this

101 research with the characteristic ratios of ^{137}Cs sources reported in the literature. In addition, the
102 proportion of each source estimated with this new tracer ($^{135}\text{Cs}/^{137}\text{Cs}$) was compared with those
103 given by other more commonly used diagnostic ratios such as $^{239+240}\text{Pu}/^{137}\text{Cs}$.

104 **Experimental section**

105 **Environmental samples.**

106 *Soils and sediments collected in France.* The selection of environmental samples was based on
107 previous work namely the cartographic reconstruction of the ^{137}Cs theoretical deposits in France
108 following NWT or the Chernobyl accident. To characterize the fallout from each of these ^{137}Cs
109 sources, samples from two regions preferentially impacted by either NWT or Chernobyl fallout were
110 studied. The investigated areas are respectively located in the mountainous areas of Pyrenees and
111 in the Mercantour (southern French Alps), both regions being devoid of any nuclear facility, so that
112 NWT and Chernobyl fallout provide the only sources of artificial radioactivity. The environmental
113 matrices analyzed were soils and lake sediments, and they were chosen because of their strong
114 capacity to fix radiocesium onto clay minerals. Indeed, in these matrices, ^{137}Cs activities ranged from
115 a few $\text{Bq}\cdot\text{kg}^{-1}$ to a few tens of $\text{Bq}\cdot\text{kg}^{-1}$ and could reach several thousands of $\text{Bq}\cdot\text{kg}^{-1}$ in mountainous
116 areas^{46,47}.

117 In this study, ten lake sediment, four surface soil (0-5 cm depth) and three subsurface soil (5-10 cm
118 depth) samples collected in the Mercantour massif between 2013 and 2021 were analyzed
119 (Figure 1). Four soil samples collected in 2014 in the Pyrenees were also investigated, including
120 three surface soils (0-10 cm depth) and one subsurface soil (10-20 cm depth). Comprehensive data
121 on the sampling of these sediment and soil samples is provided in Table S1 in the supplementary
122 material section.

123 *Accuracy verification of the applied method.* Due to the lack of certified reference samples in ^{135}Cs ,
124 the validity of the results on the collected soils and sediments was ensured by analyzing, two types
125 of materials. The first was IAEA-330 and IAEA-375 certified reference materials (CRM) from the
126 International Atomic Energy Agency (IAEA). Both CRMs were selected because of their frequent use
127 in the validation of $^{135}\text{Cs}/^{137}\text{Cs}$ analysis protocols^{1,12,32,36,37,44}. These samples of spinach (IAEA-330)
128 and soil (IAEA-375) were respectively collected in Ukraine and Russia in 1990 and they show a
129 $^{135}\text{Cs}/^{137}\text{Cs}$ ratio characteristic of Chernobyl fallout. In addition, three sediment samples exposed to
130 high levels of Fukushima fallout were used. These sediment samples were collected in 2012, 2015
131 and 2020 in the Niida River catchment, which drains a part of the main radioactive plume in the

132 Fukushima Prefecture, Northeastern Japan⁴⁸. Validity of the analytical method was evaluated by
 133 comparing the $^{135}\text{Cs}/^{137}\text{Cs}$ ratios measured in the IAEA and Niida samples with the published
 134 $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature for the Chernobyl and Fukushima accidents, respectively ^{1,12,20,32,33,36–}
 135 ³⁸.

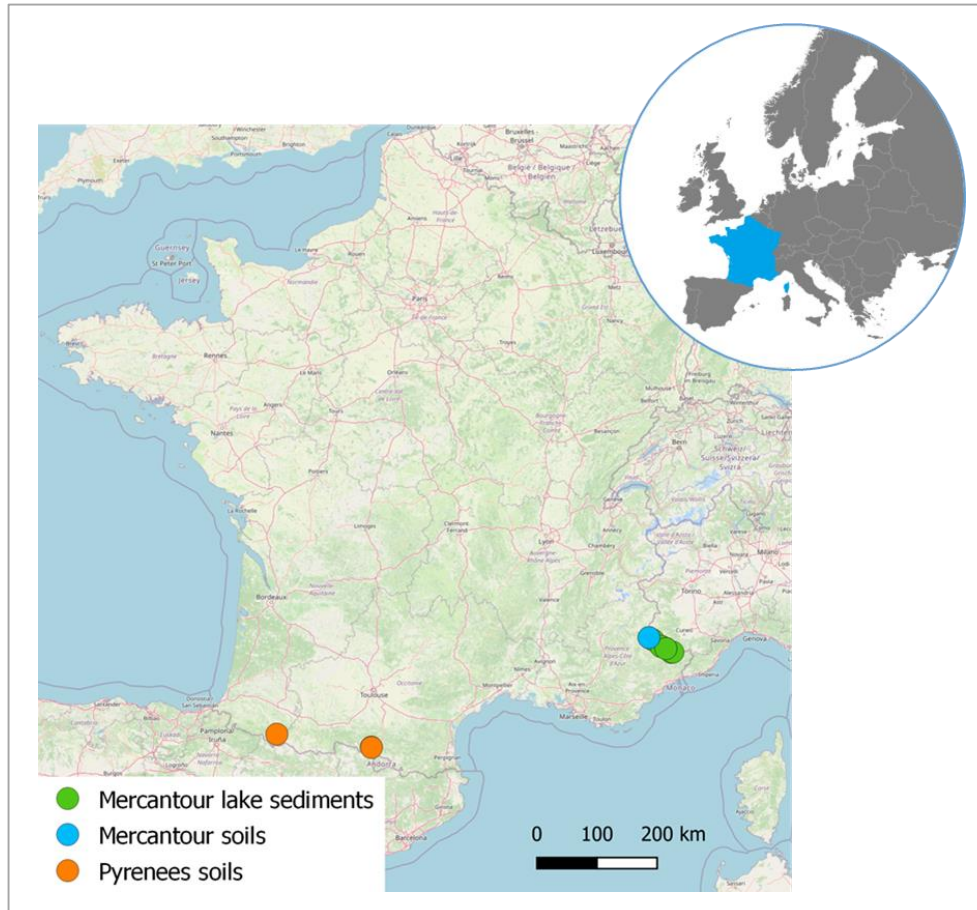


Figure 1: Location of sampling sites in France

136

137 **Estimated contribution from each source of ^{137}Cs**

138 *Using bi-elemental isotopic signature: $^{239+240}\text{Pu}/^{137}\text{Cs}$.* Nuclear Weapons Tests is considered the only
 139 source of airborne Pu in France^{49,50}. Indeed after 1st may 1986, the contaminated air masses
 140 following Chernobyl accident contained mostly volatile fission products with negligible activity of
 141 plutonium⁵¹. Thus in the current work, assuming transuranics solely derived from NWT, we have
 142 used $^{239+240}\text{Pu}/^{137}\text{Cs}$ previously derived for NWT²⁵, for which an activity $^{239+240}\text{Pu}/^{137}\text{Cs}$ ratio of $0.04 \pm$
 143 0.01 was found (decay-corrected to January 1st, 2022)²⁵ and the $^{239+340}\text{Pu}$ activity concentration
 144 ($\text{Bq}\cdot\text{kg}^{-1}$) of the samples (namely $^{239+340}\text{Pu}_{\text{sample}}$) to deduced the ^{137}Cs from NWT in the samples
 145 (hereafter denoted as $^{137}\text{Cs}_{\text{NWT}}$) following (Eq. 1).

146
$$^{137}\text{Cs}_{NWT} = \frac{^{239+240}\text{Pu}_{\text{samp}}}{(^{239+240}\text{Pu}/^{137}\text{Cs})_{REF}} \quad (1)$$

147 In this study, the activity of $^{239+240}\text{Pu}_{\text{samp}}$ was deduced from the gamma-ray or alpha spectrometry
 148 measurement of ^{241}Am (regarding $^{241}\text{Am}_{\text{mes}}$ refer to next section) and the $(^{241}\text{Am}/^{239+240}\text{Pu})_{REF}$
 149 activity ratio characteristic of the NWT, reported in the literature ($(^{241}\text{Am}/^{239+240}\text{Pu})_{REF} = 0.39 \pm 0.06$,
 150 decay-corrected to January 1st, 2022)^{23,26,52} (Eq. 2).

151
$$^{239+240}\text{Pu}_{\text{samp}} = \frac{^{241}\text{Am}_{\text{mes}}}{(^{241}\text{Am}/^{239+240}\text{Pu})_{REF}} \quad (2)$$

152 Once the ^{137}Cs activity of NWT was calculated following equation (1), the proportion of ^{137}Cs
 153 resulting from the Chernobyl accident was deduced using the total ^{137}Cs activity measured by
 154 gamma-ray spectrometry (see next section).

155 *Using a mono-elemental isotopic signature: $^{135}\text{Cs}/^{137}\text{Cs}$.* Using mixing equation proposed by
 156 Bouisset et al. (2021)⁵³, the $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios measured by mass spectrometry (ICP-MS/MS)
 157 in samples contaminated by two different sources (Chernobyl accident and NWT) is given by
 158 equation (3).

159
$$(^{135}\text{Cs}/^{137}\text{Cs})_{\text{measured}} = x_{\text{Chern}}(^{135}\text{Cs}/^{137}\text{Cs})_{\text{Chern}} + (1 - x_{\text{Chern}})(^{135}\text{Cs}/^{137}\text{Cs})_{\text{NWT}} \quad (3)$$

160 where x_{Chern} and $(1 - x_{\text{Chern}})$ were the ^{137}Cs contributions from Chernobyl and NWT fallout,
 161 respectively. The $(^{135}\text{Cs}/^{137}\text{Cs})_{\text{Chern}}$ and $(^{135}\text{Cs}/^{137}\text{Cs})_{\text{NWT}}$ atomic ratios corresponded to the
 162 characteristic atomic ratios of both sources reported in the literature: 0.66 ± 0.03 and 3.70 ± 0.68
 163 (decay-corrected to January 1st, 2022). It should be noted that the $^{135}\text{Cs}/^{137}\text{Cs}$ characteristic ratio of
 164 NWT reported was a "simple" average ratio considering the number of years since the period of
 165 testing (1950s to 1980s), assuming a $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio of 1 at the date of each detonation^{32,35}.
 166 The associated uncertainty was therefore significant compared, for example, to that of Chernobyl
 167 accident, which occurred at a specific date.

168 For each analyzed sample, the proportion of ^{137}Cs resulting from the Chernobyl accident (x_{Chern})
 169 was estimated from equation (3) using a simple two end-member un-mixing model (Eq. 4).

170
$$x_{\text{Chern}} = \frac{(^{135}\text{Cs}/^{137}\text{Cs})_{\text{measured}} - (^{135}\text{Cs}/^{137}\text{Cs})_{\text{NWT}}}{(^{135}\text{Cs}/^{137}\text{Cs})_{\text{Chern}} - (^{135}\text{Cs}/^{137}\text{Cs})_{\text{NWT}}} \quad (4)$$

171 **Methods applied to determine ^{137}Cs and ^{241}Am activities**

172 *Gamma-ray spectrometry measurements.* Once collected, the soil and sediment samples were
173 dried, crushed, sieved (< 2 mm) and then calcined at 500°C overnight in a muffle oven. The resulting
174 ash was packed into a 60 mL Petri box ($\varnothing_{\text{int}}=71$ mm; $h_{\text{int}}=15$ mm) and measured by gamma-ray
175 spectrometry. This first measurement aimed to assess the initial ^{137}Cs activity to determine the
176 amount of sample to be analyzed to quantify the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio and evaluate the
177 chemical recoveries. The ^{241}Am activity was also measured by gamma-ray spectrometry.

178 The two gamma detectors employed were High-Purity Germanium (HPGe) distributed by Ortec
179 with a crystal volume about 180 cm³. For the first detector, the relative detection efficiency and
180 resolution on the peak corresponding to ^{60}Co at 1332 keV were respectively 53% and 1.7 keV
181 (IRSN/LMRE). The corresponding values amounted to 48% and 1.9 keV for the second detector
182 (LSCE). The HPGe were previously calibrated in energy, resolution, and detection efficiency on the
183 40-1700 keV energy range using certified multigamma sources prepared by IRSN (IRSN/LEI, France).
184 The activities of ^{137}Cs and ^{241}Am were respectively quantified using their characteristic emissions at
185 661.6 keV and 59.5 keV with long counting times (up to 24h) to improve the measurement statistics.
186 The spectra analysis was performed with the GENIE 2000 software operated by Mirion Tech. Inc.
187 and the "home-made" MadOni software. Then, corrections were applied to consider the self-
188 attenuation effect according to the density and the matrix of the analyzed sample, and the used
189 geometry.

190 In five of the samples in which ^{137}Cs contents exceeded 2×10^4 Bq.kg⁻¹, the ^{241}Am activity could not
191 be quantified by gamma-ray spectrometry due to the very high Compton effect caused by the
192 significant presence of ^{137}Cs making difficult the discrimination of the peaks at low energy. In these
193 samples, the ^{241}Am activity was measured by alpha spectrometry according to the analytical
194 procedure described by Goutelard et al. (1998)⁵⁴ (see below) and used routinely in the laboratory
195 (IRSN/LMRE) under COFRAC accreditation.

196 *Alpha spectrometry for ^{241}Am activity measurements.* For each sample, 1 to 2 grams of ash were
197 introduced into a beaker and spiked with ^{243}Am to determine the chemical yield and the ^{241}Am
198 activity. The samples were then leached at 150°C during 24h with concentrated HNO₃ and HCl in
199 presence of hydrogen peroxide (H₂O₂). The solid residue was separated from the supernatant by
200 centrifugation, leached again for 2h at 150°C with concentrated HNO₃ and rinsed with ultrapure
201 water. The supernatants and rinse were combined. 15 g of oxalic acid were added to the solution
202 with 5 mL of CaCl₂ at 100 mg.g⁻¹ and the mixture was adjusted to pH 1.5 to form a calcium oxalate

203 precipitate. After centrifugation, the precipitate was dried and destroyed by heating with 10 mL of
204 concentrated HNO₃ and 5 mL of H₂O₂. The mixture was evaporated to dryness and the residue was
205 dissolved in 40 mL of 8M HNO₃ with 0.2 g of NaNO₂. The americium was then purified using a series
206 of four ion exchange resins. In detail, Am was separated from Pu(IV) using 6.4 g of AG®1-X8 resin
207 (100 – 200 mesh, Cl⁻ form, Biorad Tech.) conditioned with 30 mL of 8M HNO₃. The sample was
208 loaded and then the resin rinsed with 40 mL of 8M HNO₃. The sample eluate and rinses were
209 combined, evaporated to dryness and the residue was dissolved in 10 mL of 9M HCl. Am was
210 separated from Fe and U using a double column containing 6.5 g of AG®1-X8 resin and 2 g of
211 AG®50W-X8 resin (100 – 200 mesh, H⁺ form, Biorad Tech.). The sample loading and rinsing fractions
212 (45 mL of 9M HCl) were again combined and evaporated. The residue was dissolved in 10 mL of
213 2M HNO₃/0.5M Al(NO₃)₃. The solution was purified of metals (Cu, Ni) with 0.7 g of TRU resin (100-
214 150 µm, Triskem Int.). Once the sample was loaded and the resin rinsed (10 mL of 2M HNO₃), Am
215 was eluted with 25 mL of 0.03M HNO₃. The eluate was evaporated to dryness and then redissolved
216 in 20 mL of 1M HNO₃/93% CH₃OH mixture. Finally, Am was separated from Rare Earth Elements
217 using 4 g of AG®1-X4 resin (100 – 200 mesh, Cl⁻ form, Biorad Tech.). The sample was loaded onto
218 the resin and rinsed successively with 15 mL of 1M HNO₃/93% CH₃OH, 80 mL of 0.1M HCl/0.5M
219 NH₄SCN/80% CH₃OH and 22 mL of 1M HNO₃/93%. Am was eluted from the AG®1-X4 resin with
220 75 mL of 1.5M HCl/86% CH₃OH mixture. The eluate was evaporated and dissolved was concentrated
221 HNO₃, ultrapure H₂O and Na₂SO₄. The solution was adjusted to pH 1.90–1.95 and Am was
222 electroplated for 2h at 1A on a stainless-steel disk. The disk was counted for 5 days using a low-
223 level background α-spectrometer Alpha-Analyst (Canberra). The activity of ²⁴¹Am were quantified
224 using its emitted-alpha particles at 5,485 keV.

225 It should be noted that all activities presented in this work were given with an uncertainty at k=2.
226 For the ¹³⁷Cs and ²⁴¹Am measured activities, this uncertainty considered those related to counting
227 statistics and detector calibration. Regarding the uncertainties of the ¹³⁷Cs_{NWT} and ²³⁹⁺²⁴⁰Pu
228 activities deduced by equation 1 and 2, they included the ²⁴¹Am measurement uncertainty and
229 those associated with the ²³⁹⁺²⁴⁰Pu/¹³⁷Cs and ²⁴¹Am/²³⁹⁺²⁴⁰Pu reference ratios.

230 **Method applied for ¹³⁵Cs/¹³⁷Cs isotopic ratio determination**

231 *Cs extraction and purification from solid matrices.* The procedure of Cs extraction and purification
232 from the environmental matrix was based on the analytical method described in our previous
233 work⁴³. 1 to 100 g of sample ash (depending on the measured ¹³⁷Cs activity) were introduced into
234 a beaker. The radiocesium was extracted from the solid matrix by a succession of four acid leaching

235 steps of 8 hours on a hot plate with temperature set at 180°C. The first leaching was performed
236 with 69.5% HNO₃ in presence of 30% H₂O₂ provided by Carlo Erba. The following leaching were
237 carried out with a 69.5% HNO₃/37.5% HCl mixture (1:2, v/v) still in the presence of H₂O₂. Between
238 successive leaching steps, the solid residue was separated from the supernatant by centrifugation.
239 The supernatants were combined, evaporated to near dryness. The pH of the solution was adjusted
240 to pH 1 – 2 by diluting the residue with ultrapure H₂O milli-Q H₂O (with resistivity 18.2 MΩ.cm⁻¹)
241 produced by a Merck Millipore system. 120 mg of ammonium molybdophosphate (AMP) powder
242 (purchased from Alfa Aesar) were added to the solution to selectively complex Cs. The solution was
243 then stirred for 30 minutes at room temperature and centrifuged for 15 minutes at 3500 rpm. After
244 centrifugation, the supernatant was removed and the yellow precipitate containing Cs was filtered
245 on a polyvinylidene fluoride membrane filter (PVDF, 0.45 μm pore size, Merck Millipore). The
246 precipitate was washed with 5 mL of milli-Q H₂O and dissolved with 24 mL of 2M NH₄OH resulting
247 in the complete decomposition of the AMP molecule and consequently, the release of Cs. Cs was
248 then purified of all its interferents by combining the chemical properties of two extraction resins
249 provided by Biorad Technologies. First, 3 mL of AG®MP-1M anion exchange resin (100 – 200 mesh,
250 Cl⁻ form) conditioned with 1.5M NH₄OH were used to separate Cs from polyatomic interferents
251 such as Mo, Sb and Sn. Under these conditions, Cs⁺ ions were not adsorbed on the resin and were
252 collected in the loading and rinsing fractions (2 x 3 mL of 1.5M NH₄OH), whereas Mo, Sb and Sn,
253 present in oxide form, remained on it. Finally, Cs was separated from its isobaric interferent (Ba)
254 using 8 mL of AG®50W-X8 cationic resin (100 – 200 mesh, H⁺ form) conditioned with 20 mL of
255 milli-Q H₂O followed by 20 mL of 1.5M NH₄OH. After the loading of the sample, the resin was rinsed
256 with 50 mL of 1.5M NH₄OH and converted by 20 mL of milli-Q water followed by 20 mL of ultra-
257 pure 1.5M HNO₃. Cs was selectively eluted with 50 mL of ultra-pure 1.5M HNO₃ while Ba remained
258 fixed on the AG®50W-X8 resin. The eluate was measured by gamma-ray spectrometry, to estimate
259 the chemical yield by monitoring ¹³⁷Cs. Then, it was evaporated to dryness and dissolved in 5 mL
260 of ultrapure 0.5M HNO₃ to be measured by mass spectrometry.

261 *ICP-MS/MS for ¹³⁵Cs/¹³⁷Cs isotopic ratio and interferent concentration measurements.* Isotopic
262 ratio and interferent content measurements were performed with the Agilent 8900#100 triple-
263 quadrupole ICP-MS coupled with the SPS4 auto-sampler and controlled by the MassHunter 4.6
264 software. The formed ions in the hot plasma were extracted and focused with a Ni skimmer cone
265 and a x-lens block. The instrument is equipped with an octupole reaction-collision cell (CRC)
266 between two quadrupole mass filters (Q1 and Q2) allowing an efficient removal of interferences. All

267 measured solutions (blanks, standards, and samples) were prepared in 0.5M ultra-pure nitric acid
268 and introduced into the ICP-MS by a MicroMist nebulizer with a peristaltic pump at 0.35 mL.min⁻¹
269 flow rate. The sensitivity and oxide rate settings were optimized using a multi-element solution
270 concentrated to 2.5 ng.g⁻¹ in Cs, Ce and Ba prepared from certified solutions (Carlo Erba). Each
271 measurement was corrected with an acid blank. All the experimental conditions are listed in
272 Table S2.

273 The interferent (Ba, Mo, Sb, Sn) contents were monitored in single quadrupole mode without
274 reaction gas and calculated by an external calibration method. The standards were prepared from
275 ultra-pure milli-Q water and certified mono-elemental solutions provided by Carlo Erba. The matrix
276 effect was corrected using indium as internal standard (concentrated to 3 ng.g⁻¹).

277 The ¹³⁵Cs/¹³⁷Cs isotopic ratios were quantified in triple quadrupole mode by setting Q1 and Q2 to
278 the 135 and 137 m/z. To effectively remove the last traces of interferences, a mixture of N₂O
279 (99.998% purity, Messer), He (99.9992% purity, Air product) and NH₃/He (10/90 m/m, 99.98% purity,
280 Air product) was added in the CRC with flow rates of about 0.55, 1 and 4.79 mL.min⁻¹, respectively.
281 Isotopic ratios were corrected for mass bias by the sample standard bracketing approach with a
282 solution with a known ¹³⁵Cs/¹³⁷Cs ratio delivered by DES-SEARS (CEA). The uncertainty associated
283 with the corrected ratio were also given at k=2. It considered the variation of the ICP-MS/MS signal
284 during the measurement of the sample and the uncertainty of the mass bias correction.

285 *Evaluation of the chemical performance.* The chemical performances (recovery yield and eluate
286 purity) achieved for each sample are detailed in Table S3. Recovery yields were estimated by
287 monitoring ¹³⁷Cs by gamma-ray spectrometry in both the solid and purified liquid samples. They
288 ranged from 57% to 93%. Regarding potential spectral interferences during the analyses, the
289 radiochemical treatment of the samples allowed to significantly reduce the levels of Ba, Mo, Sb and
290 Sn in the measurement fraction, with contents ranging from 0.1 to 5.4, 0.13 to 17.5, 0.03 to 0.46,
291 and 0.2 to 12.2 ng.g⁻¹, respectively. To accurately measure the ¹³⁵Cs/¹³⁷Cs ratio, these traces of
292 interferences that remained present in solution were effectively removed by adding a mixture of
293 reaction gases (N₂O, NH₃, He) in the CRC of the mass spectrometer.

294 **Results and Discussion**

295 **Tracing the origin of radiocesium contamination by measuring ^{137}Cs and ^{241}Am** 296 **activities by nuclear counting – Use of bi-elemental isotopic signatures.**

297 The activities of ^{137}Cs and ^{241}Am in lake sediment, surface soil and subsurface soil samples collected
298 in France are presented in Table 1. Regarding ^{137}Cs , a significant heterogeneity of activities was
299 found between the two main sampling regions (Mercantour Massif or the Pyrenees) as well as,
300 within the same region, between the analyzed matrices (sediment or soil). The highest variability
301 was obtained in the Mercantour soils (including surface and subsurface soils) with values ranging
302 from a few tens (165 ± 11) to several tens of thousands ($103,308 \pm 113$) of Bq.kg^{-1} . Such a strong
303 heterogeneity is consistent with “enrichment spots”, *i.e.* surfaces of a few dm^2 strongly
304 concentrating ^{137}Cs from Chernobyl fallout⁴⁶. In contrast, ^{137}Cs activities measured in the soils of the
305 Pyrenees exhibited low heterogeneity and were about 2 to 7 times lower than in the Mercantour,
306 with levels ranging between 23 ± 4 and $93 \pm 28 \text{ Bq.kg}^{-1}$. An explanation to this lower heterogeneity
307 is that the nuclear weapon tests occurred over a longer period (between the 1950s and 1980s).
308 Overall, for both regions, ^{137}Cs activity decreased with increasing sampling depths. For the
309 sediments from the Mercantour lakes, the ^{137}Cs concentrations were significant and relatively
310 homogeneous compared to the soils, with activities varying from 249 ± 19 to $5,274 \pm 350 \text{ Bq.kg}^{-1}$.
311 For each site and each matrix studied, the distribution of ^{137}Cs activities was in good agreement
312 with that reported in the literature^{21,46,47}. High to very high levels of ^{137}Cs were expected in the
313 Mercantour resulting from a superposition of deposition from NWT and the Chernobyl accident. In
314 contrast, the Pyrenees soils showed lower activities, which was expected as they were hypothesized
315 to have been mainly supplied by the NWT. These preliminary interpretations were confirmed with
316 the assessment of the ^{137}Cs contributions of each source using the $^{241}\text{Am}/^{239+240}\text{Pu}$ and then the
317 $^{239+240}\text{Pu}/^{137}\text{Cs}$ ratios provided for the NWT (see experimental section) (Table 1). They show, overall,
318 that the proportion of ^{137}Cs from Chernobyl fallout increases significantly with the total ^{137}Cs activity
319 while the ^{137}Cs activity resulting from the NWT remains relatively homogenous (28 to 606 Bq.kg^{-1})
320 for both studied mountainous areas and both environmental matrix (cf. Figure 2). Thus, the use of
321 bi-elemental signatures ($^{241}\text{Am}/^{239+240}\text{Pu}$ and $^{239+240}\text{Pu}/^{137}\text{Cs}$) allowed, in a first step, to estimate the
322 contributions of each ^{137}Cs source. Nevertheless, the hypothesis of the fractionation of two
323 elements with different bio-geochemical properties (*i.e.*, Am vs. Pu, Pu vs. Cs) cannot be fully
324 excluded, although they were described in the literature to be relatively similar^{55,56}.

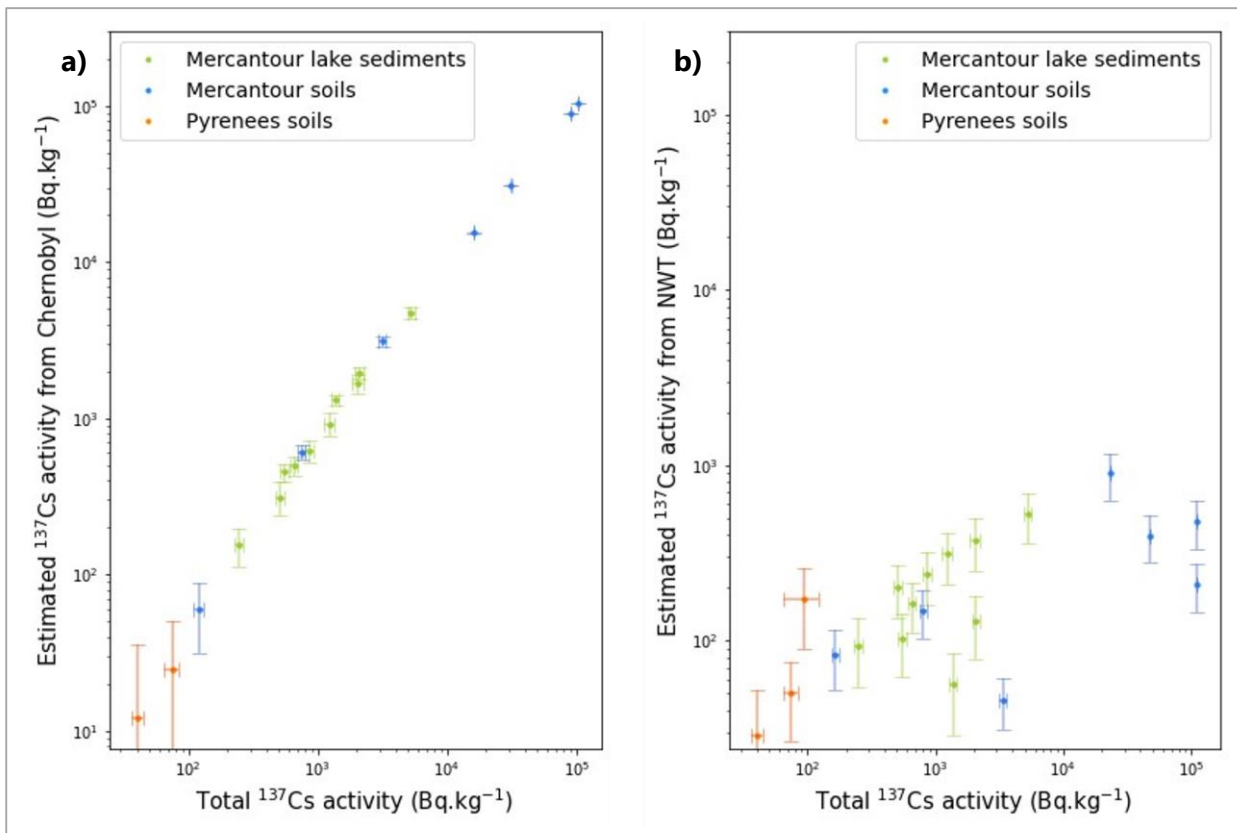


Figure 2: Distribution of the estimated ^{137}Cs activity resulting from the Chernobyl accident (a) and nuclear weapons testing (b) as a function of total ^{137}Cs activity measured by gamma-ray spectrometry in soil and sediment samples collected in France. All activities are decay-corrected to January 1, 2022, and the error bars correspond to a measurement uncertainty at $k = 2$. $^{137}\text{Cs}/^{239+240}\text{Pu}$ is used here to estimate the respective sources of ^{137}Cs . (see experimental section)

326 Table 1: ^{137}Cs and ^{241}Am activities measured by gamma-ray spectrometry in sediments and soils of the investigated sites as decay-corrected to January 1st, 2022, and with
 327 uncertainty at $k=2$. $^{239+240}\text{Pu}$, ^{137}Cs activities resulting from nuclear weapons testing (NWT) and ^{137}Cs from Chernobyl (Chern) deduced from $^{241}\text{Am}/^{239+240}\text{Pu}$ and $^{239+240}\text{Pu}/^{137}\text{Cs}$
 328 activity ratios reported in the literature for NWT contribution (0.40 ± 0.06 and 0.04 ± 0.01 respectively, and decay-corrected to January 1st, 2022) (see experimental section).

Sample name	Matrix	Study area	Sampling site	Depth (cm)	^{137}Cs activity (Bq.kg^{-1} dry)	^{241}Am activity (Bq.kg^{-1} dry)	$^{239+240}\text{Pu}_{\text{NWT}}$ activity (Bq.kg^{-1})	$^{137}\text{Cs}_{\text{NWT}}$ activity (Bq.kg^{-1})	$^{137}\text{Cs}_{\text{Chern}}$ activity (Bq.kg^{-1})
20_PNM45_1			Main Terre Rouge lake	—	1234 ± 114	4.99 ± 0.71	12.48 ± 2.59	312 ± 101	922 ± 159
20_PNM45_2			Temporary Terre rouge lake	—	2047 ± 193	5.98 ± 0.97	14.95 ± 3.30	374 ± 125	1673 ± 259
20_PNM45_3			Superior Lausfer lake	—	513 ± 38	3.21 ± 0.48	8.02 ± 1.70	200 ± 66	313 ± 76
20_PNM45_4			Inferior Lausfer lake	—	249 ± 19	1.50 ± 0.46	3.75 ± 1.27	94 ± 39	155 ± 44
13-PNM4	Lake sediment	Mercantour mountain	Cerise lake	—	1375 ± 95	0.90 ± 0.36	2.25 ± 0.96	56 ± 28	1319 ± 99
13-PNM7			Besson lake	—	2086 ± 155	2.05 ± 0.54	5.11 ± 1.56	128 ± 50	1958 ± 163
13-PNM9			Vens lake	—	555 ± 40	1.63 ± 0.42	4.08 ± 1.22	102 ± 40	453 ± 57
13-PNM19			Lausfer lake	—	862 ± 66	3.82 ± 0.57	9.54 ± 2.02	239 ± 78	624 ± 102
21_PNM24_5			Terre Rouge Main lake	—	659 ± 45	2.58 ± 0.33	6.46 ± 1.27	161 ± 51	497 ± 68
21_PNM24_6			Terre Rouge Inferior lake	—	5274 ± 350	8.43 ± 0.99	21.07 ± 4.01	527 ± 166	4747 ± 387
21_PNM24_1				0 – 5	$89,894 \pm 90$	$6.15 \pm 0.54^*$	15.37 ± 2.68	384 ± 117	$89,510 \pm 148$
				5 – 10	$103,501 \pm 97$	$3.08 \pm 0.31^*$	7.70 ± 1.39	192 ± 59	$103,308 \pm 113$
21_PNM24_2		Mercantour mountain	Restefond pass	0 – 5	165 ± 11	1.34 ± 0.32	3.34 ± 0.95	84 ± 32	82 ± 34
21_PNM24_3				0 – 5	$31,214 \pm 96$	$4.16 \pm 0.49^*$	10.40 ± 1.99	260 ± 82	$30,954 \pm 126$
				5 – 10	3169 ± 223	$0.68 \pm 0.10^*$	1.69 ± 0.36	45 ± 15	3321 ± 224
21_PNM24_4	Soil			0 – 5	$16,066 \pm 32$	$9.69 \pm 0.94^*$	24.23 ± 4.32	606 ± 186	$15,460 \pm 189$
		5 – 10	803 ± 53	2.38 ± 0.25	5.95 ± 1.09	149 ± 46	654 ± 70		
14_PYR_2			Coumebière plateau	0 – 10	75 ± 10	0.81 ± 0.31	2.02 ± 0.82	51 ± 24	25 ± 26
14_PYR_3		Pyrenees	Labant pond	0 – 10	93 ± 28	2.78 ± 1.08	6.95 ± 2.90	174 ± 84	$< 1,03$
				10 – 20	23 ± 4	< 0.36	—	—	—
14_PYR_53			Besse pass	0 – 10	40 ± 4	0.46 ± 0.35	1.14 ± 0.88	28 ± 23	12 ± 24

* Alpha spectrometry measurement

330 **Tracing the origin of radiocesium contamination using the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic**
 331 **ratio measured by ICP-MS/MS – Use of mono-elemental isotopic signature.**

332 The analytical procedure to quantify the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio in environmental samples was
 333 first applied to samples known to be contaminated with Chernobyl (IAEA-330 and
 334 IAEA-375)^{1,20,32,36,37} or Fukushima fallout (Niida_2012, Niida_2015 and Niida_2020)⁴⁸. The analytical
 335 results are presented in Table 2 and they were compared with the few data available in the literature
 336 for both sources of accidental contamination. To facilitate the comparison of results, all isotopic
 337 ratios were decay-corrected to January 1st, 2022. For both IAEA reference samples, which are
 338 generally used in the literature to validate the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio analysis methods, the measured
 339 ratios (0.66 ± 0.06 and 0.67 ± 0.02) agreed well with those reported in the literature^{1,20,32,36,37}
 340 (ranging from 0.66 ± 0.06 to 0.68 ± 0.13). In the absence of certified reference materials
 341 characteristic of Fukushima fallout, the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratios obtained in the sediments
 342 collected in the Niida river catchment were compared with the ratios published by studies
 343 characterizing the Fukushima fallout. For these sediments, the average measured $^{135}\text{Cs}/^{137}\text{Cs}$ ratios
 344 of 0.47 ± 0.02 was fully consistent with the ratios reported in the literature^{12,33,36,38} and ranging from
 345 0.45 ± 0.03 to 0.47 ± 0.04 . This comparison demonstrated the reliability of the analytical procedure.

346 *Table 2. $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratios measured by ICP-MS/MS for materials impacted by Chernobyl (IAEA-330 and*
 347 *IAEA-375) and Fukushima (Niida_2012, Niida_2015 and Niida_2020) fallout. Comparison of these ratios with*
 348 *isotopic signatures reported in the literature for these contamination sources.*

Sample name	Main source of ^{137}Cs	$^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio (at/at)	
		Current work	Literature values
IAEA-330	Chernobyl fallout	0.66 ± 0.06 (n=3)	0.66 ± 0.06 Taylor et al. (2008)
			0.66 ± 0.03 Zheng et al. (2014)
			0.66 ± 0.06 Snow et al. (2015)
			0.66 ± 0.13 Zhu et al. (2020)
IAEA-375	Chernobyl fallout	0.67 ± 0.02 (n=3)	0.68 ± 0.10 Zheng et al. (2014)
			0.66 ± 0.03 Snow et al. (2015)
			0.68 ± 0.03 Dunne et al. (2017)
			0.68 ± 0.13 Zhu et al. (2020)
Niida_2012	Fukushima fallout	0.47 ± 0.02 (n=3)	0.47 ± 0.04 Ohno et al. (2014)
Niida_2015			0.45 ± 0.03 Zheng et al. (2014)
			0.45 ± 0.02 Yang et al. (2016)
Niida_2020			0.46 ± 0.01 Zok et al. (2021)
		0.49 ± 0.04 (n=1)	

Decay-corrected to January 1st, 2022. The isotopic ratios are provided with uncertainty at $k = 2$.

349 Once the analytical procedure to measure $^{135}\text{Cs}/^{137}\text{Cs}$ was validated, it was applied to lake sediment
 350 and soil samples collected in France (Table 3).

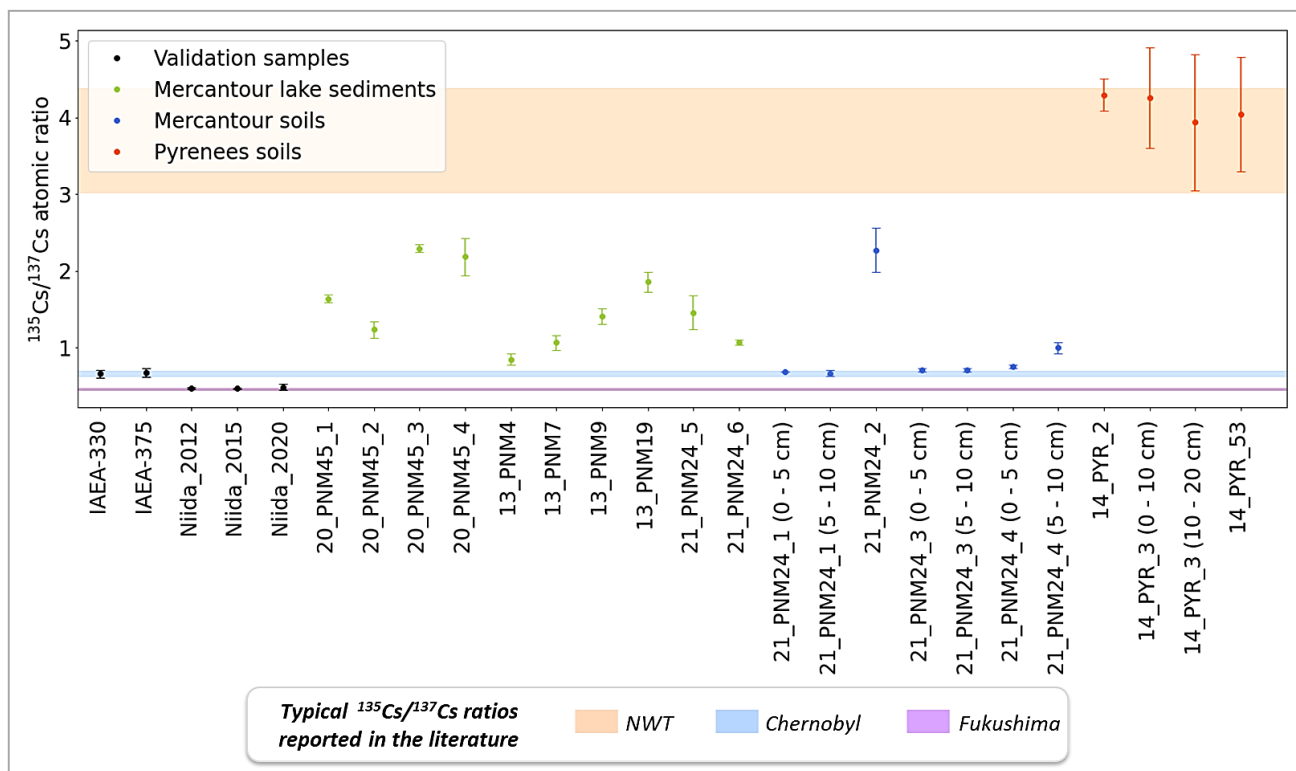
351 *Table 3. $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratios in lake sediments and soils collected in France.*

Sample name	Matrix	Study area	Sampling site	Depth (cm)	^{137}Cs activity (Bq.kg^{-1})	$^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio (at/at)	Proportion of ^{137}Cs from Chernobyl accident			
20_PNM45_1			Main Terre Rouge lake	—	1234 ± 114	1.64 ± 0.05	68%			
20_PNM45_2			Temporary Terre Rouge lake	—	2047 ± 193	1.23 ± 0.10	81%			
20_PNM45_3			Superior Lausfer lake	—	513 ± 38	2.29 ± 0.05	46%			
20_PNM45_4			Inferior Lausfer lake	—	249 ± 19	2.18 ± 0.24	50%			
13-PNM4	Lake sediment	Mercantour mountain	Cerise lake	—	1375 ± 95	0.85 ± 0.08	94%			
13-PNM7			Besson lake	—	2086 ± 155	1.06 ± 0.09	87%			
13-PNM9			Vens lake	—	555 ± 40	1.41 ± 1.86	75%			
13-PNM19			Lausfer lake	—	862 ± 66	1.86 ± 0.13	61%			
21_PNM24_5			Terre Rouge Main lake	—	659 ± 45	1.46 ± 0.22	74%			
21_PNM24_6	Terre Rouge Inferior lake	—	5274 ± 350	1.07 ± 0.03	87%					
21_PNM24_1	Soil	Mercantour mountain	Restefond pass	0 – 5	$89,894 \pm 90$	0.68 ± 0.01	99%			
				5 – 10	$103,501 \pm 97$	0.66 ± 0.04	100%			
21_PNM24_2				0 – 5	165 ± 11	2.27 ± 0.29	47%			
				0 – 5	$31,214 \pm 96$	0.71 ± 0.02	98%			
21_PNM24_3				5 – 10	3169 ± 223	0.71 ± 0.03	98%			
				0 – 5	$16,066 \pm 32$	0.75 ± 0.02	97%			
21_PNM24_4				5 – 10	803 ± 53	1.00 ± 0.07	89%			
				14_PYR_2	Pyrenees	Coumebière plateau	0 – 10	75 ± 10	4.29 ± 0.21	-19%
14_PYR_3							0 – 10	93 ± 28	4.26 ± 0.66	-18%
							10 – 20	23 ± 4	3.94 ± 0.89	-8%
14_PYR_53	Besse pass	0 – 10	40 ± 4	4.04 ± 0.75	-11%					

Data are decay-corrected to January 1st, 2022. All results presented are provided with an uncertainty at $k = 2$.

352

353 The analytical results show strongly variable $^{135}\text{Cs}/^{137}\text{Cs}$ signatures with a minimum value of $0.66 \pm$
 354 0.04 in a Mercantour soil and a maximum value of 4.29 ± 0.21 in a soil sample from the Pyrenees.
 355 It is noteworthy that soils from this area show nearly homogenous isotopic ratios, ranging from
 356 3.94 ± 0.89 to 4.29 ± 0.21 . Compared with the isotopic signatures reported for each source in the
 357 literature or in Table 2 of the current research (NWT, Chernobyl, and Fukushima accidents), such a
 358 low $^{135}\text{Cs}/^{137}\text{Cs}$ was consistent with the Chernobyl fallout signature, while the highest ratio lied
 359 within the range of values attributed to the NWT (Figure 3).



360 Accordingly, it can be deduced that the ^{137}Cs radioactive contamination of the 21_PNM24_1
 Figure 3: $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios measured by ICP-MS/MS (decay-corrected to January 1st, 2022) in the samples
 used for method validation (IAEA and Niida) and in French soils and sediments collected in the two investigated
 areas. The error bars correspond to a measurement uncertainty at $k = 2$ and the colored bands represent the
 typical $^{135}\text{Cs}/^{137}\text{Cs}$ ratios of the three main fallout sources.

361 Mercantour soil was almost exclusively due to the Chernobyl accident fallout while that of the
 362 Pyrenees soils was almost exclusively due to the fallout of nuclear weapons testing. Nevertheless,
 363 it should be noted that the ^{137}Cs contributions of Chernobyl fallout calculated for soil samples from
 364 the Pyrenees (Table 3) were slightly negative, due to the uncertainty of NWT signature, with, as
 365 underlined in the introduction, only two values of $^{135}\text{Cs}/^{137}\text{Cs}$ available for this source in the
 366 literature up to now^{32,35}. This could be also explained by the fact that these estimates relied on a
 367 $^{135}\text{Cs}/^{137}\text{Cs}$ ratio value characteristic of NWT averaged over the entire testing period (1950s to
 368 1980s) assuming a $^{135}\text{Cs}/^{137}\text{Cs}$ ratio of 1 at the date of detonation³⁵. However, the value of this ratio

369 could be refined based on the proportion of ^{137}Cs deposited during each year due to fallout from
370 NWT, while still assuming a $^{135}\text{Cs}/^{137}\text{Cs}$ ratio of 1 at the time of testing. Considering the proportion
371 of annual deposition of ^{137}Cs between 1958 and 1980 given by UNSCEAR⁴ and assuming the
372 accumulation of cesium with time in the soil or the sediments, the average $^{135}\text{Cs}/^{137}\text{Cs}$ ratio of the
373 resulting deposit would be about 3.94 to the reference time of January 1st, 2022, close to the
374 average value reported for NWT is 3.70^{32,35} (Table S4). According to experimental $^{135}\text{Cs}/^{137}\text{Cs}$ ratios
375 (3.94 ± 0.89 to 4.29 ± 0.21), actual deposition by NWT in the Pyrenees has likely mainly occurred in
376 the early period of 1950s to 1980s. Nevertheless, due to the limited data on the impact of NWT
377 fallout before the 1960s in the Pyrenees, it is difficult to determine an average value for the
378 $^{135}\text{Cs}/^{137}\text{Cs}$ ratio, specific for this region. The main limitation of this method is therefore the
379 uncertainty in the regional variation of ^{135}Cs and ^{137}Cs deposits due to nuclear weapons testing. The
380 other Mercantour soil and sediments samples with $^{135}\text{Cs}/^{137}\text{Cs}$ ranging between 0.68 ± 0.01 and
381 2.29 ± 0.05 showed radioactive contamination constituted of a mix of both sources in variable
382 proportions. Thus, for each sample, the proportion of ^{137}Cs resulting from Chernobyl fallout was
383 estimated using simple un-mixing models following methodology given in experimental section
384 (Table 3). In addition, the data highlighted a relationship between ^{137}Cs activity estimated by
385 gamma-ray spectrometry and the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio measured by ICP-MS/MS. As shown in
386 Figure 4, when the ^{137}Cs activity increased, the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio decreased until it reached the
387 $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature of Chernobyl fallout. Similarly, to the trend of $^{135}\text{Cs}/^{137}\text{Cs}$, a trend of
388 $^{134}\text{Cs}/^{137}\text{Cs}$ variations in soils of the Mercantour mountain has been shown on the one hand soils
389 strongly enriched in ^{137}Cs originating from Chernobyl and on the other hand other soils with low
390 ^{137}Cs contamination due to NWT fallout⁴⁶. Thus, both trends involving isotopes ratios of Cs suggest
391 that soils and sediments contain the two sources (NWT and Chernobyl) in various proportions from
392 one sample to another.

393 All these observations agree with what was previously predicted and, therefore,
394 demonstrate the applicability of the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio to discriminate unambiguously the sources of
395 radioactive contamination. Moreover, the use of a mono-elemental isotopic signature such as
396 $^{135}\text{Cs}/^{137}\text{Cs}$ ratio allows to get rid of any potential fractionation caused the potential difference of
397 behavior between two elements (such as Am and Pu or Pu and Cs), even if they share very similar
398 chemical properties.

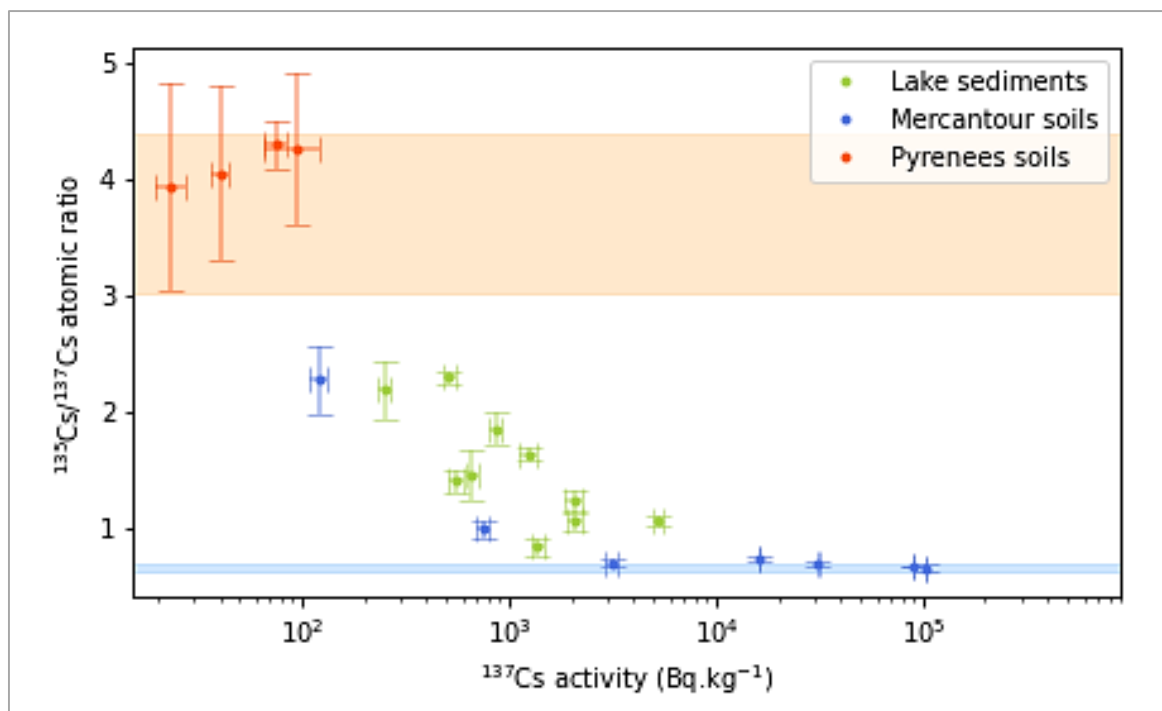


Figure 4: Relationship between $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratios and ^{137}Cs activity in sediments and soils collected in the Mercantour massif and the Pyrenees, France. The dark blue and orange bands indicate the typical $^{135}\text{Cs}/^{137}\text{Cs}$ ratios reported in the literature for fallout from nuclear weapons testing (NWT) and the Chernobyl accident. All data were decay-corrected to January 1st, 2022.

399 Conclusions

400 The main objective of the current research was to improve our knowledge of the radiological
 401 background in environments remote from nuclear tests or nuclear accident sites by analysing an
 402 isotopic signature little exploited to date, i.e., the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio. We have recently developed an
 403 analytical method to measure this ratio in solid environmental matrices and have applied it to soil
 404 and sediment samples collected in two areas of interest in France (Pyrenees and Mercantour massif).
 405 $^{135}\text{Cs}/^{137}\text{Cs}$ ratios ranging from 0.66 ± 0.04 in Mercantour soils to 4.29 ± 0.21 in Pyrenees soils were
 406 measured corresponding to typical ratios reported in the literature for Chernobyl accident fallout
 407 and from nuclear weapons tests, respectively. From these results, the contribution of each of these
 408 sources could be estimated and successfully compared with those calculated from more commonly
 409 used diagnostic ratios ($^{241}\text{Am}/^{239+240}\text{Pu}$ and $^{239+240}\text{Pu}/^{137}\text{Cs}$). Accordingly, the current work
 410 demonstrates the strength of the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio as a novel fingerprint for identifying the
 411 radioactive contamination sources and estimating their contribution in the environment. Moreover,
 412 the monitoring of this isotopic ratio in the areas that were the most affected by the Chernobyl and
 413 Fukushima accidents could provide a surrogate for the $^{134}\text{Cs}/^{137}\text{Cs}$ ratio, as the use of this ratio is

414 limited in time given the rapid decay of ^{134}Cs . In future research, it could be interesting to consider
415 the potential occurrence of diagnostic signatures of radiocesium released by nuclear facilities.

416 **Acknowledgement**

417 G. Salaün is warmly acknowledged for his excellent field work in the Alps and Pyrenees mountains
418 and his expertise for preparation of the samples in the laboratory.

419 We thank S. Aubry and S. Bonnot from the gamma team of the LMRE for the measurements of ^{137}Cs
420 and ^{241}Am by gamma-ray spectrometry and also S. Thomas for her recommendations on the ^{241}Am
421 measurement by alpha spectrometry.

422 We also warmly thank H. Isnard and S. Mialle from the Laboratory of Analytical development for
423 Nuclear Isotopic and Elemental analysis (CEA) for the supply and qualification of the spent fuel
424 sample used in this research to correct the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratios during the ICP-MS/MS
425 measurements.

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SUPPORTING INFORMATION

Identification of the origin of radiocesium into the environment in areas remote from nuclear accident and military test sites using the $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic signature

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Number of pages in Supporting Information section: 5, including cover.

Number of Tables: 4

Table S1: Characteristics of the lake sediment and soil samples investigated

Sample name	Study area	Sampling site	Latitude (°)	Longitude (°)	Sampling date	Matrix	Depth (cm)
20_PNM45_1		Terre Rouge Main lake	44.18089	7.18554	04/11/2020	Lake sediment	—
20_PNM45_2		Terre Rouge Temporary lake	—	—	04/11/2020	Lake sediment	—
20_PNM45_3		Superior Lausfer lake	44.22139	7.08944	05/11/2020	Lake sediment	—
20_PNM45_4		Inferior Lausfer lake	44.22052	7.0876	05/11/2020	Lake sediment	—
13_PNM4	Mercantour mountain	Cerise lake	44.13538	7.39015	24/09/2013	Lake sediment	—
13_PNM7		Besson lake	44.1387	7.32004	25/09/2013	Lake sediment	—
13_PNM9		Vens lake	44.31122	6.93234	09/10/2023	Lake sediment	—
13_PNM19		Lausfer lake	44.2214	7.08668	11/10/2013	Lake sediment	—
21_PNM24_5		Terre Rouge Main lake	44.190413	7.18485	16/06/2021	Lake sediment	—
21_PNM24_6		Terre Rouge Inferior lake	44.18946	7.183011	16/06/2021	Lake sediment	—
21_PNM24_1	Mercantour mountain	Restefond pass	44.344317	6.849132	15/06/2021	Surface soil	0 – 5
						Subsurface soil	5 – 10
21_PNM24_2		Restefond pass	44.344260	6.849150	15/06/2021	Surface soil	0 – 5
21_PNM24_3						Subsurface soil	5 – 10
21_PNM24_4	Restefond pass	43.341771	6.848091	15/06/2021	Surface soil	0 – 5	
					Subsurface soil	5 – 10	
14_PYR_2	Pyrenees	Coumebière plateau	42.78271	1.38986	25/06/2014	Surface soil	0 – 10
14_PYR_3		Labant pond	42.77735	1.39279	25/06/2014	Surface soil	0 – 10
						Subsurface soil	10 – 20
14_PYR_53		Besse pass	42.9697	-0.46900	08/10/2014	Surface soil	0 – 10

Table S2 : ICP-MS/MS parameters for $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio measurement

Parameters	Settings
Sample introduction	
Sample uptake	80 s (0.30 rps)
Stabilization time	40 s
Probe rinse	20 s (0.30 rps)
Spectrum acquisition	
Integration time	1 s for m/z = 115 and 138 5 s for m/z 135 and 137
Q2 peak pattern	3 points
Replicates	5
Sweeps/replicates	1000
Plasma	
RF power	1550 W
RF matching	1.27 V
Sample Depth	5.4 mm
Nebulizer gas	1.11 L.min ⁻¹
Option gas	0.0 %
Nebulizer pump	0.10 rps
S/C temperature	2 °C
Makeup gas	0.00 L.min ⁻¹
Lenses	
Extract 1	-19.0 V
Extract 2	-235.0 V
Omega bias	-110 V
Omega lens	12.0 V
Q1 entrance	2.0 V
Q1 exit	2.0 V
Cell focus	3.0 V
Cell entrance	-50 V
Cell exit	-58 V
Deflect	1.0 V
Plate bias	-50 V
Q1	
Q1 bias	-1.0 V
Q1 prefilter bias	-8.5 V
Q1 postfilter bias	-10.0 V
Cell	
He flow	1 mL.min ⁻¹
3 rd gas flow	NH ₃ /He – 48% (4.79 mL.min ⁻¹)
4 th gas flow	N ₂ O – 52 % (0.55 mL.min ⁻¹)
OctP bias	-4.0 V
Axial acceleration	2.0 V
OctP RF	160 V
Energy discrimination	-7.0 V

Table S3: Analytical performance (Cs recovery and eluate purity) achieved for each sample analyzed

Sample name	Depth (cm)	Analyzed mass (g)	¹³⁷ Cs recovery (%)	Interferent concentration in the ICP-MS measurement fraction (ng.g ⁻¹)			
				Ba	Mo	Sb	Sn
20_PNM45_1	—	63.142	83	1.09 ± 0.01	0.57 ± 0.02	0.11 ± 0.01	1.85 ± 0.02
20_PNM45_2	—	61.519	73	1.69 ± 0.03	0.28 ± 0.02	0.08 ± 0.01	1.25 ± 0.03
20_PNM45_3	—	94.853	78	1.52 ± 0.31	0.41 ± 0.09	0.08 ± 0.02	2.89 ± 0.59
20_PNM45_4	—	102.059	62	1.39 ± 0.67	17.46 ± 2.29	0.04 ± 0.02	0.24 ± 0.14
13_PNM4	—	113.369	76	1.96 ± 0.29	0.24 ± 0.03	0.06 ± 0.01	2.17 ± 0.28
13_PNM7	—	84.482	84	1.20 ± 0.19	0.28 ± 0.04	0.46 ± 0.07	1.67 ± 0.27
13_PNM9	—	60.080	84	1.15 ± 0.02	0.21 ± 0.02	0.05 ± 0.01	1.14 ± 0.01
13_PNM19	—	80.360	80	1.02 ± 0.19	0.39 ± 0.07	0.21 ± 0.04	0.81 ± 0.15
21_PNM24_5	—	99.030	77	1.16 ± 0.36	0.29 ± 0.09	0.08 ± 0.02	2.24 ± 0.66
21_PNM24_6	—	49.671	82	2.10 ± 0.02	2.45 ± 0.04	0.07 ± 0.01	1.48 ± 0.02
21_PNM24_1	0 – 5	5.131	82	0.24 ± 0.01	1.88 ± 0.04	0.04 ± 0.01	3.01 ± 0.08
	5 – 10	6.326	85	0.37 ± 0.02	0.94 ± 0.11	0.04 ± 0.01	12.16 ± 0.63
21_PNM24_2	0 – 5	109.884	57	3.39 ± 0.11	11.43 ± 0.28	0.03 ± 0.01	0.48 ± 0.03
21_PNM24_3	0 – 5	10.852	83	0.60 ± 0.01	0.18 ± 0.02	0.04 ± 0.01	7.21 ± 0.84
	5 – 10	55.037	82	5.45 ± 0.88	0.26 ± 0.04	0.05 ± 0.01	0.47 ± 0.08
21_PNM24_4	0 – 5	11.970	93	0.09 ± 0.01	0.13 ± 0.01	0.05 ± 0.01	5.64 ± 0.12
	5 – 10	100.610	71	1.03 ± 0.02	0.33 ± 0.02	0.07 ± 0.01	1.04 ± 0.02
14_PYR_2	0 – 10	113.455	65	0.34 ± 0.01	0.31 ± 0.02	0.07 ± 0.01	0.62 ± 0.03
14_PYR_3	0 – 10	34.039	72	0.52 ± 0.01	0.38 ± 0.02	0.04 ± 0.01	1.48 ± 0.02
	10 – 20	103.584	61	1.76 ± 0.03	0.31 ± 0.01	0.04 ± 0.01	1.21 ± 0.04
14_PYR_53	0 – 10	110.342	68	3.39 ± 0.01	0.30 ± 0.01	0.03 ± 0.01	0.77 ± 0.02

Table S4: Estimation of the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio characterizing NWT fallout by weighting the proportions of annual deposits with the theoretical isotopic ratio of 1 at the time of detonation.

Year	Annual deposition* (10^{16} Bq)		Proportion of annual deposition (%)	Theoretical $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio per year** (decay corrected to January 1 st , 2022)
	^{90}Sr	^{137}Cs		
Pre-1958	6.68	10.69	14.54	4.57
1958	2.33	3.73	5.07	4.37
1959	3.89	6.22	8.47	4.27
1960	0.97	1.55	2.11	4.17
1961	1.30	2.08	2.83	4.08
1962	5.34	8.54	11.62	3.98
1963	9.70	15.52	21.11	3.89
1964	6.13	9.81	13.34	3.80
1965	2.86	4.58	6.23	3.72
1966	1.21	1.94	2.63	3.63
1967	0.62	0.99	1.35	3.55
1968	0.72	1.15	1.57	3.47
1969	0.54	0.86	1.18	3.39
1970	0.76	1.22	1.65	3.31
1971	0.70	1.12	1.52	3.24
1972	0.32	0.51	0.70	3.16
1973	0.12	0.19	0.26	3.09
1974	0.45	0.72	0.98	3.02
1975	0.22	0.35	0.48	2.95
1976	0.10	0.16	0.22	2.89
1977	0.30	0.48	0.65	2.82
1978	0.37	0.59	0.81	2.76
1979	0.2	0.32	0.44	2.69
1980	0.11	0.18	0.24	2.63
TOTAL	45.94	73.50	100	3.97

*Annual ^{137}Cs deposition estimated from the annual ^{90}Sr deposition from NWT reported in the UNSCEAR report (1982) and the average $^{137}\text{Cs}/^{90}\text{Sr}$ activity ratio of 1.6.

** $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio calculated per year assuming a $^{135}\text{Cs}/^{137}\text{Cs}$ isotopic ratio of 1 at the time of detonation and for decay-correction to January 1st, 2022. The total corresponds to the $^{135}\text{Cs}/^{137}\text{Cs}$ characteristic of NWT weighted by the proportion of annual deposits.