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1 **A Fifty-year chronicle of tritium data for characterising the**
2 **functioning of the Evian and Thonon (France) glacial aquifers**

3
4 **Bernard BLAVOUX¹, Patrick LACHASSAGNE^{2*}, Abel HENRIOT^{1,2}, Bernard**
5 **LADOUCHE³, Vincent MARC¹, Jean-Jacques BELEY⁴, Gérard NICOUD⁵, Philippe**
6 **OLIVE⁶**

7
8 **1.** UMR 1114 EMMAH - Université d'Avignon et des Pays de Vaucluse, Laboratoire
9 d'Hydrogéologie, 33 rue Louis Pasteur, 84000 Avignon, France bernard.blavoux@gmail.com,
10 vincent.marc@univ-avignon.fr

11 **2.** Evian Volvic World Sources, BP 87, 11 Av. Général Dupas, 74503 Evian-les-Bains Cedex,
12 France, tel: +33-4 50 84 86 25, mob: +33-6 03 85 15 71, fax: +33-4 50 84 86 00,
13 patrick.lachassagne@danone.com, abel.henriot@danone.com

14 *** Corresponding author**

15 **3.** BRGM, Water Division, 1039 rue de Pinville, F-34000 Montpellier, France,
16 b.ladouche@brgm.fr

17 **4.** Danone Research, Water Resources & Processing Platform, BP 87, 11 Av. Général Dupas,
18 74503 Evian-les-Bains Cedex, France, jean-jacques.beley@danone.com

19 **5.** EDYTEM, Savoie University, 73000 Le Bourget du Lac, France, gnicoud@live.fr

20 **6.** Centre de Recherches Géodynamiques, Pierre et Marie Curie - Paris VI University,
21 olive87@wanadoo.fr

22

23 **Abstract¹**

24 Using lumped models and a transfer function model, this paper deals with the interpretation of
 25 exceptionally long (up to 50 years) and precise tritium chronicles characterizing the rainfall,
 26 recharge (efficient rainfall) and outflow from various types of glacial aquifers from the French
 27 Alps (Evian-Thonon area). The efficient rainfall tritium chronicle was computed from tritium
 28 measurements performed for 11 years (1969-1979) in a lysimeter. The evapotranspiration
 29 induces a mean 15% drop of the annual tritium signal. The three superficial glacial aquifers
 30 (two fluvio-glacial kame terraces and a lateral till) provide similar results: a best fit with an
 31 exponential flow model (EM) (playing the major role) combined in parallel with a piston flow
 32 model (PFM), and a rather short mean transit time (T: 5 to 7 years). The deepest mineral
 33 aquifer (Evian) can only be fitted with the in a series combination of a highly dispersive
 34 model (DM; T 68 years, DP=0.5) and a piston flow model (T 2.5 years) or, better, by the in a
 35 series combination of an EM (T 8 years) modelling the subsurface aquifer and a DM (T 60 y,
 36 DP=0.75) and the same piston flow model (T 2.5 years) modelling the deep mineral aquifer,
 37 this latest combination of models providing the following parameters: T 70 years and median
 38 transit time 45.5 years. It is also to be noted that a very small part of the efficient rainfall,
 39 about 1.3%, avoids both the EM and the DM, and directly enters the PFM (at the Northern
 40 limit of the Gavot Plateau). These models are very sensitive regarding the T (± 1 y, 0.25 y for
 41 the PFM), less so with DP. These results will prompt hydrologists to (re)work historical data

¹ Abbreviations:

amsl: above mean sea level (elevation)
 CRG: Centre de Recherches Géodynamiques
 DM: dispersion model
 DP : dispersion parameter
 EM: exponential flow model
 BMMEP: in parallel combined piston flow and exponential models
 IAEA: International Atomic Energy Agency
 LM: linear model
 LPM: combined linear flow and piston flow model
 NMW: Natural Mineral Water
 T: Mean Transit Time
 PFM: piston flow model
 TU: Tritium Unit
 y BP: year Before Present

42 to determine if important hydrologic information is available. The interest and limits of such a
43 modelling, also for other constituents than tritium, along with the future for tritium as a tracer
44 are discussed and it also provides new insights on the structure and functioning of alpine
45 paleo glacial hydrosystems.

46 **Highlights**

- 47 - interpretation of an exceptionally long tritium chronicle (rainfall, natural mineral water
- 48 and superficial springs)
- 49 - accurate characterization of a hydrological transfer function
- 50 - discussion of the interest and limits of lumped models
- 51 - new insights on the structure and functioning of glacial aquifers

52 **Keywords**

53 Evian; lumped model; natural mineral water; inverse modelling; tritium; glacial aquifers

54

55 **1. Introduction - History of isotope measurements in the Evian-Thonon area**

56 To evaluate the potential hydrogeological vulnerability of hydrosystems to anthropic pollution
57 and predict any future changes, the pattern of the transit time of water in the aquifers should
58 be defined. Isotopic measurements are presently used in field investigations and research
59 projects to improve qualitative understanding of hydrosystems and identify the processes
60 involved in water transfer (Turner and Barnes, 1998). Environmental tracers (^{18}O , ^2H and
61 tritium) and specific flow models have been used by numerous authors to estimate the transit
62 time of water in hydrological systems (Herrmann et al., 1990; Stewart and McDonnell, 1991;
63 Maloszewski et al., 1983, 1992, 1995, 2002; Maloszewski et Zuber, 1982; Holko, 1995; Amin
64 and Campana, 1996; Rodhe et al., 1996; Vitvar and Balderer, 1997; Etcheverry and Perrochet,
65 2000; Uhlenbrook et al, 2002; Viville et al., 2006; Hagedorn et al., 2011; Morgenstern and
66 Daughney, 2012). One difficulty in estimating the transit time of water is the need of the input

67 function, i.e. the concentration of tritium in the infiltrating water while only tritium in
68 precipitation and precipitation amount are available. McGuire and McDonnell (2006) tried to
69 construct better model to estimate the input function. Moreover, due to the insufficient length
70 of input and output chronicles, hydrosystems with transit times of several decades sometimes
71 cannot be studied.

72 Tritium (^3H) is a natural isotope of hydrogen (half-life 12.32 years; Lucas and Unterwenger,
73 2000), naturally present in the atmosphere at low concentrations (5 to 10 T.U.), and at higher
74 concentrations (up to about 6000 T.U.) due to above ground nuclear weapons testing
75 beginning in the mid 1940s, then dramatically increasing with the development of the
76 hydrogen bomb (first test was in November 1952) until 1963, the year when the atmospheric
77 atomic test was banned (the few small nuclear tests above ground since 1980 have just been
78 too small to make any impact on the tritium burden). However the beginning of tritium
79 recording started in August 1953 (Maloszewski and Zuber, 1994). It has been widely used in
80 hydrology to estimate aquifers' mean transit time (or residence time) since it is a constituent
81 of the water molecule and its concentration in rainfall has varied during the past sixty years,
82 giving a well-known input function for hydrological models. Tritium better captures the
83 longer term components of flow and recharge than other typical approaches (chloride or stable
84 isotopes for instance) (Stewart et al., 2010).

85 The first tritium measurements of groundwater from the Quaternary deposits of the Geneva
86 Lake basin were taken in the fifties, and have been densified since 1964, shortly after monthly
87 analyses of tritium from rainfall began in June 1963 at the Thonon (France, Fig. 1) Centre de
88 Recherches Géodynamiques (CRG, a branch of the Paris VI University), which was a member
89 of the International Atomic Energy Agency (IAEA) isotopic monitoring network. As early as
90 1963 this new isotopic tool proved useful in characterizing the hydrogeological functioning of
91 the complex glacial aquifers of the area (Blavoux et al., 1964; Fontes et al., 1967). A tritium

92 content of several hundred TU (Tritium Units) was found in 1964 in the Thonon unconfined
93 aquifer while in contrast the water from the Evian confined aquifer located about ten
94 kilometres eastwards was still only a few TU. Sampling was subsequently performed
95 quarterly in this area to monitor the evolution of the tritium signal until recently, providing
96 probably the longest available detailed temporal record of tritium in groundwater.

97 In that framework, this paper deals with the interpretation of such an exceptionally long
98 tritium chronicle characterising both the recharge and the outflow from various types of
99 glacial aquifers, using lumped models and a transfer function model. It discusses the interest
100 and limits of such modelling and also provides new insights on the structure and functioning
101 of ancient alpine glacial hydrosystems. Such glacio-fluvial hydrosystems, either quite old, or
102 “fossils” (see for instance Blavoux and Dray, 1971; Dray, 1993; Caballero et al., 2002;
103 Nicoud et al., 1993; Henriot et al., 2013; Bayer et al, 2011) or subactual (see for instance
104 McClymont et al. 2011, Rodhe and Seibert, 2011; Clow et al, 2003) are of high interest for
105 their water resources in the many regions of the world that were glaciated, mostly during the
106 Quaternary era, or are still at the margins of glaciated areas: the northern part of Eurasia,
107 North and South America, alpine regions, etc. (see for example Roy and Hayashi, 2009;
108 Beckers and Frind, 2000, 2001).

109 *Figure 1 – Location and schematic geological map of the Evian-Thonon area. Location of*
110 *springs and boreholes. Note the location of the rain gauge used since June 1963).*

111 **2. Geological and hydrogeological setting of the Evian-Thonon area**

112 The studied area is about 20 km long by 10 km wide along the southern shore of Lake Geneva
113 (Fig. 1 & 2). As in most of the Lemanic basin (Fiore et al., 2011), the land surface is almost
114 exclusively covered by thick (up to 400 m or more in Evian; Triganon et al., 2005)
115 Quaternary glacial sediments deposited over a major glacial erosion surface truncating the
116 cemented, folded and thrust Alpine rocks. The lake was dug during Quaternary glaciations

117 by ice originating from the upstream Rhône valley catchment basin. The deep valley of the
118 Dranse River (Fig. 1), the bottom of which exposes much older pre-Quaternary geological
119 formations, divides the study area into two independent zones both from a geological and a
120 hydrological viewpoint.

121 East of the Dranse River, the **Evian area** Quaternary geological formations are composed of
122 glacial sediments deposited along the Rhône glacier's southern margin (Nicoud et al. 1993),
123 well known from several kilometres of cored boreholes (Blavoux et al. 1971; Blavoux, 1988;
124 Triganon et al. 2005) (Figs 1 & 2a):

- 125 - the shape of the pre-Quaternary substratum is the result of erosion from the pre-
126 Würmian pulsations of the Rhône glacier. This paleotopography is irregular, reaches
127 an elevation less than 100 m amsl at Evian, and progressively rises towards the South,
128 up to a few pre-Quaternary outcrops at the highest points of the Gavot Plateau;
- 129 - this depression is filled by about 100 m of thick sands and gravels (older than the last
130 glacial cycle), corresponding to the northern tip of a paleodelta of the Dranse River,
131 covered by a subglacial till up to 200 m thick from the Würmian maximum (65'000 to
132 35'000 y BP, Triganon et al., 2005), during which the glacier reached an elevation of
133 about 1300 m amsl in the Evian area. This till surely prevents any groundwater flow
134 between the pre-Quaternary substratum and the sediments described here below;
- 135 - glacio-lacustrine sediments (small local streams paleodeltas within lacustrine silts)
136 from the "Inferior Complex", older than 30'000 y BP, sedimented during a major
137 retreat phase of the Rhône glacier, overlie this till up to about 390 m amsl;
- 138 - the Gavot Plateau glacial margin formation, over 200 m thick, results from the
139 progressive rise of the Rhône glacier during the Würmian "Lemanic stage" (30'000-
140 27'000 y BP, Triganon et al., 2005, Fiore et al., 2011) when the glacier reached the

141 Geneva city area. It is composed of a subglacial till in the Evian area and up to 13
142 superimposed subglacial and lateral tills with peatbog sediments below the plateau;
143 - the partial glacier retreat down to an elevation of about 480 m amsl, and then to about
144 430 m amsl at Evian, was responsible for the deposition of the glacio-lacustrine
145 sediments of the “Terminal Complex” (25’000-21’000 y BP, Triganon et al., 2005)
146 with highly permeable (10^{-3} to 10^{-4} m/s) sands and gravels in the fans of the local
147 paleostreams and low hydraulic conductivity silts laterally;
148 - finally, the last flood of the Rhône glacier, with the western tip of the glacier again
149 reaching Western Lake Geneva - “le Petit-Lac” - (Copet and Nyon readvances, Fiore
150 et al., 2011), covered all these sediments with a final subglacial till (the “terminal till”)
151 of 30 to more than 50 m thick up to an elevation of 650 to 750 m amsl in Evian. This
152 till locally comprises kame terraces, mostly deposited at the mouth of local streams
153 during the final deglaciation, and lateral tills.

154 The Natural Mineral Water (NMW) emerging from the confined aquifer of the “Terminal
155 Complex”, particularly at the Evian-Cachat spring, the highest-yield spring in Evian at 400 m
156 amsl, has been famous since 1789. Since that time, it has been widely used for its medicinal
157 properties (hydrotherapy). The Société Anonyme des Eaux Minérales d’Evian now bottles
158 “évian[®]” NMW from these mineral springs. The terminal till prevents any infiltration of
159 surface water into the aquifer and confines it in the downstream part of the aquifer. Recharge
160 occurs on the Gavot Plateau, above the 650-750 m amsl maximum elevation of the last glacier
161 advance (Blavoux, 1978; Henriot et al., 2013). Then the water slowly flows down and
162 northward within the Gavot Plateau glacial margin formation that comprises several
163 superimposed small confined and unconfined aquifers flowing mostly in the lateral tills,
164 separated one from the other by the basal till layers that act as semi-confining units (Henriot
165 et al., 2013). The mean elevation of the catchment area of the aquifer was estimated at 950-

166 1000 m amsl by comparing the ^{18}O content of the Evian NMW aquifer with the ^{18}O content of
167 precipitation at several altitudes and with the ^{18}O content of low discharge subsurface springs
168 with a well-known catchment area altitude (Blavoux, 1978). Mean annual rainfall on the
169 catchment area rises to 1'200 mm, and effective rainfall to about 750 mm. The specific
170 hydrochemical characteristics of the Evian NMW, calcium (80 mg/l) and magnesium (26
171 mg/l) (that dominate the cations) on one hand, and silica (15 mg/l) on the other hand, are
172 respectively the result of water-rock interaction with rocks of the aquifer (limestone and
173 dolomitic sands) that were eroded locally, and with rocks (granites, schists, green rocks...)
174 from buried lateral tills that were imported from the Rhône valley catchment by the glacier.
175 The pH is neutral (7.2) and bicarbonates (360 mg/l) and sulphate (13 mg/l) dominate the
176 anions. Due to the high inertia of the hydrogeological system, the mineral content and
177 temperature (11.6°C) at the spring are perfectly stable (below the analytical thresholds) and its
178 discharge shows less than 5% annual variations.

179 Small superficial aquifers are locally imbedded within the sands and gravels from the alluvial
180 kame terraces interstratified in or deposited above the terminal till. These aquifers are
181 recharged by the local precipitation. These waters can be easily distinguished from Evian
182 Natural Mineral water as the mineral content is different from that of Evian NMW, for
183 example in the Ca/Mg ratio and silica content.

184 *Figure 2 - Schematic geological cross-sections of the Evian (2a - top) and Thonon (2b -*
185 *bottom) areas (see the location of the cross-sections on Fig. 1).*

186 West of the Dranse River, the **Thonon slope** is mainly covered by the fifteen (Gagnebin
187 1933) Dranse River glacio-fluvial kame terraces (sands, gravels, and - limestone and less
188 numerous crystalline - large pebbles) progressively deposited westwards against lateral tills
189 (Figs. 1 & 2b), parallel to the Rhône glacier, during glacier retreat phases. The highest
190 terraces deposited during the Gavot Plateau retreat (Geneva stage: 25'000 to 23'000 y BP)

191 and the lowest during the final deglaciation of the “Petit Lac” stage (21’000 to 18’000 y BP).
192 They all lie on a subglacial till contemporaneous with the formation of the Gavot Plateau
193 (“Lemanic” stage), and the lowest lie on the till associated with the last flood of the Rhône
194 glacier (“Petit Lac” stage), which there confines the oldest terraces. The terrace aquifer is
195 generally unconfined and flowing northward. It exhibits a rather high hydraulic conductivity
196 (about $5.10^{-4} \text{ m.s}^{-1}$; Blavoux, 1978). Numerous springs discharge from the terraces and some
197 of them, “Les Blaves” for instance, are impounded for drinking water by Thonon town
198 waterworks (Figs. 1 & 2b). The “Versoie spring” discharges from one of the lowest terraces at
199 an elevation of 465 m amsl. Known since Roman times, it has been exploited as natural
200 mineral water, known as “Thonon Water”, for bottling and hydrotherapy since 1864. The
201 “spring” is tapped with a 15 m deep radial well equipped with a submerged pump. The mean
202 elevation of the Versoie spring catchment area has been estimated at about 600 m amsl from
203 natural ^{18}O tracing (Blavoux, 1978; Dray, 1993). It corresponds to permeable kame terraces
204 located between 650 and 465 m amsl, where mean annual precipitation reaches 1000 mm and
205 effective rainfall 550 mm.

206 **3. Material and methods - Sampling and analyses**

207 Monthly samples of rain water have been collected since July 1963 at the CRG Thonon rain
208 gauge station, at 385 m amsl on the shore of Lake Geneva and 10 km away from Evian (Fig. 1
209 and Fig. 3). Sampling consists of collecting and protecting from evaporation in a cumulative
210 rain gauge all the rain falling on a 2000 cm^2 plastic rain gauge during each month.

211 *Figure 3 CRG Thonon tritium monthly rainfall time series (since june 1963; previous annual*
212 *data reconstructed from the Ottawa time series, see details in the text). Note the logarithmic*
213 *scale of the Y axis and the 1960s very high peak.*

214 The tritium levels of three springs, two NMW (Evian-Cachat and Versoie) and one superficial
215 aquifer spring (Maxima), have been monitored since 1964; that is, during a crucial period

216 after the 1963 major tritium peak in precipitation (Figs. 4A and 4B). Evian-Cachat and
217 Versoie were sampled quarterly for 15 years (from 1964 to 1979); annual sampling continues
218 today. Although more widely spaced, measurements on the Maxima spring are sufficiently
219 numerous (22) that tritium restitution can be interpreted. Finally, the Larringes-Pugny well
220 located on the Evian impluvium was sampled from 1966 to 1969, a time sufficiently long and
221 close to the 1963 major tritium rain peak to give indications of the transformation of the
222 tritium signal upon input to the system.

223 The water catchwork of the Evian-Cachat spring, built in 1911, reaches the sandy confined
224 aquifer at the end of a 66 m long horizontal gallery crosscutting the till cover. As the aquifer
225 is confined, the gallery is completely sealed and neither the aquifer nor the water is visible
226 there. The artesian flow is limited by a valve to maintain the pressure. The samples were
227 collected at a sampling tap located in the gallery; Natural Mineral Water is not treated, and of
228 course not sterilised, consequently the samples were not subject to any treatment. Some
229 sporadic measurements were made for comparison on the other boreholes of the same mineral
230 hydrogeological system. The Versoie samples were collected on the pumping well from a tap
231 located at the top of the pumping tube. The Maxima spring (Figs. 1 & 2) emerges from a
232 superficial aquifer. It is located near the Lake's shore at 380 m amsl within a sandy kame
233 terrace of the terminal till on the lowest part of the Evian area; its more than 40 years of
234 tritium data are worth studying. The Larringes-Pugny well is located on the Gavot Plateau at
235 790 m amsl. This well exploited for drinking water taps a superficial aquifer of the Gavot
236 Plateau glacial margin formations (4 m thick sand and gravel locally covered by 2 m of clay).
237 All the water samples were analysed for tritium at the Centre de Recherches Géodynamiques
238 (CRG) in Thonon until it was closed in April 2005, and since then have been analysed at the
239 Hydrogeology Laboratory of the University of Avignon. Tritium measurements were obtained
240 by liquid scintillation counting after electrolytic enrichment. The associated error on the data

241 varies with the tritium concentration in the samples; it is 1 TU for recent samples and was
242 about 1 or 2 tens of TU for the samples which contained several hundred TU (see Figs 4A, 4B
243 and 5). The limit of detection of the CRG equipment was 5 to 8 TU during the earliest years
244 and about 1 TU since 1972 (see Fig. 5).

245 **4. Theory/calculation - Tritium restitution modelling**

246 Lumped parameter models are used in this study to estimate the transit time distribution of the
247 groundwaters discharging from the Evian - Thonon area. In the lumped parameter approach,
248 the output concentration is related to the input concentration using the following convolution
249 integral (Equ. 1) (Maloszewski and Zuber, 1982; Zuber, 1986(a) and (b)):

$$250 \quad C_{out}(t) = \int_0^{\infty} C_{in}(t - t')e^{-\lambda t'} g(t') dt' \quad (1)$$

251 where t is the sample date, t' is the transit time of single tracer particle through the system,
252 λ is the decay rate of the tracer, per year, C_{in} and C_{out} are the input and output tracer
253 contents, and $g(t')$ is the weighting function defining the transit time distribution.

254 Lumped parameter models assume a steady-state flow and that the selected tracers move with
255 the water molecules, which is why tritium is an ideal tracer. Such a steady-state flow
256 assumption is suitable for modelling the Evian and Thonon area aquifers; in fact, the water
257 volume in these aquifers does not change significantly on a seasonal and yearly time scale as
258 the variability in interannual discharge measurement is less than 5 % of the total annual
259 discharge for each spring. In addition, as two of these springs (Evian-Cachat and Versoie) are
260 bottled NMW, the spring discharges are monitored. In this paper, it is also considered that the
261 aquifer system is mono-porous, thus that the portion of immobile water is negligibly small,
262 which permits to use the mean transit time found from tritium as that of water.

263 The following lumped parameter models were considered (Yurtsever, 1995; IAEA, 1996): the
264 piston flow model (PFM), exponential flow model (EM), linear model (LM), and dispersive
265 model (DM). According to the tritium restitution curves and the hydrogeological conceptual

266 models (see chapter 2.), some of these models were also combined in parallel, thus
267 constituting Binary Mixing Models (a terminology proposed for instance by Katz et al.,
268 2001), which means a simple mixing of two - or more - endmembers occurring at the
269 spring/outlet. Piston flow and exponential model (named after BMMEP) were combined.
270 Some of these models were also combined in series. All these models take into account the
271 natural radioactive decay of tritium. The choice of model/combination of models was made as
272 a function of the appearance of the observed signal at each spring and the available
273 knowledge on their hydrogeological functioning. Among the different computer codes
274 available in the hydrological literature (for example FLOWPC, Maloszewski and Zuber 1994,
275 1996), we first used LUMPED (Ozyurt and Bayari 2003, available at
276 <http://www.sukimyasilab.hacettepe.edu.tr/english/software.shtml>). In a second phase, the
277 complex signal measured at the Evian-Cachat spring was interpreted using the TEMPO
278 software developed at BRGM by Pinault (2001) (see for instance also Dörfliger et al., 2008),
279 in which the equations of the models described by Maloszewski and Zuber (1994, 1996) have
280 been implemented (the models developed by Maloszewski and Zuber have also been used to
281 validate TEMPO). FLOWPC and TEMPO have the same input requirements and provide
282 similar outputs. The subsurface aquifers of the Versoie, Larringes-Pugny, and Maxima
283 springs were characterised using the exponential model (EM), and finally with a Binary
284 Mixing Model combining exponential and piston flow models where the exponential part
285 plays the major role. The Evian-Cachat aquifer was characterised with an in a series model
286 combining dispersive and piston flow models (Fig. 10), and secondly with an in a series
287 model combining exponential, dispersive and piston flow models (Fig. 13).
288 The piston flow model (PFM) assumes that all the flow lines have the same transit time and
289 thus, the response function is the Dirac delta function $g(t)=\delta(t-T)$, with T: mean transit time.
290 Hydrodynamic dispersion and diffusion are negligible (Maloszewski and Zuber, 1982, 1994).

291 Tracer concentration is only affected by radioactive decay. It ideally corresponds to a
292 confined aquifer with a narrow recharge area far from the sampling point.

293 In the EM, the distribution function of the transit time of water in the aquifer is exponential
294 ($g(t) = T^{-1} \exp(-t/T)$, with T = mean transit time, thus the average age of all parcels of water
295 that entered the system and reached the discharge point). Water travelling along the shortest
296 flow line has a transit time equal to zero while water travelling along the longest flow line has
297 an infinite transit time. An exponential distribution of transit times in an aquifer can
298 corresponds to multiple hydrogeological situations, including those where hydraulic
299 conductivity decreases with depth or the aquifer has uniform permeability and porosity
300 (Eriksson, 1958; Maloszewski and Zuber, 1982). Use of this model assumes that (1) there is
301 no mixing of water among the various flow lines during transfer in the hydrosystem and (2)
302 mixing of the water from the various flow lines occurs at the level of the sampling point.

303 The dispersive model (DM) allows the effects of transit time dispersion in the flow direction
304 to be taken into account. The distribution function of transit times in this model uses the one-
305 dimensional solution of the dispersion equation for a semi-infinite medium (Equ. 2)
306 (Maloszewski and Zuber, 1982):

$$307 \quad g(t) = \left(\frac{4\pi DP t}{T}\right)^{-\frac{1}{2}} \exp\left[-\frac{\tau}{4 DP T} \left(1 - \frac{t}{\tau}\right)^2\right] t^{-1} \quad (2)$$

308 with T = mean transit time and DP (without dimension) the dispersion parameter: the
309 dimension of variance of the dispersive distribution of the transit time. This additional
310 calibration parameter DP depends mainly on the distribution of transit times of the water
311 (shape of the flow lines) in the aquifer. It thus includes apparent dispersion of the tracer in the
312 system plus also apparent dispersion of the tracer in the recharge zone (recharge zone is in the
313 lumped parameter approach reduced to one point, while space distribution of the input signal
314 through the surface of the recharge zone, yields additional “dispersion”), and also the variable
315 infiltration conditions over the recharge area. DP is generally greater (by one or more orders

316 of magnitude) than the hydrodynamic dispersion parameter which usually represents only the
317 dispersive properties of the material (Maloszewski and Zuber, 1994).

318 The distribution functions of transit times providing the best correspondence of the simulated
319 concentrations to the experimental data were obtained by trial and error until a graphically
320 good fit and a “good” Nash coefficient were obtained (at best, the Nash coefficient is 1).

321 **5. Results**

322 **5.1. Observation results**

323 The annual tritium levels of the precipitation at Thonon CRG (Table 1) have been computed
324 from the monthly values weighted by the precipitation rate. For values prior to 1963, a
325 regression (Equ. 3) was established with the annual levels measured in Ottawa from 1964 to
326 1985, a station at the same latitude as Thonon that has operated since 1953 (Brown, 1970).

$$327 \text{[}^3\text{H]}_{\text{Thonon}} = 0.892\text{[}^3\text{H]}_{\text{Ottawa}} + 9, n=22, R^2=0.9 \text{ (Molicova, 1991)} \quad (3)$$

328 This chronicle of annual levels constitutes the input signal for the hydrogeological systems of
329 the Evian-Thonon area (Figs. 4A and 4B). Since the start of thermonuclear weapons testing in
330 the early 50's, continued more and more intensively until 1963, atmospheric tritium levels
331 increased enormously. The levels in rainwater at Thonon reached several thousand TU in
332 1963, with a spectacular rise between 1961 and 1963 (Fig. 4B). From 1963 to 1966, nearly all
333 atmospheric nuclear tests were stopped and levels dropped sharply with a pseudo-period close
334 to one year, thus defining a very characteristic peak on the multiyear scale. From 1967 to
335 1980, atmospheric nuclear tests were of very low capacity, with less than 3% in total of all the
336 tritium produced artificially, nevertheless leading to fallout that decreased slowly from 200 to
337 100 TU. Since 1980, there have been no atmospheric nuclear tests. With a pseudo-period of
338 one year and according to tritium natural radioactive decay (half-life: 12.32 years), the level
339 should have reached the natural level (5 to 10 TU) around 1985. However, it remained
340 between 30 and 20 TU until 1996; this is due to the feedback from the oceans and surface

341 waters that contain higher levels of tritium (Fine and Ostlund, 1977; Fine et al., 1987; Michel,
342 1992) and also the influence of the civilian nuclear industry. Since 2000, it seems that the rain
343 signal at Thonon has entered a permanent regime around a value of 9 TU.

344 *Table 1 – (i) Rainfall tritium mean annual content at the Thonon CRG rain gauge, (ii)*
345 *computed tritium efficient rainfall signal, and (iii) mean annual tritium content at the Evian-*
346 *Thonon area springs*

347 *Figure 4 – Rainfall and springs tritium mean annual content at the Thonon CRG rain gauge*
348 *and at the Evian-Thonon area springs (top: logarithmic scale; bottom: arithmetic scale)*

349 The tritium content in rainfall shows a seasonal variation. Monthly levels in Thonon have a
350 maximum in June-July and a minimum in November-December. For the temperate climate
351 zone of the Northern hemisphere, this springtime increase results from direct discharge of
352 tritium in the stratosphere toward the troposphere due to the discontinuities of the tropopause
353 (Olive, 1970). The tritium-rich rain of the summer months is much more affected by
354 evapotranspiration than that of autumn-winter, poor in tritium, therefore the transformation of
355 the rain signal upon infiltration must be investigated (Foster and Smith-Carrington, 1980). A 1
356 m² lysimetric box covered with grass and filled with fluvio-glacial earth 1 m deep was
357 installed in Thonon at the site of the rain gauge. The drainage of this box, equivalent to the
358 effective rainfall, was monitored quantitatively and qualitatively on a monthly basis from
359 1969 to 1979. During these 11 years, the average annual rainfall was 944 mm and its
360 weighted tritium content was 132 TU, while the drainage at the base of the box was 537 mm
361 and showed a weighted annual tritium content of 114 TU. The average inter-annual
362 evapotranspiration of 407 mm thus affects the tritium rain signal by a drop of 15%. This
363 mechanism was repeated each year in similar proportions during the 11 years of monitoring.
364 Consequently, the annual tritium levels in precipitation used as input data for modelling were
365 systematically adjusted by a drop of 15% to estimate the infiltration signal toward the

366 unconfined aquifers (Table 1). This correction is only really significant for the high tritium
367 values close to the 1963 peak (Fig. 6). It seems illusory to specify the infiltration signal more
368 precisely, in that the lumped models involve a steady-state regime that does not take into
369 account the inter-annual variability of input volumes.

370 *Figure 5 – Evian-Cachat spring tritium chronicle (note the increase in measurement*
371 *precision with time; arrows indicate values below the detection limit (circle))*

372 *Figure 6 - Evian-Thonon area rainfall and effective rainfall tritium mean annual content.*

373 Tritium restitution is very different according to the hydrogeological system (Fig. 4). The
374 restitution at Versoie shows high values as of 1964 and a peak in 1965 in reaction to the 1963
375 peak in rainfall, but with concentrations reduced by almost 5 times compared to that in the
376 rainfall (700 vs. about 3000 TU). The Maxima spring and the Larringes-Pugny well show
377 behaviour close to that of Versoie. On the arithmetic scale figure (Fig. 4 bottom), the Evian-
378 Cachat spring does not appear to be affected by the injection of atmospheric tritium. The use
379 of a logarithmic scale (Fig. 4 top) and use of isolated data (Fig. 5) display the multimodal
380 restitution of the tritium at the Evian-Cachat spring. An initial peak, transient and of very low
381 amplitude, is observed from 1964 to 1966 (21 TU in 1965), followed by a dip and then a very
382 broad peak, also of very low amplitude, that begins in 1969-1970 and displays a maximum
383 around 1979 with levels of about 40 TU (41 TU in 1979), 70 times less than the levels in
384 rainfall in 1963. The memory effect of this restitution is still perceptible in 2000 (16 TU).

385 From a methodological point of view, it appears (Figs. 4) that the period from the peak of
386 1963 to 1982 is decisive in distinguishing the different behaviour of the two types of
387 hydrogeological systems, systems with low transit time on one hand (Versoie, Maxima,
388 Larringes-Pugny) and that with a long transit time (Evian-Cachat) on the other hand.

389 **5.2. Results of modeling**

390 Given the relatively large variation of the tritium signal at the **Versoie spring**, at least during
391 the initial years of monitoring (1964 – 1974) (Figs. 4), the calculated annual tritium levels at
392 the spring (Table 1) were averaged from the numerous individual levels measured on samples
393 taken during the initial years of monitoring, every month until 1971, then every quarter until
394 1979. Finally, far from the 1963 thermonuclear peak in precipitation, the values used
395 correspond to a single annual check. The shape of the observed tritium signal (Fig. 7) can be
396 described using an exponential model (EM), taking a mean transit time (T) of 5 years (Fig. 7).
397 This value is close to that of 4 years put forward by Molicova (1991) using a Gamma law on a
398 shorter series, which was later confirmed by Hubert et Olive (1995) and Olive et al. (1996). A
399 PFM only is definitely not appropriate (Fig. 7). Nevertheless, the signal measured at the
400 Versoie spring shows a pronounced peak as of the beginning of monitoring in 1965, which
401 probably indicates the existence of a component of water transfer by piston effect. Use of a
402 Binary Mixing Model combining in parallel an EM with a PFM (BMMEP) thus allows the
403 measured concentrations to be well reproduced (Fig. 7) with a 5.1 years mean transit time,
404 and with the volume and flow parameters for the two reservoirs shown in Table 2. This
405 transfer model is perfectly compatible with the hydrogeological context of the Versoie spring
406 (§2. and Fig. 2) that involves two aquifers: (1) most of the flow (about 80%) comes from an
407 unconfined aquifer that is attributed to the paleo-Dranse river lower fluvio-glacial kame
408 terraces resting on the Petit Lac Stage impervious morainic substrate, and (2) a lower part of
409 the flow (about 20%) is attributed to the earlier terraces aquifer, which is confined by the Petit
410 Lac Stage impervious basal till and appears to be recharged upstream.

411 *Figure 7 – Modelling the Versoie spring tritium time series (using LUMPED, Ozyurt and*
412 *Bayari, 2003)*

413 *Table 2. – Summary of the parameters used to fit the Evian-Thonon area springs. Note that*
414 *for the exponential-piston flow model, the two models are placed in parallel*

415 The tritium signal measured at the **Maxima spring** of Amphion (380 m amsl), although
416 including less data, has an appearance very similar to that of the Versoie spring (Figs 4). The
417 same Binary Mixing Model (BMMEP) provides a very good fit (Fig. 8). Neither the PFM nor
418 the EM are able to simulate the observed data. The simulation provides a mean transit time of
419 6.7 years (Table 2). This result is in good accordance with the hydrogeological structure of the
420 Maxima spring, which outflows from a shallow semi-captive aquifer (local kame terrace)
421 interstratified within the terminal basal till that appears to comprise both a confined and an
422 unconfined component. The water molecule stable isotope content shows that this aquifer is
423 very local (mean elevation of the recharge area of about 450 m amsl).

424 *Figure 8 – Modelling the Maxima spring tritium time series (using LUMPED, Ozyurt and*
425 *Bayari, 2003)*

426 The tritium signal at the **Larringes-Pugny** well has been simulated with the same BMMEP
427 with a good fit (Fig. 9) insofar as the scarce data available allow input and output data to be
428 compared and a mean transit time of 6.3 years (Table 2). About 80% of the discharge of the
429 spring is explained by the EM, while the last 20% is the result of PFM. The well also taps a
430 shallow subhorizontal semi-confined aquifer flowing into a Gavot Plateau lateral till lying on
431 a basal till which constitutes its impervious substratum. Hydrogeological data show that this
432 aquifer is local, with a mean elevation of the recharge area of about 820 m amsl, similar to
433 that of the well (790 m amsl). As the available data at this well are scarce, they can also be
434 well fitted with an EM with $T=7$ years (Fig. 9 and Table 2), which is not incompatible with
435 the hydrogeological context (only locally confined aquifer).

436 *Figure 9 – Modelling the Larringes-Pugny well tritium time series (using LUMPED, Ozyurt*
437 *and Bayari, 2003)*

438 The time variation of the tritium levels measured at the **Evian-Cachat spring** (Figs. 4 & 6) is
439 complex and very different from the output signals observed at the springs previously studied.

440 The signal is excessively attenuated; the maximum observed tritium levels are approximately
441 20 times lower. As it propagates over a greater time period, it appears to result from a transfer
442 in a highly dispersive system. Moreover, the response of the hydrogeological system to
443 infiltration of “tritiated” water is bimodal. Even if, due to their low activities, tritium
444 measurements show a high uncertainty, an initial maximum, low in absolute value, is
445 observed around 1966; the second, of significantly greater amplitude and very extended in
446 time, appears much later, toward the 1980s. These two responses of the hydrogeological
447 system to recharge by tritiated effective rainfall are the result of two different functional
448 processes of the reservoir: (i) mainly a very highly dispersive aquifer system with very slow
449 flow dynamics and (ii) a modest contribution of water with a less slow flow dynamics that
450 doesn't flow through the highly dispersive aquifer (Fig. 10). After several trials, a conceptual
451 model with two models in a series (a DM and then a PFM) (Fig. 10) was adopted. In addition,
452 a modest (about 1.3%) contribution of efficient rainfall directly enters the PFM and
453 consequently avoids the DM.

454 *Figure 10 - Conceptual model of the Evian-Cachat spring (in a series dispersive and piston*
455 *flow model). “q” is the mean annual recharge and discharge of the spring*

456 The less slow flow component of the system was studied together with the dispersive one, but
457 was first calibrated. It was necessary first to identify the isotopic model best able to describe
458 the time variation of the first tritium maximum observed at Evian-Cachat, and then to estimate
459 the quantitative contribution of this less slow component to the overall functioning of the
460 hydrogeological system. Only the PFM allowed the initial maximum observed at Evian-
461 Cachat (Fig. 11A and B) to be satisfactorily reproduced. The mean transit time of these early
462 waters lies around 2.5 years (± 0.25 y; Fig. 11A). The contribution of this first component
463 appears to be very low, about 1.3 % (± 0.2 %; Fig 11B) of the total discharge at the spring.

464 The other models tested are not acceptable; in particular, a DM significantly overestimates
465 tritium levels during the decline that follows the initial maximum of 1966.

466 *Figure 11 Modeling (TEMPO) of the Evian-Cachat spring. Fig. 11A: Sensitivity analysis of*
467 *the PFM to the T. Fig. 11B: Sensitivity analysis of the PFM to the % of the less slow flow*
468 *component.*

469 Although not perceptible with the classical hydrochemical approaches, the computed
470 parameters of this first component are consistent with the hydrogeological knowledge:

- 471 - the PFM and the perfect mixing before the outflow is consistent with the fact that the
472 aquifer of the “terminal complex” is confined by the terminal till at and upstream from
473 the spring. An EM (unconfined aquifer) would have been totally implausible;
- 474 - with the known parameters of this aquifer in the vicinity of the spring (hydraulic
475 conductivity about 2.10^{-3} m.s⁻¹, hydraulic gradient about 1.10^{-3} , effective porosity
476 about 5%), a 2.5 years mean transit time for the first component yields a recharge area
477 about 3 km from the spring. This order of magnitude of a few kilometres
478 (northernmost part of the Gavot Plateau) is in agreement with the maximum southern
479 extension of the terminal till that, for a maximum elevation of about 650 to 750 m
480 amsl (§ 2.), respectively, lies at a horizontal distance of about 1.5 to 1.9 km from the
481 spring (Figs. 1 & 2a). Consequently, this first component is very probably a very small
482 part of the total recharge (about 1.3 %) that infiltrates on the northernmost part of the
483 Gavot Plateau and (this second condition is very important) is able to rapidly (in about
484 one year) reach the “terminal complex” high hydraulic conductivity aquifer; in fact, as
485 the Gavot Plateau is composed of several superimposed basal and lateral tills, its mean
486 hydraulic conductivity is quite low and this explains, with the capping terminal till that
487 avoids any infiltration downstream, the long transit time of Evian water (see the
488 following part of this paper). Consequently, the infiltration of this first component

489 occurs through few layers of superimposed basal and lateral tills, which is consistent
490 with the geological structure of the northernmost tip of the Gavot plateau (Fig. 2a).
491 The effect of this less slow flow component is significant up to the mid-1980s; however, it is
492 less than 5 TU starting from the mid-1970s.
493 Different types of isotopic transfer models (PFM, EM, BMM combining a PFM with an EM,
494 DM) were tested to simulate the long term second part of the observed signal. Only the DM
495 allows the restitution curve to be satisfactorily reproduced (Fig. 12) with $T = 68 (\pm 2)$; Fig.
496 12A) years, $DP = 0.5 (\pm 0.025)$; Fig. 12B), and a flow of 98.7% of the total discharge in the
497 DM, the 1.3% remaining corresponding to the less slow flow component presented above.
498 The sensitivity analysis shows that the DM is sensitive to small variations of both T and DP
499 (Fig. 12A and B). This behaviour is in good agreement with the hydrogeological knowledge.
500 The mineral aquifer recharge area, the 200 m-thick (Fig. 2a) Gavot Plateau, is composed of up
501 to 13 superimposed Würmian basal and lateral till sequences. These formations respectively
502 exhibit very low and quite low hydraulic conductivity. Hydrogeological and hydrochemical
503 data from deep piezometers drilled on the plateau (Henriot et al., 2013) show the presence of
504 several superimposed quite low hydraulic conductivity aquifers (flowing in the lateral tills)
505 with hydraulic heads decreasing with depth, which is a strong clue for a vertical component of
506 the groundwater flow. The groundwater is thus able to flow down through the basal till layers
507 (either with leakage flow and/or in places where the basal till layer(s) is (are) missing). The
508 hydrogeochemical data sampled in these deep piezometers (^{13}C and ^{14}C data, but also and
509 mainly silica content, and Mg/Ca ratio, which are all residence time indicators) also show that
510 most of the NMW mineralisation process occurs within this Gavot Plateau multilayer low
511 hydraulic conductivity system, which is not capped by the thick low hydraulic conductivity
512 superficial terminal till deposited below 650 to 750 m amsl. Consequently, such large
513 dispersion behaviour is the result of the various pathways the future NMW can follow within

514 the Gavot Plateau formation. The water then fast flows within the Terminal Complex aquifer.
515 Consequently, with this set of parameters, the mean transit time in the Evian hydrosystem is
516 about 70 years (T: 70.05 years): mostly (about 68 years) within the subsurface and deep
517 aquifers of the Gavot plateau (DM) and about 2.5 years within the high hydraulic conductivity
518 Terminal Complex (PFM). Statistical processing of the output data shows that the median
519 transit time of the Evian NMW (a less biased estimator than the arithmetic mean for such non
520 Gaussian distributions) is about 48 years (48.0 years).

521 *Figure 12 - Modelling (TEMPO) and sensitivity analysis of the slow flow component of the*
522 *Evian-Cachat spring. Fig. 12A: Sensitivity analysis of the DM to the T. Fig. 12B: Sensitivity*
523 *analysis of the DM to DP*

524 Another approach to modelling the transit time of the Evian-Cachat spring NMW in its
525 reservoir was attempted on the assumption that across the recharge area of the Gavot Plateau,
526 the infiltration component first crosses through a subsurface aquifer. In fact, the catchment
527 area of the Evian NMW system, about 35 km², has a mean elevation of about 950-1000 m
528 (see § 2.) and corresponds to the Gavot Plateau and Mont Bénant area (Fig. 1). Several local
529 subsurface aquifers of limited extent are known in this area. The rather low discharge springs
530 emerging from these aquifers are locally tapped to supply the few villages of the plateau.
531 These subsurface aquifers constitute the first step in the functioning of the mineral
532 hydrosystem. In this case, the tritium input signal of the deep mineral reservoir is transformed
533 by its stay in the subsurface aquifer and so can in fact be different from the tritium chronicle
534 resulting from effective rainfall. To simulate this new input signal, we thus assumed that the
535 functioning of the various superficial aquifers of the Evian watershed area (Gavot Plateau)
536 can be described using a mixing model (EM) with a transit time on the order of several years
537 (Fig. 13). Various simulations were performed, taking among others mean transit times in the
538 subsurface aquifer increasing from 6 to 10 years (Fig. 14). The monitoring of tritium levels in

539 one of these subsurface aquifers at Larringes-Pugny from 1966 to 1969 is actually compatible
540 with this choice (Fig. 9). The use of these data from the EM as new input data for the Evian-
541 Cachat dispersive model (the two models are in a series) requires the parameters of this latest
542 model to be revised. The tritium levels in the Evian-Cachat spring can only be well simulated
543 if it is taken into account that the mean transit time in the EM is about 8 years (Fig. 14A),
544 with a T of 60 (± 1) years (Fig. 14B) in the deep aquifer system, DP = 0.75 (± 0.025 ; Fig. 14C),
545 and still a flow of 98.7% of the total discharge in the EM and DM, the 1.3% remaining
546 corresponding to the less slow flow component presented above that only flows in the PFM
547 (Figure 13). The first result (8 years in the EM) is in good accordance with the fit obtained at
548 the Larringes-Pugny well (7 years) tapping one of the Gavot Plateau superficial aquifers (see
549 section 5. and Fig. 9). Consequently, the mean transit time in the whole Evian hydrosystem
550 computed from the 3 models in a series is about 69.5 years: 8 years within the subsurface
551 aquifers of the Gavot plateau (EM), 60 years within the deep aquifers of the Gavot plateau
552 (DM) and 2.5 years within the Terminal Complex (PFM). The median transit time of the
553 Evian NMW is then 45.5 years. More in detail, the comparison of the results obtained with
554 both in a series modelling approaches ((Model 1 - M1) DM+PFM and (Model 2 -
555 M2) EM+DM+PFM) for a perfect tracer (without the tritium radioactive decay) shows
556 interesting results (Fig. 15):

- 557 - the 4 first years are governed by the PFM and show no difference between M1 & M2;
 - 558 - during the following 14 years the difference between the two models is rather low.
- 559 The effect of the EM is nevertheless visible, with, during the first 8 years (up to a total
560 duration of about 12 years), a restitution higher for M2 (EM8 + DM 60) than for M1,
561 mostly showing the influence of the EM and of the lower T of the DM;
- 562 - after that, the differences are governed by the DM with logically a higher peak for M2.

563 Due to the difference of the two curves shapes, even if the T of both M1 and M2 are rather
564 similar (about 70 years), their median are significantly different with a higher one for M1 (48
565 y) than for M2 (45.5 y). Consequently, the two different models provide significantly
566 different results particularly during some important phases of the output, and particularly
567 during the second part of the restitution (beyond 18 years) with significant absolute
568 differences reaching about -0.12% (M1-M2), and consequently relative differences of about
569 8% $((M1-M2)/(\text{Average of } M1, M2))$.

570 *Figure 13 - Conceptual model of the Evian-Cachat spring (in a series exponential, dispersive*
571 *and piston flow model). “q” is the mean annual recharge and discharge of the spring*

572 *Figure 14 – Modelling (Tempo) of the Evian-Cachat spring for various mean transit time (T)*
573 *within the superficial aquifer (EM). Fig. 14A: Sensitivity analysis of the EM to the T. Fig.*
574 *14B: Sensitivity analysis of the DM to the T. Fig 14C: Sensitivity analysis of the DM to DP*

575 *Figure 15 – Modelling of a perfect tracer one year duration Dirac (100%, arbitrary unit;*
576 *year 0) input for the Fig. 10 D- (T 68 y, DP = 0.5) + PF- (2.5 y) model (M1), and the Fig. 13*
577 *E- (T 8 y) + D- (T 60 y, DP = 0.75) + PF- (2.5 y) model (M2). The figure also provides the*
578 *difference between the two outputs (M1 - M2)*

579 **6. Discussion**

580 *6.1. On the need of anthropogenic tracers long term database in hydrological studies*

581 It appears that, even in quite heterogeneous and complex aquifers such as those of the Evian-
582 Thonon area, the use of quite simple lumped models leads to very accurate results. Such tools
583 allow transfer model types to be obtained, their parameters inferred, and aquifer transit time
584 distributions computed.

585 Use of the exceptionally long and precise Evian-Thonon rainfall, effective rainfall and spring
586 tritium content time series allows existing knowledge about the structure and functioning of
587 such complex aquifers to be much better characterised and/or assessed. Among other results,

588 the computed median transit time in the Evian-Cachat aquifer, about 45 years, appears to be
589 much longer than previously expected from simpler approaches. Knowledge of this
590 distribution function of transit times, allowing mass transfer of chemical elements within the
591 hydrosystem to be imaged, has been especially useful in establishing a policy to protect the
592 mineral resource (see for instance Buric et al., 2011, Devier et al., 2013; Lachassagne et al.,
593 2011).

594 The long tritium chronicle available at the Evian-Cachat spring even allows a 1.3%
595 contribution to the spring discharge that, due to its low value, was not identifiable by other
596 hydrodynamical or hydrogeochemical means. However, this identification results from a very
597 opportune and exceptional combination of circumstances: the fact that tritium monitoring at
598 the Evian-Cachat spring began only a few years (2 years) after the main period of tritium
599 injection into the atmosphere, and was carried out continuously for several decades. The
600 scientists at the Centre de Recherches Géodynamiques were able to convince stakeholders to
601 carry out such monitoring.

602 These results should encourage the owners of the old tritium database, even if sparse or
603 incomplete, to make use of them, at least with such simple computational models. It should
604 also encourage young scientists to be on the lookout for emerging tracers, and consequently to
605 acquire the corresponding data on such high-stakes aquifers. A few years ago, noble gases and
606 chlorofluoromethanes were such emerging tracers. These methods are presently being tested
607 on the Evian aquifer and the results will be compared to those of this study.

608 This research also shows that the standard simple models can easily be improved with some
609 kind of plug-in, for instance, to compute the behaviour of superficial aquifers. The next steps
610 at Evian will be to more precisely compute the role of the high hydraulic conductivity aquifer
611 of the “Terminal Complex” in the framework of a complete process-based modelling of the
612 aquifer.

613 6.2. *What is the future for Tritium as a tracer?*

614 The tritium tool was especially effective in the vicinity of the 1963 rainfall peak and up to
615 approximately 1980. But new prospects are emerging. Since 2000, the mean annual tritium
616 signal in rainfall at Thonon has oscillated around a level of 9 ± 1 TU. Comparison with the data
617 available at the Orléans-BRGM station (Parisian Basin) shows the same trend around a level
618 of 6 TU, and good correlation. Thus there seems to be a return to the case of a constant influx
619 of tracer. In this case, the transit time of the water would be accessible starting from one or
620 more tritium measurements using simple empirical models that require only this parameter;
621 here, the exponential model (EM) and the Piston Flow model (PFM). For unconfined aquifers
622 likely to function according to an exponential model (of course if the vadose zone is not too
623 thick, in order to allow the arrival of water with a theoretically zero residence time), the
624 tritium level could thus be translated into the apparent age of the water, on the express
625 condition of having good knowledge of the local input rainfall signal. Given the low levels
626 and the necessary precision, correlations with a too-distant rain gauge station are now
627 inadequate, and a denser network would be necessary. This projection gives 6.7 ± 0.7 TU for
628 Versoie in the immediate future. In 2009, its content was measured at 7.1 ± 0.6 TU.
629 Measurements on such systems already studied near the 1963 peak would be worth repeating
630 today to establish these new prospects. It would be interesting to verify whether slight
631 differences still exist between families previously defined by their tritium level during former
632 regional prospecting, so as to offer new standards for interpretation.

633 **7. Conclusion**

634 This paper deals with the interpretation, with lumped models and a transfer function model, of
635 exceptionally long (up to 50 years) and precise tritium chronicles characterizing the rainfall,
636 the recharge (efficient rainfall) and the outflow from various types of glacial aquifers from the
637 French Alps (Evian-Thonon area).

638 The evapotranspiration induces a mean 15% drop of the tritium signal. The three superficial
639 glacial aquifers (two fluvio-glacial kame terraces and a lateral till) provide similar results: a
640 best fit with an exponential flow model (EM) (playing the major role) combined in parallel
641 with a piston flow model (PFM), and rather short mean transit time (T: 5 to 7 years). The
642 deepest mineral aquifer (Evian) can only be fitted with the in a series combination of a highly
643 dispersive model (DM; T 68 years, DP=0.5) and a piston flow model (2.5 years) or, better, by
644 the in a series combination of an EM (T 8 years) modelling the subsurface aquifer and a DM
645 (T 60 y, DP=0.75) and the same piston flow model (2.5 years) modelling the deep mineral
646 aquifer (note that a very small part of the efficient rainfall, about 1.3%, avoids the DM (and
647 the EM), and directly enters the PFM). This latest in a series combination of models is rarely
648 used in hydrology even if it is conceptually highly credible in such a hydrogeological context.
649 It provides the following parameters: T 69.5 years and median transit time 45.5 years. These
650 models are very sensitive regarding the T (± 1 y, 0.25 y for the PFM), less so with DP.
651 With this study the interest and limits of such a modelling and the future for tritium as a tracer
652 can be discussed and it also provides new insights on the structure and functioning of alpine
653 paleo glacial hydrosystems.

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661

662 **References**

- 663 Amin, I.E., Campana, M.E. 1996. A general lumped parameter model for the interpretation of
664 tracer data and transit time calculation in hydrologic systems. *Journal of Hydrology* 179, 1–21
- 665 Bayer, P., Huggenberger, P., Renard, P., Comunian, A. 2011. Three-dimensional high
666 resolution fluvio-glacial aquifer analog : Part 1 : Field Study, *Journal of hydrology*, 405, 1-9
- 667 Beckers, J., Frind, O.E., 2000. Simulating groundwater flow and runoff for the Oro Moraine
668 aquifer system. Part I Model formulation and conceptual analysis, *Journal of hydrology*, 229,
669 265-280
- 670 Beckers, J., Frind, O.E. 2001. Simulating groundwater flow and runoff for the Oro Moraine
671 aquifer system. Part II. Automated calibration and mass balance calculations, *Journal of*
672 *hydrology*, 243, 73-90
- 673 Blavoux, B. 1978. Etude du cycle de l'eau au moyen de l'oxygène 18 et du tritium, Thèse de
674 Doctorat d'Etat ès Sciences Naturelles, Université Pierre et Marie Curie, Paris 6, 333 p..
- 675 Blavoux, B. 1988. L'occupation de la cuvette lémanique par le glacier du Rhône au cours du
676 Würm, *Bulletin de l'Association française pour l'étude du Quaternaire*, 2/3, 69-79.
- 677 Blavoux, B., Dray, M. 1971. Les sondages dans le complexe quaternaire du Bas- Chablais et
678 leurs enseignements stratigraphiques. Leur intérêt pour l'hydrogéologie et l'hydrochimie
679 régionales, *Revue de Géographie Physique et de Géologie Dynamique* (2), Vol. XIII, Fasc.1,
680 17-34, Paris.
- 681 Blavoux, B., Glangeaud, L., Lévêque, P., Olive, Ph. 1964. Hydrodynamique et teneur en
682 tritium des eaux du bassin d'Evian. *C.R. Acad. Sc., Paris*, t.259, 4323-4326.
- 683 Brown, R.M. 1970. Distribution of hydrogen isotopes in Canadian waters. *Isotope Hydrology*,
684 *Proceed. Symp. IAEA*, 3-21, Vienna 1970

- 685 Buric, A., Gault, J., Bertoye, F. 2011. Payment for environmental services: first global
686 inventory of schemes provisioning water for cities. FAO, Natural Resources Management and
687 Environment Department, Land and Water Division. FAO Report, 165 p.
- 688 Caballero, Y., Jomelli, V., Chevallier, P., Ribstein, P. 2002. Hydrological characteristics of
689 slope deposits in high tropical mountains (Cordillera Real, Bolivia), *Catena*, 47, 101-116.
- 690 Clow, D.W., Schrott, L., Webb, R., Campbell, D.H., Torizzo, A., Dornblase, M. 2003.
691 Groundwater occurrence and contributions to streamflow in an alpine catchment, Colorado
692 Front Range, *Groundwater*, Vol. 41, 937-950
- 693 Dévier M. H., Le Menach K., Viglino L., Di Gioia L., Lachassagne P., Budzinski H. 2013.
694 Ultra-trace analysis of hormones, pharmaceutical substances, alkylphenols and phthalates in
695 two French natural mineral waters. *Science of the Total Environment*, 443 (2013) 621-632
- 696 Dörfliger, N., Fleury, P., Ladouche, B. 2008. Inverse modeling approach to allogenic karst
697 system characterization, *Ground Water*, doi: 10.1111/j.1745-6584.2008.00517.x
- 698 Dray, M. 1993. Les terrasses de Thonon : aspects géologiques de la déglaciation würmienne
699 et intérêt hydrogéologique, *Quaternaire* 4, (2-3), 1993, 77-82.
- 700 Eriksson, E. 1958. The possible use of tritium for estimating groundwater storage, *Tellus*,
701 X(4), 472-478.
- 702 Etcheverry, D., Perrochet, P. 2000. Direct simulation of groundwater transit-time distributions
703 using the reservoir theory, *Hydrogeology Journal*, 8, 200-208.
- 704 Fine, R.A., Ostlund, H.G. 1977. Source function for tritium transport models in the Pacific,
705 *Geophysical Research Letters*, vol. 4, NO. 10, 461-464.
- 706 Fine, R.A., Peterson, W.H., Ostlund, H.G. 1987. The penetration of tritium into the tropical
707 Pacific, *Journal of Physical Oceanography*, vol. 4, May 1987.

- 708 Fiore, J., Girardclos, S., Pugin, A., Gorin, G., Wildi, W. 2011. Würmian deglaciation of
709 western Lake Geneva (Switzerland) based on seismic stratigraphy, *Quaternary Science*
710 *Review*, 30 (2011), 377-393.
- 711 Fontes, J-C., Letolle, R., Olive, Ph., Blavoux, B. 1967. Oxygène-18 et tritium dans le bassin
712 d'Evian, "Isotopes in hydrology", International Atomic Energy Agency, Vienna 1967, SM-
713 83/28, 401-415.
- 714 Foster, S. S. D., Smith-Carrington, A, 1980. The interpretation of tritium in the chalk
715 unsaturated zone, *Journal of Hydrology*, 46, 343-364.
- 716 Gagnebin, E. 1933. Les terrains quaternaires des environs de Thonon (Haute-Savoie), *Eclogae*
717 *Geologicae Helveticae*, vol.6, 187-191.
- 718 Hagedorn, B., El-kadi, A.I., Mair, A., Whittier, R.B., Ha, K 2011. Estimating recharge in
719 fractured aquifers of a temperate humid to semiarid volcanic island (Jeju, Korea) from
720 fluctuations, and Cl, CFC-12 and 3H chemistry, *Journal of hydrology*, 409 (2011), 650-662
- 721 Henriot, A., Lachassagne, P. Blavoux, B. Travi, Y. 2013 (to be submitted). Geological
722 structure and hydrogeological functioning of a deeply incised glaciary margin complex
723 (Gavot Plateau, Evian, France) from a pluridisciplinary approach, *Journal of Hydrology*.
- 724 Herrmann, A, Finke, B, Schoëninger, M, Maloszewski, P, Stichler, W. 1990. The
725 environmental tracer approach as a tool for hydrological evaluation and regionalization of
726 catchment systems. In *Regionalization in Hydrology*, Beran MA, Brilly M, Becker A,
727 Bonacci O (eds). IAHS Publication No. 191. IAHS Press: Wallingford; 45–58.
- 728 Holko, L., 1995. Stable environmental isotopes of ^{18}O and ^3H in hydrological research of
729 mountainous catchment, *Journal of hydrology and Hydromechanics*, 43(4-5), 249-274
- 730 Hubert, P., Olive, Ph. 1995. Modélisation par une loi Gamma de la distribution des temps de
731 séjour de l'eau dans des systèmes hydrologiques en régime permanent, *Tracer Technologies*
732 for Hydrological Systems, I.A.H.S. Publ., vol. 229, 211-217.

- 733 IAEA 1996. Residence time distribution software analysis, user's manual. Computer Manual
734 Series n°11, International Atomic Energy Agency, Vienna, Austria, 218 pp..
- 735 Katz, B.G., Böhlke, J.K., Hornsby, H.D. 2001. Timescales for nitrate contamination of spring
736 waters, northern Florida, USA. *Chemical Geology*, 179 (2001) 167 - 186.
- 737 Lachassagne, P., Brault, Y., Béon, O., Dorrioz, M., Le Hec, C. 2011. The 20 years technical
738 and socio-economic Evian experience conciliating groundwater quality preservation,
739 collective responsibility for environment protection and local development, and its
740 transposition to other Danone water resources in the world. Proceedings of the Orléans
741 (France), March 14-16, 2011, AFEID Groundwater Conference.
- 742 Lucas, L.L., Unterweger, M.P. 2000. Comprehensive review and critical evaluation of the
743 half-life of Tritium. *Journal of Research of the National Institute of Standards and*
744 *Technology*, Vol. 105, NO 4, July-August 2000.
- 745 McClymont, A., Roy, J.W., Hayashi, M., Bentley, L.R., Maurer, H., Langston, C. 2011.
746 Investigating groundwater flow paths within proglacial moraine using multiple geophysical
747 methods, *Journal of Hydrology*, 399 (2011) 57-69.
- 748 McGuire, K. J., McDonnell, J. J. 2006. A review and evaluation of catchment transit time
749 modeling, *Journal of hydrology*, 330, 543-563
- 750 Maloszewski, P., Moser, H., Stichler, W., Trimborn, P. 1995. Isotope hydrology investigations
751 in large refuse lysimeters. *Journal of Hydrology*, 167, 149–166.
- 752 Maloszewski, P., Rauert, W., Trimborn, P., Herrmann, A., Rau, R. 1992. Isotope
753 hydrogeological study of mean transit time in alpine basin (Wimbacht, Germany), *Journal of*
754 *Hydrology*, 140, 343-360.
- 755 Maloszewski, P., Rauert, W., Stichler, W., Hermann, A. 1983. Application of flows models in
756 an alpine catchment area using tritium and deuterium data. *Journal of Hydrology*, 66, 319-
757 330.

- 758 Maloszewski, P., Stichler, W., Zuber, A., Rank, D. 2002. Identifying the flow systems in a
759 karstic-fissured-porous aquifer, the Schneealpe, Austria, by modelling of environmental ^{18}O
760 and ^3H isotopes. *Journal of Hydrology* 256, 48–59
- 761 Maloszewski, P., Zuber, A. 1982. Determining the turnover time of groundwater systems with
762 the aid of environmental tracers, I-models and their applicability, *Journal of Hydrology*, 57,
763 (3-4), 207-231.
- 764 Maloszewski, P., Zuber, A. 1994. Lumped parameter models for the interpretation of
765 environmental tracer data, User's guide of Flowpc program, GSF-Inst. Für Hydrol.,
766 Obersschleissheim, D-85764 Germany, 52 p., 25 fig.
- 767 Maloszewski, P., Zuber, A. 1996. Lumped parameter models for the interpretation of
768 environmental tracer data. In: *Manual on Mathematical Models in Isotope Hydrogeology*,
769 IAEA-TECDOC-910, Vienna, Austria, 9-58.
- 770 Michel, R. L. 1992. Residence times in river basins as determined by analysis of long-term
771 tritium records. *Journal of Hydrology*, 130 (1992) 367-378.
- 772 Molicova, H. 1991. Modélisation par une loi gamma de la distribution des temps de séjour de
773 l'eau dans des systèmes hydrologiques en régime permanent. Mémoire de Maîtrise de
774 géologie fondamentale et appliquée, 27 sept. 1991, Université Pierre et Marie Curie, Paris.
- 775 Morgenstern, U., Daughney, C.J. 2012. Groundwater age for identification of baseline
776 groundwater quality and impacts of land-use intensification – The National Groundwater
777 Monitoring Programme of New Zealand. *Journal of Hydrology*, 456-457 (2012) 79-93.
- 778 Nicoud, G., Coddet, E., Blavoux, B., Dray, M. 1993. Les complexes détritiques de marge
779 glaciaire active dans le Bas Chablais (Bassin lémanique, France). Implications
780 hydrogéologiques, *Quaternaire*, 4, (2-3), 1993, 69-76.

- 781 Olive, Ph. 1970. Contribution à l'étude géodynamique du cycle de l'eau dans l'hémisphère
782 nord par la méthode du tritium. Thèse de Doctorat d'Etat es Sciences, Université Pierre et
783 Marie Curie Paris VI.
- 784 Olive, Ph., Hubert, P., Ravailleau, S. 1996. Estimation pratique de l'âge des eaux souterraines
785 en Europe par le tritium. *Revue des Sciences de l'Eau*, 9(4), 1996, 523-533.
- 786 Ozyurt, N.N., Bayari, C.S. 2003. LUMPED: a Visual Basic code of lumped-parameter models
787 for mean residence time analyses of groundwater systems. *Computers & Geosciences* 29
788 (2003), 79-90.
- 789 Pinault, J.L. 2001. Manuel utilisateur de TEMPO : logiciel de traitement et de modélisation
790 des séries temporelles en hydrogéologie et en hydrogéochemie. BRGM report N° RP-55313-
791 FR, 274 p., 253 fig., 2 tabl., 2 ann.
- 792 Rodhe, A., Nyberg, L., Bishop, K. 1996. Transit times for water in a small till catchment from
793 a step shift in the oxygen 18 content of the water input. *Water Resources Research.*, 32, NO.
794 12, PAGES 3497-3511,
- 795 Rodhe, A., Seibert, J. 2011. Groundwater dynamics in a till hillslope: flow directions,
796 gradients and delay, *Hydrological processes*, Vol. 25, 1899-1909
- 797 Roy, J. W., Hayashi, M. 2009. Multiple, distinct groundwater flow system of a single
798 moraine-talus feature in an alpine watershed., *Journal of hydrology*, 373, 139-150
- 799 Stewart, MJ, McDonnell, JJ. 1991. Modeling baseflow soil water residence times from
800 deuterium concentration. *Water Resources Research.* **27**: 2681–2693.
801 doi:10.1029/91WR01569
- 802 Stewart, M.K., Morgenstern, U., McDonnell, J.J. 2010. Truncation of stream residence time:
803 How the use of stable isotopes has skewed our concept of streamwater age and origin,
804 *Hydrological Processes*, 24: 1646-1659.

- 805 Triganon, A., Nicoud, G., Guiter, F., Blavoux, B. 2005. Contrôle de la construction de
806 l'ensemble détritique de la région d'Evian par trois phases glaciaires durant le Würm.
807 *Quaternaire*, 16, (1), 2005, 57-63.
- 808 Turner, JV, Barnes, CJ. 1998. Modeling of isotopes and hydrogeochemical responses in
809 catchment hydrology. In *Isotope Tracers in Catchment Hydrology*. Kendall C, McDonnell JJ
810 (eds). Elsevier: Amsterdam; 723–760.
- 811 Uhlenbrook, S, Frey, M, Leibundgut, C, Maloszewski, P. 2002. Hydrograph separations in a
812 mesoscale mountainous basin at event and seasonal timescales. *Water Resources Research* 38:
813 1096. DOI: 10.1029/2001WR000938.
- 814 Vitvar T, Balderer W. 1997. Estimation of mean water residence times and runoff generation
815 by 18O measurements in a pre-alpine catchment (Rietholzbach, eastern Switzerland). *Applied*
816 *Geochemistry* 12: 787–796.
- 817 Viville, D., Ladouche, B., Bariac, T. 2006. Isotope hydrological study of mean transit time in
818 the granitic Strengbach catchment (Vosges massif, France): application of the FlowPC model
819 with modified input function. *Hydrol. Process.* 20, 1737–1751. DOI: 10.1002/hyp.5950
- 820 Yurtsever, Y. 1995. An overview of conceptual model formulations for evaluation of isotope
821 data in hydrological systems. *Tracer Technologies for Hydrological Systems*, I.A.H.S. Publ.,
822 vol. 229, 3-12.
- 823 Zuber, A. 1986(a). Mathematical models for the interpretation of environmental radioisotopes
824 in groundwater systems. In Fritz P. and Fontes J.Ch.(Eds), *Handbook of Environmental*
825 *Isotope Geochemistry*, Elsevier, Amsterdam, vol. 2, .1-59.
- 826 Zuber, A. 1986(b). On the interpretation of tracer data in variable flow systems. *Journal of*
827 *Hydrology*, 86 (1-2), 45-57.
- 828

829 **Figure captions**

830 Figure 1 – Location and schematic geological map of the Evian-Thonon area. Location of
831 springs and boreholes. Note the location of the rain gauge used since June 1963).

832

833 Figure 2 - Schematic geological cross-sections of the Evian (2a - top) and Thonon (2b -
834 bottom) areas (see the location of the cross-sections on Fig. 1).

835

836 Figure 3 - CRG Thonon tritium monthly rainfall time series (since June 1963; previous annual
837 data reconstructed from the Ottawa time series, see details in the text). Note the logarithmic
838 scale of the Y axis and the 1960s very high peak.

839

840 Figure 4 – Rainfall and springs tritium mean annual content at the Thonon CRG rain gauge
841 and at the Evian-Thonon area springs (*top: logarithmic scale; bottom: arithmetic scale*)

842

843 Figure 5 – Evian-Cachat spring tritium chronicle (note the increase in measurement precision
844 with time; arrows indicate values below the detection limit (circle))

845

846 Figure 6 - Evian-Thonon area rainfall and effective rainfall tritium mean annual content.

847

848 Figure 7 – Modelling the Versoie spring tritium time series (using LUMPED, Ozyurt and
849 Bayari, 2003)

850

851 Figure 8 – Modelling the Maxima spring tritium time series (using LUMPED Ozyurt and
852 Bayari, 2003)

853

854 Figure 9 – Modelling the Larringes-Pugny well tritium time series (using LUMPED, Ozyurt
855 and Bayari, 2003)

856

857 *Figure 10 - Conceptual model of the Evian-Cachat spring (in a series dispersive and piston*
858 *flow model). “q” is the mean annual recharge and discharge of the spring*

859

860 Figure 11 – Modelling (TEMPO) of the Evian-Cachat spring. Fig. 11A: Sensitivity analysis of
861 the PFM to the T. Fig. 11B: Sensitivity analysis of the PFM to the % of the “less slow flow
862 component”.

863

864 Figure 12 - Modelling (TEMPO) and sensitivity analysis of the slow flow component of the
865 Evian-Cachat spring. *Fig. 12A: Sensitivity analysis of the DM to the T. Fig. 12B: Sensitivity*
866 *analysis of the DM to DP*

867

868 Fig. 13 - Conceptual model of the Evian-Cachat spring (in a series exponential, dispersive and
869 piston flow model). “q” is the mean annual recharge and discharge of the spring

870

871 Figure 14 – Modelling (Tempo) of the Evian-Cachat spring for various mean transit time (T)
872 within the superficial aquifer (EM). Fig. 14A: Sensitivity analysis of the EM to the T. Fig.
873 14B: Sensitivity analysis of the DM to the T. Fig 15C: Sensitivity analysis of the DM to DP

874

875 Figure 15 – Modelling of a perfect tracer Dirac (100%, arbitrary unit; year 0) input for the
876 Fig. 10 D- (T 68 y, DP = 0.5) + PF- (2.5 y) model (M1), and the Fig. 13 E- (T 8 y) + D- (T 60
877 y, DP = 0.75) + PF- (2.5 y) model (M1). The figure also provides the difference between the
878 two outputs (M1 - M2)

879

880 **Table captions**

881

882 Table 1 – (i) Rainfall tritium mean annual content at the Thonon CRG rain gauge, (ii)
883 computed tritium efficient rainfall signal, and (iii) mean annual tritium content at the Evian-
884 Thonon area springs

885

886 Table 2 – Summary of the parameters used to fit the Evian-Thonon area springs. Note that for
887 the exponential-piston flow model, the two models are placed in parallel