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The transient distributions of nuclear weapon-generated tritium and its decay product ^{3}He in the Mediterranean Sea, 1952–2011, and their oceanographic potential

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Abstract. We present a comprehensive account of tritium and ^{3}He in the Mediterranean Sea since the appearance of the tritium generated by the atmospheric nuclear-weapon testing in the 1950s and early 1960s, based on essentially all available observations. Tritium in surface waters rose to 20–30 TU in 1964 (TU $= 10^{18} \times [^3\mathrm{H}]/[\mathrm{H}]$), a factor of about 100 above the natural level, and thereafter declined 30-fold up to 2011. The decline was largely due to radioactive tritium decay, which produced significant amounts of its stable daughter ^{3}He. We present the scheme by which we separate the tritiugenic part of ^{3}He and the part due to release from the sea floor (terrigenic part). We show that the tritiugenic component can be quantified throughout the Mediterranean waters, typically to a ± 0.15 TU equivalent, mostly because the terrigenic part is low in ^{3}He. This fact makes the Mediterranean unique in offering a potential for the use of tritiugenic ^{3}He as a tracer. The transient distributions of the two tracers are illustrated by a number of sections spanning the entire sea and relevant features of their distributions are noted. By 2011, the ^{3}He concentrations in the top few hundred metres had become low, in response to the decreasing tritium concentrations combined with a flushing out by the general westward drift of these waters. Tritium-^{3}He ages in Levantine Intermediate Water (LIW) were obtained repeated in time at different locations, defining transit times from the LIW source region east of Rhodes. The ages show an upward trend with the time elapsed since the surface-water tritium maximum, which arises because the repeated observations represent increasingly slower moving parts of the full transit time spectrum of LIW. The transit time dispersion revealed by this new application of tritium-^{3}He dating is considerable. We find mean transit times of 12 ± 2 yr up to the Strait of Sicily, 18 ± 3 yr up to the Tyrrhenian Sea, and 22 ± 4 yr up into the Western Mediterranean. Furthermore, we present full Eastern Mediterranean sections of terrigenic ^{3}He and tritium-^{3}He age in 1987, the latter one similarly showing an effect of the transit time dispersion. We conclude that the available tritium and ^{3}He data, particularly if combined with other tracer data, are useful for constraining the subsurface circulation and mixing of the Mediterranean Sea.

1 Introduction

^{3}He, the rare isotope of helium (He; atmospheric ratio $[^3\mathrm{He}]/[^4\mathrm{He}]_{\mathrm{atm}} = R_{\mathrm{a}} = 1.384 \times 10^{-6}$; Clarke et al., 1976), is, at the ocean surface, essentially in solubility equilibrium with its atmospheric concentration. In the ocean interior, however, concentrations are generally higher, one cause being ^{3}He addition by decay of radioactive tritium (tritiugenic ^{3}He), the other, release from the sea floor (terrigenic ^{3}He). The tritiugenic ^{3}He became prominent in the 1960s, when the atmospheric nuclear-weapon testing released huge amounts of tritium. Most of that tritium ended up in the ocean. The predominant transfer mechanism is exchange of tritiated water between the lower troposphere and the ocean surface ("vapour exchange", rate roughly three times the evaporation rate), and because this mechanism is virtually absent over land masses, continental tritium concentrations are distinctly higher in comparison (Weiss and Roether, 1980). Due

to the increasing continental influence, therefore, the tritium concentrations in the Mediterranean (Med) surface waters rise eastward. By now, most of the nuclear-weapon tritium has decayed ($T_{1/2} = 12.32$ yr; Lucas and Unterweger, 2000) while the resulting ^{3}He, being a stable nuclide, remained. At the same time, the competing terrigenic ^{3}He is small because the terrigenic He has a ^{3}He/^{4}He ratio that is one order of magnitude lower than in most other ocean regions (Roether et al., 1998a). The explanation is that the Med's sub-floor lithosphere is characterised by high sediment load above crust that is largely of continental type (Morelli, 1985); in both these compartments, α-decay of the natural decay series is a source of pure ^{4}He. Using the isotopic ratio of terrigenic He, measured He isotope and neon (Ne) concentrations allow one to correct for the terrigenic ^{3}He contribution (Roether et al., 1998a, 2001). The potential of using tritium and ^{3}He data jointly is based on the fact that these two tracers form a radioactive mother-daughter pair, which allows one to deduce ages, providing constraints on subsurface water transport and mixing. This methodology was pioneered by W. Jenkins (e.g., Jenkins, 1980; 1987). He dealt primarily with the North Atlantic subtropical gyre waters, which are replenished by surface water within at most a few decades, so that terrigenic ^{3}He hardly interferes.

The most prominent water mass in the Med is the Levantine Intermediate Water (LIW) formed in the northwestern Levantine Sea east of the island of Rhodes. This water mass expands westward at a few hundred metres in depth, overflows the Sicily Passage sills and eventually leaves the Med through the Strait of Gibraltar (Wüst, 1961). The loss is compensated by the inflow of Atlantic near-surface water of lower salinity. Superimposed are deep convective systems, both in the WMed and the EMed, with LIW acting as a preconditioning. Recently, however, these systems have been disturbed. In the EMed, deep water formation in the 1990s temporarily moved from the Adriatic to the Aegean Sea (Roether et al., 2007), and in the WMed, the salinity and temperature below about 1500 m were markedly raised (Schroeder et al., 2010). The deep convective systems are closed by upwelling and thus take part in the overflow of the Sicily and Gibraltar Straits. It follows that LIW and all deeper waters are subject to a general drift westward.

Tritiugenic ^{3}He appears suited to study that drift. The LIW represents the principal entrance pathway of tritium into the subsurface waters. Transfer from the LIW formation area up to Gibraltar exceeds 20 yr (Gačić et al., 2013), long enough to allow the majority of the tritium to decay into ^{3}He. Repeated tracer surveys since 1987 have documented the more recent evolution of tritium and ^{3}He rather well, especially in the EMed, while data prior to 1987 are more limited. The data of the 1987 EMed survey have been repeatedly evaluated, partly in combination with other tracers (Roether and Schlitzer, 1991; Roether and Well, 2001; Roether et al., 1994, 1998a, b, 1999). The subject of the present work is to present tritium and helium isotope data from the 2011 *Meteor* 84/3 cruise and to reconstruct the temporal evolution of the subsurface distributions of tritium and tritiugenic ^{3}He in the Med at large over the entire period since nuclear weapon-produced tritium entered the environment.

2 Turnover of Mediterranean waters

The Med circulation is driven by net evaporation, which induces salinity enhancement eastward, leading eventually to convection by way of the related density increase. The main product is the LIW (formation rate $\sim 10^6\,\mathrm{m^3\,s^{-1}}$). Deep-water source areas are for the EMed, classically, the Adriatic Sea and a region south of France for the WMed (Millot and Taupier-Letage, 2005). Newly formed Western Mediterranean Deep Water (WMDW) spreads through the sea meeting little obstruction due to the quite uniform bathymetry that extends east and south of the Baleares Islands. The classical Eastern Mediterranean Deep Water (EMDW) can similarly expand through the Ionian Basin, but toward the Levantine, the Cretan Passage acts as a topographic barrier, and the East Mediterranean Ridge (EMR) forms a similar barrier between the southern Levantine and the Hellenic Trench that adjoins the Cretan Island Arc. From a study of the chlorofluorocarbon-12 and tritium distributions in 1987, Roether and Schlitzer (1991) deduced an EMDW formation rate of about $3 \times 10^5\,\mathrm{m^3\,s^{-1}}$, equivalent to a renewal period of about 150 yr. Further analysis found that newly formed EMDW expands as near-bottom water into the Levantine Sea, where it rises up to a level of about 600 m and returns westward (Roether et al., 1994). One should realise that all these flows are subject to dispersion, mostly of large scale, i.e., in the form of recirculations and split pathways. We show below that the dispersion induces a drift in tritium-^{3}He ages as a function of time since the period of the tritium input maximum.

While for a long time the system of shallow and deep convections seemed rather stable, in the mid-1990s there was a massive outflow of unusually dense Aegean Sea waters, which were preferentially added below ~ 1500 m, lifting the residing waters upward and leading to a general salinity increase of the subsurface waters. Although the deep-water formation went back to the Adriatic in about 2000 (Rubino and Hainbucher, 2007), the effecs of the event, the so-called Eastern Mediterranean Transient (EMT; Roether et al., 2007), persist to date. The properties of the Western Mediterranean Deep Water (WMDW) have also changed distinctly since 2005 (denoted the Western Mediterranean Transition, WMT), presumably under EMT influence (Schroeder et al., 2010). The newly added deep water raised the temperature and salinity of the WMDW below about 1500 m depth.

The overflow of the Sicily Channel consisting of LIW and waters below it (Cretan Intermediate Water (CIW; Schlitzer et al., 1991) formed in the southern Aegean Sea and upper EMDW (transitional EMDW, or tEMDW)) enters the

Tyrrhenian Sea, where it mixes with resident waters. Part of the LIW component flows northward toward the Ligurian Sea, and the remainder leaves southward through the Sardinian Channel and continues adjoining the Sardinian slope. The denser part of the overflow cascades downward at the northern slope of Sicily (Sparnocchia et al., 1999), while WMDW, intruding into the Tyrrhenian across the sill of the Sardinian Channel ($\sim$1900 m sill depth), forms the near-bottom waters. The two components mix to form the Tyrrhenian Deep Water (TDW), which leaves the sea through the Sardinian Channel at depths between the components. This mechanism in effect lifts the intruding WMDW, enabling it to become involved in the outflow through the Gibraltar Strait (Millot, 1999). The mixing became reinforced by the EMT (Gasparini et al., 2005), in consequence of the enhanced density of the Sicily overflow waters. The EMT influence was also evident in a strong rise of tritiugenic ^{3}He in the Tyrrhenian Sea deep waters during 1987–2007 (Roether and Lupton, 2011).

3 Data and measurement

The cruises that contribute tracer data are listed in Table 1. Mediterranean observations of tritium began in 1965, while those of ^{3}He were delayed up to the mid 1970s. Major transient-tracer surveys in the EMed were carried out by the F.S. *Meteor* (cruises M5/6, 1987; M31/1, 1995; M44/4, 1999; M51/2, 2001; and M84/3, 2011, for which tritium/helium data are reported here). In the WMed there was a tritium survey in 1981, and surveys of both tracers in 1995 and 2011. Below we will mostly address subsets of the available data that are deemed adequate to characterise the tracer distributions and their relevant features. The full datasets are, however, available for future work.

Helium and Ne concentrations are reported in cc(STP)/kg and ^{3}He as $\delta^3\mathrm{He} = (^3\mathrm{He}/^4\mathrm{He})/R_\mathrm{a} - 1$ (R_a = atmospheric $^3He/^4He$ ratio). Concentrations are determined using highly specialised noble-gas mass spectrometers with about $\pm$ 0.3 % precision. The air-water δ^3He solubility equilibrium value is $\delta^3\mathrm{He}_0 = -$ 1.65 %, varying by $\pm$ 0.1 % over the range of Med's temperatures (Benson and Krause, 1980). Tritium concentrations are reported in tritium units (TU, 1 TU means $[^3\mathrm{H}]/[\mathrm{H}] = 10^{-18}$). Up into the 1980s, tritium measurement used low-level gas counting following isotopic enrichment, with precisions of typically 5 % or $\pm$ 0.08 TU, whichever is greater (Weiss et al., 1976). Later on, tritium was determined by measuring the ^{3}He grown in from tritium decay (Clarke et al., 1976; Jean-Baptiste et al., 1992; Sültenfuß et al., 2009), which gives precisions better than $\pm$ 3 % or $\pm$ 0.02 TU, whichever is greater. In dealing with tritiugenic ^{3}He it is advantageous to convert its concentrations into TU, on the basis that 1 TU of decayed tritium raises the ^{3}He concentration by 4.85 % (Roether et al., 1998a; varying by $\pm$ 0.05 % over the Med's ranges of temperature and salinity) relative to the ^{3}He solubility equilibrium value.

4 Separation of tritiugenic ^{3}He and tritium-^{3}He dating

To isolate the tritiugenic portion of ^{3}He, we employ the two-step procedure of Roether et al. (1998a, 2001), which was then already applied to the data of the 1987 *Meteor* cruise. Besides δ^3He data, the procedure uses concurrent values of He and Ne concentrations. Firstly, Ne, which has no sources in the ocean interior, regularly shows an excess over the ocean-atmosphere solubility equilibrium values by a few percent (Well and Roether, 2003), which we write as $\mathrm{Ne} = \mathrm{Ne}_0\ (1 + a_\mathrm{Ne})$, where Ne is the measured value and subscript 0 here and in the following denotes the solubility equilibrium value. The excess a_Ne is due to forcing at the ocean surface, which generates a similar excess also for He, i.e., $a_\mathrm{He} \approx a_\mathrm{Ne}$. But He is subject to the further effect of He released from the ocean floor (terrigenic He), so that $\mathrm{He} = \mathrm{He}_0\ (1 + a_\mathrm{He} + t_\mathrm{He})$. We re-formulate Eq. (3) of Roether et al. (1998a, 2001) to give the terrigenic He, expressed as a percentage of the solubility equilibrium value He_0, as

$$t_\mathrm{He} = \left(\frac{He}{He_0} - \frac{Ne}{Ne_0}\right) \times 100 + offset \quad (\%) \qquad (1)$$

The offset accounts for systematic errors arising from the solubility functions of He and Ne, from the He and Ne measurement calibration, and from inherent differences between a_He and a_Ne. Except for cases of pronounced upwelling, terrigenic He can be assumed to vanish in the mixed layer. We therefore analysed the mixed-layer values (depth < 20 m; more than 100 data points, some outliers excluded; solubilities of Weiss (1971)) of the *Meteor* cruises 1987–2001 and of *Poseidon* 234 (Table 1, all measured at Bremen) using (1) with $t_\mathrm{He} = 0$. The total range among the average offsets obtained for the five cruises individually was only 0.15 %, which indicates a high consistency of the offset as such and also of the He and Ne measurements. There was no positive indication of upwelling effects, nor evidence of a temperature dependence of the offset, as the average for the winter cruise M31/1 absolutely fitted in with those of the other cruises. Averaged over the five cruises, the offset was –0.8 % and the standard error of individual t_He values $\pm$ 0.4 %. Note that the offset has a different value when solubility functions other than those of Weiss (1971) are used. In the following we use an offset of -0.8 ± 0.1 % and $\pm$ 0.4 % uncertainty for individual t_He values.

For ^{3}He, secondly, an offset relative to He corresponding to that in Eq. (1) can be ignored, but one now faces two interior ocean sources, i.e., of terrigenic and of tritiugenic ^{3}He ($t_{3\mathrm{He}}$, r), so that $^3\mathrm{He} = {}^3\mathrm{He}_0\ (1 + t_{3\mathrm{He}} + r)$. The terrigenic ^{3}He is the product of the terrigenic He and its isotopic ratio R_t. The tritiugenic ^{3}He, also expressed as a percentage of

Table 1. Cruises contributing tritium and He isotope data for the present study.

Cruise or Project	Dates	Area	Reference
Exped. Odysseus 65[a]	Aug + Oct 1965	WMed, Tyrrhenian, Aegean	Östlund (1969)
Origny 1971 + 1972[b]	Jul 1971/Jul 1972	WMed	unpubl. data
Meteor 33[c]	Feb. 1974	WMed	Roether et al. (1992)
Maria Paolina G.[b]	Feb–Mar 1974	EMed	Cortecci et al. (1979)
Chain 121[c]	May 1975	WMed	unpubl. Data
Knorr 54/5[d]	Apr 1976	WMed, 0° W	Roether et al. (1992)
Bohra-2[e]	Mar–April 1977	WMed, 42° N, 4° 45′ E	Roether and Weiss (1980)
Meteor 50/3[d]	Nov–Dec 1978	WMed, EMed	Roether et al. (1992)
Phycemed 1981[c]	Apr 1981	WMed	Andrié and Merlivat (1988)
Phycemed 1983[g]	Oct 1983	WMed	unpubl. data
Meteor 5/6	Aug–Sep 1987	(WMed), EMed	Roether et al. (2007)
Meteor 31/1	Jan–Feb 1995	EMed	”
Poseidon 234	Oct–Nov 1997	WMed, Tyrrhenian.	Rhein et al. (1999)
Meteor 44/4	Apr–May 1999	EMed	Roether et al. (2007)
Meteor 51/2	Oct–Nov 2001	EMed	”
Meteor 84/3	Apr 2011	WMed, EMed	this work

[a] 4 stations, near-surface tritium only.
[b] 2 stations.
[c] Tritium only.
[d] Few stations few ^{3}He data.
[e] Repeated tritium, few ^{3}He data.
[f] Tritium only.
[g] ^{3}He only.

$^3He_0 = (1 + \delta^3\mathrm{He}_0)\ R_\mathrm{a}\ He_0$, becomes

$$r = \frac{He}{He_0} \times \frac{\delta^3\mathrm{He} - \delta^3\mathrm{He}_0}{\left(1 + \frac{\delta^3\mathrm{He}_0}{100}\right)} + \left(1 - \frac{R_\mathrm{t}}{R_\mathrm{a}}\right) \times t_\mathrm{He} \quad (\%) \qquad (2a)$$

where $\delta^3\mathrm{He}_0 = -(1.65 \pm 0.1)\,\%$ and R_t/R_a = isotopic ratio of terrigenic He relative to the atmospheric ratio. For the EMed the isotopic ratio is 0.42 ± 0.1 (Roether et al., 1998a), values in the Med elsewhere are addressed below (Sect. 7.2).

Using (1), Eq. (2a) converts into

$$r = \frac{He}{He_0} \times \frac{\delta^3\mathrm{He} - \delta^3\mathrm{He}_0}{\left(1 + \frac{\delta^3\mathrm{He}_0}{100}\right)} + \left(1 - \frac{R_\mathrm{t}}{R_\mathrm{a}}\right) \times \left[\left(\frac{He}{He_0} - \frac{Ne}{Ne_0}\right) \times 100 - 0.8\right] \quad (\%) \qquad (2b)$$

The tritiugenic ^{3}He thus depends on observed values of δ^3He, He and Ne concentrations, and on temperature and salinity to obtain the solubility equilibrium values. Dividing r by 4.85 ± 0.05 %/TU one obtains the tritiugenic ^{3}He ($^3\mathrm{He}_\mathrm{tri}$) in TU. The negative sign of $\delta^3\mathrm{He}_0$ and the low value of R_t/R_a raise r relative to δ^3He. A shift of about 1.7 % arises from $\delta^3\mathrm{He}_0$, and, in the LIW layer ($t_\mathrm{He} \sim 3\,\%$) for example, the t_He term adds 1.3 %, so that one has $r - \delta^3\mathrm{He} \approx 3\,\%$, which corresponds to about 0.6 TU of tritiugenic ^{3}He.

The value from Eq. (2b) together with the concurrent tritium concentration gives the tritium-^{3}He age as

$$\tau = t_{1/e} \times \ln\left(1 + \frac{^3He_{tri}}{tritium}\right) = t_{1/e} \times \ln\left(1 + \frac{r}{4.85 \times tritium}\right) \quad \text{(years)} \qquad (3)$$

where $t_{1/e}$ = radioactive mean life of tritium (17.8 yr), and both tritium and the tritiugenic ^{3}He are in TU. To show that the tracer measurement errors generate only rather moderate age uncertainties, consider a typical value pair of 3 TU for tritiugenic ^{3}He and 2 TU for tritium (see below), for which (3) gives an age of about 16 yr. The expected uncertainty of r, combining those of δ^3He, R_t/R_a, He/He_0 minus Ne/Ne_0, and the standard error for individual t_He values is about $\pm 0.6\,\%$ or 0.15 TU absolute, or 5 % relative to 3 TU, and the uncertainty of tritium is $\pm 3\,\%$. The uncertainty of the ratio becomes about $\pm 6\,\%$, for which Eq. (3) gives an age uncertainty of about 5 %, or less than 1 yr. For tritium concentrations below about 0.5 TU, however, the relative uncertainty of tritium, and hence also the age uncertainty, will be larger.

Because in the mixed layer, one has $\delta^3\mathrm{He} = \delta^3\mathrm{He}_0$ and $t_\mathrm{He} = 0$ (in the absence of strong upwelling), it follows from Eq. (2) that the upper boundary condition for tritium-^{3}He dating in the interior is $r = 0$ for $t = 0$. It is useful to compare stable tritium (the sum of tritium and tritiugenic ^{3}He) between the interior location and the formation region at the deduced time of subduction (Fig. 1). The two values must agree in the absence of mixing, so that any difference in the

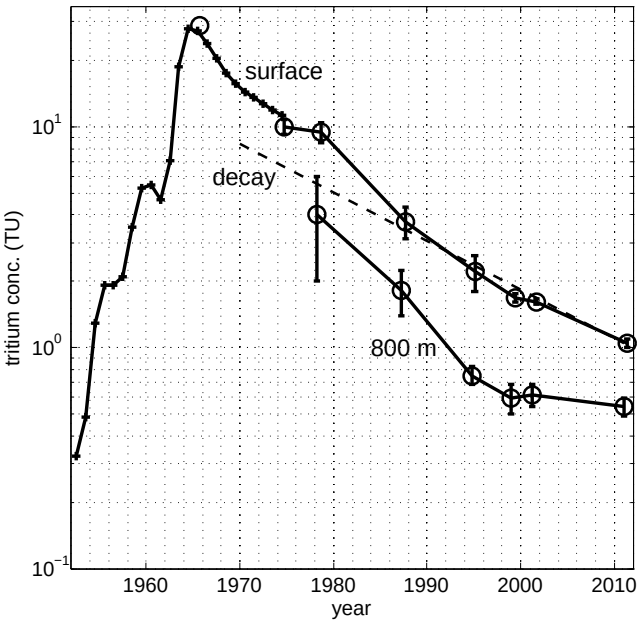

Fig. 1. Tritium concentrations (TU) in the Mediterranean south of Crete vs. time, 1952–2011, at the surface and at 800 m depth (see text). Year marks are 1st January. Typically averages of 3 stations are shown (numerical values for surface water in Appendix A). The error bars represent one standard deviation of the apparent scatter between individual values, plus interpolation and estimated measurement errors. For the part up to 1974 the uncertainty should not exceed 20 %, while that of the pre-nuclear value of 1952 is probably somewhat larger. For reference, tritium decay is shown by the dashed line. The mean concentration during 1952 to 2011 was about 6.7 TU, about 20 times the natural one.

stable tritium values reflects mixing effects or escape of ^{3}He into the atmosphere at the air-water boundary. Other consequences of mixing will be that (a) the age will be biased towards that of the components of the highest tritium and ^{3}He concentrations, and that (b) mixing with waters from the pre-nuclear period that contain tritiugenic ^{3}He while being old enough to be free of tritium will enhance the ages, as discussed next.

As shown in the following section, the pre-nuclear (prior to 1952), i.e., natural surface-water tritium concentration is about 0.3 TU. Upon sinking below contact with the atmosphere, its decay gradually accumulates ^{3}He. Eventually, after long subsurface travel, a maximum of 0.3 TU equivalent, or $r_{\mathrm{nat}} = 1.5\,\%$ ($= 0.3\,\mathrm{TU} \times 4.85\,\%/\mathrm{TU}$) can be reached. Close to the sinking region the effect remains small, and the water may leave the system before the tritium conversion is complete. Furthermore, the generated ^{3}He suffers a loss whenever contact with the atmosphere is resumed, such as in deep-water formation. Since our evaluation below accounts for the tritium input function beginning in 1952, only the pre-1952 part of r_{nat} is a concern, which adds the period between 1952 and sampling for leaving the system. We conclude that, by the combined effects mentioned, the natural tritiugenic ^{3}He becomes sufficiently small to be ignored.

5 Assessing the evolution of nuclear weapon-generated tritium

The mixed layer concentrations of tritium are determined by the interplay of tritium entering from the atmosphere and tritium loss into the ocean interior. The resulting concentrations must therefore be obtained using observations. The temporal evolution in the Eastern Mediterranean, 1952 to 2011, is shown in Fig. 1 (for the numerical values see Appendix A). For the period prior to the mid-1970s, we use values derived for the North Atlantic (Dreisigacker and Roether, 1978), recalibrated to the Med using the observations of 1965 (tentatively interpolated between the Tyrrhenian and the Aegean Seas) and 1974 (Fig. 1). Thereafter, actual observations are shown. The curves represent the situation south of Crete, i.e., near to the LIW formation region. The concurrent tritium concentrations in newly formed LIW are virtually identical to those at the surface (not shown). At 800 m depth, concentrations are a factor of 3 to 4 smaller; that curve is to represent the tEMDW that contributes, as mentioned above, to the westward outflow in the Sicily Channel. The EMT enhanced the exchange with deeper waters of lower tritium content, inducing dips in the tritium concentration in the 1990s, primarily in the 800 m curve.

The 1952 surface-water value in Fig. 1 (0.3 TU) represents the natural tritium background (Dreisigacker and Roether, 1978). In that year, an impressive, $\sim$ 100-fold rise started culminating in the mid-sixties, followed by a 30-fold decline up to the year 2011. As mentioned, the elevated concentrations are overwhelmingly due to the atmospheric nuclear-weapon testing, and the decline was governed by transfer into the interior waters early on, but later predominantly by radioactive decay. By 2011 the anthropogenic tritium in the mixed layer was reduced to as little as about twice the natural component. Figure 1 demonstrates that, by now, generation of tritiugenic ^{3}He has become small relative to the situation in the previous decades. The decline will presumably not quite reach the natural level, because smaller tritium sources, such as nuclear-fuel processing and medical or technical uses of tritium, continue to be operative.

Table 2 gives an overview of the temporal evolution of tritium concentrations elsewhere in the Med in the form of concentration ratios. For the EMed, the table presents ratios of the tritium concentrations near to the Entrance into Sicily Strait (ESS in the table) in the LIW and at 800 m depth to the corresponding values south of Crete (columns 2–3). Furthermore, ratios are shown between the WMed and EMed surface waters (column 4). For the WMed, columns 5–6 list ratios of tritium concentrations in LIW and at 800 m to surface water values. One notes clear upward trends with time in the LIW ratios between Sicily Strait and south of Crete

Table 2. Ratios of tritium concentrations between various water masses. Data sources see Table 1, EMed surface water values see Fig. 1. Free space if no available data. The LIW at the entrance into Sicily Strait (ESS) is represented by data near to 250 m and in the WMed in 450–500 m. The WMed/EMed surface water ratios for 1971–1972, 1981, and 1997 use EMed values of Fig. 1 interpolated in time between observations.

Year	LIW ESS to source region[a]	800 m ESS to 800 m Fig. 1	Surface WMed/EMed	WMed LIW/surface	WMed 800 m/surface
1965			0.62		
1971–1972			0.62	0.27	0.14
1974			0.65	0.30	0.15
1975				0.36	0.20
1978			0.68	0.43	0.20
1981			0.70	0.39	
1987	0.29	1.40			
1995	0.66	1.20			
1997			0.84	0.65	0.40
1999	0.83	1.38			
2001	0.97	1.33			
2011	1	1.23	0.75	0.79	0.65

[a] Tritium concentrations in the source region are identical to surface values in Fig. 1, see text.

(approaching unity in 2011; column 2 of Table 2) and in the LIW and the 800 m to surface ratios in the WMed (by factors of about 2 (column 5) and 3 (column 6) between 1975 and 2011). These trends reflect the fact that the subsurface tritium concentrations are subject to a time lag enforced by the subsurface advection from their respective formation regions. Consequently, the subsurface tritium concentrations increase, while the surface values decrease (Fig. 1). For the WMed to EMed surface water ratios the increase is more subtle; after 1965 the ratios average 0.74 ± 0.06. The EMed 800 m ESS/Fig. 1 ratios (column 3) exceed unity (average ratio 1.3 ± 0.1) because the ESS waters near to this depth receive waters from the Adriatic. Such water largely proceeds toward the Levantine Sea, making the ESS region upstream of that south of Crete. Both these average ratios have apparent uncertainties of about 10 %, which should also apply to the column 1 values, while the errors for LIW and 800 m in the WMed are possibly somewhat larger. Figure 1 and Table 2 provide a basis for estimating tritium concentrations in the Med's top kilometre with a useful precision. One should note that not only the observations on which the ratios are based contribute to the uncertainty, but partly also required interpolation in depth between available values.

Further source regions of subsurface EMed waters (EMDW, CIW, EMT-formed waters) are the southern parts of the Adriatic and Aegean Seas. The few tritium data available for these regions yield scattering ratios, presumable because the regions are rather small, water mass mixing and convection vary with season, and the mixing recipes were affected by the EMT. However, we find little evidence for significantly enhanced tritium concentrations relative to the EMed at large. While enhancement might arise from a comparably stronger effect of the land masses around these seas, it appears that their strong exchange with the EMed at large prevents this. In summary, the tritium concentrations for these source regions should agree with those of Fig. 1 within a factor of 1 ± 0.15 on average.

6 Tracer distributions

To illustrate the temporal evolution of tritium in the EMed, Figs. 2 and 3 show the distributions of tritium for the *Meteor* cruises of 1987–2001 (Table 1) in the form of along-basin (quasi-zonal) sections. The Fig. 2 values are decay-corrected to the period of the first survey in September 1987. The 1987 distribution is characterised by fairly high concentrations (>3 TU) down to several 100 m depth, reaching somewhat less deep in the Levantine and the deepest in mid-section near to Crete. At greater depths one finds a strong eastward decrease from moderately high values toward the Malta Escarpment, associated with the descending branch of the thermohaline circulation, to quite low ones in the east, with minimum values < 0.2 TU in the western Levantine. The 1995 section reflects the downward transport of near-surface waters and the upwelling of deep waters (Klein et al., 1999) imposed by the EMT. A reduction of tritium in, and a thinning of, the top layer is manifest, accompanied by a distinct tritium rise further down. One notes enhanced tritium values below about 1500 m in mid-section and the deep minimum of 1987 in the east being largely filled in. By 1999, the mid-section enhancement has vanished, giving way to a mid-depth minimum reaching all along the section. The surface layer has shrunk in depth somewhat more, with tritium concentrations being reduced relative to the 1995 survey. The 2001 section is rather similar, except for a somewhat deeper-reaching surface layer and the mid-depth minimum being

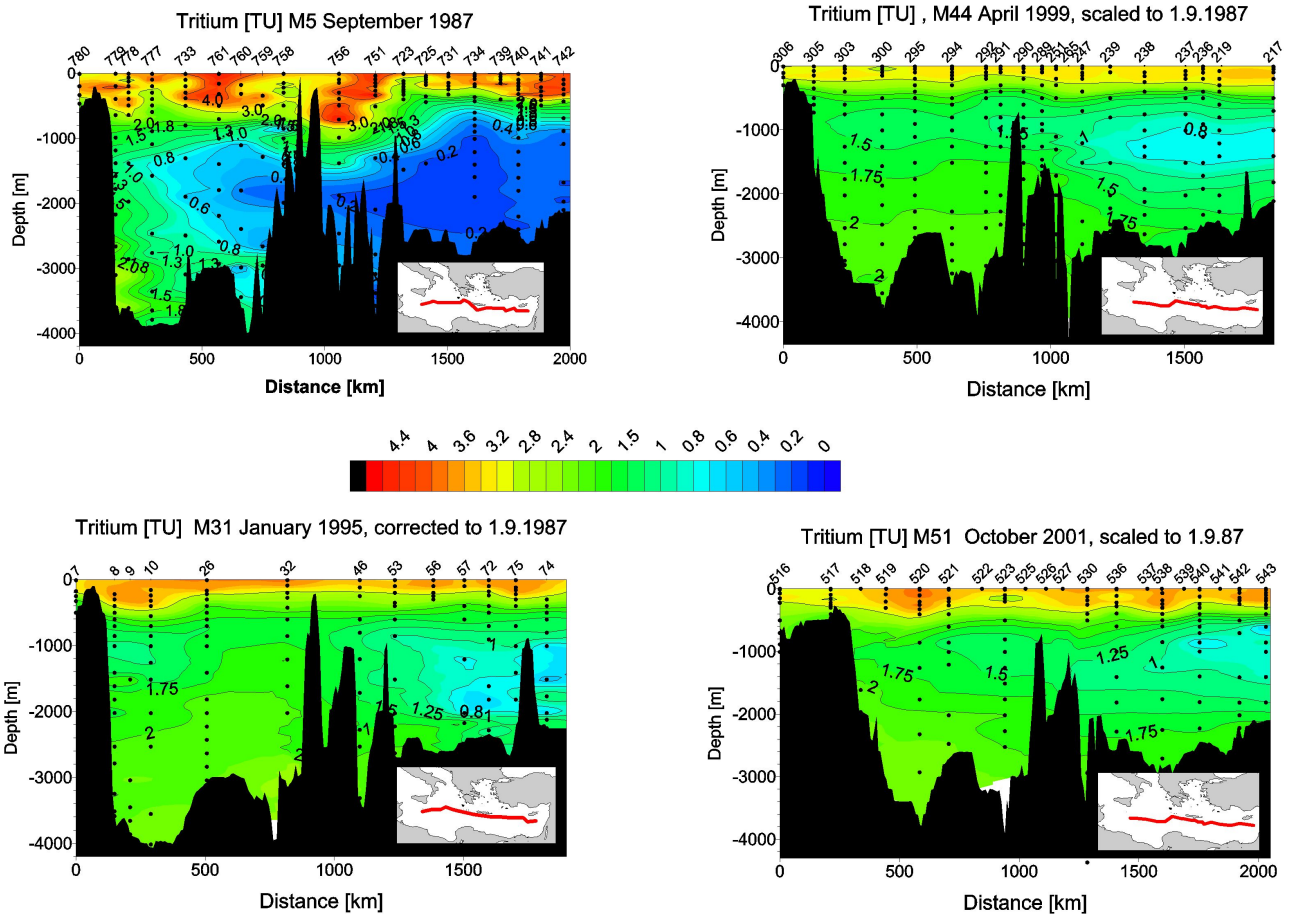

Fig. 2. Tritium sections (TU) of the *Meteor* cruises in 1987, 1995, 1999 and 2001 (cf. Table 1; for concentrations see colour bar and values at isolines), decay-corrected to the date of the 1987 cruise (1 September 1987; the factors are 1.51 for M31/1, 1.92 for M44/4, and 2.20 for M51/2). Numbers on top are station numbers, observations are indicated by dots, and the actual sections are shown in the inset maps. Isolines by objective mapping.

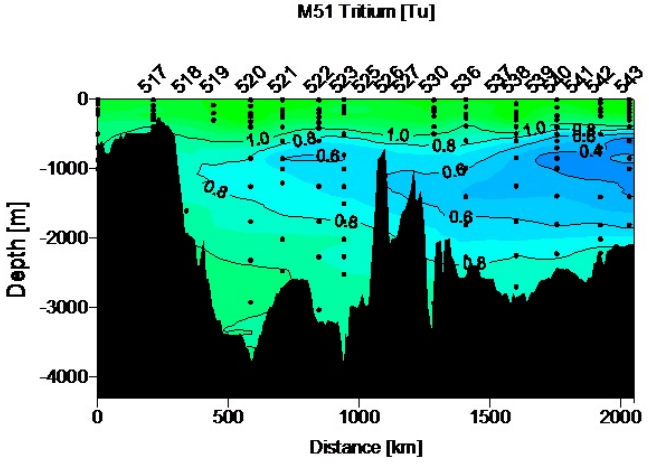

Fig. 3. The 2001 *Meteor* tritium section with the decay correction omitted. For the actual section and color bar, see Fig. 2.

filled in further. In comparison with 1987, the mid-depth tritium values are now distinctly higher and the minimum is centered at shallower depth (∼ 1200 m vs. ∼ 1800 in 1987).

As mentioned, the Fig. 2 tritium values are decay-corrected to 1987, in order to reveal the effects of the EMT and of dispersion. To give a feel for the concentration changes due to decay, Fig. 3 repeats the 2001 section with the original data. While decay amounts to more than a factor of 2, the tritium concentrations in the minimum layer, which has moved toward the eastern end of the section, are about twice those of 1987.

Figure 4 presents two sections in the WMed of the *Poseidon* 1997 cruise and Fig. 5 the WMed and EMed parts of the *Meteor* section of 2011. The southern *Poseidon* section (Fig. 4, left) shows a steady decline from about 1.8 TU at the surface to a weak minimum between 0.8 TU isolines near to 1000 m and 1500 m depth. In particular the lower one of these isolines sinks towards the Tyrrhenian, demonstrating that this sea feeds into the minimum layer and waters

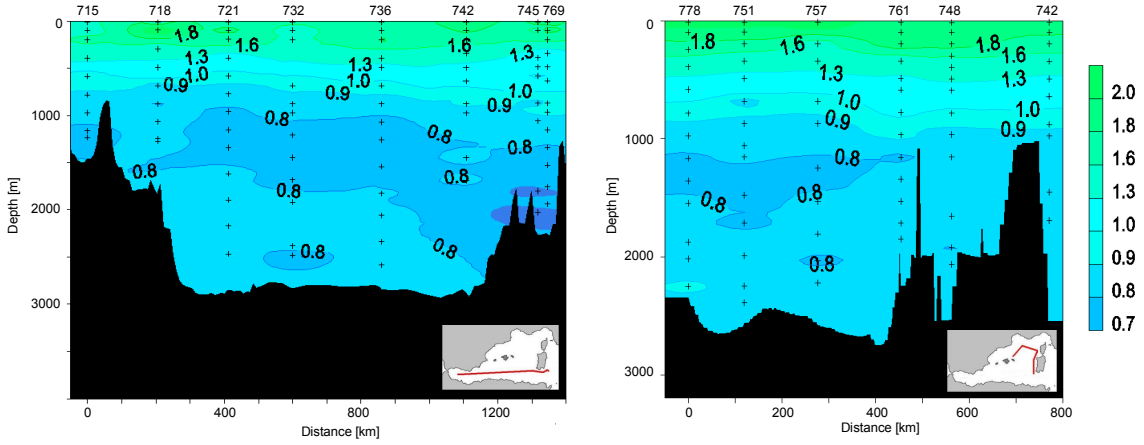

Fig. 4. Tritium sections (TU) of *Poseidon* 234, 1997, left extended southern section, right northern curved section. Numbers on top are station numbers, station positions see inset maps.

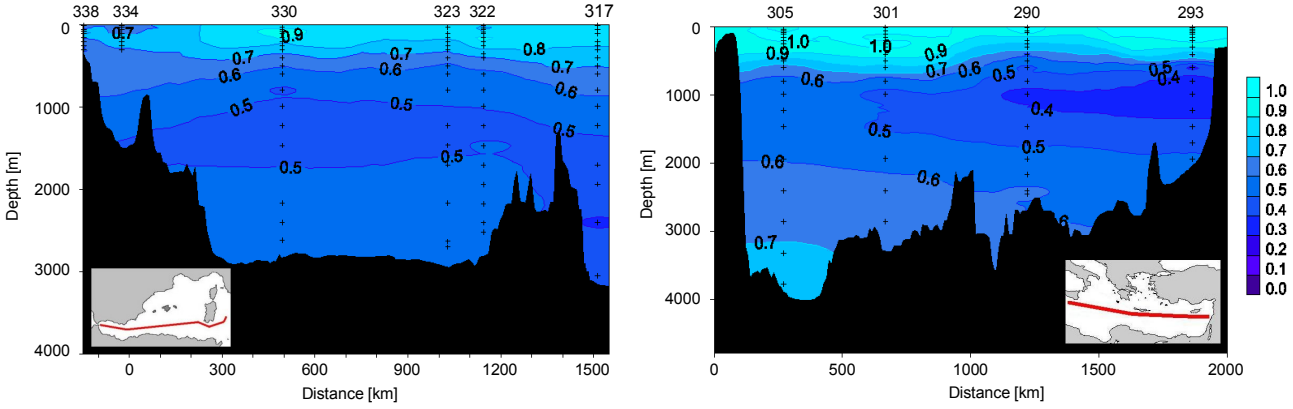

Fig. 5. As Fig. 4, but *Meteor* 84/3, 2011, left WMed, right EMed.

below it (see remark on TDW outflow in Sect. 2). At the northern section (Fig. 4, right), the deep-water tritium concentrations are slightly lower without revealing a connection toward the Tyrrhenian. In the 2011 WMed section (Fig. 5, left), the deep-water structure is basically the same as in Fig. 4, left, including the connection toward the Tyrrhenian, with concentrations descending from 0.85 TU at the surface and the minimum between 0.5 TU isolines near to 1000 and to 1600 m depth. The similarity between the two sections holds despite the fact that the WMT added upper waters below about 1500 m in the period between the two surveys. (Schroeder et al., 2010). The EMed section of 2011 (Fig. 5, right) has about 1 TU at the surface. The lowest tritium concentrations in its mid-depth minimum (center near to 1000 m) are similar to those in 2001 ($\sim$ 0.4 TU; Fig. 3) The highest concentrations in the deep waters ($\sim$ 0.7 TU) are found toward the western end of the section, reduced by roughly 30 % relative to 2001. This means that toward the east there is still a tritium addition compensating decay, while in the west decay predominates.

Some older tritium profiles (1971–1972) from the northern part of the WMed are shown in Fig. 6 in comparison with profiles of 1981 and 1997. A drastic decrease between 1971–1972 and 1997 in the upper waters is revealed, in keeping with Fig. 1 and Table 2. Below 1000 m the temporal decrease is small; apparently, tritium decay is largely compensated by admixture from waters further up.

δ^3He sections concurrent with the tritium sections of Fig. 2 are presented in Fig. 7. Basic features are surface values close to the solubility equilibrium δ^3He_0, a maximum in the LIW layer, with the lowest values near to the LIW formation region and the highest towards Sicily Strait (ESS region; 11 %), the latter extending below the classical LIW depth range. Further down there is a minimum layer, descending in depth and strongly decreasing in δ^3He toward the east, and still deeper one finds higher values concentrated toward the western end of the section, associated with the higher tritium concentrations observed there. The mid-depth minimum layer in the Levantine, descending eastward from $\sim$ 1800 m to 2000 m, showed an extended region with values below -3 %.

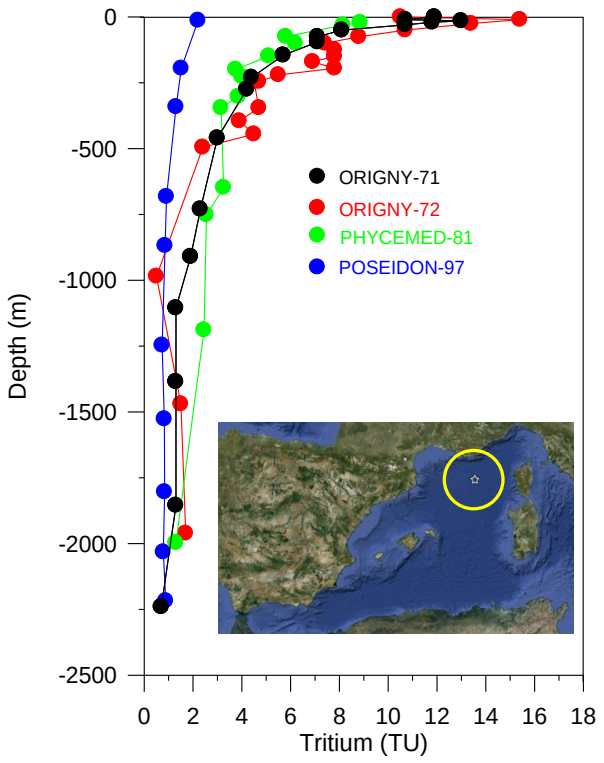

Fig. 6. Tritium profiles in 1971–1972, 1981 and 1997 in the WMed, for positions see inset map.

Such values are significantly below δ^3He_0, demonstrating the presence of terrigenic He of low ^{3}He content (Roether et al., 1998a), as similarly observed in EMed brine basins (Winckler et al., 1997; Charlou et al., 2003).

By 1995, the δ^3He values in LIW were significantly reduced, to 8 % in the ESS region, about 3 % in the east, and 0 %–1 % at the LIW level in the formation region. The mid-depth minimum in the east now displayed values between −1 % and −2 %, i.e., close to δ^3He_0, so that the definitive evidence of the ^{3}He-poor terrigenic He is lost. The centre of the minimum layer was displaced upward to 1800–1400 m. The maximum deep value in the west was near to 5 % and found above the bottom. In 1999, the LIW ESS value was 7 %, and was about 0 % near to the formation region and less than 2 % in the east. The mid-depth minimum layer, now centred in 1600–1300 m depth, showed values between 0 % and −1 % in the east, and the maximum deep value in the west was similar to 1995. In 2001 the LIW ESS value was at most 5 %, that in the formation region below 0 %, and that in the east 2 %–3 %. The minimum had risen in depth further, ranging between 1200 m and 1000 m. The maximum deep value in the west had become slightly larger, i.e., 5 % to 6 %.

Figure 8 shows δ^3He in the WMed at the two *Poseidon* sections corresponding to Fig. 4. They reveal maximum δ^3He-values of 9 % to 10 % in the LIW layer centred near to 500 m depth. The southern, quasi-zonal section (Fig. 8, left) reaches into the Tyrrhenian Sea. Here one finds the highest δ^3He values in LIW and also in the deep waters. Upward of the LIW, the values decrease strongly first and then more gradually into the surface layer, which has $\delta^3He < 0$, while below the LIW, the decrease is moderate, leading to 7.5 % near to 1000 m. Fig. 8 (right) has somewhat higher values in the LIW, and the 7.5 % isoline is found at somewhat greater depths, about 1500 m in the east and 1100 in the more western part of the section. We ascribe the structure to the effect of the Tyrrhenian Sea (cf. Sect. 2).

Figure 9 gives the two δ^3He sections of 2011 in correspondence to Fig. 5. In the WMed (Fig. 9, left) a striking feature is that, in contrast to 1997, the δ^3He maximum in LIW is lost, and instead, a maximum appears between 700 and 1200 m depth. Like in Fig. 8, the highest values are found at stations located in the Tyrrhenian Sea. Further down the values are slightly lower than in Fig. 8, possibly due to upper-water addition by the WMT. Also in the EMed part (Fig. 9, right) there is no longer a maximum in the LIW layer. Further down there is still a δ^3He minimum in the east, but the value (< 2 %) has become significantly larger than in 2001 (cf. Fig. 7). Below the minimum, one finds isolines rising westward, with the levels increasing from 2 % to 3 % in the east to 4 % to 5 % toward the Malta Escarpment.

Figure 10, finally, presents WMed δ^3He profiles of 1983, which consistently show maxima in the LIW layer. The highest value of about 16 % is observed at Sta. SRS in the Sardinian Channel, which exceeds the concurrent value at the upstream Sta. BAOR located in the EMed off the Malta Escarpment, and in fact, is the largest in all our datasets. One further notes that, especially at the northern stations, the δ^3He maximum partly occurs at a lower depth than usually ascribed to LIW in the WMed (i.e., ∼ 200 m instead of 500 m).

Lastly, we have a few early δ^3He and tritium values in the WMed from cruises in 1976 and 1977 (Table 1), which are far closer in time to the surface tritium maximum (Fig. 1) but have only survived in graphical form (Roether and Weiss, 1980; Roether et al., 1992). These data are addressed in Sect. 7.3.

7 Discussion

7.1 Features of the tracer distributions

The 1987 distributions of tritium and δ^3He in the EMed (Figs. 2 and 7) represent the pre-EMT situation. They reflect the classical thermohaline cells of the LIW in the upper waters and of the EMDW at greater depths. The LIW layer is characterised by low δ^3He the closest to the formation area east of Rhodes, rising strongly westward, where the values reach up to 11% just upstream of the entrance into Sicily Strait (ESS region); the high values extend downward to about 800 m depth, which we ascribe to presence of Cretan

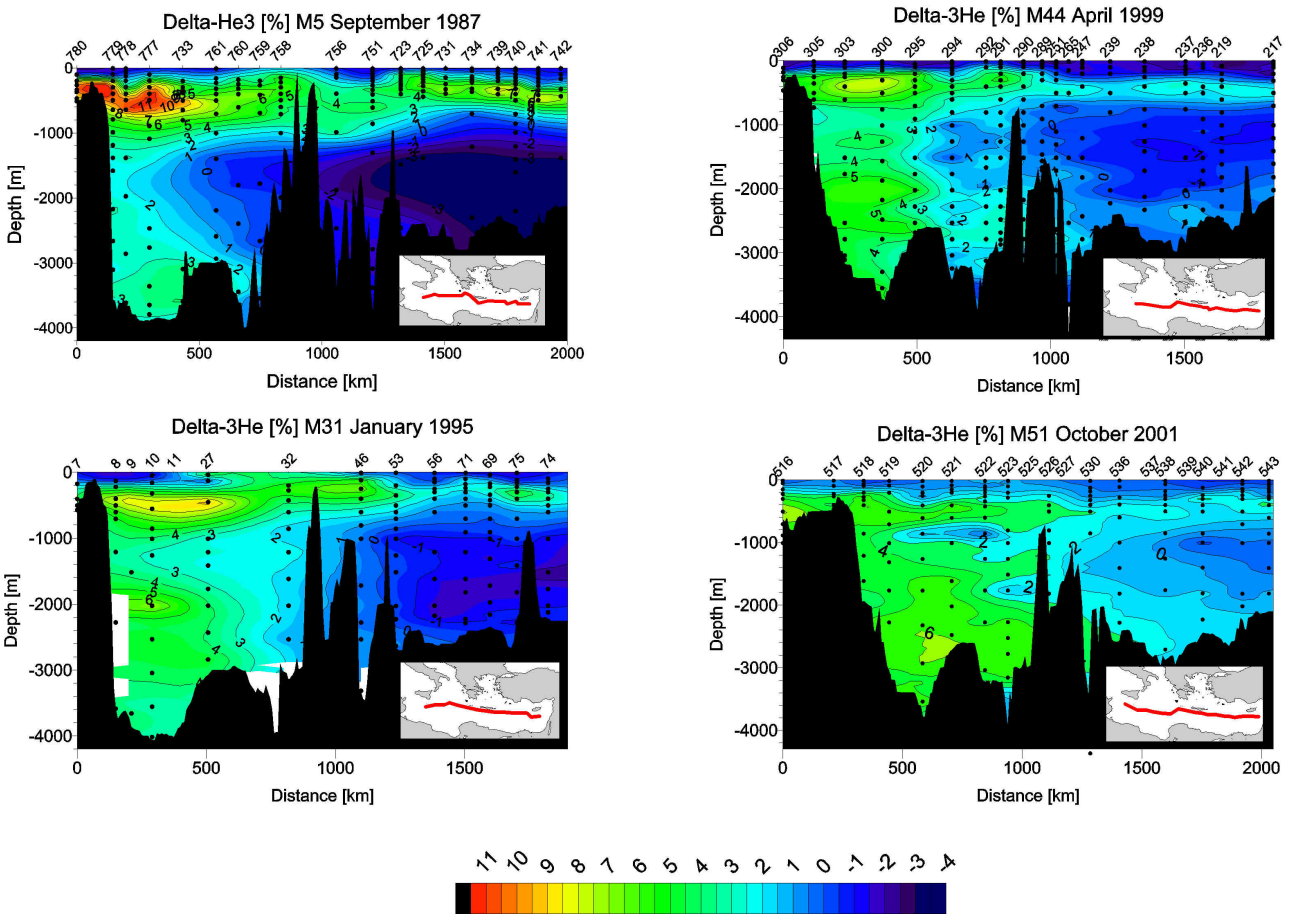

Fig. 7. Same as Fig. 2 but δ^3He sections (%). Note that in 1987 the deep waters in the Levantine Sea were largely below the solubility equilibrium value.

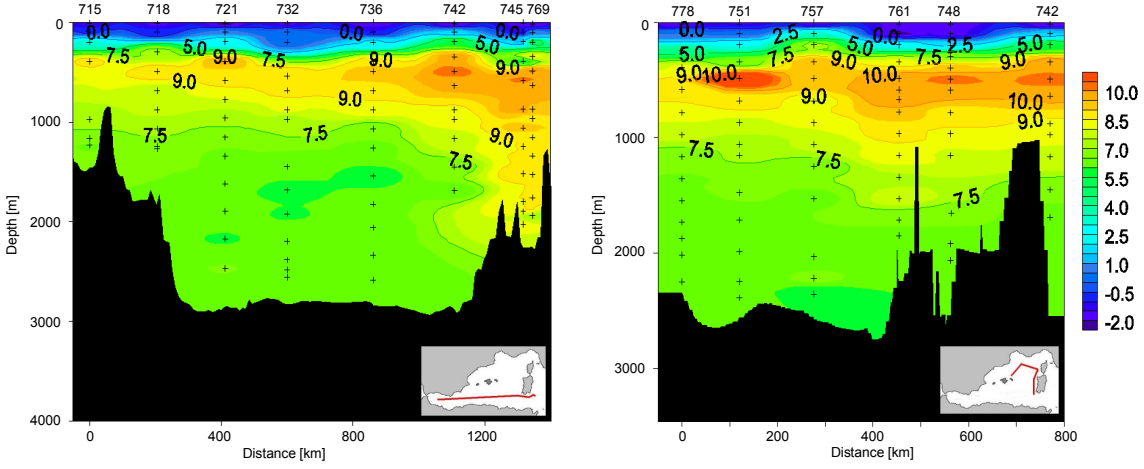

Fig. 8. WMed δ^3He sections (%) of *Poseidon* 234, 1997, extended southern section left, northern curved section right. Numbers on top are station numbers, sections cf. inset maps.

Intermediate Water (CIW) that adjoined the LIW from below (Schlitzer et al., 1991; Roether et al., 1999). The smaller rise in δ^3He eastward of the formation region indicates a restricted expansion of LIW in that direction. The spreading of the EMDW along the western slope of the Ionian Sea, followed by a slow, near-bottom transfer eastward across the

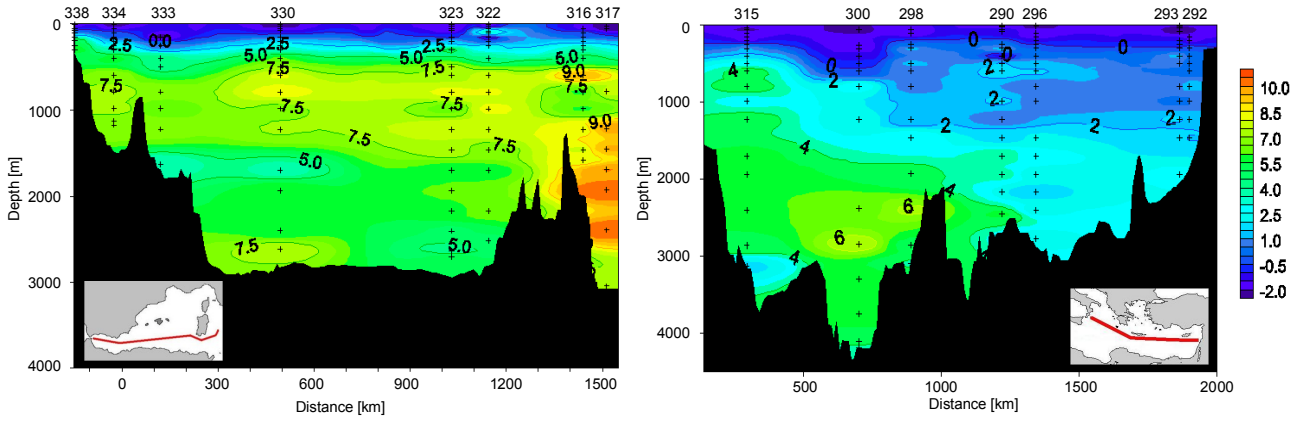

Fig. 9. δ^3He sections (%) of *Meteor* M84/3, 2011, left WMed, right EMed. Numbers on top are station numbers, sections cf. inset maps. The track in the EMed part differs from that in Fig. 5 because, close to Sicily, He and tritium were sampled on different stations.

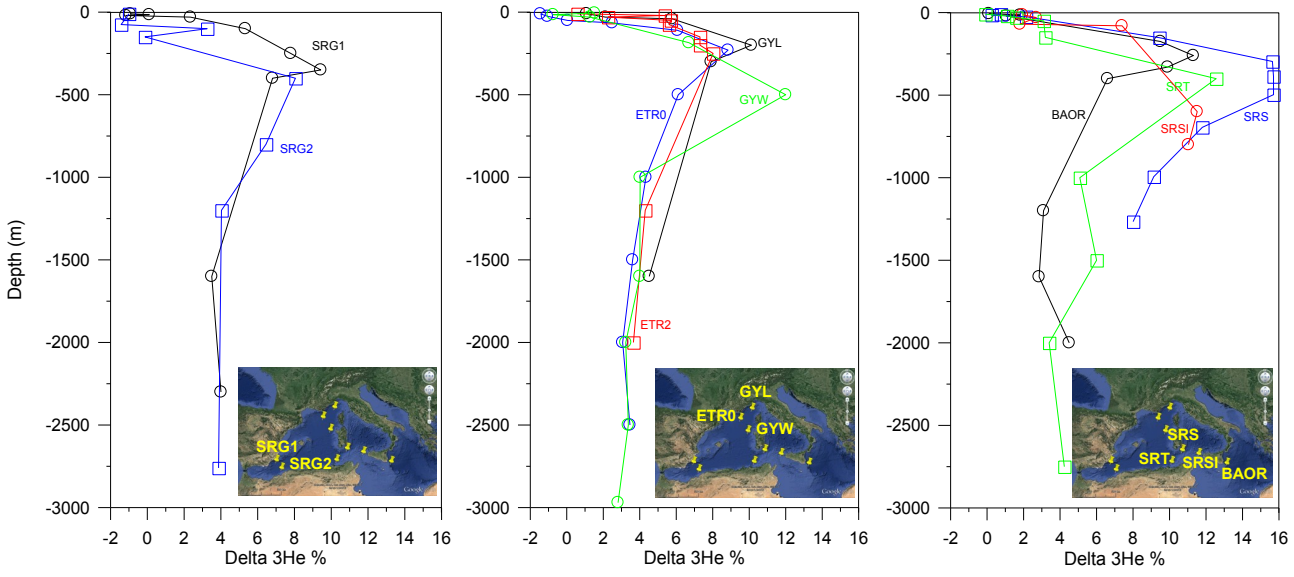

Fig. 10. δ^3He profiles (%) of *Phycemed* 1983, left: western stations, centre: northern stations, right: southeastern stations. For station positions see inset maps.

Ionian and into the Levantine and closure of the EMDW circulation by upwelling (Roether et al., 1994; Roether and Well, 2001), is visualised impressively in the distributions of both tracers: the concentrations strongly decrease eastward forming mid-depth tracer minima, in which the lowest tritium and δ^3He values of our entire data set are found. A special feature is δ^3He values below the equilibrium with the atmosphere, from which the mentioned low isotopic ratio of terrigenic He (R_t, Sect. 4) in the EMed has been deduced (Roether et al., 1998a).

The subsequent observations up to 2001 (Figs. 2 and 7) document the severe impact of the EMT, which transferred large amounts of tritium-rich upper waters into the deep waters, with highest contributions toward the bottom and south of Crete, and induced a lifting of the deep and mid-depth waters that was felt up into the photic zone (Klein et al., 1999). By expanding eastward, the newly added near-bottom waters displaced the residing waters upward (accompanied by mixing). This is demonstrated in the rise of the mid-depth minima from about 1800 m in 1987 (Figs. 2 and 7) to 1000 m by 2011 (Figs. 5 and 9, right), accompanied by increasing tracer concentrations due to vertical mixing. One consequence was that in particular the tritium distribution in 2011 was far smoother than in 1987. Because the formation of the dense Aegean waters involved upper waters and was subject to ventilation, the EMT had, in contrast to tritium, but a small impact on the average δ^3He in the deep waters. Furthermore, the ^{3}He ingrowth from tritium decay gradually became small because of the decreasing tritium concentrations, which eventually made δ^3He a rather conservative

tracer. In consequence, the δ^3He in the LIW layer decreased after 1987 (Fig. 7), primarily as a result of flushing of the layer by the westward flow. By 2011, the ^{3}He-depleted region reached down to approximately 1200 m over the eastern half of the section (Fig. 9, right), while further down and further westward, the δ^3He values remained similar to those found earlier. The depletion of δ^3He testifies to displacement by upwelling that fed into the westward return flow, to be eventually transferred into the WMed.

The tritium concentrations in the WMed were distinctly less structured than those in the EMed, with the isolines being more level. In 1997 (Fig. 4), one finds a moderate minimum centered in roughly 1500 m depth, indicating that newly formed WMDW was preferentially added below that minimum. In the Tyrrhenian at the eastern end of the southern section (Fig. 4, left), the minimum reached deeper and the values were the lowest. In 2011 (Fig. 5, left) the minimum was found at a somewhat shallower depth, presumably in response to the WMT.

The δ^3He sections of 1997 (Fig. 8) show distinct maxima in the LIW, with values only moderately less than found in the ESS region in 1987 and rather higher than the ESS values in 1995, which is due to continued tritium decay on the way. Further down, the values decrease with depth rather gradually. In the Tyrrhenian Sea (Fig. 8, left) higher values were observed, which is opposite to the situation for tritium. Our interpretation is that water turnover in the Tyrrhenian is sufficiently slow to support significant tritium decay and ^{3}He ingrowth. In 2011 (Fig. 9, left), a mid-depth δ^3He maximum and the effect of the Tyrrhenian are still present. However, the δ^3He maximum is now below that of salinity, i.e., below the centre of the LIW; also this feature is opposite to the corresponding one for tritium. Presumably, these somewhat deeper waters travel slower allowing more time for tritium decay, while in new inflow via Sicily Strait, which is the principal source of LIW in the west, the δ^3He values have become low (Fig. 9, right). Further west, the LIW layer values in both years gradually decrease westward.

The WMed δ^3He profiles of 1983 (Fig. 10) give additional information. Most importantly, Sta. SRS near to the southern entrance of the Tyrrhenian at LIW depths has a value of 16 %, which is the highest value that we found anywhere in the Med. This certainly reflects the fact that 1983 is, considering also the transit time from the LIW source region (see Sect. 7.3), distinctly closer to the tritium maximum in surface waters in the mid-1960s (Fig. 1) than is the case for the later tracer surveys. In all years for which we have observations (1983, 1997, 2011), the WMed δ^3He values in the LIW layer consistently decreased westward. Because there is no indication of the 1983 peak moving further downstream, i.e., westward, it appears that the LIW flow is subject to strong along-flow, or transit time, dispersion.

7.2 Terrigenic ^{3}He

While the concentrations of terrigenic He can be obtained from Eq. (1) rather accurately, the critical part in applying tritium-^{3}He dating is the isotopic ratio of the terrigenic He. As mentioned, a definite value $(0.42 \pm 0.1) \times R_a$ is available only for the EMed (cf. Sect. 4). For the WMed, geological similarity indicates a low isotopic ratio also there. On the other hand, both the Tyrrhenian and Aegean Seas are regions of geodynamic activity so that mantle-derived He with a far higher isotopic ratio might interfere. We show in the following that such input is of minor relevance.

For the Aegean, we inspected values of t_{He}, non-atmospheric ^{3}He (tritiugenic + terrigenic), and age for (a) the pre-EMT *Meteor* cruise M5/6 (1987) and (b) the cruise following the Aegean outflow maximum (M31/1, 1995) in the Cretan Sea (southern Aegean). For 1987, the t_{He} values were the highest in the depressions in the east of the sea (up to 7 % >2000 m) and low at LIW depths ($\sim$ 1%), reflecting slow renewal in the depressions and denying a significant impact of local terrigenic ^{3}He sources at LIW depths. By 1995, in contrast, the depressions had been flushed due to the enhanced water density during the peak outflow (Roether et al., 2007), reducing their t_{He} to 1 % or less. At LIW depths, t_{He} had increased to about 4 %, which must be due to the EMT-induced upwelling outside of the Aegean, which also explains the relatively high age of $\sim$ 12 yr (using the EMed R_t/R_a of 0.42). The terrigenic He ratio R_t might actually be higher than that value but must be less than R_t/R_a= 2, because that value would imply the unrealistic result of vanishing tritiugenic ^{3}He. The EMT-related Aegean peak outflow was concentrated between roughly 600 and 1000 m depth (Roether et al., 2007), where the t_{He} values of 1995 are below 2 %. We conclude that the EMT-related outflow hardly added any significant amounts of extra terrigenic ^{3}He into the EMed at large, while inside the Cretan Sea an elevated R_t/R_a ratio, at most about unity, might be indicated.

In the Tyrrhenian, Lupton et al. (2011) found δ^3He elevated up to 20 % (but mostly less) above submarine vents along the Aeolian Arc (southern Tyrrhenian Sea) between 200 and 800 m depth. Away from the vents, however, values only slightly above background (by at most 1 %) were observed, excluding a substantial impact on the terrigenic ^{3}He. A significant effect was also denied by Roether and Lupton (2011) noting conformity of Tyrrhenian values at LIW depths (the range that would be affected most by the hydrothermal ^{3}He) with values just upstream of the Sicily Channel. Following these authors, we allow for a small effect, i.e., use $R_t/R_a = 1$ in the Tyrrhenian Sea. For a typical t_{He} value of 3 %, this ratio lowers the tritiugenic ^{3}He by 0.4 TU compared to using the EMed value of 0.42.

A transition between the Tyrrhenian Sea and the WMed with t_{He} values decreasing westward is found in the observations of *Poseidon* 234 in 1997. At that time the Tyrrhenian was subject to a strong EMT impact (Roether and Lupton

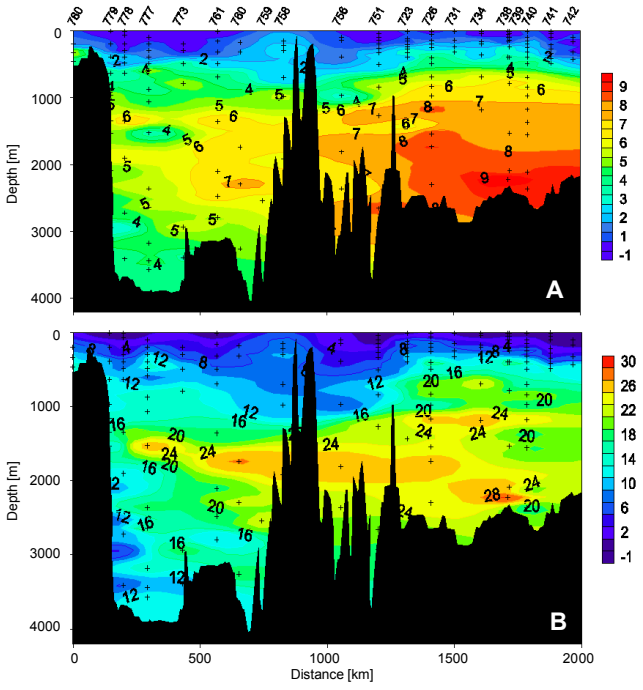

Fig. 11. Terrigenic He in percent of the He solubility equilibrium values **(A)** and tritium-^{3}He age (**B**; years) in the EMed for cruise M5/6, 1987; for track see Fig. 7. Station numbers at top of figure, dots indicate data points.

2011), while the WMed proper was still but moderately affected. Near to the southern Tyrrhenian outlet (the Sardinian Channel), maximum t_{He} values of about 3.5 % are found between 500 and 1500 m depth, compatible with values in the deeper waters overflowing the Strait of Sicily sills (Roether and Lupton, 2011; see also Fig. 11 below). At greater depths, t_{He} decreases to meet the WMDW value of ~ 1 % at 3500 m. West of the transition zone, the values decrease to less than 2 % in the LIW layer (around 500 m) and to ~ 1 % below 1000 m. The latter value is distinctly less than in the Sicily Strait overflow waters, indicating that in the WMDW formation a substantial fraction of terrigenic He gets lost, with little compensation by new input from the sea floor. Thus, it appears that in the WMed much of its terrigenic He is imported from the EMed so that it appears safe to assume $R_t/R_a = 0.42$ also here.

7.3 Tritium-^{3} He dating

Tritium-^{3}He ages τ are obtained using Eq. (3) with input from Eq. (2b), with an upper boundary condition of vanishing tritiugenic ^{3}He in the mixed layer ($r = 0$ for $t = 0$). Our first example is ages in LIW at various locations and in different years, which represent transit times from the LIW formation region. We averaged the input data over the LIW layer according to the LIW salinity signals. The data resolve the LIW only coarsely, which leads to an age uncertainty that we estimate at ± 10 %. The earliest observations are from 1976 near to the entrance into the Alboran Sea, and 1977 in the WMDW formation region. Table 3 summarises the input data (columns 2 and 3), the resulting terrigenic He, its isotopic ratio, and the resulting tritiugenic ^{3}He and age. Column (8) gives the ratios of stable tritium (tritium + tritiugenic ^{3}He) between (a) the interior location at the time of observation and (b) at the surface in the formation area (Fig. 1, Table 2) τ years back in time. The latter value is often denoted by "initial tritium" since there is no tritiugenic ^{3}He to contribute ($r = 0$, see above). All ages show a trend of increasing values with the calendar time of observation and also with distance from the source region.

An exception is low ages for the WMed 1976/77 observations, which is particularly surprising for the *Knorr* station located in the far west of the Med. The explanation is that 1976/77 was that close to the surface tritium maximum that only the fastest travelling LIW carried tritium-rich water from near to the surface-water tritium peak ($\sim$ 1965, Fig. 1), while tritium in the slower travelling parts was still of the lower pre-peak level, which is supported by the ages obtained from the later observations of no less than 20 yr. Additional support is that the initial tritium values for the 1976/77 observations ($\sim$ 11 TU) are typical of near-peak values. Because the ages in a water mixture are biased toward the components with the highest tracer concentrations, it follows that in this case the ages refer preferentially to the fast travelling component. One must conclude that the LIW flow up to the WMed is subject to a transit time dispersion from the source region on the order of the age difference fast LIW versus bulk, i.e., roughly 10 yr.

For the later observations the upward age trend continues but apparently at a distinctly smaller rate (Table 3). We ascribe this to the fact that the dispersing LIW flow no longer covers substantial contributions of pre-peak surface waters, so that the ages over the range of the dispersion combine to a more realistic mean age. The LIW ages are furthermore affected by vertical mixing: Because ^{3}He forms a maximum in LIW while tritium monotonically declines downward through the LIW layer (see the tracer sections above), any vertical mixing lowers the ^{3}He/tritium ratio, which reduces the age. Also this effect was largest early on when the vertical gradients must have been distinctly higher than later. We believe that for the later observations this effect is secondary, considering that vertical mixing in the ocean is generally rather small. We note that the particularly large age increase in the ESS region between 1995 and 1999 is ascribed to contributions of older water that was uplifted during the EMT peak Aegean outflow. At the time of the 1995 cruise, that peak had ended but in the ESS area the impact was still present (Roether et al., 1996).

The stable tritium ratios in Table 3 mostly decrease in time and also with distance from the LIW source. The cause is mixing with waters of lower tritium or ^{3}He content, which gradually reduces the stable tritium in the interior. An

Table 3. Tritium-^{3}He ages (yr) in LIW at various locations in different years. The tritium and δ^3He values are averaged over the LIW layer. For the EES region, just upstream of Sicily Strait, values between about 200 and 600 m are used to include the CIW, further west the range is about 400 to 600 m. For the stable tritium ratio, see text. The initial tritium values are given by the sum of the (2) and (6) values, divided by (8).

Location and year	Obs. tritium (TU)	Obs. δ^3He (%)	Terrig. He (%)	R_t/R_a	Tritiug. ^{3}He (TU)[a]	Tritium-^{3}He age	Stable tritium ratio
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
ESS region 1987 M5/6, Sta. 779	3.4	9.5	2.3	0.42	2.7	11	0.66
ESS region 1995 M31/1, Sta. 8	2.1	6.7	2.1	0.42	2.1	12	0.62
ESS region 1999 M44/4, Sta. 305	1.2	5.4	2.0	0.42	2.0	17	0.5
Tyrrh. Sea, 1987 M5/6, Sta. 786	1.92	12.1	2.2	1	3.0	17	0.65
Tyrrh. Sea 1997 *Poseid.* 234, Sta 764	1.2	7.8	3.6	1	2.5	19	0.49
WMed 1976[b] *Knorr* 54/5 Sta. 727	2.1	3.8	1.7	0.42	1.5	9.5	0.34
WMed, 1977[c] *Bohra*-2	3.1	5.5	1.7	0.42	1.8	8.0	0.41
WMed 1983[d] Phycemed, Sta. SRS	2.1	15.7	2.0	0.8	4.5	20	0.55
WMed center 1997 *Poseid*. 234, Sta. 736	1.2	9.4	1.7	0.42	2.6	21	0.42
WMed center 2011[e] M84/3, Sta. 323	0.62	6.7	1.7	0.42	1.9	25	0.28

[a] Conversion 4.85 % TU^{-1}.
[b] 37° N 0° W, April 1976; δ^3He and tritium: Roether and Weiss 1980, columns (4) and (5) = 1997 values.
[c] 42° N 4° 45′ E, 30 March and 3 April 1977; δ^3He: Roether and Weiss (1980); tritium: Roether et al. (1992); columns (4) and (5) = 1997 values.
[d] Close to southern exit of Tyrrhenian Sea; column (2) estimated from Fig. 1/Table 2; column (1) and sampling location cf. Fig. 10, columns (4) and (5) interpolated values.
[e] Columns (4) and (5) = 1997 values.

exception is low values early on (see the 1976/77 values in Table 3) when the (relative) tracer gradients were still particularly high. We note in passing that the WMed *Knorr* and *Borha-2* cruises of 1976 and 1977 show unrealistically low ages not only in the LIW (Table 3) but also at greater depths. At 800 m and 2000 m, the ages amount to 12.5 and 14 yr (stable tritium ratios 0.1 and 0.34), respectively, for the *Knorr* data, and for *Borha*-2 to 10.5 and 13 yr (stable tritium ratios 0.14 and 0.09). The rather low stable tritium ratios indicate particularly strong mixing since formation.

To obtain average transit times in view of these findings, we selected ages for which the related mean formation time is at least a decade after the surface-water tritium maximum, when also the ages no longer change much. We concluded that realistic mean LIW transit times are 12 ± 2 yr at the entrance into the Strait of Sicily, 18 ± 3 yr in the Tyrrhenian, and 22 ± 4 yr in the WMed. These ages are quite compatible with values obtained in a very different way (delayed correlation of salinity extrema) by Gacic et al. (2013).

Our other example is sections of terrigenic ^{3}He and age in the EMed for 1987 (Fig. 11) along the section shown in Fig. 2. The distribution of the former parameter is virtually an inverted mirror image of the δ^3He minimum in the corresponding section in Fig. 7. The highest value, 8 %, is found toward the bottom in the east of the section. The LIW layer has about 2 %, the δ^3He minimum layer 5 % to 8 % and the waters further down in the west 4 % to 6 %. The age section displays a mid-depth maximum extending over most of the section. At the eastern end, the ages decrease again, which is due to rising tritium values (Fig. 2). Rather low ages are found in the deep waters at the western end of the section, reflecting the input from the Adriatic Sea. The low ages in the upper waters reach the deepest at Sta. 756 south of Crete. That water has been reported to originate from the Aegean on the basis of a multi-parameter water analysis (Schlitzer et al, 1991), which is well compatible with the low ages. The feature might represent a precursor of the EMT, which began in about 1990 (Roether et al., 2007). We note that all

mixed-layer ages are close to zero, supporting our determination of tritiugenic ^{3}He using Eq. (2).

That the ages in Fig. 11 hardly exceed 24 yr even in the EMDW is again a matter of transit time dispersion, considering that 24 yr prior to 1987 point to 1963, i.e., shortly prior to the surface-water tritium maximum. The 24 yr is the age of the youngest contribution to the EMDW, which makes it well compatible with the turnover time of the deep waters of more than 100 yr (Roether and Schlitzer, 1991). Note that even if one would wait long enough for the deep waters in question to approach a steady state of tracer input, tritium decay and tracer loss by water leaving the system we would still not obtain an age near to the turnover time. The fact is that such a turnover time is defined as the ratio of the volume of a well-mixed box divided by the annual flux through that box: Assuming the water input Φ to be free of tritiugenic ^{3}He, the balance at equilibrium is $C_{^3\mathrm{He}} \times \Phi = V \times C_{\mathrm{tritium}}/t_{1/e}$, so that the ^{3}He/tritium ratio amounts to $\tau_{\mathrm{turn}}/t_{1/e}$. Converting that into a tritium-^{3}He age (Eq. 3) one finds that the tritium-^{3}He age is far smaller than the turnover time, but related to it in a defined way, i.e., age $= t_{1/e} \times \ln(1 + \tau_{\mathrm{turn}}/t_{1/e})$.

Both these examples show that the ages need to be interpreted with care. A basic problem is that tritium-^{3}He dating virtually cannot account for any age bias caused by mixing. It appears from this study that the main effect arises from large-scale flow dispersion, but preferential gain or loss for either tritium or tritiugenic ^{3}He by vertical mixing may contribute. A further point is that long turnover times mean that the deep water still contains water that was formed during the pre-nuclear period (Fig. 1). It was shown above that the contribution should be small (Sect. 4), and the ages, furthermore, hardly account for such pre-nuclear contributions because the tritium-^{3}He ages are biased toward contributions of higher tracer concentration.

8 Conclusions

The tritium and δ^3He sections presented above visualise many features of the subsurface circulation and mixing of the Med. Examples are the eastward expansion and upwelling of the EMDW, the spreading of the LIW with a strong dispersion along its flow, and the tremendous impact of the EMT, such as in the upward water displacement of deep water in the Levantine Sea. An important feature is the recent depletion in tritiugenic ^{3}He in the top 1500 m of the Levantine Sea and in the LIW throughout the Med (Fig. 9). The depletion is caused by westward transfer of the residing waters, while in the waters replacing them the generation of new ^{3}He has become small due to low tritium concentrations. By now, the Med's subsurface tritium concentrations range between 0.4 and 0.7 TU (Fig. 5), so that the ^{3}He ingrowth over the next 10 yr will amount to 0.2 to 0.3 TU, or only 1 to 1.5 % in δ^3He. The current δ^3He values range between 4 % and 8 % except in the mentioned depletion zone in the Levantine. New ingrowth over the 10 year period will thus be smaller than the current concentrations of tritiugenic ^{3}He. Therefore, a new tracer survey around the year 2020 is desirable, which would demonstrate the further westward transfer of the Med's subsurface cloud of ^{3}He, an information that could hardly be obtained otherwise. Such a survey would allow one to deduce the time scales of the westward transfer, including the loss into the Atlantic by the Strait of Gibraltar outflow.

We quantified tritiugenic and terrigenic ^{3}He with a useful precision over the entire water column of the Med (a byproduct is terrigenic He), using observations of δ^3He and of He and Ne concentrations. This achievement depends on the particularly low ^{3}He content of terrigenic He and on tritium concentrations high enough to allow precise measurement. The resulting dataset of tritium and tritiugenic ^{3}He is useful to study the circulation and mixing of the Med. One tool is tritium-^{3}He dating, which we applied in the LIW at different locations and repeated in time. We find trends of increasing age with the calendar year of observation, which we ascribe to transit time dispersion of the LIW flow. We deduce average LIW transit times (between 12 and 22 yr), which are compatible with other estimates. As a further application we present detailed, quasi-zonal sections through the EMed of tritium-^{3}He age and terrigenic He for 1987. The highest ages in the East Mediterranean Deep Water (EMDW) are approximately 24 yr, far lower than the turnover time of this water mass ($\sim$ 100 yr; Roether and Schlitzer, 1991). The tracer age largely represents the portion of the deep water formed in the vicinity of the tritium peak in the mid-1960 and thereafter, which is again a manifestation of transit time dispersion. The LIW ages in the first application are realistic, while those in the second application (EMed) represent more recent water renewal only. This demonstrates that tritium-^{3}He ages have to be interpreted with care, basically because they place a higher weight on water components of higher tracer concentrations and ignore mixing. As Schneider et al. (2013) state, tracer ages such as the tritium-^{3}He age are often only proxies of age, while they do contain useful information. These authors show that the concept of Transit Time Distributions (TTDs) (Hall and Plumb, 1994) is generally superior to using tracer ages. The point is that, in contrast to the tracer ages, the TTD approach explicitly accounts for mixing.

Evaluation using the TTD concept is thus a way to proceed. CFC-12 data exist for all cruises since 1987, so that three transient tracers are available, i.e., tritium, tritiugenic ^{3}He, and CFC-12 (for the 2011 cruise even SF6 additionally; cf. Schneider et al., 2013). The concept splits the actual tracer concentrations in the interior into yearly contributions of their formation back in time, which defines tritium decay and thus also ^{3}He ingrowth. The tracers have very different input functions, and the observations repeated in time give additional constraints, so that a detailed treatment should be possible. It is true that the uncertainty of the input function of tritium is higher than that of CFC-12. However, we believe that the uncertainty arising from data gaps in space and time

Table A1. Surface-water tritium values 1952–1974. Time is given in fraction of a full year, i.e., 1952.5 is mid-1952. These are the original Dreisigacker and Roether (1978) data, for calibration to the northwestern Levantine Sea, the values have to be multiplied by 1.61.

Year	Tritium concentration (TU)
1952.5	0.2
1953.5	0.3
1954.5	0.8
1955.5	1.2
1956.5	1.2
1957.5	1.3
1958.5	2.2
1959.5	3.3
1060.5	3.4
1961.5	2.9
1962.5	4.4
1963.5	11.7
1964.5	17.4
1965.5	16.9
1966.5	14.8
1967.5	12.7
1968.5	10.9
1969.5	9.8
1970.5	9.0
1971.5	8.5
1972.5	7.9
1973.5	7.4
1974.5	7.0

and from the approximate nature of any concept of evaluation is often dominating. An example of the latter is vertical mixing across the LIW layer, which, due to different vertical distributions of tritium and ^{3}He, potentially alters the tracer concentration ratio in the LIW (Sect. 7.3).

Another promising approach would be to use the tracer data to verify OGCM simulations in the subsurface waters. A special challenge will be to deal with the fundamental changes in the deep and intermediate waters caused by the East Mediterranean Transient (EMT) and the West Mediterranean Transition (WMT). We are at least fortunate that in both cases pre-event tracer surveys (EMed: 1987, WMed: 1997) exist.

Appendix A

The data basis for the surface water part of Fig. 1.

The part up to 1974 is listed in Table A1. It goes back to Dreisigacker and Roether (1978), who obtained their set using a zero-order mixing model of the upper waters of the North Atlantic forced by the rather well defined tropospheric histories of tritium and ^{90}Sr, with a few free parameters that were adjusted using North Atlantic surface water observations of both tracers in 20° to 60° N. The fine structure shown for this part is therefore realistic. The further values, listed in Table A2, are averages of surface water values in or near to the northwestern Levantine Sea from the cruises listed in Table 1. Their errors account for the scatter in, or interpolation error between, the data from which the actual values were computed. The two earliest values in Table A2 (1965, 1974) serve to recalibrate the Dreisigacker and Roether (1978) values to the northwestern Levantine. Their individual errors result in a formal uncertainty of the calibration factor (1.61) of about 7 %. The true uncertainty is certainly larger but should not exceed 20 %, except possibly for the pre-nuclear value of 1952. To obtain the curve in Fig. 1, the values listed here were connected by straight lines (semi-logarithmic plot!).

Table A2. Surface water tritium values 1965–2011. Years as in Table A1, errors are standard error.

Year	Tritium concentration (TU)
1965.7	29 ± 4
1974.7	10.05 ± 0.8
1978.7	9.5 ± 1
1987.7	3.73 ± 0.6
1995.1	2.21 ± 0.4
1999.4	1.69 ± 0.07
2001.7	1.62 ± 0.05
2011.4	1.05 ± 0.05

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