Ocean Sci. Discuss., 10, 649–690, 2013 www.ocean-sci-discuss.net/10/649/2013/ doi:10.5194/osd-10-649-2013 © Author(s) 2013. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Ocean Science (OS). Please refer to the corresponding final paper in OS if available.

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

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Received: 20 March 2013 - Accepted: 21 March 2013 - Published: 3 April 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.



Abstract

We present a comprehensive account of tritium and ³He in the Mediterranean Sea since the appearance of the tritium generated by the atmospheric nuclear-weapon testing in the 1950's and early 1960's, based on essentially all available observations. Tritium in surface waters rose to 20–30 TU in 1964 (TU = $10^{18} \cdot [^{3}H]/[H]$), 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 ³He. We present the scheme by which we separate the tritiugenic part of ³He and the part due to release from the sea floor (terrigenic part). We show that the tritiugenic component can be guantified throughout the Mediterranean 10 waters, typically to a ±0.15 TU equivalent, mostly because the terrigenic part is low in ³He. This fact makes the Mediterranean unique in offering a potential for the use of tritiugenic ³He 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 ³He concentrations in the top few hundred meters 15 had become low, in response to the decreasing tritium concentrations combined with a flushing out by the general westward drift of these waters. Tritium-³He 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 20 arises because the repeated observations represent increasingly slower moving parts of the full transit time spectrum of LIW. The transit time dispersion found by this new application of tritium-³He 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. We furthermore present full Eastern Mediterranean sections 25 of terrigenic ³He and tritium-³He age in 1987, the latter one similarly showing an effect of the transit time dispersion. We conclude that the available tritium and ³He data, in



particular if combined with other tracer data, are useful for constraining the subsurface circulation and mixing of the Mediterranean Sea.

1 Introduction

³He, the rare isotope of helium (He; atmospheric ratio [³He]/[⁴He]_{atm}= R_a =1.384×10⁻⁶; ⁵Clarke 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 ³He addition by decay of radioactive tritium (tritiugenic ³He), the other, release from the sea floor (terrigenic ³He). The tritiugenic ³He 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, with only a minor part taking a detour through the land hydrosphere and the cryosphere. By now, most of the nuclear-weapon tritium has decayed ($T_{1/2}$ = 12.32 yr; Lucas and Unterweger, 2000) while the resulting ³He, being a stable nuclide, remained. In the Mediterranean (Med), the tritium concentrations were comparatively high as a result of its intra-continental

- situation. At the same time, the competing terrigenic ³He is small because the terrigenic He has a ³He/⁴He ratio that is one order of magnitude lower than in most other ocean regions (Roether et al., 1998a). The Med's sub-floor lithosphere is characterized by high sediment load above crust that is largely of continental type (Morelli, 1985); in both, α -decay of the natural decay series is a source of pure ⁴He. Using the isotopic
- ratio of terrigenic He, measured He isotope and neon (Ne) concentrations allow one to correct for the terrigenic ³He contribution (Roether et al., 1998a, 2001). The potential of using tritium and ³He 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.
- 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 in a few hundred m depth, overflows the Sicily Passage



sills and eventually leaves the Med through the Strait of Gibraltar (Wüst, 1961). The loss is compensated by 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. These 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.

Tritiugenic³He 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, this issue), long enough to allow the majority of the tritium to decay into ³He. Repeated tracer surveys since 1987 have

- documented the more recent evolution of tritium and ³He in the EMed rather well, 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 ³He in the Med at large over the entire period since nuclear weapon-produced tritium entered the environment.

2 Turnover of Mediterranean waters

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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 ~ 10⁶ m³ 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) similarly 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 × 10⁵ m³ s⁻¹, equivalent to a renewal period of about 150 yr. Further analysis found that newly formed EMDW expands as bottom water into the Levantine Sea, where it rises upward to a depth of about 600 m and returns westward (Roether et al., 1994). One should realize 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-³He 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, there was in the mid-1990s a massive outflow of unusually dense Aegean Sea waters, which were preferentially added below $\sim 1500 \text{ m}$, lifting the residing waters

¹⁵ upward and leading to a general salinity increase of the subsurface waters. The event, the so-called Eastern Mediterranean Transient (EMT; Roether et al., 2007), persists 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 (Schröder et al., 2010). The newly added deep water raised the temperature and salinity of the WMDW below about 1500 m.

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. At greater depth, WMDW intrudes into the Tyrrhenian across the sill of the Sardinian Channel (~ 1900m sill depth). These two components mix to feed outflow back through the Sardinian Channel at intermediate



depths. 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. That influence was also evident in a strong rise of tritiugenic ³He in the Tyrrhenian Sea deep waters during 1987–2007, which was in full accordance with the ³He and tritium values upstream in the EMed (Roether and Lupton, 2011). That work also noted enhanced mid-depth outflow of particularly saline water into the WMDW depth range.

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 ³He 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 characterize the tracer distributions and their relevant features. The full data sets are, however, available for future work.

Helium concentrations are reported in cc(STP) kg⁻¹ and ³He as δ^{3} He = $({}^{3}He/{}^{4}He)/R_{a}$ -1, where R_{a} = atmospheric ${}^{3}He/{}^{4}He$ ratio. Concentrations are

determined using highly specialized noble-gas mass spectrometers with about ±0.3% precision. The air-water δ³He solubility equilibrium value is δ³He₀=-1.65%, varying by ±0.1% over the range of Med's temperatures (Benson and Krause, 1980). Tritium concentrations are reported in tritium units (TU, 1TU means [³H]/[H]=10⁻¹⁸). Up into the 1980's, tritium measurement used low-level gas counting following isotopic
enrichment, with precisions of typically 5% or ±0.08TU, whichever is greater (Weiss et al., 1976). Later on, tritium was determined by measuring ³He 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 ± 0.02 TU, whichever is greater. In dealing with tritiugenic ³He it is advantageous to convert its concentrations into TU, on the basis that 1 TU of decayed tritium raises the ³He 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 ³He solubility equilibrium value.

4 Separation of tritiugenic ³He and tritium-³He dating

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To isolate the tritiugenic portion of ³He, 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^3 He 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 $Ne = Ne_0(1 + a_{Ne})$, 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. $a_{He} \approx a_{Ne}$. But He is subject to the further effect of He released from the ocean floor (terrigenic He), so that $He = He_0(1 + a_{He} + t_{He})$. 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, as

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

The offset accounts for systematic errors arising from the solubility functions of He and Ne, from the He and Ne measurement calibration, and from 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 analyzed 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)



(1)

using (1) with $t_{He} = 0$. 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

- ⁵ 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 ± 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 ± 0.4 % uncertainty for individual t_{He} values.
- ¹⁰ For ³He, 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 ³He. The terrigenic ³He₀ is the product of the terrigenic He and its isotopic ratio R_t . The tritiugenic ³He, also expressed as a percentage of ³ $He_0 = (1 + \delta^3 He_0)R_aHe$, becomes

$$r = \frac{He}{He_0} \times \frac{\delta^3 He - \delta^3 He_0}{\left(1 + \frac{\delta^3 He_0}{100}\right)} + \left(1 - \frac{R_t}{R_a}\right) \times t_{He} \quad (\%)$$
(2a)

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

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

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$$r = \frac{He}{He_0} \times \frac{\delta^3 He - \delta^3 He_0}{\left(1 + \frac{\delta^3 He_0}{100}\right)} + \left(1 - \frac{R_t}{R_a}\right) \times \left(\frac{He}{He_0} - \frac{Ne}{Ne_0}\right) \times 100 - 0.8 \quad (\%)$$
(2b)

The tritiugenic ³He thus depends on observed values of δ^3 He, He and Ne concentrations, and on temperature and salinity to obtain the solubility equilibrium values. Dividing *r* by 4.85 ± 0.05 % TU⁻¹ one obtains the tritiugenic ³He in TU. The negative sign of



 δ^3 He and the low value of R_t/R_a raise *r* relative to δ^3 He. A shift of about 1.7% arises from δ^3 He, and, in the LIW layer ($t_{\text{He}} \sim 3\%$) for example, the t_{He} term adds 1.3%, so that one has $r - \delta^3$ He $\approx 3\%$, which corresponds to about 0.6 TU of tritiugenic ³He.

The value from (2b) together with the concurrent tritium concentration gives the $_{5}$ tritium-³He age as

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

where $t_{1/e}$ = radioactive mean life of tritium (17.8 yr), and both tritium and the tritiugenic ³He 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 ³He and 2 TU for tritium (see below), for which Eq. (3) gives an age of about 16 yr. The expected uncertainty of *r*, combining those of δ^3 He, R_t/R_a , He/He_0 minus Ne/Ne_0 , and the standard error for individual t_{He} values is about ±0.6 % or 0.15 TU absolute, or 5 % relative to 3 TU, and the uncertainty of tritium is ±3 %. The uncertainty of the ratio becomes about ±6 %, for which Eq. (3) gives an age uncertainty of about 5 %, or 15 less than 1 yr. For tritium concentrations less than 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 $\delta^3 \text{He} = \delta^3 \text{He}_0$ and $t_{\text{He}} = 0$ (in the absence of strong upwelling), it follows from Eq. (2) that the upper boundary condition for tritium-³He dating in the interior is r = 0 for t = 0. It is useful to compare stable tritium (the sum of tritium and tritiugenic ³He) between the interior location and the formation re-

gion at the deduced time of subduction (Fig. 1). In the absence of mixing the values must agree, so that any difference in the stable tritium values reflects mixing effects or escape of ³He into the atmosphere at the air–water boundary. Other consequences of mixing will be that the age will be biased towards that of the components of the highest tritium and ³He concentrations, and that mixing with waters containing tritiugonic ³He

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²⁵ tritium and ³He concentrations, and that mixing with waters containing tritiugenic ³He



while being old enough to be free of tritium will enhance the ages. The latter effect can be ignored in the present context.

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 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 ob-

servations 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 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

- ²⁰ 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,
- ²⁵ a comforting environmental result. Figure 1 demonstrates that, by now, generation of tritiugenic ³He 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. Note that the EMed surface-water tritium concentrations have always exceeded those in the WMed. This reflects the fact that continental tritium levels have been up to about four-fold higher than the oceanic ones with a wide transition 5 in between (~ 1000 km; Weiss and Roether, 1980). The continental influence is clearly

stronger in the EMed and this holds even more for the Adriatic and Aegean Seas.

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 taha) in the LIW and at 200 m donth to the corresponding values pauth of Crote (columns

- ble) 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 (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, making the ESS region upstream of that south of Crete. Both these average ratios have apparent uncertainties of about 10%, but the uncertainty of
- the values for LIW and 800 m in the WMed are probably larger. Figure 1 and Table 2 provide a basis for estimating tritium concentrations in the Med's top kilometer with a fair 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.



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 alongbasin (quasi-zonal) sections. The Fig. 2 values are decay-corrected to the period of the first survey in September 1987. The 1987 distribution is characterized 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 midsection 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 filled in further. In comparison with 1987, the mid-depth tritium values are

now distinctly higher and the minimum is centered at shallower depth (\sim 1200 m vs. \sim 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 de-

²⁵ 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 *Poseidon* sections show a steady decline from about 1.8 TU at the surface to 0.8 TU near to 1000 m depth, with slightly ascending isolines at the northern section (Fig. 4, right) from southwest of Sardinia northward and then westward. In the 2011 WMed section (Fig. 5, left) the

- surface value is about 0.85 TU and one finds about 0.5 TU near to 800 and to 2000 m depth with a minimum in between. The latter structure is probably an effect of the WMT, which added upper waters below about 1500 m (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
- ¹⁰ concentrations in its mid-depth minimum (center near to 1000 m) are similar to those in 2001 (~ 0.4 TU; Fig. 3) The highest concentrations in the deep waters (~ 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 net tritium addition, while in the west decay prevails.
- Some older tritium profiles (1971–72) from the northern part of the WMed are shown in Fig. 6 in comparison with profiles of 1981 and 1997. A drastic decrease between 1971–72 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^{3} He 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^{3} He₀, a maximum in the LIW layer, with the lowest values near to the LIW formation region and the highest ones 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^{3} He 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, decreasing eastward from ~ 1800m to 2000 m, showed an extended region with values below – 3 %. Such values are significantly below δ^{3} He₀, demonstrating the presence



of terrigenic He of low ³He content (Roether et al., 1998a), as similarly observed in EMed brine basins (Winckler et al., 1997; Charlou et al., 2003).

By 1995, the δ^3 He 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 middepth minimum in the east now displayed values between –1 % and –2 %, i.e. close to δ^3 He₀, so that the definitive evidence of the ³He-poor terrigenic He is lost. The center 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 there was about 0 % near to the formation region and less than 2 % in the east. The mid-depth minimum layer, now centered 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^3 He in the WMed at the two *Poseidon* sections corresponding to Fig. 4. They reveal maximum δ^3 He-values of 9% to 10% in the LIW layer centered near to 500 m depth. The southern, quasi-zonal section (Fig. 8, left) reaches into the Tyrrhenian Sea. Here one finds the highest δ^3 He 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 δ^3 He < 0, while below the LIW, the decrease is moderate, leading to 7.5% near to 1000 m. Figure 8 (right) has somewhat higher values in the LIW, and a less steep decline upwards. The 7.5% isoline is found at somewhat greater depths, of 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^3 He 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^3 He 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^3 He 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^3 He 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 data sets. One further notes that, especially at the northern stations, the δ^3 He maximum partly occurs at a lower depth than usually ascribed to LIW in the WMed (i.e.

 $\sim 200\,m$ instead of 500 m).

Lastly, we have a few early δ^3 He 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

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7.1 Features of the tracer distributions

²⁰ The 1987 distributions of tritium and δ^3 He distributions 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 characterized by low δ^3 He 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 ²⁵ Strait (ESS region); the high values extend downward to about 800 m depth, which we



ascribe to presence of Cretan Intermediate Water (CIW) that adjoined the LIW from

below (Schlitzer et al., 1991; Roether et al., 1999). The smaller rise in δ^3 He eastward 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 Ionian and into the Levantine and closure of the EMDW circulation by upwelling (Roether et al., 1994; Roether and Well, 2001), is visualized impressively in the distributions of both tracers: the concentrations strongly decrease eastward forming mid-depth tracer minima, in which the lowest tritium and δ^3 He values of our entire data set are found. A special feature is δ^3 He values below the equilibrium with the atmosphere, from which the mentioned low isotopic ratio of terrigenic He (R_t ,

¹⁰ 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 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
- ²⁰ than originally, i.e. 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^3 He in the deep waters. Furthermore, the ³He ingrowth from tritium decay gradually became small because of the decreasing tritium concentrations, which eventually made δ^3 He a rather conservative tracer. In conse-
- ²⁵ quence, the δ^3 He 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 ³He-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^3 He values remained similar to those found



earlier. The depletion of δ^3 He 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 δ³He 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 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 ³He ingrowth. In 2011 (Fig. 9, left), a mid-depth δ³He maximum and the effect of the Tyrrhenian are still present. However, the δ³He maximum is now below that of

salinity, i.e. below the center of the LIW; also this feature is opposite to the corresponding one for tritium. Presumably, these somewhat deeper waters travel slower allowing ²⁰ more time for tritium decay, while in new inflow via Sicily Strait, which is the principal source of LIW in the west, the δ^3 He values have become low (Fig. 9, right). Further west, the LIW layer values in both years gradually decrease westward.

The WMed δ^3 He profiles of 1983 (Fig. 10) give additional information. Most importantly, Sta. SRS near to the southern entrance of the Tyrrhenian at LIW depths has

²⁵ 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-1960's (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^3 He 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 ³He

⁵ While the concentrations of terrigenic He can be obtained from Eq. (1) rather accurately, the critical part in applying tritium-³He dating is the isotopic ratio of the terrigenic He. As mentioned, a definite value (0.42 ± 0.1) · 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 ³He (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

- ¹⁵ Aegean). For 1987, the t_{He} values were the highest in the depressions in the east of the sea (up to 7% > 2000m) and low at LIW depths (~ 1%), reflecting slow renewal in the depressions and denying a significant impact of local terrigenic ³He 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
- ²⁰ less. At LIW depths, t_{He} had increased to about 4% due to the EMT-induced upwelling, which also explains the relatively high age of ~ 12yr (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 ³He. The EMT-related Aegean peak outflow was concentrated between roughly
- ²⁵ 600 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 ³He into the EMed at large, while inside the Cretan Sea an elevated $R_{\text{t}}/R_{\text{a}}$ ratio, at most about unity, might be indicated.



In the Tyrrhenian, Lupton et al. (2011) found δ^3 He 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 ³He. 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 ³He) 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 ³He by 0.4 TU compared to using the EMed value of 0.42.

A transition between the Tyrrhenian Sea and the WMed with $t_{\rm He}$ 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, 2011), while the WMed proper was still but moderately affected. Near to the southern Tyrrhenian outlet (the Sardinian Channel), maximum $t_{\rm He}$ 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 %
- ²⁰ 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. It thus 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.

25 7.3 Tritium-³He dating

Tritium-³He ages τ are obtained using Eq. (3) with input from Eq. (2b), with an upper boundary condition of vanishing tritiugenic ³He 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

- ⁵ are from 1976 near to the entrance into the Alboran Sea, and 1977 in the WMDW formation region. Table 3 summarizes the input data (columns (2) and (3)), the resulting terrigenic He, its isotopic ratio, and the resulting tritiugenic ³He and age. Column (8) gives the ratios of stable tritium (tritium + tritiugenic ³He) between (a) the interior location at the time of observation and (b) at the surface in the formation area (Fig. 1, Table
- ¹⁰ 2) τ years back in time. The latter value is often denoted by "initial tritium" since there is no tritiugenic ³He to contribute (r = 0, see above). All ages show a trend of increasing values with 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

- ¹⁵ 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 (~ 1965, Fig. 1), while tritium in the slower travelling parts was still of the lower prepeak 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
- ²⁰ observations (~ 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 components travelling the fastest. 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 the dispersing LIW flow no longer covers 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 ³He forms a maximum in LIW while tritium monotonically declines downward through the LIW layer (see the tracer sections above), any vertical mixing lowers the ³He/tritium ratio, which reduces the age. Also this effect was largest early on when the vertical gradients were the highest and decreased thereafter.

- ⁵ We believe that for the later observations this effect is secondary, considering that vertical mixing is generally rather small. We note that the particularly large age increase in the ESS region between 1995 and 1999 is to be 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 low (Roether et al., 1996).
- ¹⁰ 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 ³He content, which gradually reduces the stable tritium in the interior. An 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, this issue).

Our other example is sections of terrigenic ³He 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^3 He 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^3 He minimum layer 5–8% and the waters further down in the west 4–6%. 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 ³He 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 contri-15 bution to the EMDW, which is 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, τ_{turn} . Fact is that such a turnover time is defined as the 20 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 ³He, the balance at equilibrium is $C_{^{3}\text{He}} \times \Phi = V \times C_{\text{tritium}}/t_{1/e}$, so that the ³He/tritium ratio amounts to $\tau_{\text{turn}}/t_{1/e}$. Converting that into a tritium-³He age (Eq. 3) one finds that the tritium-³He age is far smaller than the turnover time, but related to it in a defined way, i.e. age = $t_{1/e} \times \ln(1 + \tau_{turn}/t_{1/e})$. 25

Both these examples show that the ages need to be interpreted with care. A basic problem is that tritium-³He 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 ³He 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) and thus has extremely low tracer concentrations. Because the tritium-³He ages are biased toward contributions of higher tracer concentration, the ages hardly account for such pre-nuclear contributions.

8 Conclusions

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Apart from characterizing the tritium and ³He distributions over the nuclear era, we show that the available data of δ³He and of He and Ne concentration for the Mediterranean Sea allow one to quantify tritiugenic and terrigenic ³He with a useful precision over the entire water column. This fact depends on the particularly low ³He content of terrigenic He and on tracer concentrations high enough to allow precise measurement. Together with the large number of data available, this makes the Mediterranean unique in allowing application of tritium-³He dating. Applying this tool in the LIW at different locations and repeated in time, we find trends of increasing age with the calendar year of observation, which arise primarily from transit time dispersion of the LIW flow. We deduce average LIW transit times (between 12 and 22 yr) that are compatible

- with other estimates. As a further application we present detailed, quasi-zonal sections through the EMed of tritium-³He age and terrigenic He for 1987. The highest ages in the East Mediterranean Deep Water (EMDW) are approximately 24 yr. That result is
- again due to transit time dispersion, in that 24 yr prior to 1987 points to 1963, close to the surface-water tritium maximum. In other words, these tracer ages characterize the youngest contributions due to the tritium of the nuclear era. Evidently, the information obtained is quite different from the far longer turnover time of this water mass of more than 100 yr as derived previously. Fact is that tritium-³He ages as such account for
- advection only and are biased whenever mixing becomes relevant and, because they place a higher weight on water components of higher tracer concentrations, virtually ignore contributions formed prior to the nuclear era when the concentrations of the two



tracers were extremely low. We find that stable tritium (the sum of tritium and tritiugenic ³He) can serve as a proxy for mixing effects.

From a more general point of view, our analysis offers a transient-tracer data set consisting of tritium and tritiugenic ³He, which are interrelated in the combination as tritium ³He are on the and and an the other set the stable tritium deficit in the

- ⁵ tritium-³He age on the one hand, and on the other as the stable tritium deficit in the interior relative to the tritium concentration at the surface when that water was sub-ducted; a by-product is terrigenic He. A promising approach will be the combination with other tracer data such as the chlorofluorocarbons 11 and 12, for which a similarly large data base exists, and sulfur hexafluoride, which is available from *Meteor* cruise
- ¹⁰ M84/3 in 2011. An approach using the concept of transit time distribution (TTD; e.g. Huhn et al., 2008) could account for mixing and can be extended back in time to cover water contributions of pre-nuclear tracer concentrations. Another promising approach would be to interpret the tracer data by OGCM simulation. A special challenge will be to deal with the fundamental changes in the deep and intermediate waters caused by the Last 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.

By now, the Med's subsurface tritium concentrations range between 0.4 and 0.7 TU (Fig. 5), so that the ³He ingrowth over the next 10 years will amount to 0.2 to 0.3 TU, or to only 1 to 1.5 % in δ^3 He. The current δ^3 He values range between 4 and 8 % except for still lower concentrations in the top ~ 1500 m in the eastern Levantine (Fig. 9). Evidently the 10 yr ingrowth is mostly smaller than the current concentrations of tritiugenic ³He. Therefore, a new tracer survey around the year 2020 should be very useful. It would

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- specifically serve to demonstrate the further westward transfer of the Med's subsurface
- ²⁵ cloud of ³He generated in consequence of the nuclear weapon testing, which currently is already apparent in the Levantine Sea (Fig. 9) and in LIW generally. This would allow one to deduce the time scales of the westward transfer, including the loss into Atlantic by the Strait of Gibraltar outflow.



Acknowledgement. We thank Toste Tanhua, Kiel, for organizing the 2011 *Meteor* cruise and supporting our participation; E. Hümpel, Kiel, took the helium and tritium samples. Figs. 2, 3 and 7 were contributed by B. Klein, Hamburg. All *Meteor* cruises that delivered data for the present work and the M84/3 tracer measurement carried out at Bremen were funded by the

⁵ Deutsche Forschungsgemeinschaft, Bonn–Bad Godesberg, Germany. We are grateful to the masters and crew of the various cruises and to the people that helped to produce the data set used in this work.

References

10

20

Andrie, C. and Merlivat, L.: Tritium in the western Mediterranean during the 1981 *Phycemed* cruise, Deep-Sea Res. Pt. I, 35, 247–267, 1988.

- Benson, B. B. and Krause, D.: Isotopic fractionation of helium during solution: a probe for the liquid state, J. Solut. Chem., 9, 895–909, 1980.
- Charlou, J. L., Donval, J. P., Roy, N., Jean-Baptiste, P., Foucher, J. P., Woodside, J., and the MEDINAUT Scientific Party: Evidence of methane venting and geochemistry of brines as-
- sociated with mud volcanoes of the eastern Mediterranean sea (MEDINAUT diving cruise, 1998), Deep-Sea Res. Pt. I, 50, 941–958, 2003.
 - Clarke, W. B., Jenkins, W. J., and Top, Z.: Determination of tritium by mass spectrometric measurement of ³He, Int. J. Appl. Radiat. Isotopes, 27, 515–522, 1976.

Cortecci, G., Noto, P., and Tonarelli, B.: Tritium and oxygen profiles in the eastern Mediterranean, Tellus 31, 179–183, 1979.

Dreisigacker, E. and Roether, W.: Tritium and 90-strontium in North Atlantic surface water, Earth Planet. Sci. Lett., 38, 301–312, 1978.

Gačić, M., Schroeder, K., Civitarese, G., Cosoli, S., Vetrano, A., and Eusebi Borzelli, G. L.: Salinity in the Sicily Channel corroborates the role of the Adriatic-Ionian Bimodal Oscillating

- ²⁵ System (BiOS) in shaping the decadal variability of the Mediterranean overturning circulation, Ocean Sci., 9, 83–90, doi:10.5194/os-9-83-2013, 2013.
 - Gasparini, G. P., Ortona, A., Budillon, B., Astraldi, M., and Sansone, E.: The effect of the Eastern Mediterranean Transient on the hydrographic characteristics in the Strait of Sicily and in the Tyrrhenian Sea, Deep-Sea Res. Pt. I, 52, 915–935, 2005.



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Huhn, O., Roether, W., and Steinfeldt, R.: Age spectra in North Atlantic Deep Water along the South American continental slope, 10° N–30° S, based on tracer observations, Deep-Sea Res. Pt. I, 55, 1252–1276, doi:10.1016/j.dsr.2008.05.016, 2008.

Jean-Baptiste, P., Mantisi, F., Dapoigny, A., and Stievenard, M.: Design and performance of

- a mass spectrometric facility for measuring helium isotopes in natural waters and for low-levle tritium determination by the ³He ingrowth method, Appl. Radiat. Isot., 43, 881–891, 1992.
 - Klein, B., Roether, W., Manca, B., Bregant, D., Beitzel, V., Kovacevic, V., and Luchetta, A.: The large deep water transient in the Eastern Mediterranean, Deep-Sea Res. Pt. I, 46, 371–414, 1999.
 - Lucas, L. L. and Unterweger, M. P.: Comprehensive review and critical evaluation of the half-life of tritium, J. Res. Natl. Inst. Stand. Tech., 105, 541–549, 2000.

10

25

30

- Lupton, J., de Ronde, C., Spovieri, M., Baker, E. T., Bruno, P. P., Italiano, F., Walker, S., Faure, K., Leybourne, M., Britten, K., and Greene, R.: Active hydrothermal discharge on the
- ¹⁵ submarine Aeolian Arc, J. Geophys, Res., 116, B02102, doi:10.1029/2010JB007738, 2011.
 Millot, C.: Circulation in the Western Mediterranean Sea, J. Mar. Systems, 20, 423–442, 1999.
 Millot, C. and Taupier-Letage, I.: Circulation in the Mediterranean Sea, in: The Handbook of Environmental Chemistry, vol. 5, Part K, edited by: Saliot, A., Springer-Verlag, New York, 29–66, doi:10.1007/b107143, 2005.
- Morelli, C.: Geophysical contribution to knowledge of the Mediterranean crust, in: Geological Evolution of the Mediterranean Basin, edited by: Stanley, D. J. and Wenzel, F.-C., Springer Verlag, New York, 65–82, 1985.
 - Östlund, H. G.: Expedition Odysseus: Tritium and Radiocarbon in the Mediterranean and Black Seas, Report ML 69167, Inst. of Marine and Atmosph. Sciences, University of Miami, Miami, 1969.
 - Rhein, M., Send, U., Klein, B., and Krahmann, G.: Interbasin deep water exchange in the western Mediterranean, J. Geophys. Res., 104, 23495–24508, 1999.
 - Roether, W. and Lupton, J. E.: Tracers confirm downward mixing of Tyrrhenian Sea upper waters associated with the Eastern Mediterranean Transient, Ocean Sci., 7, 91–99, doi:10.5194/os-7-91-2011, 2011.
 - Roether, W. and Schlitzer, R.: Eastern Mediterranean deep water renewal on the basis of chlorofluoromethane and tritium data, Dynam. Atm. Oceans, 15, 333–354, 1991.

Discussion Pape OSD 10, 649-690, 2013 Tritium and ³He in the Mediterranean Sea W. Roether et al. Paper **Title Page** Introduction Abstract Conclusions References Discussion Paper Tables Figures Back Close Discussion Full Screen / Esc Printer-friendly Version Pape Interactive Discussion



- Roether, W. and Weiss, W.: Die groß-skalige thermohaline Zirkulation des Mittelmeers, Annal. Meteorol. (Neue Folge), 15, 135–137, 1980.
- Roether, W. and Well, R.: Oxygen consumption in the Eastern Mediterranean, Deep-Sea Res. Pt. I, 48, 1535–1551, 2001.
- ⁵ Roether, W., Schlosser, P., Kuntz, R., and Weiss, W.: Transient-tracer studies of the thermohaline circulation of the Mediterranean, in: Winds and Currents of the Mediterranean Basin, Proc. NATO workshop "Atmospheric and Oceanic Circulations in the Mediterranean Basin", 7–14 September 1983, Santa Teresa, Italy, edited by: Charnock, H., Harvard University, Cambridge MA, Vol. II, 291–317, 1992.
- Roether, W., Roussenov, V., and Well, R.: A tracer study of the thermohaline circulation of the Eastern Mediterranean, in: Ocean Processes in Climate Dynamics: Global and Mediterranean Examples, edited by: Malanotte-Rizzoli, P. and Robinson, A. R., Kluwer Academic Publishers, Dordrecht, 371–394, 1994.

Roether, W., Manca, B. B., Klein, B., Bregant, D., Georgopoulos, D., Beitzel, V., Kovacevich, V.,

- and Lucchetta, A.: Recent changes in Eastern Mediterranean deep waters, Science, 271, 333–335, 1996.
 - Roether, W., Well, R., Putzka, A., and Rüth, C.: Component separation of oceanic helium, J. Geophys. Res., 103, 27931–27946, 1998a.

Roether, W., Klein, B., Beitzel, V., and Manca, B. B.: Property distributions and transient-tracer

- ²⁰ ages in Levantine Intermediate Water in the Eastern Mediterranean, J. Marine Systems, 18, 71–87, 1998b.
 - Roether, W., Beitzel, V., Sültenfuß, J., and Putzka, A.: The Eastern Mediterranean tritium distribution in 1987, J. Marine Systems, 20, 49–61, 1999.

Roether, W., Well, R., Putzka, A., and Rüth, C.: Correction to "Component separation of oceanic helium", J. Geophys. Res., 106, 4679, 2001.

25

- Roether, W., Klein, B., Manca, B. B., Theocharis, A., and Kioroglou, S.: Transient Eastern Mediterranean deep waters in response to the massive dense-water output of the Aegean Sea in the 1990s, Prog. Oceanogr., 74, 540–571, doi:10.1016/j.pocean.2007.03.001, 2007.
- Schlitzer, R., Roether, W., Hausmann, M., Junghans, H. G., Oster, H., Johannsen, H., and Michelato, A.: Chlorofluoromethane and oxygen in the Eastern Mediterraniean, Deep-Sea
- ³⁰ Michelato, A.: Chlorofluoromethane and oxygen in the Eastern Mediterraniean, Deep-Res. Pt. I, 38, 1531–1551, 1991.
 - Schroeder, K., Josey, S. A., Herrmann, M., Grignon, L., Gasparini, G. P., and Bryden, H. L.: Abrupt warming and salting of the Western Mediterranean Deep Water af-

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ter 2005: atmospheric forcings and lateral advection, J. Geophys. Res., 115, C08029, doi:10.1029/2009JC005749, 2010.

- Sültenfuß, J., Roether, W., and Rhein, M.: The Bremen mass spectrometric facility for the measurement of helium isotopes, neon, and tritium in water, Isotopes Environ. Health Stud., 45,
- ⁵ 83–95, doi:10.1080/10256010902871929, 2009.
 - Weiss, R. F.: The solubility of helium and neon in water and seawater, J. Chem. Engin. Data, 16, 235–241, 1971.

- ¹⁰ Weiss, W., Roether, W., and Bader, G.: Determination of blanks in low-level tritium measurement, Int. J. Appl. Radiat. Isotopes, 27, 217–225, 1976.
 - Well, R. and Roether, W.: Neon in South Atlantic and South Pacific waters, Deep-Sea Res. Pt. I, 50, 721–735, 2003.

Winckler, G., Suess, E., Wallmann, K., De Lange, G. T., Westbrook, G. K., and Bayer R.: Excess

- helium and argon of radiogenic origin in the Mediterranean brine basins, Earth Planet. Sci. Lett., 151, 225–231, 1997.
 - Wüst, G.: On the vertical circulation of the Mediterranean Sea, J. Geophys. Res., 66, 3261–3271, 1961.

Weiss, W. and Roether, W.: The rates of tritium input to the world oceans, Earth Planet. Sci. Lett., 49, 435–446, 1980.

Cruise or Project	Dates	Area	Reference	
Exped. Odysseus 65 ^a	Aug + Oct 1965	WMed, Tyrrhenian, Aegean	Östlund (1969)	
<i>Origny</i> 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 [°]	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 ⁹	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	

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

^a 4 stations, near-surface tritium only.

- ^b 2 stations. ^c Tritium only.
- ^d Few stations few ³He data. ^e Repeated tritium, few ³He data.
- ^f Tritium only.
- ^{g 3}He only.



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 1971–72, 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		
1971–72			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.



Table 3. Tritium-³He ages (yr) in LIW at various locations in different years. The tritium and δ^3 He 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^3 He (%)	Terrig. He (%)	$R_{\rm t}/R_{\rm a}$	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 <i>Poseid.</i> 234, Sta 764	1.2	7.8	3.6	1	2.5	19	0.49
WMed 1976 ^b <i>Knorr</i> 54/5 Sta. 727	2.1	3.8	1.7	0.42	1.5	9.5	0.34
WMed, 1977 ^c <i>Bohra</i> -2	3.1	5.5	1.7	0.42	1.8	8.0	0.41
WMed 1983 ^d Phycemed Sta SBS	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^3 He and tritium: Roether and Weiss 1980, columns (4) and (5) = 1997 values.

^c 42° N 4° 45′ E. 30 March and 3 April 1977: δ³He: 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.





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). For data sources, see Table 1, year marks are 1 January. Typically averages of 3 stations are shown. 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 be around 20 %, and that of the pre-nuclear value of 1952 is probably still somewhat larger. For reference, tritium decay is shown by the dashed line. The inset shows the tritium concentration above the natural background (~ 0.3 TU) integrated in time, normalized to unity in 2011 (the 2011 value is 376 TU yr); the 50 % mark is reached in 1970 and the mean concentration during the period was 6.4 TU (376 TU yr/59 yr), about 20 times the natural one.





Fig. 2. Tritium sections (TU) of the *Meteor* cruises in 1987, 1995, 1999 and 2001 (cf. Table 1; for concentrations see color 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.



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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.





Fig. 6. Tritium profiles in 1971–72, 1981 and 1997 in the WMed, for positions see inset map.











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





Fig. 9. δ^3 He sections (%) of *Meteor* M84/3, 2011, left WMed, right EMed. Numbers on top are station numbers, sections cf. inset maps.





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





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

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