

Carbon isotope measurements reveal unexpected cycling of dissolved organic matter in the deep Mediterranean Sea



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ABSTRACT

One of the most intriguing aspects of dissolved organic carbon (DOC) dynamics in the Mediterranean Sea (Med Sea) is that in the intermediate and deep waters, DOC concentrations are equal to the lowest values found in the deep Atlantic and Pacific (36–42 μM). The very low DOC values in the deep Med Sea were unexpected since the renewal time of deep waters in the basin is only 20–126 years. Over this short timescale, we expected just a very small, nearly undetectable, fraction of refractory DOC (RDOC) to be removed. The first DOC isotope data show that DOC in Med Sea deep water is more depleted in both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ than in the deep Atlantic Ocean, with an estimated age of 4500–5100 years. These data suggest that at least 10%, and up to 45%, of the Atlantic RDOC entering the Med Sea is removed and replaced by isotopically lighter DOC in less than 126 years. Potential allochthonous sources include: fossil methane and methane derived DOC seeps from sediments, anthropogenic combustion products and terrestrial organic matter delivered by the atmosphere, rivers, and groundwaters. Using current information, it is not possible to quantify the relative contribution of these potential sources. Based on estimated flux and isotopic value, atmospheric input of soluble organic carbon from soils or combustion products as well as DOC from groundwater are the most likely sources of allochthonous DOC. Our results suggest that DOC cycling in the deep Med Sea is dynamic and support the idea that a substantial fraction (up to 45%) of what has traditionally been defined as “refractory” DOC imported from the Atlantic Ocean, can be removed on temporal scales of <126 y, thereby opening intriguing questions about deep sea DOC cycling.

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1. Introduction

In the global ocean, dissolved organic carbon (DOC) concentrations range between 34 μM in the deep North Pacific and ~80 μM in oligotrophic surface waters of mid ocean gyres. DOC concentrations are generally high in the surface layer, where most of the production processes occur, undergo a marked reduction in the mesopelagic layer, due to net microbial mineralization, and have low values in the deep ocean (>1000 m). The fraction of deep ocean DOC remaining when concentrations reach values <42 μM , is considered “refractory” (RDOC), indicating little potential for additional removal by microbial respiration on short time scales (lifetime of ~16,000 years; Hansell, 2013). DOC stable carbon isotopes values ($\text{DOC}\delta^{13}\text{C}$) are ~–21‰ to –22‰ throughout the whole water column, indicating an autochthonous microbial source for most marine DOC (Druffel et al., 1992). DOC concentrations decrease along the pathway of abyssal circulation, from ~48 μM in the deep North

Atlantic (Carlson et al., 2010), to ~40 μM in the Southern Ocean (Hansell and Carlson, 2013) and ~34–38 μM in the deep North Pacific (Hansell and Carlson, 1998, 2013). The decrease in DOC concentration along the trajectory of abyssal circulation suggests slow, continuous removal of RDOC in the deep ocean, of the order ~3 nM C y^{-1} (Hansell, 2013). However, looking at the deep RDOC distribution more in detail, it appears that the removal of RDOC may not be a continuous process. Localized sinks for RDOC have been proposed in the deep, far North Pacific and at mid depth in the subtropical South Pacific, while localized sources may be present in the Indian Ocean, the Arabian Sea (Hansell and Carlson, 1998) and at the Equator (Hansell and Carlson, 2013).

Radiocarbon measurements support the concept of a very old pool of DOC in the deep ocean. Radiocarbon values for RDOC are highly depleted (~–400 to –530‰), compared to DIC (–80 to –230‰), indicating that RDOC is markedly older than DIC (4000–6000 vs. 100–1000 y). RDOC becomes further depleted in $\Delta^{14}\text{C}$ as water ages and moves from the deep North Atlantic (~–390‰) to the North Pacific (–530‰), in good agreement with the depletion in $\text{DIC}\Delta^{14}\text{C}$ (from –80 to –230‰) (Druffel et al., 1992). Due to its long apparent residence time in the ocean, RDOC should be well mixed throughout the water column.

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In surface waters of the N. Atlantic, $\text{DOC}\Delta^{14}\text{C}$ is strongly depleted relative to $\text{DIC}\Delta^{14}\text{C}$ (Druffel et al., 1992). The $\text{DOC}\Delta^{14}\text{C}$ depth profile, with $\sim 70\text{--}80\ \mu\text{M}$ DOC of $\Delta^{14}\text{C} - 230\text{‰}$ in surface water and $\sim 40\ \mu\text{M}$ DOC of $\Delta^{14}\text{C} \sim -390\text{‰}$ in deep water, is therefore well described by a two-component model (TCM) of $36\text{--}42\ \mu\text{M}$ RDOC ($\sim -390\text{‰}$) mixed throughout the entire water column, and a second, semi-labile component (SLDOC) with a modern radiocarbon age that is cycled within the upper ocean ($< 1000\ \text{m}$) (Williams and Druffel, 1987).

Recently, Follett et al. (2014) proposed that the TCM is not adequate to fully describe the complexity and richness of marine DOC cycle. Follett et al. (2014) used stepwise oxidation of DOC to estimate the isotopic distribution of components within DOC in order to uncover carbon fluxes that may be obscured by the TCM. Their results suggest that a significant fraction of deep DOC is modern and supported by a $1\ \text{Pg}\cdot\text{y}^{-1}$ carbon flux from sinking particles. These results open new and intriguing hypothesis about DOC cycle.

The Mediterranean Sea (Med Sea) is a natural laboratory where these hypotheses may be tested. The major physical processes occurring in the oceans (i.e.: thermohaline circulation, deep water formation, seasonal cycle of stratification, intense meso and sub-mesoscale activity) all occur within the basin and Med Sea DOC concentrations and vertical profiles are similar to the oceanic ones (Santinelli, 2015). It is important to remember that the Med Sea is a small semi-enclosed basin characterized by low primary production (Lazzari et al., 2012) and low sinking particle fluxes; only $\sim 10\%$ of open ocean values (Speicher et al., 2006). It is ultra-oligotrophic and shows an anomalous N/P ratio (N:P > 25 in the eastern Med Sea; N:P ~ 20 in the western Med Sea; Krom et al., 2005; Ribera d'Alcalà et al., 2003). Its deep waters are $\sim 10\ ^\circ\text{C}$ warmer than deep waters in the ocean and they are characterized by (i) fast ventilation rates and short residence times; (ii) enhanced respiration (Christensen et al., 1989) and DOC mineralization rates (Santinelli et al., 2010). The Med Sea thermohaline circulation is driven by the inflow of the Atlantic Water (AW) at the Gibraltar strait. The AW increases its salinity during its west to east transit through the basin, as a result of intense evaporation that is characteristic of the region. Due to its increased salinity, AW sinks in the Levantine Basin forming the Levantine Intermediate Water (LIW). LIW crosses the entire basin at $200\text{--}500\ \text{m}$ moving from east to west and finally exits through the Gibraltar Strait at depths $> 100\ \text{m}$. Deep water formation occurs every winter in both the western (West Med) and eastern (East Med) basins by a mechanism analogous to the polar Atlantic deep convection.

An intriguing observation is that in the intermediate and deep waters of the Med Sea, DOC concentrations are equal to the lowest values found in the deep Atlantic and Pacific ($36\text{--}42\ \mu\text{M}$; Santinelli, 2015 and literature therein). The lowest DOC values in the deep Med Sea ($\sim 36\ \mu\text{M}$) are unexpected since the renewal time of deep waters in the basin is only $20\text{--}126$ years (Andrie and Merlivat, 1988; Schlitzer et al., 1991). Applying removal rates of RDOM characteristic of the deep global ocean ($\sim 3\ \text{nM}\ \text{y}^{-1}$; Hansell, 2013), we expected that just a very small ($\sim 0.06\text{--}0.38\ \mu\text{M}$), nearly undetectable fraction of RDOC should be removed over the residence time of deep water in the basin. The Med Sea is a concentration basin (evaporation is higher than the input of freshwater) with significant influxes of terrestrial carbon from Europe and North Africa. As a consequence, the concentration of DOC in the deep Med Sea should be slightly higher than in the deep Atlantic Ocean ($\sim 42\ \mu\text{M}$). The surprisingly low DOC concentrations measured in the intermediate and deep waters can be explained by different hypothesis:

- 1) The processes that remove RDOC are much faster in the deep Med Sea than in the deep ocean, as suggested by Hansell and Carlson (2013). The net removal of $\sim 8\ \mu\text{M}$ RDOC takes less than 126 years in the Med Sea compared to ~ 1000 years in the deep ocean. Faster rates of RDOC removal could be explained by (i) the higher ($\sim 13\text{--}14\ ^\circ\text{C}$) temperature, characteristic of the deep Med Sea; (ii) different communities of RDOC-degrading microbes; and/or (iii) priming of

bathypelagic RDOC-degrading microbes by the input of labile DOC to depth after wintertime deep mixing events. The faster removal of RDOC should not affect its radiocarbon value, we therefore expect radiocarbon values to be similar for DOC in the deep Med Sea and deep Atlantic Ocean.

- 2) The concentration of RDOC is $< 36\ \mu\text{M}$ in both the oceans and the Med Sea, but deep Atlantic oceanic DOC values are elevated due to the input of semi-labile DOC (SLDOC) from sinking particles (Follett et al., 2014). Here we define SLDOC as any carbon that accumulates in the ocean but is removed on timescales of decades or less. Our definition does not distinguish between carbon removed on seasonal and decadal timescales, and includes the semi-labile (seasonal removal) and semi-refractory (decadal removal) DOC as defined by Hansell (2013). In this scenario, a fraction of deep DOC that has been traditionally defined as RDOC ($< 42\ \mu\text{M}$; lifetime of $\sim 16,000\ \text{y}$) is not refractory with respect to the timescale of its removal, but is semi-labile, and in steady-state through supply by dissolution of sinking particles and removal by as yet unquantified processes, but most likely through microbial oxidation. The generally lower fluxes of sinking particles characteristic of the Med Sea (Speicher et al., 2006) would reduce the supply of SLDOC to depth, resulting in lower steady state concentrations of DOC. A reduction in the supply of autochthonous, surface derived, semi-labile, modern radiocarbon fraction from deep DOC will lower the radiocarbon value of the remaining organic matter. We therefore expect radiocarbon values to be more depleted (older age) in the deep Med Sea than in the deep Atlantic Ocean.

These two hypotheses represent different scenarios for deep sea DOC cycling that are not easily tested in the global ocean. The hypotheses are not mutually exclusive, and higher degradation rates for RDOC could be made more visible by lower supply of SLDOC at depth. Here we present the first stable and radioisotope data for DOC in the West Med, these data will help elucidate sources, sinks and cycling pathways for DOC in the deep ocean.

2. Materials and methods

2.1. Study area and sampling stations

Seawater samples for DOC, $\text{DOC}\Delta^{14}\text{C}$ and $\text{DOC}\delta^{13}\text{C}$ were collected in three stations located in the Tyrrhenian Sea (St. A), Sardinian Channel (St. B) and Sardinian Sea (St. C) during the oceanographic cruise WMED-BIOOPT 2012, carried out on the R/V Urania, from March 22nd to April 10th 2012 (Fig. 1, Table 1). Samples for $\text{DIC}\Delta^{14}\text{C}$ were collected in the Tyrrhenian Sea during the oceanographic cruise WMED-BIOOPT 2013, carried out on the R/V Minerva I, April 14th 2013 (Fig. 1, Table 3). Pressure, conductivity, temperature and dissolved oxygen concentration were measured with a SBE 911 plus CTD, equipped with a rosette sampler fitted with 10 l Niskin bottles. CTD-oxygen was calibrated by Winkler titration of select discrete samples. CTD data were kindly provided by the Rome section of the Institute of Atmospheric Sciences and Climate (ISAC), Italian National Research Council (CNR) (Dr. R. Santoleri and Dr. F. Bignami).

2.2. Sample collection and storage

2.2.1. DOC

DOC samples were collected at 5, 10, 25, 50, 75, 100, 150, 200, 300, 400, 500 m and every 250 m from 500 m to the bottom. Water was collected directly from the Niskin bottles into amber glass sample bottles that were preconditioned with filtered open-sea deep water and rinsed three times with the sample before its collection. Samples were immediately filtered through sterile $0.2\ \mu\text{m}$ nylon membrane filters (Minisart Nylon 25 mm, 17,845 ACK) under low pressure by high-purity air. The first $\sim 200\ \text{ml}$ of the filtrate was discarded. Filtered samples were stored

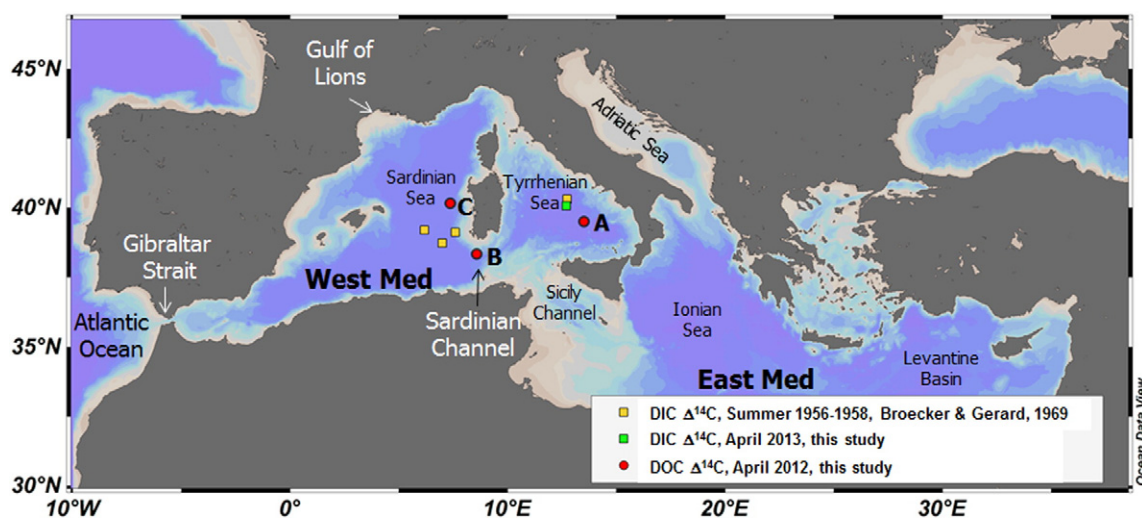


Fig. 1. Study area and sampling stations. The position of the stations reported in Broecker and Gerard (1969) is also indicated (yellow squares).

at 4 °C in the dark until analysis (within 3 months). DOC was also measured directly from the samples used for radiocarbon analysis.

2.2.2. $DOC\Delta^{14}C$ and $DOC\delta^{13}C$

All radio and stable isotope samples were collected and processed using protocols recommended by the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility in Woods Hole, MA. The protocols were developed to minimize the potential for contamination by radiocarbon used in shipboard ^{14}C tracer measurements. No contamination of shipboard work areas or Niskin sampling bottles was detected by swipe test. Samples were returned to Woods Hole for processing in a radiocarbon clean facility.

$DOC\Delta^{14}C/\delta^{13}C$ samples were collected in new, 2–10 l polycarbonate bottles cleaned by soaking in 10% bleach (1 week) and 1% HCl (>1 week) followed by >5 rinses with high purity (>18 M Ω) water. Samples were drawn directly from the Niskin bottles and filtered in-line through Whatman Polycap 36 TC capsule filters (0.2 μ m, cleaned by soaking in 1% HCl overnight, followed by 5 l high purity water rinse and 1 l sample rinse). Samples were capped, triple-bagged and frozen immediately after collection.

2.2.3. $DIC\Delta^{14}C$

Samples for dissolved inorganic carbon were collected in 500 ml glass bottles supplied by NOSAMS. Bottles were filled to overflow directly from the Niskin bottles. A small amount of the sample was removed, the bottle was poisoned with 100 μ l of a saturated solution of HgCl₂, sealed, and stored in the dark at room temperature. Further processing was done at NOSAMS using established protocols (McNichol et al., 1994).

2.3. Sample measurement

2.3.1. DOC

The DOC measurements were carried out in the laboratory at the Pisa section of the Institute of Biophysics (IBF), CNR, with a Shimadzu TOC-VCSN, equipped with a quartz combustion column filled with 1.2% Pt on alumina pillows of ~2 mm diameter. Samples were acidified with 2 N high purity HCl and sparged for 3 min with CO₂-free ultra-high purity air in order to remove inorganic carbon. 150 μ l of the sample were injected in the furnace after a three-fold rinsing with the sample to be analyzed. From 3 to 5 replicate injections were performed until the analytical precision was lower than 1%. A four-point calibration curve was done with standard solutions of potassium hydrogen phthalate in the same concentration range as the samples. The system blank was measured every day at the beginning and the end of analyses using low-carbon water (2–3 μ M C) produced by a Milli-Q system. Measurement reliability was assessed twice daily by comparison of data with DOC Consensus Reference Waters (CRM) (Hansell, 2005) (batch #12, measured concentration: 41.7 ± 1.2 μ M, standard error 0.10 μ M, n = 28). This quality assurance procedure ensures the integrity of the calibration curve (Sharp et al., 2002).

2.3.2. $DOC\Delta^{14}C$ and $DOC\delta^{13}C$

Samples for $DOC\Delta^{14}C/\delta^{13}C$ were processed at NOSAMS using protocols detailed in Beupr e et al. (2007). Briefly, approximately 1 l of sample was transferred to an all-quartz reaction flask and acidified to pH ~2 with high purity phosphoric acid. The flask was placed in a gas extraction apparatus and sparged with helium to remove carbon dioxide. DOC was oxidized by UV irradiation, and the resulting carbon

Table 1
Site information for the three DOC stations and physical chemical characteristics at the sampling depths.

Station	Latitude °N	Longitude °E	Date	Bottom depth (m)	Area	Sampling depth (m)	Pot temp (°C)	Salinity	σ_θ (Kg m ⁻³)	DO (μ M)	AOU (μ M)
A	38.50	13.50	Apr-7-2012	3440	Tyrrhenian Sea	2	16.79	37.90	27.79	244.7	–
						1500	13.20	38.55	29.11	186.5	71.2
						2500	13.04	38.51	29.10	188.0	70.6
						3429	12.99	38.49	29.10	188.5	70.4
B	38.33	8.57	Apr-1-2012	1894	Sardinian Channel	2	16.57	37.02	27.17	248.7	–
						480 (LIW)	13.84	38.70	29.08	177.9	76.2
						1851	12.89	38.47	29.11	197.2	62.2
C	40.16	7.36	Apr-4-2012	2702	Sardinian Sea	2	16.01	37.84	27.93	249.7	–
						1500	12.89	38.46	29.10	193.7	65.8
						2680	12.89	38.47	29.11	196.7	62.8

dioxide stripped with a helium sparge and cryogenically trapped. Further details are provided on the NOSAMS website at http://www.who.edu/nosams/Submitting_Guidelines.

3. Results

3.1. Hydrologic characteristics

Potential temperature/salinity (θ/S) diagrams allow for the identification of the major water masses occurring in the study area: Atlantic Water (AW), Levantine Intermediate Water (LIW), Western Mediterranean Deep Water (WMDW) and Tyrrhenian Deep Water (TDW) (Fig. 2). The AW ($S < 37.2$, $\theta = 15.0$ – 16.5 °C), occupies the surface layer of station B, the marked increase in S at stations A and C ($S = 37.9$ – 38.1) indicates

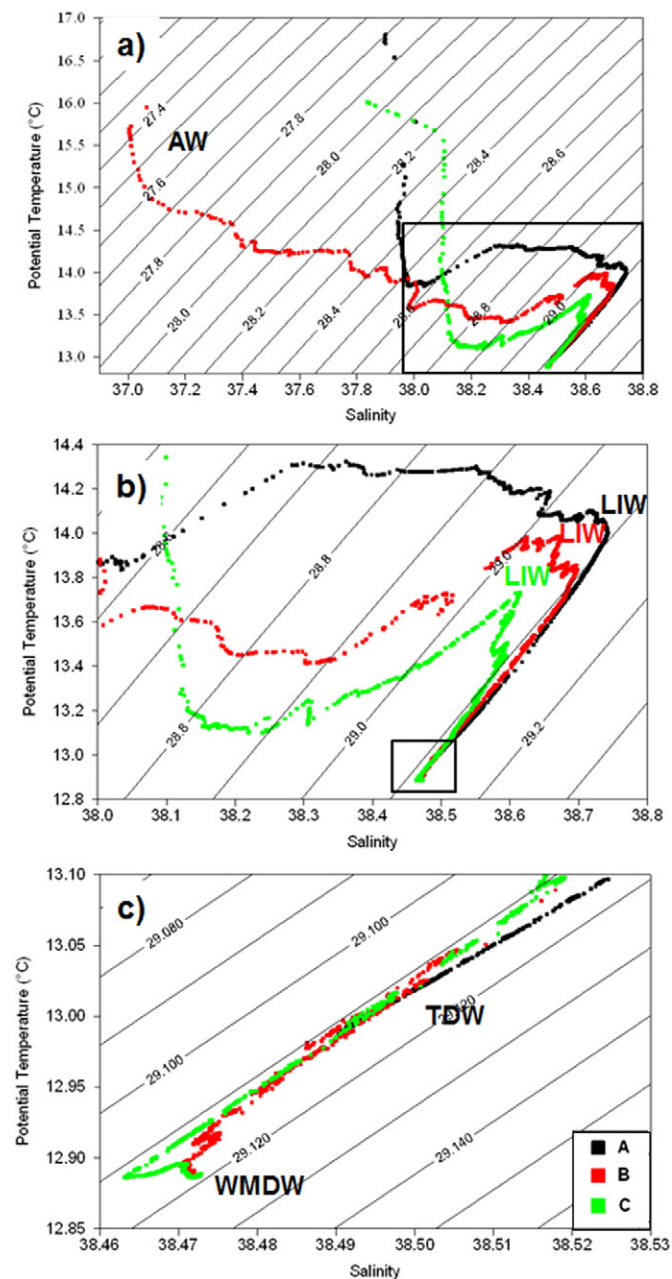


Fig. 2. Potential temperature/Salinity (θ/S) diagrams for the DOC sampling stations. The Levantine Intermediate Water (LIW, maximum of salinity) is clearly visible at the three stations. AW: Atlantic Water; WMDW: Western Mediterranean Deep Water; TDW: Tyrrhenian Deep Water. The black rectangles indicate the area that is enlarged and referred to in the subsequent plots for intermediate (b) and deep (c) water.

that these stations are affected by a modified vein of AW, probably coming from the East Med. The thermocline is not very strong, with surface temperatures (0–10 m) between 15.0–16.8 °C at all three stations (Figs. 2a and 3).

The LIW is easily recognizable by its salinity maximum (38.6–38.74). Its core becomes more mixed (less salty and colder) moving from station A (330–600 m; $S = 38.70$ – 38.74 , $\theta = 13.9$ – 14.1 °C) to station B (280–600 m; $S = 38.65$ – 38.70 , $\theta = 13.7$ – 14.0 °C) and station C (250–600 m, $S = 38.55$ – 38.61 , $\theta = 13.25$ – 13.73 °C), where it is still visible (Figs. 2b and 3). The vertical profiles of oxygen clearly show a minimum (< 183 μM) in the core of LIW (200–500 m), with ~ 10 μM decrease moving from station A to C (Fig. 3).

The WMDW ($S \sim 38.47$; $\theta = 12.89$ – 12.92 °C; $\text{DO} = 194$ – 198 μM) can be observed at stations B and C (Figs. 2c and 3). This water mass forms during intense, wintertime cooling events in the Gulf of Lions and spreads throughout the deep western basin. At both stations a very dense ($\sigma_\theta > 29.11$ Kg m^{-3}), salty ($S > 38.47$) tongue of WMDW is clearly visible. WMDW is slightly warmer at station B (Fig. 2c). This water mass is most likely the residual of the “anomalous” deep water formation event in 2005–2006 (López-Jurado et al., 2005; Schroeder et al., 2006). Changes in the physical properties of the WMDW were related either to the severity of weather conditions at the time of formation in winter 2004/2005 or to the transfer of the Eastern Mediterranean Transient (EMT) (Malanotte-Rizzoli et al., 1999; Roether et al., 1996) signal to the West Med (López-Jurado et al., 2005; Schroeder et al., 2006). At station A, deep water is warmer (12.99– 13.04 °C), saltier (38.49– 38.51) and lower in oxygen (186– 188 μM) than the WMDW (Figs. 2c and 3). These characteristics are typical of the TDW, formed by the mixing between the LIW and the WMDW. The very low oxygen values indicate the absence of recently ventilated deep water in the Tyrrhenian Sea (Fig. 3).

Apparent Oxygen Utilization (AOU) values (Table 1) are in the range of those reported for the TDW (57– 71 μM) and the WMDW (52– 73 μM) in 2008 (Santinelli et al., 2010), while they are higher than those observed in the WMDW in 2005 (43– 56 μM), confirming the exceptional characteristics of the WMDW formed in winter 2005 and the removal of oxygen with time due to the mixing with the resident waters and the microbial respiration.

3.2. DOC vertical profiles

DOC vertical profiles show the classical shape with the highest concentrations in the surface water (60– 65 μM), similar to values in the North Atlantic subtropical gyre, and a gradual decrease to 39– 40 μM at ~ 500 m. Below 500 m, the values remain very low (38– 42 μM) until the bottom (Table 2 and Fig. 4). DOC concentration and vertical distribution is in agreement with the data reported for the Tyrrhenian Sea (Santinelli et al., 2013) and the West Med (Santinelli et al., 2010).

Focusing on the deep water, it is noteworthy that DOC concentrations are the same as those reported in 2008 in the region, but they are markedly lower than those observed in 2005 in the WMDW (56 ± 9 μM , Santinelli et al., 2010). The 14 μM (56– 42 μM) decrease is in agreement with the AOU increase and suggests that a fraction of DOC, exported to depth during the exceptional event of deep water formation in winter 2005, was removed on the short temporal scale.

3.3. Carbon isotopes

Samples for radiocarbon measurements were collected in the surface layer (2 m), in the core of LIW (480 m, maximum of S) at station B, in the WMDW (the deepest samples at stations B and C), in the TDW (the deepest sample at station A), and at intermediate depths (1500 m at stations A and C; 2500 m at station A) (Table 1).

In the surface layer, $\text{DOC}\Delta^{14}\text{C}$ ranges between -237 to -286 ‰, suggesting a radiocarbon age of 2120–2640 years. $\text{DOC}\delta^{13}\text{C}$ values range from -21.9 to -22.7 ‰ (Table 2 and Fig. 4). Just one sample

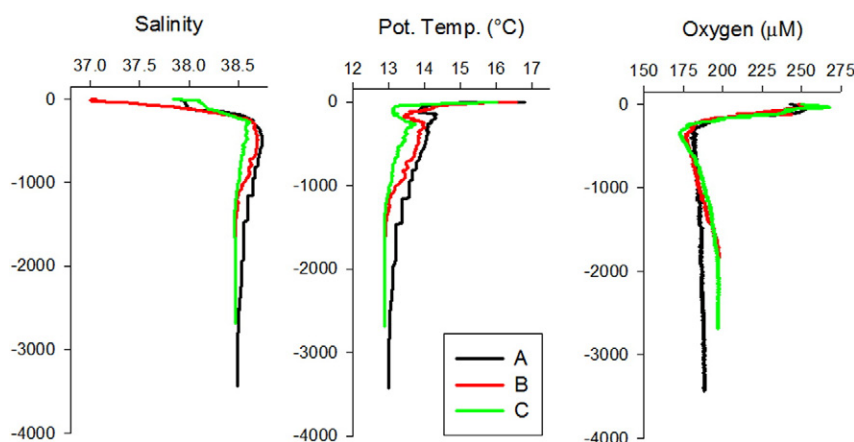


Fig. 3. Vertical profiles of salinity, potential temperature and oxygen at the three stations.

was collected in the LIW with $\text{DOC}\Delta^{14}\text{C}$ of -425‰ and $\text{DOC}\delta^{13}\text{C}$ of -22.8‰ , indicating the presence of DOC that is older than in the surface layer, but younger than in the deep waters (Table 2 and Fig. 4). $\text{DOC}\Delta^{14}\text{C}$ in the deep waters (1500–bottom) have values between -445 to -475‰ , indicating a radiocarbon age of 4670–5120 years old. $\text{DOC}\delta^{13}\text{C}$ ranges between -23.0 and -24.2‰ (Table 2 and Fig. 4).

$\text{DIC}\Delta^{14}\text{C}$ values for the Tyrrhenian Sea (Station A, Table 3) decrease from $+31.3\text{‰}$ in the surface to $+18.6\text{‰}$ in the core of the LIW at 400 m, reach a minimum of -34.6‰ at 2500 m, before rebounding slightly to -22.6‰ in the deepest sample collected at 3390 m. These values confirm that the Med Sea waters are renewed in less than 126 years (post-bomb values).

4. Discussion

4.1. $\text{DIC}\Delta^{14}\text{C}$ and ventilation time of Med Sea waters

The vertical pattern of $\text{DIC}\Delta^{14}\text{C}$ values is similar to an earlier report by Broecker and Gerard (1969) for samples collected in the West Med and in the Tyrrhenian Sea in summer 1956 and 1958, before significant bomb radiocarbon had penetrated the basin (Fig. 1 and Table 3). In the West Med Broecker and Gerard (1969) reported a value of -48‰ for surface water, -60‰ for LIW (320 m), and -69‰ for deep water (2700 m) (Table 3). A fourth sample collected from the deep

(3390 m) Tyrrhenian Sea, close to our station A (Fig. 1), was significantly older, with a $\text{DIC}\Delta^{14}\text{C}$ value of -83‰ . The difference in radiocarbon values from the deep West Med and the Tyrrhenian Sea reflects more active deep water formation in the West Med, as indicated by higher oxygen concentrations and lower values for AOU at our stations B and C compared to station A (Table 1). The $\sim+80\text{‰}$ increase in surface and intermediate water $\text{DIC}\Delta^{14}\text{C}$ values, and the $\sim+40$ to $+50\text{‰}$ increase in deep water values are indicative of the rapid penetration of bomb radiocarbon to all depths in the basin, in agreement with Broecker and Gerard's earlier assessment of deep Mediterranean ventilation times of <100 y for the West Med and <200 y for the Tyrrhenian Sea.

4.2. Radiocarbon in surface water, source and age of SLDOC in the Med Sea

As expected from past studies on radiocarbon at open ocean sites, $\text{DOC}\Delta^{14}\text{C}$ values are more highly depleted than $\text{DIC}\Delta^{14}\text{C}$ throughout the entire water column, reflecting the longer residence time of organic carbon in seawater. In the euphotic zone, photosynthesis fixes carbon with $\Delta^{14}\text{C} \sim \text{DIC}\Delta^{14}\text{C} (+31\text{‰})$ into SLDOC that is slowly degraded by microbial cycling. The depletion in surface water $\text{DOC}\Delta^{14}\text{C}$ (~-237 to -286‰ , Table 2) relative to $\text{DIC}\Delta^{14}\text{C}$ ($+31\text{‰}$, Table 3) can be explained by a two-component mixture of modern radiocarbon age SLDOC and old radiocarbon age DOC. Since no strong upwelling regions occur in the Med Sea (excluding the Gulf of Lions) the source of the old

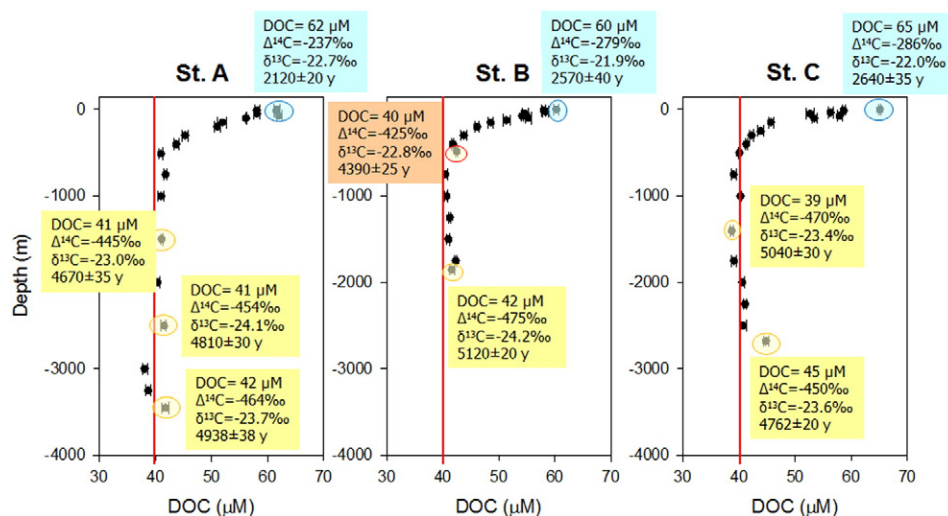


Fig. 4. Vertical profiles of DOC, with radiocarbon values and ages superimposed. DOC concentration refers to those measured in the bottle used for radiocarbon analysis. Cyan boxes: surface samples, Red boxes: LIW samples; Yellow boxes deep water samples (>1000 m).

Table 2
DOC concentrations and isotopic values at the three stations.

Station	Depth (m)	DOC_in bottle (μM) ^a	DOC NOSAMS (μM) ^b	DOC (μM) ^c	F modern	Fm Err	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Age years	Age Err years
A	1	61.6	59.2	58.3	0.768	0.002	−22.7	−237	2120	20
	1500	41.1	45.6	40.1	0.559	0.002	−23.0	−445	4670	35
	2500	41.5	39.2	39.3	0.550	0.002	−24.1	−454	4810	30
	3429	–	–	41.8	0.538	0.002	−23.7	−464	4938	38
B	1	60.0	60.0	60.2	0.726	0.004	−21.9	−279	2570	40
	480 (LIW)	39.7	42.5	41.7	0.579	0.002	−22.8	−425	4390	25
	1851	41.6	46.0	40.3	0.529	0.001	−24.2	−475	5120	20
C	1	65.1	67.0	59.1	0.719	0.003	−22.0	−286	2640	35
	1500	38.7	42.0	41.3	0.534	0.002	−23.4	−470	5040	30
	2680	44.8	44.8	41.4	0.548	0.001	−23.6	−450	4762	20

^a DOC concentration in the bottle used for carbon isotopes measurements.

^b DOC concentration estimated by the CO_2 produced during sample processing for carbon isotopes measurements.

^c DOC concentration in the replicate collected in amber glass bottle (see [Material and methods](#) section for further details).

DOC in the surface layer is most likely the AW inflow. Surface carbon isotope values for both the $\text{DOC}\delta^{13}\text{C}$ (−21.9 to −22.7‰) and the $\text{DOC}\Delta^{14}\text{C}$ (−237 to −286‰) are slightly lower (more negative) than those measured in the surface Atlantic Ocean ($\text{DOC}\delta^{13}\text{C}$ = −21.0 to −21.3‰, $\text{DOC}\Delta^{14}\text{C}$ = −210 to −253‰) (Druffel et al., 1992) even though DOC values are quite similar (59–65 μM for the North Atlantic vs. 60–65 μM for the Mediterranean Sea) (Table 2 and Fig. 4). For radiocarbon, these differences could arise from changes in the isotopic value of SLDOC due to differences in location and time of sampling. Bomb radiocarbon reached maximal values in ocean subtropical gyres in the mid to late 1970s (McNichol and Aluwihare, 2007) and has been decreasing since that time. $\text{DIC}\Delta^{14}\text{C}$ values measured by Druffel et al. (1992) in North Atlantic surface waters (<100 m) in 1991 were $\sim +115\%$, considerably higher than values we measured in the Med Sea 21–22 years later (+31%). Assuming the RDOC in AW inflow has an isotopic value similar to RDOC in deep Atlantic Ocean water (>1000 m, DOC = 43 μM ; $\text{DOC}\Delta^{14}\text{C}$ = −394‰; Druffel et al., 1992), we can calculate that in the Med Sea surface waters (mean DOC = 62 μM ; mean $\text{DOC}\Delta^{14}\text{C}$ = −267‰, Fig. 4 and Table 2), $\text{SLDOC}\Delta^{14}\text{C}$ would have a value of $\sim +20\%$, similar to the $\text{DIC}\Delta^{14}\text{C}$, using the following equation:

$$\left(\text{DOC}\Delta^{14}\text{C}\right)_{\text{surfMed}} \cdot [\text{DOC}]_{\text{surfMed}} = \left(\text{DOC}\Delta^{14}\text{C}\right)_{\text{deepNA}} \cdot [\text{DOC}]_{\text{deepNA}} + \left(\text{SLDOC}\Delta^{14}\text{C}\right) \cdot \left([\text{DOC}]_{\text{surfMed}} - [\text{DOC}]_{\text{deepNA}}\right) \quad (1)$$

where surfMed is the average of the surface (2 m) Med Sea samples (Fig. 4 and Table 2) and deepNA is the average of samples collected in the deep (>1000 m) North Atlantic.

4.3. Radiocarbon in deep water, source and age of RDOC in the Med Sea

The small number of samples and spatial placement of our study sites does not allow for meaningful interpretation of differences in $\text{DOC}\Delta^{14}\text{C}$ between deep water samples. For the purposes of the following discussion, we therefore take a deep water average value of

−460 ± 12‰ (>1000 m, n = 6) to be representative of deep Med Sea $\text{DOC}\Delta^{14}\text{C}$. This value is lower than the average RDOC $\Delta^{14}\text{C}$ value of −394 ± 13‰ for the deep (>1000 m, n = 9) North Atlantic reported by Druffel et al. (1992), even though DOC concentrations in the two studies were comparable (43 ± 1 μM in the deep North Atlantic, 42 ± 2 μM in the deep Mediterranean Sea). Flerus et al. (2012) reported $\text{DOC}\Delta^{14}\text{C}$ values for a fraction of RDOC that was recovered by solid phase extraction onto a hydrophobic resin along a North–south cruise track that passed just west of the Gibraltar Strait. Solid phase extractable $\text{RDOC}\Delta^{14}\text{C}$ values ranged from ~ -225 to -370% in surface (<100 m) water and $\sim -450\%$ in deep (>500 m) water. Druffel et al. (1992) found similar values (−329 to −402‰ surface, −454 to −587‰ deep) for humic substances adsorbed onto hydrophobic solid phases (XAD) from Sargasso seawater. In all cases, the $\Delta^{14}\text{C}$ value of adsorbed DOC in deep water was more depleted (older) than in whole DOC by −40 to −173‰. These studies demonstrate that within deep North Atlantic DOC, there is a fraction (at least 20–25%) with radiocarbon values as depleted as deep Med Sea $\text{DOC}\Delta^{14}\text{C}$.

Atlantic DOC enters the Med Sea through Gibraltar in the AW inflow. During AW transit into the basin and its transformation into Med Sea intermediate and deep waters, Atlantic SLDOC is removed and replaced by SLDOC released in the surface layer of the Med Sea. However, Atlantic RDOC, which makes up $\sim 70\%$ of the total DOC, should remain. Due to the comparable concentrations of DOC in the deep Atlantic and Med Sea and the relatively short ventilation time of the Med Sea, a similar age for DOC was expected. The $\sim 66\%$ depletion of deep Med Sea $\text{DOC}\Delta^{14}\text{C}$ (−460‰), compared to deep North Atlantic $\text{DOC}\Delta^{14}\text{C}$ (−394‰) was therefore surprising. The depletion in $\text{DOC}\Delta^{14}\text{C}$ cannot be due to radioactive decay of ^{14}C , since renewal of water in the Med Sea is too fast (<126 y) compared to the half-life of ^{14}C (5730 y). The depletion must therefore arise from the rapid replacement of a fraction of “refractory” DOC coming from the Atlantic (RDOC_{Atl}) with Med Sea DOC having an older radiocarbon age (DOC_{Med}).

The minimum amount of RDOC_{Atl} replacement needed to explain the older deep Mediterranean values can be calculated if we assume DOC_{Med} to be fully depleted in ^{14}C (−1000‰). In this case, a 4 μM

Table 3
 $\text{DIC}\Delta^{14}\text{C}$ values in the Med Sea compared to values reported in the literature. The position of the stations is reported in Fig. 1.

Station	Latitude °N	Longitude °E	Date	Area	Depth m	DIC Conc (mmol/kg)	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Age years	Age Err years	Reference
A	40.07	12.70	Apr 2013	Tyrrhenian Sea	2	2.19	0.98	31.3	>Modern	–	This study
					400	2.32	0.75	18.6	>Modern	–	
					2500	2.31	0.99	−34.6	220	20	
					3390	2.31	0.99	−22.6	120	20	
367 N	40.31	12.73	Aug 1956	Tyrrhenian Sea	3390	n.a.	0.70	−83 ± 6	n.a.	n.a.	Broecker and Gerard (1969)
492X	39.2	6.17	Jul 1958	West Med	1	n.a.	−48 ± 10	n.a.	n.a.		
492 W	39.12	7.60	Jul 1958	West Med	320	n.a.	−60 ± 10	n.a.	n.a.		
492U	38.73	7.00	Jul 1958	West Med	2700	n.a.	−69 ± 7	n.a.	n.a.		

n.a.: not available.

(~10%) replacement of RDOC_{Atl} with DOC_{Med} will yield the observed deep $\text{DOC}\Delta^{14}\text{C}$ value. Carbon autochthonous to Med Sea, produced by microbes, cannot be older than 126 y (the renewal time of Med Sea waters) and therefore should have $\Delta^{14}\text{C}$ values similar to DIC (–34 to +31‰, Table 3). As a consequence, to lower the $\Delta^{14}\text{C}$ value of deep Med Sea DOC, DOC_{Med} must have a source external to the basin.

The average deep Mediterranean $\text{DOC}\delta^{13}\text{C}$ value is –23.7‰, which is significantly lighter than $\text{DOC}\delta^{13}\text{C}$ in the deep Atlantic or Pacific (–20.8‰ and –21.1‰ respectively), but similar to $\text{DOC}\delta^{13}\text{C}$ in the Canada Basin (Griffith et al., 2012). The more negative $\text{DOC}\delta^{13}\text{C}$ value can be explained by the replacement of a fraction of RDOC_{Atl} by isotopically light DOC_{Med} . Assuming that the minimum 4 μM DOC_{Med} needed to account for low $\text{DOC}\Delta^{14}\text{C}$ is the same carbon that lowers $\text{DOC}\delta^{13}\text{C}$, DOC_{Med} should have a $\delta^{13}\text{C}$ value of ~–48‰, and an annual flux of $1.9\text{--}2.5 \times 10^{+12} \text{ g C y}^{-1}$, obtained by multiplying the amount of carbon replaced (4 μM) by the inflow at the Gibraltar Strait (1.28–1.68 Sv; Hopkins, 1999; Bethoux and Gentili, 1999). Isotopically light carbon with annual fluxes of this magnitude is not a characteristic of most sources allochthonous to the Med Sea (Table 4).

Potential sources of DOC_{Med} that need to be evaluated for their flux and isotopic value include (1) fossil methane and methane derived DOC seeps from sediments, and (2) anthropogenic combustion products and terrestrial organic matter delivered by the atmosphere, rivers, and groundwaters.

4.4. Potential sources of DOC_{Med}

4.4.1. Methane

Methane arises from the microbial reduction of sedimentary organic matter and carbon dioxide during diagenesis (biogenic methane) or from thermal cracking of sedimentary carbon, usually deep in the geosphere under elevated temperatures over long periods of time (thermogenic methane). Biogenic processes yield methane that is isotopically lighter (typically –50‰ to –80‰) than thermogenic methane (typically –40‰ to –55‰), although there is some overlap (Whiticar et al., 1986). Transformation of methane into biomass by methanotrophs leads to further fractionation of ~–30‰ (Summons et al., 1994). The radiocarbon value of biogenic methane can range from fully modern to highly depleted, depending on the radiocarbon content of the organic matter or carbon dioxide used as substrate,

while thermogenic methane is thought to be fully depleted in radiocarbon (~–1000‰). We are not aware of any isotopic measurements of methane in the Med Sea. A few measurements of $^{13}\text{C}\text{--CH}_4$ from pore waters of the Adriatic Sea and Gulf of Lions sediments suggest a biogenic origin for shallow gas in the Adriatic Sea ($^{13}\text{C} = 70$ to -92‰ ; García-García et al., 2007) and perhaps mixed biogenic/thermogenic origin in the Gulf of Lions ($^{13}\text{C} = 53$ to -82‰ ; García-García et al., 2006).

The total flux of methane from sediments places an upper bound on the potential contribution of methane to DOC_{Med} . Biogenic and thermogenic methane enters the Med Sea either by direct injection of methane charged muds (mud volcanoes), venting from pockmarks and fissures (gas bubbles and flares) or through diffusive fluxes from subsurface sediments with high methane concentrations (Boetius and Wenzhöfer, 2013; Römer et al., 2014). The large number of potential input mechanisms, and the spatial and temporal variability of these inputs makes a basin-wide estimate of methane flux difficult. Using hydroacoustic profiling of methane flares in the water column, sediment core incubations, and benthic chambers, Römer et al. (2014) estimated the annual flux of methane to the water column to range from 0.4 to $94 \times 10^{+9} \text{ g C y}^{-1}$ in a 225 km^2 section of the Nile deep sea fan. If this flux is scaled to the entire Med Sea, the annual flux of methane from sediments would range from 0.4 to $104 \times 10^{+13} \text{ g C y}^{-1}$. This value most likely overestimates the flux of methane into the deep Med Sea by a significant amount, since many areas of the Med Sea floor lie outside the methane hydrate stability zone and are characterized by carbon-lean sediments, with little potential for methane generation or storage.

As a second approach, we weighted the estimated global sediment to seawater flux of methane ($3\text{--}5 \times 10^{+13} \text{ g C y}^{-1}$, with an additional $3 \times 10^{+13} \text{ g C y}^{-1}$ from deep sea mud volcanoes) (Kvenvolden et al., 2001; Milkov et al., 2003) to the areal extent of sediments that lie within the methane hydrate stability zone in the Med Sea. Using this approach the basin-wide annual methane flux is markedly lower $\sim 3\text{--}4 \times 10^{+11} \text{ g C y}^{-1}$.

In the water column, methane can escape to the atmosphere, be oxidized to CO_2 , or fixed into microbial biomass with a fraction subsequently released as DOC. We are unaware of any measurements of the conversion efficiency of methane to DOC by either aerobic or anaerobic methane oxidizers. If, from estimates of bacterial growth efficiency on marine DOC, we assume 10–30% of methane is fixed into biomass by bacteria, that 10% of the fixed carbon is released as DOC (Carlson,

Table 4

Literature stable and radiocarbon isotopes values for organic carbon measured in the possible allochthonous sources to the Med Sea.

Source	DOC (μM)	DOC Flux ($10^{12} \text{ g C y}^{-1}$) ^a	$\text{DOC}\Delta^{14}\text{C}$ (‰)	$\text{DOC}\delta^{13}\text{C}$ (‰)	References	
Atlantic Atmosphere	Western North Atlantic, 1987 (0–100 m)	62	30–39	–238	–21.2	Druffel et al. (1992)
	TC in Aereosol in Milan urban area		0.4–13	–354 to –522		Bernardoni et al. (2013)
	Organic carbon in PM10 in Amsterdam urban area			–325		Dusek et al. (2013)
	Organic carbon in PM10 in a coastal location of Petten.			–177		
	Organic carbon in PM1–PM10 in various locations in Europe.			–118 to –453		Dusek et al. (2013) (Table 2 and literature therein)
Rivers	Rainwater North Carolina	132–540		49 to –102	–21.8 to –28.2	Avery et al. (2006)
	Rhone River 2004–2005 (POC)	8 to 62.5	0.6–0.7		–25.46 to –28.55	Harmelin-Vivien et al. (2010)
	Po River 2000–2001 (POC)	16–171			–21.3 to 28.9	Boldrin et al. (2005)
	Amazon (Brazil), Hudson (New York, USA), York (Virginia, USA) and Parker (Massachusetts, USA) rivers			364 to –158	–	Raymond and Bauer (2001)
Submarine groundwater Methane	Island of Majorca (Spain)	80–169	0.3–9.7			Basterretx et al. (2010)
	Adriatic Sea		0.003–10	–	–70 to –92‰	García-García et al. (2007)
	Gulf of Lions			–	–53 to –82‰	García-García et al. (2006)

^a Fluxes estimated in Santinelli, 2015 and in this work.

2002), and that ~10% of this DOC is refractory (Ogawa et al., 2001), methane could potentially contribute to DOC_{Med}.

Alternatively, we might assume that the conversion of methane to DOC has an efficiency similar to the conversion of net marine primary production to RDOC. Taking into account that less than 1% of the net annual production in the open ocean is required to maintain the marine reservoir of RDOC at steady state with a radiocarbon age of 16,000 y (Hansell, 2013), then the contribution of fossil methane carbon to DOC_{Med} is probably less than $3 \times 10^{+9}$ to $1 \times 10^{+13}$ g C y⁻¹.

Methanotrophy in surface sediments may add isotopically depleted DOC directly into the water column (Pohlman et al., 2011; Boetius and Wenzhöfer, 2013) further increasing the flux of methane sourced carbon to DOC_{Med}. We are not aware of any current estimates of direct input of methane derived DOC from sediments at any site, and we cannot estimate the magnitude of this additional flux. Uncertainties in the annual flux of fossil methane into the deep Med Sea, and the amount of methane carbon that is transformed into RDOC are so large that it is unclear if fossil methane contributes significantly to DOC_{Med}. However, unless future estimates of methane flux for the region or the methane to DOC conversion efficiency by methanotrophs are revised substantially upwards, it seems unlikely that methane contributes more than a fraction to DOC_{Med}, and other sources of aged carbon are needed to explain the isotopic depletion of deep Med Sea DOC.

4.4.2. Rivers and atmosphere

Assuming that DOC in Med Sea deep water is a mixture of marine DOC ($\delta^{13}\text{C} \sim -21\%$) coming from the Atlantic Ocean and terrestrial DOC ($\delta^{13}\text{C} \sim -27\%$) coming from rivers, atmosphere and marine groundwaters surrounding the Med Sea, we can calculate that 55% (~23 μM) of deep Med Sea DOC is marine, and 45% (~19 μM) is of terrestrial origin. If the 23 μM of marine DOC had a $\Delta^{14}\text{C}$ value equal to deep North Atlantic DOC (-394%) then the $\Delta^{14}\text{C}$ value of the terrestrial component would be ~-540% and it should have an annual flux of $9\text{--}12 \times 10^{+12}$ g C y⁻¹, estimated multiplying the Atlantic inflow at Gibraltar (1.28–1.68 Sv) by 19 μM . The total estimated terrestrial input of DOC to the Med Sea is $1\text{--}13 \times 10^{+12}$ g C y⁻¹, including both river ($0.6\text{--}0.7 \times 10^{+12}$ g C y⁻¹) and atmospheric ($0.4\text{--}13 \times 10^{+12}$ g C y⁻¹) DOC inputs (Santinelli, 2015 and literature therein). Additionally, rivers deliver between $0.7\text{--}1.0 \times 10^{+12}$ g C y⁻¹ of particulate organic carbon to the Med Sea, some fraction of which may become solubilized as DOC after delivery.

River input was estimated considering all the available data that include the major Med Sea rivers (Rhône, Po and Ebro) and some of the minor ones. DOC concentrations are from multi-year observations in the Rhône river (Sempéré et al., 2000; Panagiotopoulos et al., 2012), Po river (Pettine et al., 1998) and Arno river (Retelletti Brogi et al., 2015). In contrast, DOC data are taken sporadically in the other rivers. If we consider the discharge (Ludwig et al., 2009), DOC data are available for 50% of the rivers (81% in the West Med and 34% in the East Med). DOC concentrations ranged between 133 and 366 μM in the West Med and between 92 and 292 μM in the East Med. The lack of DOC data in some rivers was overcome by using the mean DOC concentration computed by all the available data (176–225 μM in the West Med and 157 μM in the East Med) and multiplying this value by the discharge of the rivers without DOC data (for further details refer to Santinelli, 2015).

Data on wet and dry DOC depositions from the atmosphere are scarce for the Med Sea. DOC fluxes from the atmosphere were therefore estimated by using the largest range calculated referring to three papers. Pulido-Villena et al. (2008) report direct DOC concentration on total atmospheric deposition, collected at the Cap Ferrat (West Med Sea) continuously from December 2005 to December 2006. These authors observed an atmospheric DOC input ranging from 0.04 to 1.2 mmol m⁻² d⁻¹, with the highest values associated with Saharan dust deposition events. Economou and Mihalopoulos (2002) measured TOC in 47 rain samples collected at Heraklion (Crete Island, East Med

Sea) from September 1999 to May 2000. They observed concentrations ranging from 16.6 to 358 μM , with a volume weighted mean of 100 μM . An annual wet deposition for TOC of $0.14 \text{ mmol m}^{-2} \text{ d}^{-1}$ was calculated multiplying 100 μM by an annual precipitation rate of 0.5 m. De Vicente et al. (2012) measured the concentration of water-soluble organic carbon (WSOC), in both dry and wet deposition, collected in 2004 and 2005 by a passive sampler deployed in three reservoirs located in Southern Spain within an area that experienced intense dust deposition. The annual average concentrations of WSOC, considering both dry and wet depositions, ranged from 0.18 to 0.42 mmol m⁻² d⁻¹.

The minimum and maximum of the fluxes reported in these three papers were multiplied by the Med Sea area ($2.5 \times 10^{+6} \text{ km}^2$), in order to have a regional estimate of atmospheric input. This estimate is affected by large uncertainties, since it is based on the assumption that this range is valid for the whole basin and for the whole year. The flux could be underestimated since Saharan dust deposition, which seems to play a major role on DOC input, is probably more intense and frequent in the southern part of the West Med, where no data are available. On the other hand, Saharan dust deposition does not occur every day, leading to an overestimation of the fluxes if the highest values are taken into account. The most reasonable range is the one based on annual average (0.14 to $0.42 \text{ mmol m}^{-2} \text{ d}^{-1}$) and it suggests an average DOC flux of $1.3\text{--}4.6 \times 10^{+12}$ g C y⁻¹.

Recently, Total Dissolved Nitrogen (TDN) and Phosphorus (TDP) fluxes from the atmosphere were studied in bulk deposition samples simultaneously collected at 10 locations, around the Med Sea, during one year period (June 2001–May 2002) (Markaki et al., 2010). These data are more representative of integrated fluxes to the basin, but no DOC data are available in this study. The authors observed dissolved inorganic nitrogen (DIN) fluxes ranging from 33.2 to 36.6 mmol m⁻² y⁻¹ and dissolved organic nitrogen (DON) to be on average 32% of TDN, DON fluxes should therefore be 15.6–17.2 mmol m⁻² y⁻¹. Assuming a DOC/DON ratio in atmospheric dissolved organic matter (DOM) ranging between 10 and 18, typical ranges of Med Sea DOM (Pujo-Pay et al., 2011; Santinelli et al., 2012), atmospheric DOC input should range from 4.7 to $9.3 \times 10^{+12}$ g C y⁻¹. These values are slightly higher than those estimated by taking into consideration direct DOC measurements on atmospheric deposition.

No DOC $\Delta^{14}\text{C}$ data is available for Med Sea rivers, however we assume that the values are similar to the range (+364 to -158%) reported by Raymond and Bauer (2001) for temperate and tropical rivers that drain a wide variety of terrestrial watershed types, including large population centers (Potomac, Washington D.C.; Susquehanna, Philadelphia; Hudson, New York; all USA). Wastewater treatment associated with population centers may contribute a substantial fraction of petroleum derived carbon (Griffith et al., 2009).

Atmospheric DOC $\Delta^{14}\text{C}$ spans a slightly wider range of values from +49 to -522%, reflecting inputs from modern terrestrial biomass to fossil fuel combustion in urban areas (Table 4).

Estimates of carbon flux and isotopic range for terrestrial DOC inputs are based on only a small number of measurements, and have large uncertainties when extrapolated to the entire basin over decadal time-scales. However, the low flux, enriched isotopic values, and lability of riverine DOC (5–50% removed in months) (Holmes et al., 2008; Lønborg et al., 2009; Retelletti Brogi et al., 2015) suggest rivers contribute only a minor fraction of DOC_{Med}, although processing of riverine particulate organic matter ($0.7\text{--}1.0 \times 10^{+12}$ g C y⁻¹) may further increase this contribution. It is noteworthy that most of the carbon in the Rhône River continental shelf is much older (POC $\Delta^{14}\text{C} = -310 \pm 66\%$) than would be expected if it had been derived from contemporarily synthesized sources. The authors explained these heavily depleted values with the presence of aged organic carbon, such as kerogens, graphite, petroleum residues or black carbon (Cathalot et al., 2013). The flux and isotopic value of DOC delivered from the atmosphere, however, could be sufficient to supply DOC_{Med}, even if only a fraction of this carbon is refractory.

4.4.3. Submarine groundwater

Submarine groundwater may represent another crucial source of pre-aged terrestrial DOC and DIC to the Med Sea (Moore, 2010). Recently, using ^{228}Ra mass balance, Rodellas et al. (2015) estimated that submarine groundwater discharge (SGD) to the Med Sea is $0.3\text{--}4.8 \times 10^{+12} \text{ m}^3 \text{ y}^{-1}$. This flux is equal to or up to 16 times larger than river input ($0.3 \times 10^{+12} \text{ m}^3 \text{ y}^{-1}$) and it represents a significant source of nutrients (N, P, Si) to the Med Sea DIN: $(20\text{--}1500) \times 10^{+9} \text{ mol y}^{-1}$; DIP: $(0.1\text{--}4.6) \times 10^{+9} \text{ mol y}^{-1}$; DSi $(20\text{--}650) \times 10^{+9} \text{ mol y}^{-1}$ (Rodellas et al., 2015). The only paper reporting total organic carbon concentration (TOC) in Mediterranean SGD refers to the coast of the island of Majorca (Basterretx et al., 2010). These authors measured a TOC concentration ranging between 80 and 169 μM in 4 embayments. Assuming these values are representative of SGD to the Med Sea SGD could account for a TOC flux of $0.3\text{--}9.7 \times 10^{+12} \text{ g C y}^{-1}$. This estimate includes uncertainties, but suggests that the magnitude of SGD can be relevant and cannot be overlooked. It is also important to remember that submarine groundwaters are an important source of aged DIC (Gramling et al., 2003), and that if recycled through bacteria to DOC, SGD could contribute to the synthesis of pre-aged DOC.

4.5. Refractory DOC cycling

Stable and radiocarbon isotope values of deep Med Sea DOC suggest at least 10% and up to 45% of the Atlantic RDOC entering the Med Sea is removed and replaced by isotopically depleted DOC in less than 126 years. This finding can be explained by two hypothesis:

1. Unique conditions of the deep Med Sea allow for the removal of a substantial fraction (up to 45%) of “refractory” DOC imported from the Atlantic. Carbon that is refractory in the global ocean becomes semi-labile in the Med Sea.
2. Not all of the $\sim 42 \mu\text{M}$ RDOC entering to the Med Sea is refractory (cycles on timescales of 1000s of years). A fraction of RDOC is in fact semi-labile since it can be removed in < 126 years, and the true “refractory” fraction of DOC_{Atl} is only $\sim 20\text{--}25 \mu\text{M}$. This hypothesis posits that the deep DOC inventory is at a steady state. A fraction is continuously removed and replaced by semi-labile DOC released by sinking POC or produced by chemoautotrophy and/or other processes (Follett et al., 2014). In the Med Sea primary production and the flux of sinking autochthonous POC are both low (Lazzari et al., 2012; Speicher et al., 2006), and some RDOC is replaced by older and lighter DOC from allochthonous sources. Using current information, it is not possible to clearly identify the relative contribution of potential allochthonous sources. However, based on estimated flux and isotopic value, atmospheric inputs of soluble organic carbon from soils or combustion products and DOC from submarine groundwaters are the most likely sources of DOC_{Med} . Atmospheric soluble organic carbon and DOC by SGD can be then transported to depth by deep water formation or by sorption onto/desorption off of sinking particles.

We can think of no reason or evidence to suggest that the Med Sea should be different from the global ocean with respect to the lability of RDOC (hypothesis 1). If RDOC persists in the ocean for several millennia, then it spends significant time in the surface ocean where temperature, salinity, and nutrient concentrations all bracket conditions found in the deep Med Sea. Exposure to elevated temperatures in surface waters should draw down RDOC values to the values $\sim 20\text{--}25 \mu\text{M}$ that we find in the deep Med Sea. However, the high fidelity with which the two-component model (TCM) replicates the observed distribution of DOC radiocarbon values in the surface ocean (Williams and Druffel, 1987; Druffel et al., 1992; Beupré and Aluwihare, 2010) suggests RDOC is not substantially degraded. Additionally, Griffith et al. (2012) report $\text{DOC}\delta^{13}\text{C}$ (~ -23 to -24%) and $\text{DOC}\Delta^{14}\text{C}$ values (-400 to -500%) for deep sea DOC in the Canadian Basin of the Arctic Ocean, similar to values we observe in the deep Med Sea. DOC

concentration values in Griffith's samples are $\sim 40\text{--}42 \mu\text{M}$. The $\text{DOC}\delta^{13}\text{C}$ values in particular suggest that replacement of 30% RDOC has occurred, even though temperatures are $0 \text{ }^\circ\text{C}$ to $-1 \text{ }^\circ\text{C}$ throughout the deep basin.

Hypothesis 2 is consistent with a growing body of radiocarbon measurements made in the deep sea (Druffel and Bauer, 2000; Griffith et al., 2012; Follett et al., 2014) that are otherwise difficult to explain. In this scenario, replacement of SLDOC upwelled from the deep ocean with SLDOC in the surface ocean would not impact its radiocarbon value, and the distribution of radiocarbon predicted by the TCM would be unaffected.

Our calculations assume that the RDOC_{Atl} has an isotopic value equal to DOC in the deep North Atlantic ($43 \mu\text{M}$; $\delta^{13}\text{C} = -21\%$; $\Delta^{14}\text{C} = -394\%$). Recently, Follett et al. (2014) used serial oxidation of deep sea DOC from the North Pacific to measure its isotopic diversity and distribution. The results show a continuum of isotopic values from -1000% to $+150\%$ indicating that deep Pacific DOC includes organic matter from post-bomb to fossil carbon sources. The authors divided deep Pacific DOC into three fractions: refractory carbon ($\sim 24 \mu\text{M}$) with $\Delta^{14}\text{C}$ between -1000% and -600% , semi-labile carbon ($\sim 9 \mu\text{M}$) with a modern ($+50\%$) radiocarbon value, probably supplied by sinking particles, and an aged carbon fraction ($\sim 7 \mu\text{M}$, $\sim -275\%$, similar to deep sea $\text{DIC}\Delta^{14}\text{C}$) that could represent carbon derived from meso- and bathypelagic chemoautotrophy or from entrainment and advection of semi-labile DOC. If the concentration of RDOC in the deep North Atlantic is equal to the North Pacific, and the radiocarbon values of these fractions are adjusted for aging by the difference in $\text{DIC}\Delta^{14}\text{C}$ value (-146%) between the deep North Atlantic (-84%) and Pacific (-230%), we can calculate the amount and radiocarbon value of RDOC in the deep North Atlantic as $24 \mu\text{M}$ at -654% and $7 \mu\text{M}$ at -129% (Fig. 5a). By this scenario, only $12 \mu\text{M}$ of labile, modern ($\Delta^{14}\text{C} \sim -28\%$) carbon would need to be replaced by $11 \mu\text{M}$ carbon with $\Delta^{14}\text{C}$ of -247% and $\delta^{13}\text{C}$ of -31% to achieve the deep Med Sea $\text{DOC}\Delta^{14}\text{C}$ value of -460% and $\delta^{13}\text{C}$ value of -23.7% (Fig. 5b). An annual flux of $5.3\text{--}7.0 \times 10^{+12} \text{ g C y}^{-1}$ would be needed to support this replacement. Alternatively, if the $7 \mu\text{M}$ of aged carbon is supplied by chemoautotrophy and is included in the semi-labile fraction, then $19 \mu\text{M}$ of carbon could be replaced by $18 \mu\text{M}$ DOC_{Med} with isotopic values of -201% and -27% , in the range of $\text{DOC}\Delta^{14}\text{C}$ and $\text{DOC}\delta^{13}\text{C}$ values for riverine and atmospheric input (Fig. 5c).

The two hypotheses are not mutually exclusive. They represent different scenarios for deep sea DOC cycling that can be addressed with further measurement and modeling. If hypothesis 2 is correct, then this would necessitate a re-evaluation of traditional definitions and inventories of refractory marine DOC in the deep ocean. Further, the hypothesis more intimately ties the distribution of deep sea DOC to production in the surface and the to the flux and dissolution of sinking particulate organic matter. It suggests that a significant fraction of accumulated DOC in the deep sea is ultimately utilized by the microbial community.

5. Conclusions

The first radiocarbon data on DOC in the Med Sea indicate that at least 10% and up to 45% of the Atlantic RDOC entering the Med Sea is removed and replaced by isotopically lighter and older DOC in less than 126 years. Large uncertainties are associated to atmospheric, riverine, ground water and methane fluxes, limiting an estimate of their relative importance. However, based on measured fluxes and isotopic values, atmospheric inputs of soluble organic carbon from soils or combustion products as well as DOC from groundwaters are the most likely sources of allochthonous DOC. These data suggest that the true “refractory” fraction of DOC (the fraction that cycles on millennial timescales) could be as low as $\sim 20\text{--}25 \mu\text{M}$. The Med Sea can be viewed as a reactor, where marine DOC imported from the Atlantic is replaced by terrestrial DOC, with the net release of $0.5\text{--}0.6 \times 10^{+12} \text{ g CO}_2 \text{ y}^{-1}$ to the atmosphere.

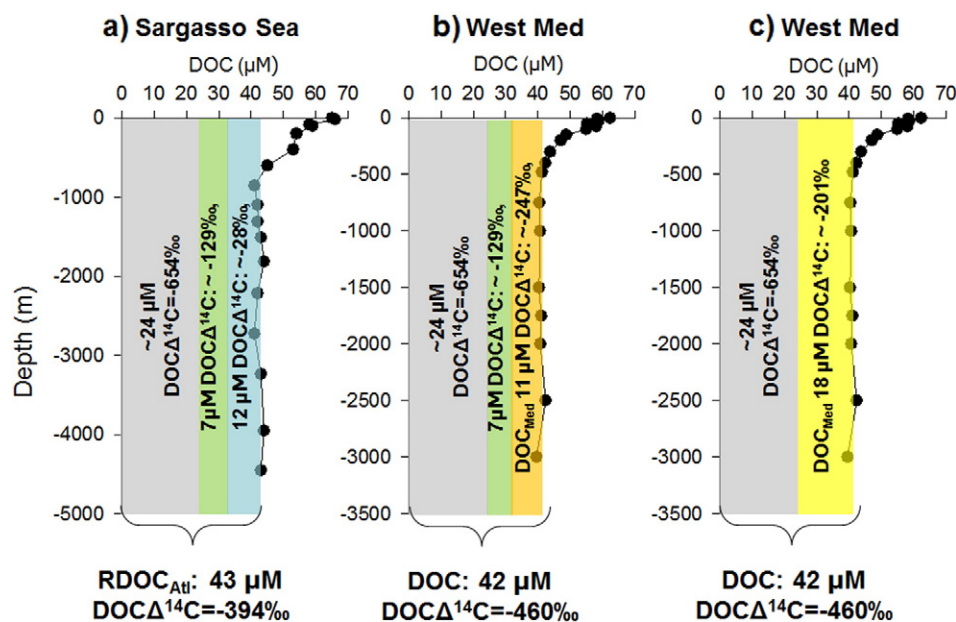


Fig. 5. Vertical profiles of DOC for the Sargasso sea (a) (data from Druffel et al., 1992) and the average DOC profile for the West Med (b, c) (this study), with the hypothetical distribution of different radiocarbon fractions superimposed. In b we assume that the 7 μM of aged DOC at -129‰ is refractory; in c we assume this DOC is SLDOC from chemosynthesis, so it can be easily replaced.

The outflow of deep Med Sea water through Gibraltar may be a source of terrestrial DOC to the ocean, with a flux of $8.2\text{--}10.9 \times 10^{+12} \text{ g C y}^{-1}$, estimated multiplying 18 μM by the outflow of Med waters (1.2–1.6 Sv) (Hopkins, 1999; Bethoux and Gentili, 1999). By this account, the Med Sea would add about $\sim 1\text{--}2\%$ of total DOC as terrestrial carbon to the deep North Atlantic. Although this amount would become rapidly undetectable in the Atlantic after mixing, it may be possible to detect this source at stations close to Gibraltar through measurements of $\text{DOC}\delta^{13}\text{C}$.

The mechanisms that lead to RDOC replacement are unknown. If replacement is common in the deep ocean (Follett et al., 2014), then replacement by isotopically lighter terrestrial carbon in the Med Sea and Arctic Ocean only makes the process in these basins more visible than in the global ocean. If however, unique processes or microbial communities in the deep Med Sea and Arctic Ocean convert RDOC into semi-labile DOC, then the mechanisms involved are of great interest.

Our results highlight the need for additional data on radiocarbon in both the West and East Med Sea as well as additional information about radiocarbon in the external sources to the basin (atmosphere, rivers, groundwaters) and further studies on DOC cycling in this peculiar basin. The idea that the concentration of refractory DOC could be lower than 36–42 μM further strengthens the importance of DOC in the global carbon cycle, and elevates the possibility that DOC could represent a key element in maintaining dark ocean metabolism.

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