Seasonality of Dissolved Organic Carbon Exchange Across the Strait of Gibraltar

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Abstract Exchange of mass, heat, and solutes across the Strait of Gibraltar is fundamental to understand the circulation and biogeochemistry of the Mediterranean. Here we focus on the exchange of dissolved organic carbon (DOC) using data from 12 surveys conducted between 2008 and 2015. DOC exchange exhibits a marked bimodal distribution with minima in late June and late October and maxima in mid-April and late August. This pattern is mainly due to seasonal variation of the DOC gradient between the Atlantic Surface Water entering the Mediterranean and the deep opposite flow of Mediterranean Overflow Water. The gradient is controlled by the different seasonal cycles followed by the DOC in the two layers. Annual average DOC import from the Atlantic is equivalent to $4.2 \pm 1.5$ Tg C yr$^{-1}$, which represents 53% of the external DOC inputs and contributes to support 32% of the net heterotrophy of the Mediterranean.

Plain Language Summary The Mediterranean Sea is a semienclosed basin connected with the Atlantic Ocean through the Strait of Gibraltar. At this hot spot of ocean circulation, about 0.8 Sv ($1 \text{ Sv } = 10^6 \text{ m}^3\text{ s}^{-1}$) of dissolved organic carbon (DOC) rich Atlantic Surface Water enters the Mediterranean Sea and the same volume of DOC poor Mediterranean Overflow Water flows oppositely to the Atlantic Ocean. Both DOC concentrations and water flows are not stationary but vary seasonally. Differences in the amplitude and timing of those seasonal cycles produce a marked bimodal variation in the net DOC flux of Atlantic water that enters the Mediterranean Sea, with minima in late June and late October and maxima in mid-April and late August. This pattern has been observed for the first time and allowed us to better constrain this organic carbon flux, which represents about half of the total input of DOC in the Mediterranean Sea and supports about one third of its net organic carbon demand.

1. Introduction

The two-layer water circulation in the Strait of Gibraltar (Figure 1) ties the overturning circulation cells of the North Atlantic and the Mediterranean Sea (Bryden & Kinder, 1991; Carracedo-Segade et al., 2016; Reid, 1979; Volkov et al., 2019). Atlantic Surface Water (ASW) enters the Mediterranean basin across the strait and flows eastward until the Levantine basin, progressively gaining salinity due to evaporation. At the Rhodes gyre, it sinks and returns westward as Levantine Intermediate Water (LIW) in the Eastern basin and Eastern Intermediate Water (EIW) in the Western basin, constituting the shallow overturning circulation cell of the Mediterranean Sea (Schneider et al., 2014; Tsimpis et al., 2006). EIW mixes mostly with Western Mediterranean Deep Water (WMDW) to form the Mediterranean Overflow water (MOW) that leaves the Mediterranean Sea through the Strait of Gibraltar (Bryden & Stommel, 1982; García-Lafuente et al., 2007; Naranjo et al., 2015). This conspicuous circulation pattern is the reason behind the extreme oligotrophy and net heterotrophy that dictate the carbon and nutrient biogeochemistry of the Mediterranean (Luna et al., 2012; Reygondeau et al., 2017) and makes this basin a transient anthropogenic CO$_2$ sink (Palmié et al., 2015). Given that the strait is a “hot spot” of this circulation cell, it has been repeatedly visited to study its hydrography (García-Lafuente et al., 2015; Millot, 2014; Naranjo et al., 2015) and dynamics (Bryden et al., 1994; García-Lafuente et al., 2011; Naranjo et al., 2017; Sammartino et al., 2013). Similarly, the quantification of the exchange of ASW and MOW carrying contrasting biogeochemical properties has been crucial to constrain the net heterotrophy of the Mediterranean sea in terms of dissolved inorganic nutrients (Dafner et al., 2003; Huertas et al., 2012) and CO$_2$ system components (Flecha et al., 2019; Huertas et al., 2009). Furthermore, the MOW leaving the strait also impacts on the hydrography, circulation, and biogeochemistry of the adjacent Northeast Atlantic: It causes the massive subduction of Eastern North Atlantic Central Water (ENACW) in the Gulf of Cadiz (GC) (Barbosoa Aguilar et al., 2015; Baringer & Price, 1997;
Rhein & Hinrichsen, 1993; Sánchez-Leal et al., 2017) and likely affects the formation of North Atlantic Deep water (NADW) in the high latitudes of the North Atlantic, with direct implications for the Atlantic Meridional Overturning Circulation (Carracedo-Segade et al., 2016). Particularly, the impact of the subduction of ENACW: MOW has been quantified in terms of the downward transports of CO2 (Álvarez et al., 2005) and dissolved organic carbon (DOC) (Santana-Falcón et al., 2017) to intermediate depths of the Northeast Atlantic, where anthropogenic CO2 is stored and DOC is a major substrate for microbial growth.

While the assessment of net inorganic carbon and nutrient fluxes between the North Atlantic and the Mediterranean Sea is based on time series of water transport records and repeated bottle measurements in ASW and MOW (Huertas et al., 2009, 2012), previous estimates of the net exchange of DOC through the Strait of Gibraltar are limited to discrete DOC measurements performed more than two decades ago (September 1997 and April 1998) and a constant value of water transport taken from the literature (Dafner, González-Dávila, et al., 2001; Dafner, Sempéré, & Bryden, 2001). Latter, Santinelli (2015) also provided an estimate based on Dafner’s and her own data. These estimations have been considered as representative of a stationary net import of DOC from the Atlantic toward the Mediterranean.

This steady-state assumption would not be accurate if water flows and DOC concentration profiles are not stationary throughout the year. In this regard, a marked seasonality in the thermohaline characteristics and water flow of the MOW at the Strait of Gibraltar have been reported in response to basin scale processes, such as the seasonal and interannual variability in the formation of WMDW in the Gulf of Lions (Garcia-Lafuente et al., 2007; Naranjo et al., 2015, 2017; Sammartino et al., 2015; Schroeder et al., 2016). Furthermore, DOC profiles in temperate and subtropical areas are also characterized by well-defined seasonal cycles (Carlson et al., 1994; Doval et al., 2016; Romera-Castillo et al., 2013). Recently, Amaral et al. (2020) have also reported seasonal differences in the DOC of the GC. Therefore, there are solid evidences to hypothesize that the net DOC exchange fluxes along the Strait of Gibraltar are not stationary but exhibit a marked seasonal variability. To test the hypothesis we combined periodic measurements of DOC taken in the ASW and the MOW from 2008 to 2015 and water flows through the channel, to calculate net DOC exchange.
exchange fluxes throughout the seasonal cycle. We further revisited the role of the Strait of Gibraltar in the DOC budget of the Mediterranean Sea on the light of this new estimate.

2. Materials and Methods

2.1. Sampling Program

Data were acquired at the Gibraltar Fixed Time series (GIFT, Figure 1b) during 12 surveys carried out between 2008 and 2015 (Table S1 in the supporting information). Measurements were taken in the three stations that form the GIFT, G1 (5°58.60’W, 35°51.68’N), G2 (5°44.75’W, 35°54.71’N) and G3 (5°22.10’W, 35°59.19’N) by following an identical procedure. In all surveys, a temperature and salinity profile was obtained with a Seabird 911Plus conductivity/temperature depth probe connected to a rosette sampler containing 10 L Niskin PVC bottles. Conductivity measurements were converted into practical values of the salinity scale with the UNESCO equation (1986). The accuracy of CTD measurements for temperature and salinity were 0.004°C and 0.005, respectively. Seawater samples for dissolved oxygen, nutrient salts, and chlorophyll measurements were subsequently collected with the rosette. Sampling occurred at variable depths (from five to eight levels) depending on the instant position of the interface between the ASW and the MOW in the water column (Figure 1c), which had been previously identified by the CTD profiles. On average, 21 (range 16 to 26) water samples were collected on each survey. Dissolved oxygen concentration was determined by automated potentiometric modification of the original Winkler method using a Titroprocessor (model Metrohm 794). Upon collection, Winkler flasks were sealed, stored in darkness, and measured within 24 hr. The error of measurements was ±2 μmol kg⁻¹ (n = 252). Apparent oxygen utilization (AOU) values were calculated with the solubility equation (Benson & Krause, 1984). For nutrients (nitrate, phosphate, and silicate) determination, water samples (5 ml, two replicates) were taken from the Niskin bottles in 50 ml polyethylene bottles, filtered immediately through Whatman GF/F glass fiber filters (0.7 μm pore size), and stored frozen at −20°C for later analyses in the shore-based laboratory. Nutrients concentrations were measured with a continuous flow analyzer using standard colorimetric techniques (Hansen & Koroleff, 1999). Analytical precisions were always better than ±3%. Chlorophyll analysis was conducted by filtering 0.5 L samples through Whatman GF/F filters, extracting in 90% acetone, and measuring concentration by standard fluorometric methods (Parsons et al., 1984) using a Turner Designs Model 10 fluorometer. The fluorometer was calibrated using pure chlorophyll a from the cyanobacterium Anacystis nidulans (Sigma chemical Co.) with the concentration determined spectrophotometrically.

2.2. DOC Measurements

Seawater samples for the determination of DOC were collected in 0.25 L acid-cleaned glass bottles and immediately filtered through precombusted (450°C, 4 hr) Whatman GF/F filters with an acid-cleaned all-glass filtration system previously rinsed with about 50 ml of the sample. Aliquots of 20 ml were collected for DOC analysis in precombusted (450°C, 12 hr) 24 ml glass vials. After acidification with H₃PO₄ (85%) to pH < 2, they were sealed with Teflon-lined caps and stored in the dark at 4°C until analyzed in the shore-based laboratory within 1 month after collection. DOC content in samples was measured with a commercial Shimadzu TOC-VPCH organic carbon analyzer working under the principle of high-temperature catalytic oxidation according to the protocol described by Álvarez-Salgado and Miller (1998). Potassium hydrogen phthalate (99.95–100.05%, p.a., Merck) was used to calibrate the system. The precision of the analyzer was ±0.5 μmol L⁻¹. Accuracy was checked with consensus reference materials provided by D. A. Hansell (University of Miami, USA).

2.3. Seasonal Cycles Modeling

Generalized additive models (GAMs) (Wood, 2006) were used to infer the seasonal cycles of DOC and companion variables in the two opposite flowing layers of the strait. The surface eastward flowing ASW was demarcated by salinity <37.5 and the bottom westward flowing MOW by salinity >37.5 (Figure 1c; Huertas et al., 2009, 2012). Data collected deeper than 500 m (n = 7 cases) were excluded from the analyses. Independent GAMs were fitted to the ASW and MOW data.

A GAM is a nonparametric regression technique that allows inspecting the relationship between a response variable and one (or more) explanatory variable(s) without the need to choose a particular parametric form for describing the shape of the relationship(s). In this work, we modeled the variability of DOC and other
variables (Chl $a$, dissolved oxygen, and nutrients) using the day of the year (DoY), salinity ($S$) and potential temperature ($T$) as explanatory variables. DoY accounts for the seasonal cycle while salinity and temperature standardize the effect of thermohaline variability within the two layers. Salinity and temperature ranged from 37.483 to 35.876 and from 13.208 to 23.446°C in ASW, respectively. In MOW they varied from 37.504 to 38.513 and from 12.965 to 14.632°C.

GAMs were formulated as follows:

$$ Y_{i,j} = \alpha + g(DoY_{i,j}) + h_1(S_{i,j}) + h_2(T_{i,j}) + \epsilon_{i,j} $$

where $Y$ is the DOC, or any other variable of interest, measured at a day $i$ and depth level $j$, $\alpha$ is the intercept, and $\epsilon_{i,j}$ is the error term assumed to be normally distributed; $g$ and $h_k$ are nonparametric smoothing functions specifying the effect of the covariates ($DoY$, $S$, and $T$) on the response variable $Y$. Smoothing functions $g$ and $h$ were fit by penalized cyclic cubic and cubic regression splines, respectively, and the number of knots were restricted to a maximum of six and three knots for each smoothing function type. Note that when modeling $S$ and $T$ we included in the model the covariate depth (in m).

3. Results and Discussion

3.1. Seasonal Variability of DOC at the Strait of Gibraltar

Average DOC profiles along the Strait of Gibraltar (Figure S1a) and year round (Figure S1b) show well-defined spatial and temporal patterns. The DOC-rich ASW is characterized by higher concentrations at the Atlantic side of the strait (stn G1). Conversely, the DOC-poor MOW presents lower concentration in the bottom layer of the Mediterranean side of the strait (stn G3) (Figure S1a). The annual cycle of the average DOC profile (Figure S1b) shows a differential seasonal accumulation of DOC in both the ASW and MOW. Individual GAMs were tested for the three stations along the strait (Figure 1b) finding roughly equivalent patterns between stations (Figure S2 and Table S2). Therefore, GAMs were fit to data for the three stations together to obtain average seasonal distributions of DOC along the strait, which is more convenient to calculate net exchange fluxes rather than taking individual stations at both ends of the strait.

These statistical models described well the seasonal cycle of DOC (Table S3) and the rest of variables in both ASW (Table S4) and MOW (Table S5) flowing layers. Regarding the DOC in ASW, although the model explained 36.4% of the variance, the standard error of the estimate was low (about 1 µmol L$^{-1}$) and the significance of DoY as explanatory variable was very high ($p < 0.001$) (Table S3). The time course of DOC in ASW was characterized by a well-defined annual cycle with minimum levels of 64 µmol L$^{-1}$ by mid-June and maximum of 88 µmol L$^{-1}$ by late August (Figure 2a). In the MOW the model produced comparable results in terms of the error of the estimate and significance of DoY and showed also a clear annual cycle although with a lower seasonal amplitude and decoupled from the ASW as the seasonal minimum of 49 µmol L$^{-1}$ happens by early May and the maximum of 66 µmol L$^{-1}$ by early August (Figure 2a). Thus, the seasonal DOC extremes occurred 20–30 days later in the ASW than in the MOW.

The contrasting origin of the water masses that meet in the Strait of Gibraltar and their opposed circulation are the reasons behind the observed differences in the amplitude and timing of the seasonal cycles of DOC. ASW flowing eastward in the upper layer and MOW flowing westward in depth constitute the shallow open overturning circulation cell of the Mediterranean Sea (Schneider et al., 2014; Tsimplis et al., 2006). Thus, ASW is a well-ventilated DOC-rich water mass originated in the Eastern North Atlantic Ocean and transported to the Strait of Gibraltar by the Portugal and Azores currents (García-Lafuente et al., 2015; Sánchez-Leal & Relvas, 2003; Santana-Falcón et al., 2017). ASW also modifies further while crossing the GC (Amaral et al., 2020; Criado-Aldeanueva et al., 2006) (Figure 1a), a basin characterized by the classical seasonal cycle of primary production of temperate regions (Navarro & Ruiz, 2006). Furthermore, a considerable discharge of DOC from the Guadalquivir river estuary to the continental shelf of the GC has been documented (Amaral et al., 2020; de la Paz et al., 2007; Flecha et al., 2015). Therefore, the ASW likely receives regional inputs of organic matter with a marked temporal pattern during transit toward the Strait.

On the other hand, the MOW is largely a mixture of EIW and WMDW. EIW is an aged water mass ultimately formed in the Levantine basin and it is characterized by its high salinity (38.84) and low DOC (51 µmol L$^{-1}$) (Catalá et al., 2018; Santinelli, 2015; Santinelli et al., 2010). WMDW forms by deep convection in the Gulf of
Lions. Several varieties of this water mass, previous and posterior to the Western Mediterranean Transient (WMT), coexist in the Western Mediterranean basin, with salinities ranging from 38.46 to 38.49 and DOC 42–43 μmol L⁻¹ (Catalá et al., 2018).

A time series study of the seasonal variability of DOC in surface ocean waters of the temperate Eastern North Atlantic has not been reported yet. The nearest available time series observations are in the oligotrophic waters of the Bermuda Atlantic Time Series station (BATS), in the western side of the North Atlantic subtropical gyre. DOC at BATS displays a marked seasonal cycle characterized by a minimum in February-March and a maximum in July-August (Carlson et al., 1994). Thus, the DOC minimum overlaps with the winter convective mixing period due to DOC dilution within the winter mixed layer. The DOC maximum happens during summer stratification due to “malfunctioning” of the microbial food web caused by nutrient limitation in warm, highly stratified waters (Thingstad et al., 1997). By contrast, the DOC minimum in ASW of the Strait of Gibraltar does not occur during winter mixing: the lowest temperature in ASW is observed in early February (Figure S3), that is, about 3 months before the DOC minimum. Conversely, the DOC maximum overlaps with the highest value of temperature and lowest concentrations of Chl a and nitrate (Figure S3), that is, the period of maximum stratification. In this sense, the seasonal cycle of primary production in the GC (Navarro & Ruiz, 2006) would be coupled to the fluctuations in DOC concentrations measured in the ASW in the same way as already described in BATS. Interestingly, a quasi-permanent phytoplankton proliferation is found around the Trafalgar Cape (NW of the Strait), which has been attributed to local fertilization by the injection of nutrients from the MOW due to tidal effect, but which is particularly pronounced at the end of summer (Macías et al., 2007; Navarro & Ruiz, 2006; Sala et al., 2018). Macías et al. (2007) also showed an eastward advection of phytoplankton toward the Alboran Sea by the Atlantic jet, which could well carry the DOC formed by the local bloom occurring at the end of summer, contributing to the DOC maximum detected over this period of the year.

In the case of the MOW, seasonal minimum levels of DOC at the Strait of Gibraltar are coincident with the DOC concentration in the EIW (Catalá et al., 2018). The remarkable amplitude of the seasonal change of DOC in the MOW, 17 μmol L⁻¹ (Figure 2a), suggests a vertical transference from the ASW by the strong shear and tidal induced mixing between both water masses while crossing the Strait in opposite directions, particularly at the Camarinal sill (Figures 1b and 1c) area (Dafner, González-Dávila, et al., 2001; García-Lafuente et al., 2007; Macías et al., 2007). Even though salinity, potential temperature, AOU, and inorganic nutrients in the MOW also experience seasonal changes (Figure S4), they are small compared with the temporal changes in DOC. In this regard, Santinelli et al. (2012) found a highly significant linear relationship between DOC and AOU in the core of the LIW, with DOC representing 49% of the oxygen demand of this water mass in the Eastern Mediterranean. However, the DOC-AOU relationship was lost in the Western Mediterranean, as we observed in the Strait of Gibraltar.

3.2. DOC Exchange Across the Strait of Gibraltar

The decoupling between the annual cycles of DOC in the upper Atlantic layer and Mediterranean bottom waters in the Strait of Gibraltar results...
in a marked bimodal distribution of the annual cycle of the difference between the DOC in the ASW and the MOW (ΔDOC; Figure 2b). Two ΔDOC maxima of 18 and 22 μmol L⁻¹ occur by mid-April and end of August whereas two ΔDOC minima of 6 and 8 μmol L⁻¹ are observed by the beginning of summer and fall at these latitudes. When ΔDOC is multiplied by the value of the Mediterranean water transport (Q) measured in the Atlantic side of the Strait (at the Espartel sill area, Figure 1b) the net exchange of DOC across the channel can be obtained (F = ΔDOC × Q). Here we have used the modeled seasonal variability of the DOC gradient in the Strait (Figure 2b) and the seasonal pattern observed in the Mediterranean water transport (Figure 2c) provided by Sammartino et al. (2015). This procedure allows to calculate the seasonal cycle of the net exchange of DOC between the Atlantic and the Mediterranean (Figure 2d).

As expected, the annual distribution of DOC fluxes is also bimodal, although the spring and summer maxima of F are of about the same magnitude (15–10¹² g C day⁻¹) compared with the two ΔDOC maxima, 20% higher in summer than in spring. This can be explained by the seasonal pattern of Q, which is 20% faster in spring (0.90 Sv) than in summer (0.75 Sv) (Sammartino et al., 2015) (Figure 2c). DOC exchange at the Strait of Gibraltar varies over a wide range of values, from 5 to 15·10¹² g C day⁻¹ and our work suggests that the periods of minimum and maximum DOC import from the Atlantic toward the Mediterranean can be anticipated.

Previous estimates of net DOC exchange through the Strait are restricted to two values obtained with discrete measurements collected in September 1997 (Dafner, González-Dávila, et al., 2001) and April 1998 (Dafner, Sempéré, & Bryden, 2001). The small differences between both estimates, 0.28–0.35 and 0.30–0.56·10¹² mol C yr⁻¹ (or 10–18 and 9–12·10¹⁰ g C day⁻¹) would not lead to infer the occurrence of a seasonal cycle of net DOC transport. However, when the estimates by Dafner and coworkers are superimposed on the seasonal cycle of the net DOC exchange provided here, they fit conveniently (Figure 2d). These authors used data taken in spring and late summer, when the fluxes between both basins are relatively high. Hence, considering the large seasonal variability of DOC fluxes, any estimate based in observations gathered at a short time period should be expressed on daily (day⁻¹) or monthly basis (month⁻¹) whereas annual extrapolations should be avoided.

### 3.3. Contribution of Water Exchange Through the Strait of Gibraltar to the DOC Budget of the Mediterranean Sea

The annual average net transport of DOC from the North Atlantic toward the Mediterranean Sea through the Strait of Gibraltar is 4.2 ± 1.5·10¹² g C yr⁻¹, as calculated from the seasonal cycle of DOC exchange (Figure 2d). Note that our flux estimates cover from DoY 58 to 338, the period comprised by the surveys (Table S1). Therefore, our annual average net DOC transport does not take into account the fluxes from December to February. Extrapolation of the modeled DOC gradient (Figure 2b) to the winter months does not alter significantly the annual average net flux. Our estimate is half than the 7.7–9.7·10¹² g C yr⁻¹ reported by Santinelli (2015) because we have used more recent and accurate water flows. In order to contextualize the net DOC transport from the Atlantic with other DOC sources to the Mediterranean, we obtained that the atmospheric DOC inputs represent 0.45–1.80·10¹² g C yr⁻¹ (Copin-Montegut, 1993; Djoudi et al., 2018; Galletti et al., 2020; Loïé-Pilot et al., 1992; Violaki et al., 2018; Willey et al., 2000) and riverine inputs account for by 1.0–1.6·10¹² g C yr⁻¹. These fluvial fluxes were calculated from the average DOC concentrations in rivers Po (215 μmol C L⁻¹) Rhone (250 μmol C L⁻¹) and Nile (301 μmol C L⁻¹) recently reviewed by Dai et al. (2012) and using the total freshwater flow to the Mediterranean Sea provided by Lionello et al. (2012) (12.7–14.3; Violaki et al., 2018·10⁵ m³ s⁻¹). Our estimates are lower than the atmospheric input of 0.4–13·10¹² g C yr⁻¹ and slightly higher than the fluvial input of 0.6–0.7·10¹² g C yr⁻¹ provided by Santinelli (2015). The discrepancy in the range of atmospheric DOC inputs is because we have discarded outliers when extrapolating to the entire Mediterranean. In fact, Santinelli et al. (2015) state that 1.3–4.6 g C yr⁻¹ would be a more reasonable range. Finally, the net DOC input from the Black Sea across the Dardanelles strait has been estimated in 1.21–1.26·10¹² g C yr⁻¹ (Copin-Montegut, 1993; Polat & Tugrul, 1996). Therefore, according to our assessment, the Atlantic Ocean can be considered the main source of DOC to the Mediterranean Sea, representing 53% of the total DOC input of 7.9 ± 1.6·10¹² g C yr⁻¹. This percentage is very consistent with the 55% contribution of the ASW inflow to the DOC of the deep Mediterranean Sea based on δ¹³C-DOC measurements by Santinelli et al. (2015) despite our disagreements in the estimates of next fluxes.
Applying a similar two-layer model of water mass exchange, Huertas et al. (2009) estimated the net export of dissolved inorganic carbon (C\textsubscript{I}) from the Mediterranean Sea to the adjacent Atlantic Ocean as 29.2 ± 0.6·10\textsuperscript{12} g C yr\textsuperscript{−1}, after discounting the anthropogenic C\textsubscript{I} signal. These authors also reported that 45% of such export (13.2 ± 0.2·10\textsuperscript{12} C yr\textsuperscript{−1}) corresponded to C\textsubscript{I} produced during organic matter mineralization. Therefore, total DOC inputs to the Mediterranean Sea constitute 60 ± 12% of the organic carbon mineralization in this semienclosed basin, with 32 ± 12% of an Atlantic origin. The DOC transported eastward in the ASW has an immediate impact on the heterotrophy of the adjacent Alboran Sea (Sempéré et al., 2003). The remaining 40% should come from the mineralization of organic particles suspended in fluvial discharge, Dardanelle and Gibraltar straits flows, as well as that deposited from the atmosphere. Concerning fluvial particulate organic carbon (POC), the annual flux from river Rhone is about twice the flux of DOC (Sempéré et al., 2000). If this ratio is applicable to all Mediterranean rivers, the total fluvial flux of POC would be 2.0–3.2·10\textsuperscript{12} g C yr\textsuperscript{−1}, which would explain about 50% of the POC demand. The net POC exchange across the Dardanelle strait has been estimated in 0.17–0.18 10\textsuperscript{12} g C yr\textsuperscript{−1} (Polat & Tugrul, 1996). For the case of the Strait of Gibraltar, Santana-Falcón et al. (2017) estimated a net POC exchange of 0.6 10\textsuperscript{12} g C yr\textsuperscript{−1} from a single POC profile obtained in May 2014. Therefore, POC imported from the surface NE Atlantic Ocean and Marmara Sea would represent about 15% of the POC demand. The remaining 35% could be explained by the organic content of particles deposited from the atmosphere, likely during the frequent and massive Sahara dust events (Gallaisi et al., 2016). Submarine groundwater discharge has also been suggested as a source of DOC to the Mediterranean but it would be essentially refractory (Santinelli et al., 2015). All these estimates are just based on the product of DOC or POC concentrations in marine, atmospheric, and fluvial waters to the Mediterranean multiplied by their respective water flows. Therefore, what we obtain is a net budget of inputs minus outputs, assuming steady state, and treating the Mediterranean as a “black box.” Despite all these limitations, our numbers reveal the major role played by DOC in the carbon cycle of the Mediterranean Sea and particularly by the DOC transported from the Atlantic Ocean by the ASW through the Strait of Gibraltar.

4. Conclusions

Straits connecting ocean basins are “hot spots” of ocean circulation and biogeochemical cycles. Despite their importance, studies on the seasonal variability of the net exchange fluxes of essential compounds across straits are still scarce. Here we have shown that differences in the amplitude and timing of the seasonal cycles of DOC concentrations in ASW and MOW as well as water exchange fluxes across the Strait of Gibraltar produced a marked bimodal distribution of the net DOC flux to the Mediterranean basin. These fluxes are about threefold during the seasonal maxima that during the seasonal minima. Quantification of this seasonality is crucial to better constraining this significant flux of 4.2 Tg C yr\textsuperscript{−1}, which represents 53% of the external DOC input to the Mediterranean Sea and supports 32% of the net heterotrophy of this basin. Our estimate is based on discrete DOC measurements along the strait occupied on different months through several years. Using our data to validate a 3-D hydrodynamic + biogeochemical model would provide better-constrained results. Furthermore, application of DOC isotope, optical, or molecular proxies would allow gaining new insights on the role of the DOC transported by the Atlantic jet into the Mediterranean.

Data Availability Statement

Data used in this study correspond to the database generated at the GIFT (Gibraltar Fixed Time Series) observatory and are available at Digital CSIC repository (https://digital.csic.es/handle/10261/205367).

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