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Key Points:

- Global DOC export from coastal ocean to the open ocean varied between 4.4 to 27.0 Pg C yr^{-1}
- Global DOC export is consistent with regional estimates

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Dissolved organic carbon pools and export from the coastal ocean

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Abstract The distribution of dissolved organic carbon (DOC) concentration across coastal waters was characterized based on the compilation of 3510 individual estimates of DOC in coastal waters worldwide. We estimated the DOC concentration in the coastal waters that directly exchange with open ocean waters in two different ways, as the DOC concentration at the edge of the shelf break and as the DOC concentration in coastal waters with salinity close to the average salinity in the open ocean. Using these estimates of DOC concentration in the coastal waters that directly exchange with open ocean waters, the mean DOC concentration in the open ocean and the estimated volume of water annually exchanged between coastal and open ocean, we estimated a median ± SE (and average ± SE) global DOC export from coastal to open ocean waters ranging from 4.4 ± 1.0 Pg C yr^{-1} to 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} to 29.0 ± 8.0 Pg C yr^{-1}) depending on the global hydrological exchange. These values correspond to a median and mean median (and average) range between 14.7 ± 3.3 to 90.0 ± 6.0 (23.3 ± 19.3 to 96.7 ± 26.7) Gg C yr^{-1} per km of shelf break, which is consistent with the range between 1.4 to 66.1 Gg C yr^{-1} per km of shelf break of available regional estimates of DOC export. The estimated global DOC export from coastal to open ocean waters is also consistent with independent estimates of the net metabolic balance of the coastal ocean. The DOC export from the coastal to the open ocean is likely to be a sizeable flux and is likely to be an important term in the carbon budget of the open ocean, potentially providing an important subsidy to support heterotrophic activity in the open ocean.

1. Introduction

Dissolved organic carbon (DOC) is the second largest carbon pool in the ocean and the least understood [*Hansell and Carlson*, 2001]. Even though DOC represents only 2% of the carbon inventory in the water column, this pool is the largest exchangeable reservoir of carbon in the marine environment [*Druffel et al*., 1992; *Hansell and Carlson*, 2002]. DOC is an important component of the global carbon cycle and has been shown to be a sizeable and dynamic component of the carbon budget in surface and deep waters of the open ocean [*Carlson et al*., 1994; *Hansell and Carlson*, 1998].

Models of the organic carbon cycle in the open ocean typically ignore coastal inputs [*Sarmiento and Gruber*, 2006], implicitly assuming the exchange of organic carbon between open and coastal waters to be negligible [*del Giorgio and Duarte*, 2002]. As a result, the carbon budget of the open ocean is typically treated as a one-dimensional, vertical process with exchanges of carbon between different layers and with the boundaries above (atmosphere), and below (sediments), but no significant lateral exchange with the coastal ocean [*Sarmiento and Gruber*, 2006]. However, examination of regional carbon budgets consistently provides evidence for a significant export of organic carbon from the coastal to the open ocean [*Liu et al*., 2000a; *Chen and Borges*, 2009]. Although the importance of the coastal ocean as a component of the marine carbon cycle is well recognized [*Walsh*, 1991], efforts to elucidate the fate and cycling of organic carbon in the coastal ocean and its export to the open ocean have been limited [*Hung et al*., 2000; *Bauer et al*., 2001; *Vlahos et al*., 2002].

Although continental shelves represent only about 7% of the oceanic surface area, the coastal zone is a productive and dynamic system that accounts for about 20% of the total oceanic organic matter production. The coastal ocean receives organic carbon inputs mainly from rivers [*Cauwet*, 2002], groundwater discharge [*Burnett et al*., 2003], and relatively small atmospheric inputs [*Willey et al*., 2000]. Riverine organic C inputs to the coastal ocean have been estimated at about 426 Tg C yr^{-1} [*Cauwet*, 2002], where 58.7% is delivered as DOC and the rest as particulate organic carbon (POC) [*Cauwet*, 2002]. Therefore, the coastal ocean receives 250 Tg C yr^{-1} of DOC from land [*Cauwet*, 2002]. Because this terrestrial DOC pool is generally refractory [*le Clercq et al*., 1997; *Stubbins et al*., 2010], much of it is believed to be exported to the open ocean [*Liu et al*., 2000a]. However, the relative contribution of riverine DOC to the open ocean pool is small [*Opsahl and Benner*, 1997], probably because riverine DOC is buried [*Duarte et al*., 2005] and photooxidized within the coastal zone [*Moran and Zepp*, 1997; *Opsahl and Benner*, 1998; *Stubbins et al*., 2010].

Hence, DOC in the coastal ocean is dominated by autochthonous sources, as the coastal ocean is inhabited by highly productive communities (plankton, macrophyte, and coral dominated communities) [*Gattuso et al*., 1998]. Indeed, coastal ecosystems typically produce organic carbon in excess relative to respiratory demands [*Duarte and Cebrián*, 1996; *Gattuso et al*., 1998; *Duarte et al*., 2010]. Some of the excess organic carbon is buried in the sediments; however, the rest of the organic carbon is available to be exported to the open ocean [*Duarte et al*., 2005], where it may subsidize heterotrophic activity [*del Giorgio and Duarte*, 2002].

Organic carbon can be exported from the coastal to the open ocean as POC and DOC. Earlier studies of carbon export from ocean margins to the open ocean considered POC export alone [*Wollast*, 1991]. However, DOC concentrations are 1 to 2 orders of magnitude greater than that of POC in surface waters [*Druffel et al*., 1992; *Bauer and Druffel*, 1998], suggesting that the DOC pool may dominate organic carbon (OC) export from shelf regions to the open ocean. In addition, the C:N ratio of DOC exceeds the Redfield ratio [*Hopkinson et al*., 1997] implying that a given nitrogen input would support a greater C export if occurring as DOC than as POC.

The suspension time of particles in the ocean is less than 1 month [*Lande and Wood*, 1987], much shorter than the residence time of the coastal ocean (about 130 days) [*Huthnance*, 1995], implying that most of the POC produced in the coastal zone may not reach the open ocean and will be retained within the coastal ocean. Thus, DOC is expected to dominate the excess organic carbon exported from the coastal to the open ocean. Indeed, regional studies of organic carbon export (OC export) from continental margins indicate that about 80% of the C export occurs as DOC [*Hung et al*., 2000; *Bauer et al*., 2001; *Vlahos et al*., 2002].

The elucidation of organic carbon export from the coastal ocean can help improve our understanding of the metabolic balance of the open ocean [*del Giorgio and Duarte*, 2002; *Duarte et al*., 2013]. Indeed, arguments on the role that organic C export from the coastal ocean may play in the carbon budget of the global ocean have been thus far derived indirectly from mass balance considerations, as the inventory of DOC in the coastal ocean needed to formulate a direct estimate was not available.

Here we provide an overview of the role of the coastal ocean in supporting organic C export to the open ocean. We first review available estimates of organic carbon export from the coastal to the open ocean inferred from carbon mass balances. We then provide a synthesis of estimates of DOC concentration in coastal waters. These estimates are then combined with estimates of hydrological exchanges between the coastal and open ocean to yield a direct estimate of the global DOC export from the coastal to the open ocean. The robustness of this estimate is then discussed by examining the consistency of the export flux derived here with those assessed in regional studies and with existing estimates of organic carbon mass balances in the coastal zone.

2. Methods

We searched the literature for estimates of DOC concentrations in the coastal ocean, as well as the salinity at the site of DOC sampling and the distance from the nearest shoreline. Whenever the distance to the nearest shoreline was not reported, the minimum distance from the sampling station to the coastline was derived from latitude and longitude using global shoreline contours or from maps provided in the papers. DOC data were averaged, when provided as vertical profiles, to yield depth-averaged estimates of coastal DOC concentrations. Coastal waters were defined as those comprised between estuarine head waters and the shelf break. The coastal locations where DOC estimates were available were classified as estuaries, open coastal zone, and vegetated coastal waters (including coastal lagoons). Open coastal waters were defined as those outside estuarine and vegetated areas. We acknowledge that the data derived from the published literature on estimates of DOC concentration in coastal waters do not represent a random sample of the coastal ocean but portray the current state of knowledge on DOC concentrations in coastal waters. Depth-averaged DOC concentration in coastal waters was not normally distributed (Kolmogorov-Smirnov normality test). Hence, we used median values to represent the central tendency and used nonparametric analyses to test for differences. Differences in DOC concentrations across bioregions were assessed using a Post Hoc test (Dunn test) after a nonparametric Kruskal-Wallis test.

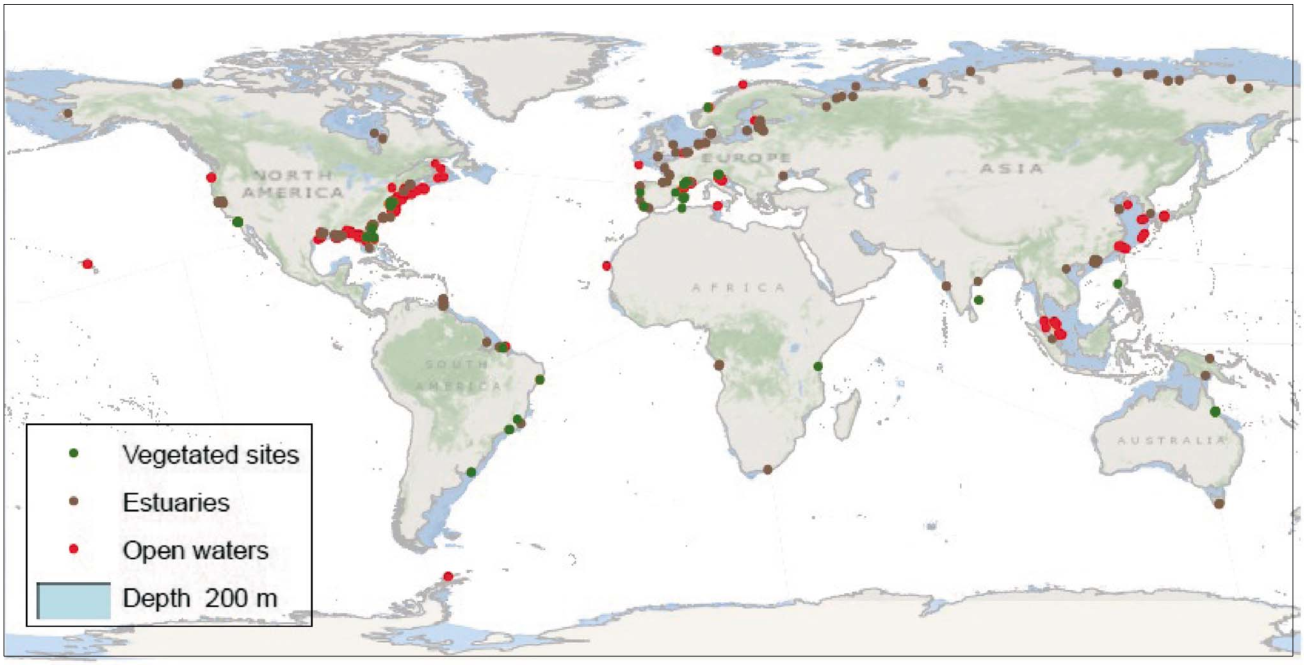

Figure 1. Location of the sites where DOC concentrations were compiled from the literature and from our own unpublished results. Brown circles represent estuaries, red circles represent open coastal waters, green circles represent vegetated sites. The yellow-shaded area represents the extent of the coastal ocean.

We used two approaches to estimate the DOC concentration in the coastal waters directly exchanging with open ocean waters. First, we estimated this concentration as the median (and average) DOC concentration at the edge of the coastal zone estimated from the relationship between DOC concentrations in coastal waters and the distance from the coastline, assuming an average width of the coastal ocean of 78 km [*Shepard*, 1963]; unfortunately, no error is shown, and no uncertainty related with this estimate could be computed. We also used the salinity field to estimate the DOC concentration in the coastal waters directly exchanging with open ocean waters as the median (and average) DOC concentration in coastal waters with salinity above 35, representing the average salinity in the open ocean, derived from the relationship between the DOC concentration versus salinity in coastal waters. The relationships between coastal DOC concentrations and salinity were fitted using least squares regression analysis on DOC data binned by three salinity units, thereby representing the median (and average) DOC within salinity classes. The relationships between coastal DOC concentrations and distance from the coast were fitted using least squares regression analysis after transforming the raw data using a $\log_2$ distance bins, as raw data showed an exponential distribution.

The global DOC export from the coastal to the open ocean (mol C yr^{-1}) was calculated from the simple equation:

$$\text{Global DOC export} = (\text{DOC}_c - \text{DOC}_o) \times E \tag{1}$$

where DOC_c represents the average DOC concentration in the coastal waters directly exchanging with open ocean waters (mol m^{-3}), estimated by the two alternative approaches indicated above, DOC_o represents the average DOC concentration in the open ocean (mol m^{-3}), derived from *Arístegui et al*. [2002], and E represents the water exchanged between the coastal and the open ocean in 1 year ($\text{m}^3\,\text{year}^{-1}$), calculated from the data provided by *Huthnance* [1995]. The uncertainty associated to our estimates was evaluated using bootstrapping by resampling the components involved in the calculations (DOC at the self-break, full-strength salinity and in the open ocean; and hydrological exchange across the shelf break) randomly from normal distributions with the mean and SD calculated in this study. No error estimate was available for the global length of the shelf break of 300,000 km [*Huthnance*, 1995], so the uncertainty on this could not be included. The uncertainty around the hydrological exchange across the shelf break was estimated as the SD for the values derived for the regional studies available, but we used both the mean for those studies as well as the more conservative value of 1 Sv for 1000 km of shelf break derived as a global value

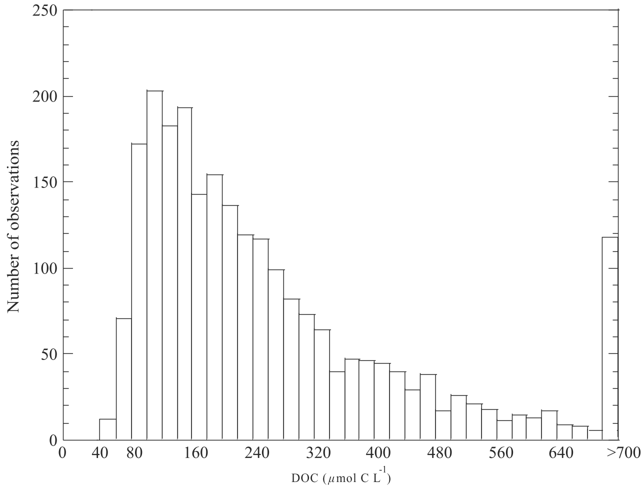

Figure 2. Frequency distribution of depth-averaged DOC concentration in coastal waters.

by *Huthnance* [1995]. Twenty sets of 10 independent combinations of values were generated for each simulation, each providing a mean and SD for global DOC export. The mean average and mean SD for the 20 simulation sets was then used as a robust estimate of the DOC exchange and the associated uncertainty. Thereby, we estimated a median ± SE and mean ± SE global DOC export. The resulting estimates of global DOC export were then compared with independent estimates of the organic carbon export from available regional studies. We searched the literature for regional estimates of DOC export from shelf waters, which were converted to Gg C yr^{-1} per km of shelf break to allow comparison. Whenever the length of the shelf break for the region studied was not provided, this was calculated from maps provided in the papers.

3. Results

3.1. Inventory and Patterns of Variability of DOC in the Coastal Ocean

The data set on DOC concentrations developed here amended with our own unpublished results comprised 3510 individual estimates of DOC in coastal waters worldwide [*Barrón and Duarte*, 2013]. These estimates were not evenly distributed across the coastal ocean, with most estimates located in the Northern Hemisphere and a deficit of studies in the coast of Africa, South America, Australia, and Asia, which support high riverine inputs (Figure 1). Depth-averaged DOC concentration in coastal waters was not normally distributed and showed a skewed distribution (Figure 2). Depth-averaged DOC concentration in coastal waters ranged over an order of magnitude, with a few estimates, from estuarine environments, exceeding 700 μmol C L^{-1}, and a mean ± standard error (SE) and median concentration of 285.7 ± 5.7 μmol C L^{-1} and 208.5 μmol C L^{-1}, respectively (Figure 2). Estuarine waters comprise a minor fraction of the volume of the coastal ocean, but most (73.7%) of the DOC estimates from the 2384 coastal locations reported derived from estuaries (Table 1), with an average DOC concentration of 329.8 ± 7.0 μmol C L^{-1}. Only 19.3% and 6.9% of the coastal areas where DOC concentrations were available corresponded to open coastal areas and shallow vegetated areas with average DOC concentrations of 126.4 ± 2.6 and 246.0 ± 17.6 μmol C L^{-1}, respectively (Table 1). Most (60.7%) of the estimates of DOC concentration from open coastal waters were derived from the North Atlantic coastal zone, and 17.4% of the estimates were derived from coastal waters in the Mediterranean Sea (Figure 3). DOC concentrations across coastal regions did not show overall major differences across regions, although DOC concentrations from West Pacific coastal waters were significantly lower than DOC concentrations from the Mediterranean Sea and the Tropical West Atlantic (Dunn test, $p < 0.05$, Figure 3).

Table 1. Mean ± SE and Median of Depth-Averaged DOC (μmol C L^{-1}) Concentration From 2384 Coastal Locations (*n*)

	Mean (μmol C L^{-1})	±	SE	Median (μmol C L^{-1})	*n*
Coastal waters	285.7	±	5.7	208.5	2384
Open coastal zone	126.4	±	2.6	111.3	461
Vegetated coastal waters	246.0	±	17.6	180.4	165
Estuaries	329.8	±	7.0	250.0	1758
Coastal water with salinity >35	139.5	±	7.9	111.7	
Shelf break (78 km from coastal line)	109	±	41	97	

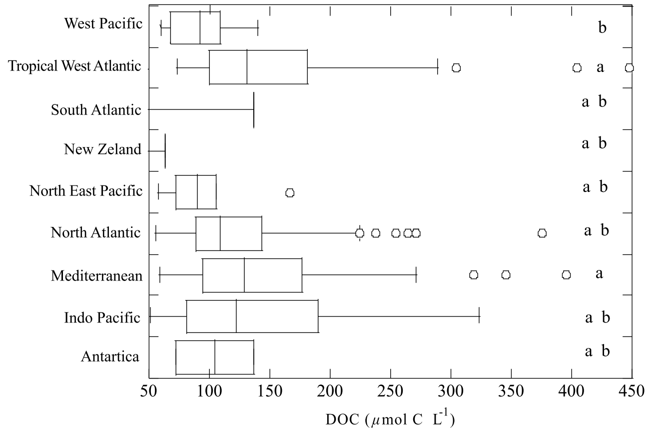

Figure 3. Box plot showing the distribution of DOC concentrations in the open coastal zone across different bioregions. Open coastal waters were defined as those outside estuarine and vegetated areas. Different letters in the plot indicate significant differences ($p < 0.05$).

The average DOC concentration in open ocean surface waters has been estimated at 63.4 ± 0.2 µmol C L^{-1} [*Arístegui et al.*, 2002], well below that of coastal waters. This implies that the mixing of open and coastal ocean waters involves a net offshore export of DOC to the open ocean. However, DOC-rich estuarine waters do not exchange directly with open ocean waters, as this mixing occurs at the shelf break. It is, therefore, important to consider what is the differential DOC concentration between coastal waters at the shelf break and open ocean waters.

The median DOC concentration in coastal waters also decreased significantly ($r^2 = 0.95$, $p < 0.001$) with increasing salinity, from an average of about 488 µmol C L^{-1} in estuarine headwaters to reach 139.5 ± 7.9 µmol C L^{-1}, on average, in open coastal waters with salinity > 35 (Figure 4, Table 1) and a median value of 111.7 µmol C L^{-1}. The median DOC concentration in coastal waters declined significantly with increasing distance from the coastline ($r^2 = 0.77$, $p < 0.01$, Figure 5), as a result of dilution and dynamic turnover, involving DOC release and microbial and photochemical removal, within the coastal zone. The concentration of DOC at the edge of the coastal ocean directly exchanging with the open sea water, calculated from the fitted linear regression between DOC concentration and distance from the shoreline (Figure 5) assuming an 78 km average width of the coastal ocean [*Shepard*, 1963] was, on average, 109 ± 41 µmol C L^{-1} with a median concentration of 97 µmol C L^{-1}.

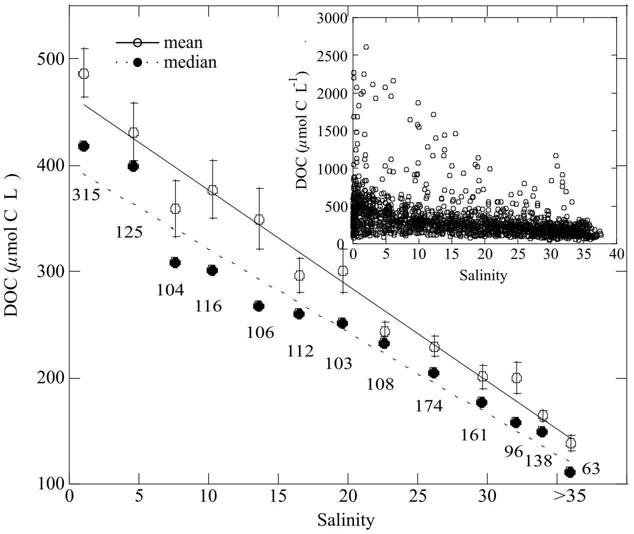

Figure 4. The relationship between DOC concentration and salinity in coastal waters. The data points represent the average ± SE and median of DOC concentration of data grouped in three salinity unit bins. The number below each data point represents number of data of each data point. The solid line represent the fitted linear regression equation of the means: DOC (µmol C L^{-1}) = 465.70 (±11.60) − 8.93 (±0.55) salinity, $r^2 = 0.96$, $p < 0.001$. The dot line represents the fitted linear regression equation of the median: DOC (µmol C L^{-1}) = 398.87 − 7.76 salinity, $r^2 = 0.95$, $p < 0.001$. The last two circles represent the mean and median of DOC concentration with salinity > 35. The insert shows the relationship with the raw data ($n = 1721$).

3.2. Mixing and DOC Export From Coastal to Open Ocean Waters

The water exchange between the coastal and open ocean is the result of multiple and complex processes (e.g., Ekman transport and upwelling) including storm surges, tides, and thermohaline circulation driven by density gradients [*Huthnance*, 1995]. When integrated, these processes have been estimated to yield an average exchange rate of about 1 sverdrup (1 Sv = 10^6 m^3 s^{-1}) per 1000 km of shelf break length [*Huthnance*, 1995]. This exchange rate between continental shelves and the open ocean remains the only global estimate available and has been used recently to estimate the nitrogen budget in the coastal zone [*Voss et al.*, 2011]. With a global shelf break length of 300,000 km, the resulting water exchange between the coastal and open ocean is 300 sverdrup, within the range of 50–1500 sverdrups calculated to be required to transport sufficient excess production to meet the putative organic matter in the open ocean [*Williams and Bowers*, 1999]. This transport represents the integral of exchanges driven by a wide diversity of processes operating across the length of the shelf break [*Huthnance*, 1995]. For instance, *Jahnke* [2010] estimated that cascades of high-density waters from continental shelves support an exchange of 75–120 Sv between shelves and ocean interiors using a global shelf edge length of approximately 150,000 km (excluding many marginal seas). The estimated annual water exchange (*E*) between the coastal and open ocean corresponds, therefore, to about 9.46×10^{15} m^3, which considering a volume of the coastal ocean of 3.38×10^{15} m^3 yields a residence time for the global coastal ocean of about 130 days.

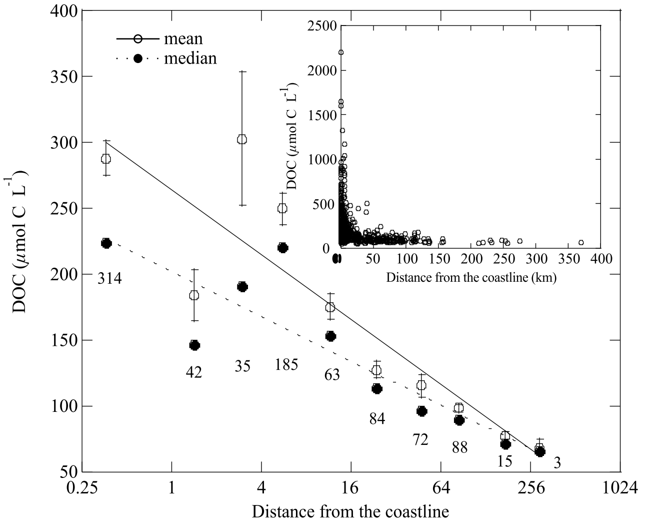

Figure 5. The relationship between DOC concentration in coastal waters and the distance offshore from the coastline. The data points represent the average ± SE and median of DOC concentration of data grouped in $\log_2$ distance bins. The number below each data point represents number of data of each data point. The solid line represents the fitted regression equation of the means: DOC (μmol C L^{-1}) = 263.87 (±21.49) − 24.53 (±4.40) $\log_2$ distance (km), $r^2 = 0.77$, $p < 0.01$. The dot line represents the fitted regression equation of the median: DOC (μmol C L^{-1}) = 203.76 − 17.11 $\log_2$ distance (km), $r^2 = 0.77$, $p < 0.01$. The insert shows the relationship with the raw data ($n = 901$).

The median (and average) DOC concentration in the coastal waters (DOC$_c$) calculated above in open coastal waters of 112 μmol C L^{-1} (139 ± 8 μmol C L^{-1}) and at the shelf break of 97 μmol C L^{-1} (109 ± 41 μmol C L^{-1}) far exceeds the average DOC concentration in open ocean (DOC$_o$) surface waters of 63.4 ± 0.2 μmol C L^{-1} [*Arístegui et al.*, 2002]. This implies that the mixing of open and coastal ocean water involves a median (and average) net offshore DOC export of 41 μmol C L^{-1} (61.2 ± 47.2 μmol C L^{-1}) of water exchanged. The average net DOC export from open coastal water is 76.1 ± 8.1 μmol C L^{-1} and at the shelf break is 46.3 ± 41.6 μmol C L^{-1},

Table 2. DOC Export (Gg C yr^{-1}), Estimated Shelf Length (km), Calculated DOC Export Per Shelf Break Length Per Year (Gg C km^{-1} yr^{-1}), Water Exchange (Sv; 1 Sv = 10^6 m^3 s^{-1}), and Exchange Rate in Sv Per 1000 km in Regional Studies of Shelf DOC Export

Shelf region	DOC Export Gg C yr^{-1}	Shelf Length (km)	DOC Export per km Shelf Break Length Gg C km^{-1} yr^{-1}	Sv	Sv per 1000 km	References
East China Sea	4968	250.0	19.9	0.7	2.9	*Hung et al.* [2000]
Mid-Atlantic Bight	19150	777.8	24.6	0.3	0.3	*Vlahos et al.* [2002]
East China Sea	35700	666.7	53.5	1.2	1.8	*Hung et al.* [2003]
Cape Ghir (northwest Africa)	2974	45.0^a	66.1	0.3	7.1	*García-Muñoz et al.* [2005]
Mid-Atlantic Bight	6000	950.0	6.3	0.4	0.4	*Bauer et al.* [2001]
North Brazilian Shelf	1440	212.5	6.8	0.2	0.8	*Dittmar et al.* [2006]
Ría de Vigo (Spain)	551	32.0^a	17.2	0.1	3.4	*Álvarez-Salgado et al.* [2001]
Bengala upwelling (model)	6000	600.0	10.0			*Waldron et al.* [2009]
Gulf of Lion	307.8	222.2	1.4	1.5	6.7	*Durrieu de Madron et al.* [2009]
Southern California coast			33.4^b			*Munro et al.* [2013]
Median of regional studies			18.5		2.4	
Average of regional studies			23.9			
Median of global estimate			14.7–90.0			This study
Average of global estimate			23.3–96.7			This study

^{a}Width of the filament in the offshore flowing section reported.
^{b}DOC and POC export.

with an uncertainty of 10.6% and 89.9%, respectively. Regional estimates of water exchange in coastal regions where hydrological exchange rates across the shelf break range between 0.3 and 7.1 Sv per 1000 km with a median (and average ± SE) of 2.4 Sv per 1000 km (3.0 ± 1.0 Sv per 1000 km) in these specific regions (Table 2) higher, but not significantly so, than the global estimate of 1 Sv per 1000 km derived by *Huthnance* [1995]. Using the mean and SD hydrological exchange from regional studies and the net DOC export from open coastal waters reported above, the median (± SE), and mean (± SE) global export of DOC from the coastal to the global ocean was estimated at 18.6 ± 2.8 Pg C yr^{-1} and 16.2 ± 12.8 Pg C yr^{-1}, respectively, when the mean DOC concentration at the shelf break was used to calculate the coastal end-member mixing with open ocean water and an export estimate of 27.0 ± 1.8 Pg C yr^{-1} and 29.0 ± 8.0 Pg C yr^{-1}, respectively, was derived when the mean DOC at full-strength salinity was used. Using the more conservative global hydrological exchange of 1 Sv per 1000 km of shelf break, the corresponding median (± SE) and mean (± SE) global export of DOC from the coastal to the global ocean was estimated at 4.4 ± 1.0 Pg C yr^{-1} and 7.0 ± 5.8 Pg C yr^{-1}, respectively, when the mean DOC concentration at the shelf break was used to calculate the coastal end-member mixing with open ocean water and an export estimate of 8.6 ± 1.0 Pg C yr^{-1} and 10.6 ± 4.4 Pg C yr^{-1}, respectively, was derived when the mean DOC at full-strength salinity was used. Therefore, median (± SE) global DOC export varied between 4.4 ± 1.0 Pg C yr^{-1} and 27.0 ± 1.8 Pg C yr^{-1}, and average (± SE) global DOC export ranged between 7.0 ± 5.8 Pg C yr^{-1} and 29.0 ± 8.0 Pg C yr^{-1} depending on the global hydrological exchange.

4. Discussion

The compilation of coastal DOC estimates were dominated by measurements derived from the Northern Hemisphere, with 78% of the DOC estimates in open coastal waters derived from the North Atlantic and the Mediterranean Sea. The estimate of a median ± SE (and average ± SE) global DOC export varied between 4.4 ± 1.0 Pg C yr^{-1} and 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} and 29.0 ± 8.0 Pg C yr^{-1}) from the coastal to the open ocean provided here is, to the best of our knowledge, the first estimate of organic carbon exchange between the coastal and open ocean derived from consideration of mixing between these two compartments. Large offshore gradients of terrigenous DOC across the coastal zone suggest that this component is mineralized through photochemical and microbial oxidation before being exported to the open ocean [*Moran et al.*, 1991]. Microbial degradation of aromatic carbon compounds is slower than photochemical degradation [*Opsahl*, 2005]. However, *Bianchi et al.* [2013] showed that aromatic compounds such as lignin breaks down faster during a flooding event in the Gulf of Mexico. Photooxidation of terrestrial DOC also plays a role in the cycling of carbon in the coastal zone [*Opsahl and Benner*, 1998; *Stubbins et al.*, 2010]. Solar radiation is responsible for the photochemical transformation of dissolved organic matter (DOM) to low molecular weight compounds, carbon monoxide (CO), and ultimately carbon dioxide [CO_2, *Moran and Zepp*, 1997]. Photochemical processes also transform refractory terrestrial compounds into more labile molecules [*Stubbins et al.*, 2010] that can be used more readily by bacteria [*Moran and Zepp*, 1997]. For instance, in the Gulf of Mexico, *Bianchi et al.* [2009] reported a decline in DOC concentration and dissolved lignin phenols across a transect from a marsh ecosystem to the adjacent continental shelf, suggesting photochemical breakdown of lignin and subsequent microbial use of the more labile products.

In addition, highly productive coastal ecosystems such as marine macrophyte habitats are likely to be the source of much of the exported DOC. Seagrass meadows export significant amounts of organic carbon to adjacent ecosystems as DOC [*Ziegler and Benner*, 1999; *Stabenau et al.*, 2004; *Barrón and Duarte*, 2009]. For instance, a Mediterranean seagrass meadow supported a net DOC export of 4.3 mol C m^{-2} yr^{-1} [*Barrón and Duarte*, 2009] and globally seagrass meadows had a net release rate of 4.5 ± 1.1 mol C m^{-2} yr^{-1} [*Barrón et al.*, 2014]. Macroalgae have also been reported to be sizeable sources of DOC [*Hughes et al.*, 2012; *Wada*, 2012], with net release rates averaging 8.5 ± 4.6 mol C m^{-2} yr^{-1} [*Barrón et al.*, 2014]. The high net DOC release from marine macrophytes may be supported by photosynthetically derived carbohydrates, which dominate nonstructural (storage) compounds. These newly produced compounds may be labile and used by bacteria so that only a fraction of the DOC released by marine macrophytes supports DOC export to the open ocean. Other marine benthic communities such as mangroves, coral reefs, and salt marshes have been reported to release DOC at rates of 12 mol C m^{-2} yr^{-1} [*Dittmar et al.*, 2006], 28.25 mol C m^{-2} yr^{-1} [*Nakajima et al.*, 2009], and 7.40 mol C m^{-2} yr^{-1} [*Hassen*, 2000], respectively. In contrast, DOC release by bare sediment has been estimated to be low, at 0.33 mol C m^{-2} yr^{-1} [*Burdige et al.*, 1999], well below that of vegetated sediments [*Ziegler and Benner*, 1999; *Barrón and Duarte*, 2009; *Barrón et al.*, 2014]. In addition to benthic DOC release, plankton [*Souchu et al.*, 1997; *Romera-Castillo et al.*, 2010] and krill [*Ortega-Retuerta et al.*, 2009; *Ruiz-Halpern et al.*, 2011] act as sources of DOC in coastal ecosystems. Moreover, leaching from decomposing organic material can also be an important source of DOC in coastal systems [*Ziegler and Benner*, 1999; *Mai et al.*, 2006; *Wang et al.*, 2007].

Earlier suggestions that a significant flux of organic carbon exported from the coastal ocean could reach the open ocean, subsidizing heterotrophic metabolism therein [*Duarte and Agustí*, 1998], was met with the criticism that this "…would also require massive water transport—perhaps 50–1500 Sverdrups, i.e., comparable to or many times greater than the Gulf Stream" [*Williams and Bowers*, 1999]. Rather than a single current system, the required transport mechanism is provided by mixing between coastal and open ocean waters, involving a broad range of complex mechanisms, which is estimated to exchange $9.46 \times 10^{15}\,\mathrm{m^3\,yr^{-1}}$ [*Huthnance*, 1995] equivalent to 300 sverdrups, within the middle of the range calculated to be necessary by *Williams and Bowers* [1999]. This large hydrological exchange, involving 1 sverdrup per 1000 km along the 300,000 km of shelf break in the global ocean coupled with a differential in DOC concentration between open coastal and open ocean waters drive a globally significant export flux of DOC from the coastal to the open ocean.

We acknowledge several sources of uncertainty in our analysis. First, uncertainties derived from limited availability of estimates of DOC concentration in the coastal zone, particularly in the Southern Hemisphere. Indeed, the Southern Hemisphere is underrepresented in the empirical basis available on DOC concentration in coastal waters and exchange with the open ocean. Addressing this imbalance through a concerted effort to develop regional studies targeting the Southern Hemisphere will help improve the precision of current estimates of global DOC export from the coastal to the open ocean. A second source of uncertainty is our primitive understanding of hydrological exchange processes between the coastal and the open ocean, which are not adequately implemented in global ocean circulation models. In addition, the processes involved, from hydrological exchanges to OC inputs and metabolic rates in the coastal ocean are not static but dynamic over time, also adding to variability about global estimates. Lastly, our estimates do not account for depth variability, whereas DOC concentrations and hydrological exchange at the shelf break may differ with depth, but the required data are not available. Efforts to improve our understanding of the connectivity and hydrological exchange processes between the coastal and open ocean and its variability, largely ignored in current global carbon budgets and ocean circulation models, are, therefore, essential to understand carbon fluxes and the associated metabolic balance of the ocean.

Provided the uncertainties associated with the estimate of global DOC export, its robustness should be tested further by assessing its consistency with independent constrains. We do so by assessing the consistency of the estimate provided above with mass balance calculations of the carbon budget of the global coastal ocean and also assessing its consistency with regional estimates of OC export from the coastal to the open ocean.

4.1. Export of Organic Carbon From the Coastal Ocean Inferred From Carbon Mass Balances

The global export from coastal to open ocean (Ex, $\mathrm{Tg\,C\,yr^{-1}}$) can be calculated from the mass balance equation:

$$\mathrm{Ex} = I + \mathrm{NEP} - B \qquad (2)$$

where I represents the allochthonous C inputs to the coastal ocean, NEP represents the net ecosystem production of coastal ecosystems, and B represents the rate of C burial in the coastal zone.

Riverine organic C inputs to the coastal ocean have been estimated at about $426\,\mathrm{Tg\,C\,yr^{-1}}$ (Table 3) where 58.7% is delivered as DOC and the rest as POC [*Cauwet*, 2002]. Sewage inputs deliver an estimated $150\,\mathrm{Tg\,C\,yr^{-1}}$ to the coastal ocean [*Smith and Hollibaugh*, 1993]. Generally, terrestrial derived fresh submarine groundwater discharge range from 6 to 10% of surface water inputs in the coastal zone by rivers; hence, we estimated, assuming DOC concentrations in groundwater to be similar to those in surface runoff, that groundwater discharge provides an additional $34\,\mathrm{Tg\,C\,yr^{-1}}$. Atmospheric DOC inputs deliver $90\,\mathrm{Tg\,C\,yr^{-1}}$ to the marine system [*Willey et al.*, 2000]. Assuming that continental shelves represent 7% of the oceanic surface area, the rainwater DOC flux to the coastal ocean would be about $6.3\,\mathrm{Tg\,C\,yr^{-1}}$. This represents an upper estimate to atmospheric allochthonous organic inputs, since a fraction of this input may represent DOC emitted from the ocean to the atmosphere. Hence, the total allochthonous input (I in the equation above) of organic carbon to the coastal ocean is estimated at $616.4\,\mathrm{Tg\,C\,yr^{-1}}$. Part of this OC, representing the most

Table 3. Organic Carbon Budget and Export (OC Export) From the Coastal Ocean to the Ocean[a]

	Component	(Tg C year^{-1})	References
Allochthonous inputs	Rivers	426	*Cauwet* [2002]
	Sewage	150	*Smith and Hollibaugh* [1993]
	Atmosphere	6.3	*Willey et al.* [2000]
	Groundwater	34.1	*Burnett et al.* [2003]
Authochthonous NEP	Macroalgae	730	*Duarte and Cebrián* [1996]
	Coral reefs	−30	*Duarte and Cebrián* [1996]
	Microphytobenthos	80	*Duarte and Cebrián* [1996]
	Marsh plants	0	*Duarte and Cebrián* [1996]
	Seagrass (average)	53.6	*Duarte et al.* [2010]
	Mangroves	450	*Duarte and Cebrián* [1996]
	Coastal phytoplankton	720	*Duarte and Cebrián* [1996]
Coastal burial		210.3	*Duarte et al.* [2005]
OC export	Global coastal ocean	2410	This study

[a] This estimate is calculated as the sum of allochthonous inputs to the coastal zone and net ecosystem production (NEP) of coastal ecosystems minus the burial of carbon in the coastal zone. See explanation of the mass balance equation (2) in the text.

labile components such as those with sewage inputs, is respired in the near-shore coastal zone, sustaining the relatively large CO_2 efflux of estuaries [*Frankignoulle et al.*, 1998] and near-shore waters [*Borges*, 2005], estimated globally for inner estuaries, salt marshes, and mangroves, with some uncertainty, at 500 Tg C yr^{-1} [*Chen and Borges*, 2009]. In addition, photodegradation of riverine DOC during transport along the estuary can be a significant loss factor [*Stubbins et al.*, 2010] estimated to remove up to 30% of the DOC inputs from the Satilla River [*Moran et al.*, 2000]. The carbon released as CO_2 from coastal waters is sufficient to account for almost all the allochthonous inputs of organic carbon (Table 3). Export of organic carbon from the coastal to the open ocean must be, therefore, supported by the net production of benthic habitats and plankton communities.

Coastal ecosystems include macrophyte-dominated communities such as macroalgae, seagrasses, salt marshes, and mangroves [*Alongi et al.*, 1998], tend to be net autotrophic [*Duarte and Cebrián*, 1996; *Gattuso et al.*, 1998; *Duarte et al.*, 2010]. A fraction of their net production is buried in coastal sediments [*Duarte and Cebrián*, 1996; *Duarte et al.*, 2005], and the remaining is available for export (Table 3) [*Duarte and Cebrián*, 1996]. On the basis of community carbon budgets seagrass meadows have been reported to support globally a net ecosystem production (NEP) of 35.7–71.4 Tg C yr^{-1} [*Duarte et al.*, 2010, Table 3] and export of 16 to 33 Tg C yr^{-1} [*Maher and Eyre*, 2010; *Barrón et al.*, 2014]. The NEP of mangroves communities has been estimated to be 450 Tg C yr^{-1} [*Duarte and Cebrián*, 1996], with 60% of this organic matter exported as DOC [*Bouillon et al.*, 2008]. The NEP of salt marshes and macroalgal beds has been estimated at 0 and 730 Tg C yr^{-1}, respectively (Table 3). Together, coastal plankton communities have been calculated to support a NEP of 720 Tg C yr^{-1} [*Duarte and Cebrián*, 1996]. Hence, the production of organic carbon in the coastal zone available for export to the open ocean can be calculated following the mass balance equation above as the sum of allochthonous inputs and net ecosystem production minus the coastal organic C burial (B) of 210.3 Tg C yr^{-1} [*Duarte et al.*, 2005]. This calculation yields an estimate of organic carbon available to be exported from the coastal to the open ocean of 2410 Tg C yr^{-1} (Table 3). Recently, using mass balance calculation net inorganic and organic C export from the coastal ocean to the open ocean has been estimated to be 750 Tg C yr^{-1} [*Regnier et al.*, 2013] and 850 Tg C yr^{-1} [*Bauer et al.*, 2013]. *Regnier et al.* [2013] estimate is conservative as it takes into account estuarine vegetation of mangroves and salt marshes and other coastal habitats such as seagrass, macroalgae, and coral reefs are not taken in consideration. Our estimate of organic carbon export (OC export) from mass balance calculation can be compared with previous estimates of OC export from the coastal to the open ocean, which ranges between 216 and 6000 Tg C yr^{-1} (Table 4), with a median estimate of 1000 to 2196 Tg C yr^{-1}. The estimate derived from a mass balance calculation considering all coastal inputs and outputs, whereas the OC export estimates reported in Table 4 consider only some of these processes or are extrapolated from specific sites. For instance, the estimate by *Wollast* [1991, 1998] considering the export of particulate C alone. Also, global DOC export ranging from 480 to 600 Tg C yr^{-1} reported by *Chen et al.* [2003]; *Chen and Borges* [2009] and *Chen* [2010], is based on extrapolating DOC export from two regions. In contrast, our estimate is based on 63 estimates of DOC concentrations in coastal waters with salinity above 35 and the relationship between DOC concentrations in coastal waters and the distance from

Table 4. Published Estimates of Global Organic Carbon Export (OC Export) From the Coastal to the Open Ocean

OC Export (Tg C year^{-1})	Comments	References
6000	Maximum estimate	*del Giorgio and Duarte* [2002]
1000	Particulate organic matter	*Wollast* [1991]
216		*Smith and Hollibaugh* [1993]
5520	From ecosystem carbon budget	*Duarte and Cebrián* [1996]
2200	Particulate organic matter	*Wollast* [1998]
2350		*Liu et al.* [2000a]
1126–3534	Including vegetated ecosystems	*Duarte et al.* [2005]
2400	Export coastal production	*Ducklow and McCallister* [2004]
216–2196	Median	*Mackenzie et al.* [2005]
600	DOC (including new production in shelves)	*Chen and Borges* [2009]
480	DOC	*Chen et al.* [2003]
840	export coastal production	*Liu et al.* [2000b]
600	DOC (including new production in shelves)	*Chen* [2010]
1000–2196	Median	

the coastline based on 901 estimates. The range estimated of median ± SE (and average ± SE) global DOC export of 4.4 ± 1.0 Pg C yr^{-1} and 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} and 29.0 ± 8.0 Pg C yr^{-1}) derived here is also in the midrange of previous estimates of OC export from the coastal ocean (216–6000 Tg C yr^{-1}) and is also consistent with that derived from mass balance considerations (2410 Tg C yr^{-1}; Table 3).

4.2. Consistency With Regional Coastal C Export Estimates

Shepard [1963] provided an average width of the coastal ocean of 78 km and the range of width of the different coastal ocean regions. However, recently, *Jahnke* [2010] calculated the shelf width of the major margin regions, ranging from 34 to 693 km. These recent calculations were used to estimate the concentration of DOC at the edge of the shelf break in specific coastal regions where enough DOC estimates were available to estimate the DOC at the shelf edge using a regional regression between DOC concentration and distance from the shore. It was assumed that regional margins had an average exchange rate of about 1 sverdrup (1 Sv = 10^6 m^3 s^{-1}) per 1000 km of shelf break length, which the DOC concentration of the adjacent open ocean of each regions is 63.4 ± 0.2 μmol C L^{-1}. In the slope-dominated margin of NE Pacific Eastern Boundary Current margin with a shelf width of only 47 km, the median (and average) net DOC export at the shelf break was estimated at 86 μmol C L^{-1} (77.9 ± 8.1 μmol C L^{-1}), yielding a median (and average) DOC export of 70.3 Tg C yr^{-1} (45.8 ± 25.5 Tg C yr^{-1}) in this specific zone of the NE Pacific coastal ocean. As a contrast, in the shelf-dominated NW Atlantic western Boundary current margin, characterized by a broad continental 136 km wide, on average, the median (and average) DOC export is estimated to be of 32.4 Tg C yr^{-1} (63.0 ± 218.5 Tg C yr^{-1}) as the net DOC export per unit volume exchange was estimated at 71 μmol C L^{-1} (78.1 ± 51.0 μmol C L^{-1}). Unfortunately, there is no estimate of the width of the Mediterranean coastal zone, and the DOC export from this coastal region could not possible be estimated. Consequently, these examples suggest that coastal regions with narrow continental shelves are likely to export more DOC than those with width shelves.

Huthnance [1995] estimated that about 1 Sv (10^6 m^3 s^{-1}) is exchanged for each 1000 km of shelf edge. This assessment remains the only global estimate available and is consistent with the range of values derived from regional assessments. For instance, regional estimates show that the on-off shelf water exchange, based on a model, from Brittany to Norway (about 2000 km of shelf edge) is 2.5 Sv [*Huthnance et al.*, 2009]. The water exchange of 1.25 Sv per 1000 km in this coastal zone is in the range of global water exchange reported by *Huthnance* [1995]. However, seven upwelling coastal provinces reported by *Chen et al.* [2003] had a water transport of 27.3 Sv along 15,000 km of coastal length, so on average, the water exchange of these coastal upwelling system was 1.82 Sv per 1000 km, slightly higher than the global water exchange reported by *Huthnance* [1995]. Moreover, Huthnance's consideration of export by cascades of high-density water off the shelf were conservative, as these have been recently revised to represent a globally significant export of continental shelf water of 75–120 Sv [*Jahnke*, 2010]. Hence, the estimate of 1 Sv (10^6 m^3 s^{-1}) exchanged for each 1000 km of shelf edge in *Huthnance* [1995] appears a conservative one when compared with regional estimates (e.g., Table 2), thereby rendering our estimate of DOC export conservative.

Regional estimates of water exchange in coastal regions range between 0.3 and 7.1 Sv per 1000 km of shelf break. The highest water exchanges correspond to regions supporting an upwelling filament and a large river plume, which are features that contribute significantly to enhance organic carbon export from the coastal ocean. For instance, filaments accounts for 2.5 to 4.5 times more carbon export offshore than the Ekman transport in the subtropical Northeast Atlantic Ocean [*Álvarez-Salgado et al*., 2007], suggesting than filaments must represent a significant conduit to deliver coastal organic carbon to the open ocean. Hence, we consider the estimate of 1 Sv (10^6 m^3 s^{-1}) to be conservative, possibly because more recent assessments have added export by upwelling filaments [*Álvarez-Salgado et al*., 2001; *García-Muñoz et al*., 2005] and cascades of high-density water off the shelf, to the range of processes considered by *Huthnance* [1995]. As a consequence estimates of carbon export, using *Huthnance's* [1995] global estimate of 1 Sv per 1000 km of shelf break would deliver conservative values. Hence, we have also calculated the DOC export using the mean hydrological export derived from empirical regional studies (Table 2) and bootstrapping to provide an estimate of uncertainty.

The estimate of coastal DOC export derived here is consistent with estimates of export inferred from mass balance considerations in the coastal ocean (Table 3) and is also consistent with available regional estimates of OC exchange across the shelf break (Table 2). Our estimate of median ± SE (and average ± SE) global DOC export of 4.4 ± 1.0 Pg C yr^{-1} to 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} to 29.0 ± 8.0 Pg C yr^{-1}) entering the open ocean across the shelf break corresponds to median (and average) range between 14.7 ± 3.3 Gg C to 90.0 ± 6.0 Gg C (23.3 ± 19.3 Gg C to 96.7 ± 26.7 Gg C) annually exported to the open ocean per kilometer of shelf break. Regional estimates of annual DOC export from coastal areas to the open ocean range between 1.4 and 66.1 Gg C yr^{-1} per km of shelf break with a median (and average ± SE) export rate of 18.5 (23.9 ± 6.8) Gg C yr^{-1} per km of shelf break (Table 2), consistent with the global value calculated independently here. Recently, *Munro et al*. [2013] estimated the net community production (integrating POC export and net DOC production) in the Southern California coastal zone using triple O_2 isotopes and O_2: Ar gas ratios, to arrive to an estimated OC carbon export in this coastal zone was 210 mg C m^{-2} d^{-1}. Using the area of the California Cooperative Oceanic Fisheries Investigation (CalCOFI) grid reported in their web page, we estimated an OC export of 33.4 Gg C yr^{-1} per km of shelf break, which is within the range of DOC export from different coastal areas to the open ocean. The median (and average) DOC exchange rate varies between 14.7 ± 3.3 and 90.0 ± 6.0 (23.3 ± 19.3 to 96.7 ± 26.7) Gg C yr^{-1} per km of shelf break estimated from the global inventory of DOC and the global water exchange rate provided here is consistent with regional estimates of DOC export from continental margins to adjacent open ocean (Table 2).

4.3. Coastal OC Export and the Metabolic Balance of the Open Ocean

The estimated export of coastal OC to the open ocean is consistent with estimates derived from carbon mass balances in the coastal ocean and with those derived from regional studies assessing OC export from the coastal zone to the open ocean. However, this estimate needs also be reconciled with the carbon budget of the open ocean. The metabolic balance of the open ocean remains a controversial issue. Some analyses conclude that the open ocean is in metabolic balance [*Williams*, 1998; *Williams et al*., 2013], whereas others consider that it is heterotrophic, therefore requiring inputs of organic carbon to subsidize excess respiration. *Smith and Hollibaugh* [1993] postulated that the open ocean must be a net heterotrophic ecosystem and *Duarte and Agustí* [1998] and *Duarte et al*. [2013] concluded that the oligotrophic ocean, encompassing 80% of the ocean surface, is net heterotrophic, while the rest, including the coastal zone, is net autotrophic. The carbon deficit in the open ocean has been reported to represent up to 6000 Tg C yr^{-1} [*Duarte et al*., 1999; *del Giorgio and Duarte*, 2002; *Ducklow and McCallister*, 2004]. One of the arguments to question the proposition that the open ocean may be a heterotrophic ecosystem is that this will require a sizeable source of organic carbon subsidizing excess respiration, which had not yet been identified. The analysis presented here identifies the coastal ocean as a source of organic carbon delivering a median ± SE (and average ± SE) range of 4.4 ± 1.0 Pg C yr^{-1} to 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} to 29.0 ± 8.0 Pg C yr^{-1}) to the open zone, an amount comparable to that required to balance the metabolic deficit of the open ocean [*del Giorgio and Duarte*, 2002]. Whereas our estimate has broad uncertainty brackets, it shows that the export of DOC from the coastal to be open ocean could be a globally significant flux. This should provide an impetus to improve the precision of the estimate by expanding the current data set on estimates for DOC concentrations from coastal zones and improving the estimate of global water exchange between the coastal and the open ocean.

The comparison of the global average hydrological and DOC fluxes per 1000 km of shelf break with more precise regional estimates reported in the literature shows that the global average values are consistent with regional ones, and probably are conservative ones, further supporting our conclusion that the export of DOC from the coastal to be open ocean is likely to be a globally significant flux. The large estimate of DOC export from the coastal to the open ocean results from an input of DOC from land [*Cauwet*, 2002] and mainly from an excess DOC production over consumption in the coastal ocean [*Duarte et al*., 2005], which may subsidize the metabolism of the open ocean, providing an additional element to help reconcile the metabolic and carbon budgets of the open ocean.

In conclusion, the inventory of coastal DOC pools and the patterns of decline in concentration toward the shelf break reported here allowed, when combined with estimates of the exchange between coastal and open ocean waters across the shelf break the identification of coastal ocean as a source of organic carbon delivering a median ± SE (and average ± SE) range of 4.4 ± 1.0 Pg C yr^{-1} to 27.0 ± 1.8 Pg C yr^{-1} (7.0 ± 5.8 Pg C yr^{-1} to 29.0 ± 8.0 Pg C yr^{-1}) to the open zone. These estimates can be reconciled both with the carbon budget of coastal and the open ocean and is also consistent with detailed regional estimates of coastal carbon export. Mixing between coastal and open ocean waters is a complex process affected by multiple mechanisms, which taken in concert rivals, in terms of the hydrological fluxes involved, some of the largest current systems in the ocean. Improving our estimates of the regional and global magnitude and variability of these mixing processes is fundamental to improve our understanding of the connectivity between the coastal and open ocean and its consequences for the carbon budget of the ocean.

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