Net removal of dissolved organic carbon in the anoxic waters of the Black Sea

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ABSTRACT

Dissolved organic carbon (DOC) concentrations in the deep Black Sea are ~2.5 times higher than found in the global ocean. The two major external sources of DOC are rivers and the Sea of Marmara, a transit point for waters from the Mediterranean Sea. In addition, expansive phytoplankton blooms contribute autochthonous carbon to the Black Sea’s ~800 Tg C DOC reservoir. Here, a basin-wide zonal section of DOC is explored using data from the 2013 Dutch GEOTRACES GA04-N, cruise 64PE373. DOC distributions are interpreted with respect to well-described hydrographic and biogeochemical layers of the Black Sea. Observed DOC concentrations were >180 μmol kg⁻¹ at the surface, decreasing to ~125 μmol kg⁻¹ at the base of the oxic layer and reaching a minimum of ~113 μmol kg⁻¹ in the upper anoxic layer between ~150 and 500 m. At greater depths the concentrations increased; maximum anoxic layer concentrations of 122 μmol kg⁻¹ were found in the homogeneous benthic bottom layer (~1775 m). Concentrations are then predicted based on conservation with respect to salinity using linear end-member mixing models, and predictions are compared with observations to estimate net removal (i.e., deficits) and accumulation (i.e., surpluses). A maximum surplus of ~10 μmol kg⁻¹ was identified at the surface, likely due to local primary production. DOC exported to depth was non-conservative: up to ~34-41 μmol kg⁻¹ was removed from the basin’s oxic layer in ~5 years, and an additional 13 ± 5 μmol kg⁻¹ was removed from the anoxic layer during its ~300 to 600-year residence time, given steady state. These deficits represent a removal of ~19% in the oxic water and a further removal of ~10% under anoxia, for a net removal of 48 μmol kg⁻¹ (or ~29%) of allochthonous DOC, with respect to predicted concentrations. We find no evidence for DOC accumulation (i.e., net production) in the anoxic Black Sea, and suggest that concentrations are elevated relative to the ocean due to input of terrigenous DOC from rivers; we estimate that ~50% of DOC in the deep Black Sea is terrigenous. The Black Sea’s relatively elevated DOC pool may be analogous to a hypothesized anoxic Eocene ocean’s elevated reservoir only if the Eocene ocean received a substantial amount of terrigenous DOC.

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1. Introduction

The Black Sea is the world’s largest anoxic basin and inland sea Fig. 1. With a volume of 547,000 km³ and a maximum depth of ~2200 m (Oguz et al., 2004), it is characterized by dissolved organic carbon (DOC) concentrations ~2.5 times higher than the open ocean (Ducklow et al., 2007). Concentrations in the ocean range from ~40 μM in deep water to ~75 μM at the surface (Hansell et al., 2009), while they are ~120 μM in the anoxic water of the Black Sea and ~200 μM or higher at its surface (Tugrul, 1993; Ducklow et al., 2007). Sexton et al. (2011) suggested that concentrations are high in the Black Sea due to mineralization being inhibited under anoxic conditions, causing DOC to accumulate. They also suggested that the Black Sea may be analogous to the early Eocene’s abyssal ocean, which was at times anoxic, postulating that this past ocean stored a massive DOC reservoir as a result of anoxia-inhibited mineralization.

However, in the Black Sea, mineralization removes organic matter even under anoxic conditions (Murray et al., 1995; Hiscock and Millero, 2006). Ducklow et al. (2007) found that DOC in the Black Sea is removed in the subsurface, contrary to anoxic inhibition and obviating an associated DOC accumulation. They also suggested that concentrations are high relative to the ocean because, unlike the ocean, the Black Sea receives a proportionately large amount of terrigenous DOC from rivers such as the Danube (Fig. 1; Cauwet et al., 2002; Saliot et al., 2002; Raymond and Spencer, 2015). Similar to concentrations in the anoxic Black Sea, Lake Baikal’s oxygenated deep water has DOC concentrations of 90-100 μM (Weiss et al., 1991; Yoshioka et al., 2002), suggesting that Black Sea concentrations are likewise high because of terrigenous input. Furthermore, DOC concentrations in the hypoxic...
layer of the Arabian Sea (~47 μM) and anoxic Cariaco Basin (56 μM) are similar to oceanic values (Hansell and Peltzer, 1998; Lorenzoni et al., 2013).

Here we present a DOC section across the Black Sea, which we interpret with respect to the basin’s well-described hydrographic and biogeochemical layers (Murray et al., 1991; Tugrul et al., 1992; Ivanov et al., 1997; Ducklow et al., 2007). DOC concentrations are predicted based on conservation with respect to salinity using linear end-member mixing models, similar to Ducklow et al. (2007). Differences between observed and predicted concentrations are calculated to determine the net DOC deficit for the basin and its layers (the deficit is net since there is the potential for a small net contribution of autochthonous DOC). The component of the deficit that occurs exclusively in the anoxic water of the Black Sea is also determined. Processes responsible for the observed DOC distributions and net deficits are explored, while the Black Sea as a paradigm for the anoxic Eocene ocean is considered. In order to understand the dynamics of this ~800 Tg C reservoir, it is first put into the context of the basin circulation.

1.1. Hydrographic context

The surface circulation of the Black Sea is dominated by the cyclonic, meandering Rim Current (Fig. 1; Oguz et al., 1993). The Rim Current encompasses the western and eastern (upwelling, cyclonic) gyres, along with the semi-permanent anti-cyclonic central basin eddy; on the eastern margin of the basin is the anti-cyclonic Batumi eddy (Fig. 1). The Rim Current and its associated eddies and meanders exchange water between the northwest shelf and central basin, bringing highly productive shelf waters to the basin interior (Zhou et al., 2014). These cross-shelf exchanges also deliver river water enriched with nutrients and DOC to the basin interior (Cauwet et al., 2002). The four major rivers that enter the Black Sea are the Danube, Dnieper, Dniester, and Rioni, with the first three located on the northwest shelf (Fig. 1; Jaoshvili, 2002). Some of the river water that enters the Black Sea on the northwest shelf is rapidly transported south by a coastal current, exiting the basin via the upper layer of the Bosporus Strait, carrying this relatively fresh water to the Sea of Marmara (Oguz et al., 2004). Water entering the Black Sea in the deep layer of the Bosporus Strait (~50 m sill) has high salinity and density, characteristic of Mediterranean seawater, which sinks to ventilate the deeper layers of the Black Sea (Ozsoy et al., 1993; Ivanov and Samodurov, 2001; Oguz et al., 2004).

1.1.1. Biogeochemical and hydrographic layers

The Black Sea layers are distinguished by their chemical distributions, with these in turn being controlled by biogeochemical processes that vary throughout the water column, such as photosynthesis, aerobic mineralization, denitrification and sulfate reduction (Dyrssen, 1986; Tugrul et al., 1992, 2014; Murray et al., 1995; Ducklow et al., 2007). The upper ~100 m of the water column is oxygenated and referred to as the oxic layer (OL), including the euphotic zone (upper ~50 m) where nutrients are depleted (Tugrul et al., 1992; Ducklow et al., 2007). The upper ~100 m of the water column is oxygenated and referred to as the oxic layer (OL), including the euphotic zone (OL), the OL-SOL interface is approximately coincident with the depth of the nitrate maximum (Murray et al., 1995), marking the transition from aerobic to anaerobic mineralization. The SOL is defined by oxygen and hydrogen sulfide (H₂S) concentrations <20 μM and <1 μM, respectively (Tugrul et al., 2014); denitrification is evident by nitrate decreasing with depth in this layer. Below the SOL, in the anoxic layer (AOL), oxygen and nitrate are absent, with H₂S increasing with depth due to sulfate reduction (Dyrssen, 1986).

Fig. 1. Distributions of chlorophyll a (µg L⁻¹) and stations occupied during the cruise. The generalized upper layer circulation of the Black Sea is added with gray arrows adapted from Oguz et al., 1993. Chlorophyll a is from July 12–19, 2013 and stations were occupied from July 14–23, 2013. CBE is the central basin eddy. DOC was not sampled at station 1, marked by the “×” in the western gyre. White in the chlorophyll a field represents no data due to cloud cover. Aqua MODIS chlorophyll a data from oceancolor.gsfc.nasa.gov/.
Overlapping the Black Sea’s biogeochemical layers are hydrographic layers defined by conservative properties (i.e., temperature, salinity). Near the bottom of the OL is the cold intermediate layer (CIL), formed by winter mixing and defined by temperatures ~8 °C; it is the coldest layer of the Black Sea (Tolmazin, 1985; Ozguz et al., 1991; Ivanov et al., 1997; Gregg and Yakushev, 2005; Korotaev et al., 2014). Chlorofluorocarbons (CFCs) were detectable in the upper AOL (UAOL, depths ~500 m), while they were either near or below the detection limit in the underlying water (Lee et al., 2002; Staney et al., 2004). The presence of CFCs in the UAOL shows that it is a distinct layer, ventilated on a shorter timescale than the deeper AOL. Another hydrographic layer in the AOL is the homogeneous benthic bottom layer (BBL) in the lower ~400 m of the water column, formed by convective mixing induced by mild geothermal heating (Murray et al., 1991; Ozsoy et al., 1991; Ozsoy and Unluata, 1997). The layer between the UAOL and the BBL is referred to here as the deep AOL (DAOL); together, the UAOL, DAOL and BBL compose the AOL.

1.1.2. Deep water renewal and residence times

The deep layers of the Black Sea are formed when the brackish water of the CIL (salinity ≈ 19) is entrained by salty Marmara seawater (salinity ≈ 36) entering the Black Sea via the Bosporus Strait (Unluata et al., 1990; Murray et al., 1991); the resulting dense water sinks to form the AOL (Ozsoy et al., 1993; Ozguz et al., 2004). As it sinks, much of this newly formed water is laterally injected into the AOL at intermediate depths, resulting in small potential temperature (θ) and practical salinity (Sθ) anomalies within or slightly below the UAOL (Murray et al., 1991; Ozsoy et al., 1991, 1993). Some of this new water sinks to the bottom of the basin, delivering elevated Sθ to the BBL (Ivanov and Samodurov, 2001). Following the formation of the BBL, there is a net upward flux of water (and salt) as the AOL overturns during the deep-basin’s residence time (Ozguz et al., 2004).

Deep Black Sea residence time estimates are wide ranging (Ostlund, 1974; Top and Clark, 1983; Dyrrsen, 1986; Top et al., 1990; Murray et al., 1991; Lee et al., 2002). Among these, Lee et al. (2002) calculated a residence time of 625 ± 430 years for the AOL using CFC observations at ~500 m. In the UAOL, there was a vertical gradient in residence times, ranging from 21.1 ± 8.9 years below the SOL-UAOL interface to 235 ± 110 years above ~500 m (Lee et al., 2002). Lee et al. (2002) also calculated residence times for the CIL (~5 years) and SOL (~5 years), taken here to be representative estimates for the sub-euphotic OL and SOL. A 600-year residence time is assumed here to be a realistic figure for the DAOL and BBL, while for the water between the SOL and ~500 m, a gradient from 5 to 600 (or ~300) years is inferred.

1.2. The Black Sea DOC pool in context

During a 2001 expedition to the western gyre and northwest shelf, DOC concentrations ranged from ~150 to ~200 μM in the OL and decreased with depth (Ducklow et al., 2007). Concentrations were ~120 μM in the AOL, with the full water column profiles generally agreeing with results from Tugrul (1993). DOC is introduced into the Black Sea from two major sources: one is rivers enriched with terrigenous DOC, having concentrations of ~300 μM (Cauwet et al., 2002; Saliot et al., 2002); the second is the Sea of Marmara, bringing moderate concentrations (~70 μM) via the Bosporus Strait (Polat and Tugrul, 1995). The Sea of Azov (Fig. 1) also contributes to the DOC pool, however its influence is negligible due to relatively small volume exchanges (Efimov et al., 2012). Phytoplankton blooms contribute by producing autochthonous DOC in the OL (Yunev et al., 2002), while inputs from sediments, particle solubilization, and chemosynthesis may also contribute (Mopper and Kieber, 1991; Ducklow et al., 2007). Aside from bacterial consumption (i.e., mineralization), DOC may be removed abiotically by flocculation within estuaries, photo-oxidation, or by scavenging and co-precipitation (Sholkovitz, 1976; Mopper and Kieber, 1991; Mopper et al., 1991).

Ducklow et al. (2007) predicted DOC concentrations resulting from conservative mixing between marine (Aegean Sea) and fresh (Danube River) end-members. A surplus of DOC was identified at the surface on the northwest shelf and in the western gyre, likely resulting from autochthonous DOC production. In the underlying water, DOC concentrations were up to ~50 μM lower than predicted by conservation. Of the 50 μM deficit identified in the AOL, Ducklow et al. (2007) suggested that half was removed in the upper water column over the course of a few years, while the remainder was removed over the 600-year residence time of the basin’s deep water.

2. Materials and methods

2.1. Sample collection and analysis

Samples were collected from July 14-23, 2013 aboard the R/V Pelagia during cruise 64P373, executed as part of the GEOTRACES GA04-N transect. Water was collected at stations 1-12, while DOC was determined at stations 2-12 (Fig. 1, Table 1). The water column was sampled using 24 × 24.4-L polyvinylidene fluoride (PVDF) bottles housed in a titanium frame (Rijkenberg et al., 2015), equipped with a Sea-Bird Electronic, Inc. (SBE) 9Pius CTD sensor package. Temperature was calibrated with a high-accuracy reference thermometer (SBE 35) and Sθ (Lewis and Perkin, 1978) was calibrated using a Guideline Model 8400B Laboratory Salinometer with Ocean Scientific International Ltd. (OSIL) salinity standard, batch P155. The temperature had an accuracy of ~0.001 °C when compared to the SBE 35 and the Sθ sensor differed from calibration measurements by ~0.001, with two standard deviations (2σ) of 0.0016 °C and 0.001, respectively. Both θ and the potential density anomaly (σθ) were calculated using the 2010 Thermodynamic Equation of Seawater (TEOS-10) with the Gibbs-SeaWater (CSW) Toolbox (version 3.04; McDougall and Barker, 2011) for MATLAB (R2014a) and plotted using Ocean Data View (Schlitzer, 2014).

Dissolved oxygen was measured using a SBE 43 sensor, calibrated by collecting samples at three depths from eleven casts using 25 L Niskin bottles mounted on a standard rosette, and spectrophotometrically analyzed with a precision of ±0.1 μM (Winkler, 1888; Reinhalter et al., 2006). H2S was measured following the procedures of Grasshoff (1969) with an estimated precision of ±0.263 μM. Nitrate was calculated by subtracting measured nitrite concentrations (did not exceed 0.22 μM) from measured nitrate plus nitrite concentrations; both were measured on board following the procedures of Grasshoff et al. (1983) with a propagated precision of ±0.018 μM. Photosynthetically active radiation (PAR) was measured using a Satlantic PAR sensor to estimate the base of the euphotic zone (~3–10% cosine error), in conjunction with oxygen measurements.

Water for DOC analysis was collected from the PVDF bottles by filtering through Sartorius Sartobran® P 0.2 μm pore size, 300 cm² filtration area capsules and into pre-cleaned, 60 mL high-density polyethylene (HDPE) bottles. The HDPE bottles were cleaned by soaking in 10% HCl for 24 h and rinsed thoroughly with Milli-Q® water before rinsing three times with sample water. Samples were stored in the dark and frozen at ~20 °C until analysis using a Shimadzu TOC-L Total Organic Carbon Analyzer by combusting pre-acidified samples at 680 °C and measuring the resulting CO2 (Dickson et al., 2007). Analysis was verified with a precision of ±1.5 μM using DOC consensus reference material (CRM; Hansell, 2005) Batch 14, Lot # 01-14 (www.rsmas.miami.edu/groups/biogeochem/CRM.html).

2.2. Mixing scenarios

Black Sea mixing relevant to this analysis is described in the Introduction and depicted in Fig. 2 as mixing scenarios #1 and #2. The formation of water in the upper layers of the Black Sea is modeled with mixing scenario #1 based on the conservation of Sθ, representing mixing between the Bosporus Strait and Danube River waters (end-members...
Table 1

<table>
<thead>
<tr>
<th>Region and station</th>
<th>Date</th>
<th>Position</th>
<th>Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bosporus Strait</td>
<td>July 23, 2013</td>
<td>41° 13.44’ N, 29° 07.55’ E</td>
<td>59 m</td>
</tr>
<tr>
<td>Bosporus Plume</td>
<td>July 23, 2013</td>
<td>41° 34.31’ N, 29° 08.80’ E</td>
<td>576 m</td>
</tr>
<tr>
<td>Western Gyre</td>
<td>July 14, 2013</td>
<td>42° 15.96’ N, 30° 00.94’ E</td>
<td>2081 m</td>
</tr>
<tr>
<td>Eastern Gyre</td>
<td>July 14-15, 2013</td>
<td>42° 31.29’ N, 31° 24.11’ E</td>
<td>2120 m</td>
</tr>
<tr>
<td>Central Basin Eddy</td>
<td>July 22, 2013</td>
<td>42° 44.33’ N, 32° 30.31’ E</td>
<td>2133 m</td>
</tr>
<tr>
<td>Batumi Eddy</td>
<td>July 16, 2013</td>
<td>43° 01.65’ N, 33° 43.85’ E</td>
<td>2164 m</td>
</tr>
<tr>
<td>12 July 23, 2013 41° 13.44’ N, 29° 07.55’ E</td>
<td>59 m</td>
<td>59 m</td>
<td></td>
</tr>
<tr>
<td>11 July 23, 2013 41° 34.31’ N, 29° 08.80’ E</td>
<td>576 m</td>
<td>576 m</td>
<td></td>
</tr>
<tr>
<td>1 July 14, 2013 42° 15.96’ N, 30° 00.94’ E</td>
<td>2081 m</td>
<td>2081 m</td>
<td></td>
</tr>
<tr>
<td>2 July 14-15, 2013 42° 31.29’ N, 31° 24.11’ E</td>
<td>2120 m</td>
<td>2120 m</td>
<td></td>
</tr>
<tr>
<td>10 July 22, 2013 42° 44.33’ N, 32° 30.31’ E</td>
<td>2133 m</td>
<td>2133 m</td>
<td></td>
</tr>
<tr>
<td>3 July 16, 2013 43° 01.65’ N, 33° 43.85’ E</td>
<td>2164 m</td>
<td>2164 m</td>
<td></td>
</tr>
<tr>
<td>9 July 21, 2013 43° 12.01’ N, 34° 46.21’ E</td>
<td>2157 m</td>
<td>2157 m</td>
<td></td>
</tr>
<tr>
<td>4 July 17, 2013 43° 08.55’ N, 35° 13.78’ E</td>
<td>2136 m</td>
<td>2136 m</td>
<td></td>
</tr>
<tr>
<td>8 July 20, 2013 42° 48.67’ N, 37° 34.03’ E</td>
<td>2105 m</td>
<td>2105 m</td>
<td></td>
</tr>
<tr>
<td>5 July 18, 2013 42° 20.93’ N, 38° 41.03’ E</td>
<td>2040 m</td>
<td>2040 m</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Schematic of the Black Sea’s generalized circulation, mixing scenarios #1 and #2, and biogeochemical and hydrographic layers. Approximate depth boundaries are marked on the right and left sides of the figure. The cyclonic flow of the Rim Current is illustrated by vector arrowheads in the upper OL, also illustrating the coastal current that brings water southward and out of the Bosporus Strait.

Fig. 3. Vertical profiles of oxygen, nitrate, hydrogen sulfide, and temperature (°C) against potential density in the Black Sea, sampled at all 12 stations during the cruise. The biogeochemical layers (oxic, suboxic, anoxic) are defined by distributions of these geochemical variables; their boundaries are defined by \( \sigma_t \). Approximate layer boundary depths are marked on the right side of the y-axis.

3. Results

Samples were collected in the western gyre, central basin eddy, eastern gyre and Batumi eddy, along with the Bosporus Strait and its plume (Fig. 1, Table 1). All biogeochemical and hydrographic layers were sampled (Fig. 3). The boundaries of the biogeochemical and hydrographic layers during cruise 64PE373 are defined in Table 2 following previous studies, with further partitioning of the AOL (i.e., UAOL and DAOL).

The euphotic zone extended to ~50 m, where oxygen concentrations were elevated, ranging from ~230 to 340 \( \mu \text{mol kg}^{-1} \); oxygen decreased to ~20 \( \mu \text{mol kg}^{-1} \) at the bottom of the OL (Fig. 3). Nitrate was detectable at depths \( > \sigma_t \approx 14 \text{ kg m}^{-3} \), with concentrations increasing to a maximum of 4.6 \( \mu \text{mol kg}^{-1} \) just above the OL-SOL interface (Fig. 3). The upper \( \sigma_t \) boundary of the SOL was 15.64 ± 0.24 \( \text{kg m}^{-3} \) (2\( \sigma_t \), \( n = 12 \)) where oxygen concentrations were 20 ± 4 \( \mu \text{mol kg}^{-1} \), while its lower \( \sigma_t \) boundary was 16.20 ± 0.10 \( \text{kg m}^{-3} \) (7 \( \sigma_t \), \( n = 12 \)) where \( H_2S \) concentrations reached 1.0 ± 0.9 \( \mu \text{mol kg}^{-1} \). Oxygen and nitrate decreased to undetectable levels in the SOL, while \( H_2S \) remained > 1 \( \mu \text{mol kg}^{-1} \) (Fig. 3). In the AOL, oxygen and nitrate were virtually absent and \( H_2S \) increased with depth, reaching ~450 \( \mu \text{mol kg}^{-1} \) at the bottom of the basin (Fig. 3).
Temperature was ~25 °C at the surface, then decreased with depth to the water column minimum of 7.663 °C at \( c_{\theta_0} = 14.690 \text{ kg m}^{-3} \) near the center of the CIL (Fig. 3, showing ~8 °C). The CIL spanned from \( c_{\theta} = 14.250 \text{ kg m}^{-3} \) to 15.185 kg m\(^{-3}\), having a \( \theta \) of 7.853 ± 0.174 °C and a \( S_P \) of 19.166 ± 0.632 (20, n = 58). The upper boundary of the CIL was approximately coincident with the lower boundary of the euphotic zone. Below the CIL, \( \theta \) increased to a local maximum of 8.85 °C at stations 3, 4 and 9 in the central basin at ~500 m, corresponding to the lower boundaries of the euphotic zone. Below the CIL, \( \theta \) increased from ~18 at the surface to 22.3482 ± 0.0016 (n = 1775 m, i.e., within the BBL (Fig. 4a). \( S_P \) generally increased from ~18 at the surface to 36.25 ± 1.25 from Unluata et al., 1990) and observed \( S_P \):

\[
\% \text{ Freshwater} = \left(1 - \frac{S_P}{36.25}\right) \times 100. \tag{1}
\]

The distribution (Fig. 6) shows that ~40-50% of the water in the basin has a freshwater origin, with the exception of the inflowing Marmara seawater at station 12. The highest percentages are at the surface near the margins, where riverine influence is largest. The layer least influenced by river input (BBL) is still ~38% fresh, illustrating the importance of rivers to the basin’s water budget. Since nearly half of the basin’s water originates from rivers, the observed DOC concentrations likely reflect that.

### 4.1.2. Mixing scenario #2

To evaluate DOC concentrations in the basin’s deep water, AOL formation is modeled using the mean \( \theta \) and \( S_P \) of its source end-members (i.e., Bosphorus and CIL waters) to trace the conservative mixing depicted by mixing scenario #2 (Fig. 2). Here we first seek to establish the validity of the assumptions behind that mixing. The Bosphorus end-member is defined using the temperature reported by Unluata et al. (1990) (here converted to a \( \theta \) of 13.49 ± 1.0 °C) and \( S_P \) used in Eq. (1). Mean \( \theta \) (7.853 °C) and \( S_P \) (19.166) in the CIL were calculated from samples collected during the cruise (Section 3). Together, the Bosphorus and CIL end-members are employed to produce two conservative mixing equations:

\[
o_2 = 0.330 \times S_P + 1.529. \tag{2}
\]

\[
S_{O2} = 3.031 \times 0 - 4.634. \tag{3}
\]

The equations for mixing scenario #2 predict \( \theta \) and \( S_P \) (\( \theta_2 \) and \( S_{P2} \)) in the AOL (blue line in Fig. 7), with overall root mean square errors

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### Table 2

Biogeochemical and hydrographic layers of the Black Sea, and definitions of upper and lower boundaries.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Upper boundary</th>
<th>Lower boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxic layer</td>
<td>Surface</td>
<td>( c_{\theta_0} = 15.64 \text{ kg m}^{-3} )</td>
</tr>
<tr>
<td>Euphotic zone</td>
<td>Surface</td>
<td>Depth ≈ 200 m</td>
</tr>
<tr>
<td>Cold intermediate layer</td>
<td>Temperature = 8 °C</td>
<td>Temperature = 8 °C</td>
</tr>
<tr>
<td>Suboxic layer</td>
<td>( c_{\theta} = 15.64 \text{ kg m}^{-3} )</td>
<td>( c_{\theta} = 16.20 \text{ kg m}^{-3} )</td>
</tr>
<tr>
<td>Anoxic layer</td>
<td>( c_{\theta} = 16.20 \text{ kg m}^{-3} )</td>
<td>Seafloor</td>
</tr>
<tr>
<td>Upper anoxic layer</td>
<td>( c_{\theta} = 16.20 \text{ kg m}^{-3} )</td>
<td>( c_{\theta} = 17.04 \text{ kg m}^{-3} )</td>
</tr>
<tr>
<td>Deep anoxic layer</td>
<td>( c_{\theta} = 17.04 \text{ kg m}^{-3} )</td>
<td>Depth = 1775 m</td>
</tr>
<tr>
<td>Benthic bottom layer</td>
<td>Depth = 1775 m</td>
<td>Seafloor</td>
</tr>
</tbody>
</table>

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Fig. 4. Depth profiles of (a) potential temperature, (b) practical salinity and (c) potential density below 900 m to illustrate the homogenous character of the BBL. The BBL is filled in with gray, and its upper boundary (1775 m) is marked with the horizontal line.
(RMSEs) of 0.068 °C and 0.211, respectively. Mixing scenario #2 predicts observations best in the BBL (single point of overlapping data on blue line in Fig. 7) and DAOL, where their respective $\theta_2$ and SP2 RMSEs are 0.003 °C and 0.004, and 0.019 °C and 0.057. UAOL observations, however, are not predicted well, as there is an offset between mixing scenario #2 and observations (Fig. 7), having RMSEs of 0.084 °C for $\theta_2$ and 0.261 for SP.

For $\theta$ and SP exclusive to the UAOL, linear regressions from the observed data are employed:

$$\theta_{UAOL} = 0.301 \times S_P + 2.239.$$  \hspace{1cm} (4)

$$S_{P-UAOL} = 3.261 \times \theta - 6.884.$$ \hspace{1cm} (5)

Fig. 5. DOC section from depths (a) 0-200 m and (b) 0-2250 m, where station numbers are given at the top of the section. The z-axis is non-linear to more clearly show DOC gradients in the deep water column. Isopycnal surfaces (from potential density) and the depth of 1775 m, as boundaries between the different biochemical environments (in Table 2) are indicated with black lines. Section plotted using Ocean Data View (Schlitzer, 2014).

Fig. 6. Percent freshwater from (a) 0 to 200 m and (b) 0 to 2250 m, where station numbers are given at the top of the section. Isopycnal surfaces (from potential density) and the depth of 1775 m, as boundaries between the different biochemical environments (in Table 2) are indicated with black lines. Section plotted using Ocean Data View (Schlitzer, 2014).
The ~20 μmol kg⁻¹ difference between UAOL observations and UAOL SP of 19.166 ± 0.040, respectively, agreeing with UAOL observations better than the end-members employed in mixing scenario #2 (green and orange lines in Fig. 7). Furthermore, the UAOL regressions fall within the ranges of the Bosporus and CIL end-members, suggesting that mixing scenario #2 assumptions are supported by these regressions.

Sub-layers of the AOL are formed by mixing of the Bosporus and CIL waters, however the UAOL appears to be formed uniquely when compared to the DAOL and BBL (Fig. 7); seasonal variability (e.g., in temperature) may cause this difference. Seasonal temperature variations influence both end-members (Unluata et al., 1990; Gregg and Yakushev, 2005), which may result in the formation of the relatively warm UAOL (Fig. 7). The deviations of θ and SP from the UAOL regressions near the bottom of the layer suggest that the DAOL may be entrained upwards into the lower UAOL (Fig. 7), while the θ-SP curvatures within the DAOL and BBL is evidence for geothermal input at the bottom of the basin (Murray et al., 1991; Ozsoy et al., 1991). Considering the AOL as a whole, these subtle θ and SP variations are unlikely to affect DOC estimates significantly, so only mixing scenario #2 is used to predict DOC in all of the AOL's sub-layers.

4.2. Predicting basin-wide DOC concentrations

4.2.1. Predicting DOC with mixing scenario #1

We first establish the Bosporus and Danube AOL end-members for mixing scenario #1. Inflowing Bosporus seawater has an annual average concentration of 71 ± 8 μmol kg⁻¹ (here converted from μM reported by Polat and Tugrul, 1995), while the Sₚ of 36.25 from Unluata et al. (1990) is used for consistency with Eqs. (2) and (3). The concentration of 300 μmol kg⁻¹ and Sₚ of 0 from the Danube River, reported by Cauwet et al. (2002), is assumed to be representative of the river end-member. The relationship between these DOC and Sₚ end-members is described by:

\[
\text{DOC}_1 = 300 - 6.32 \times S_p.
\]

where DOC₁ is the predicted concentrations from Sₚ, represented by the red line in Fig. 8. Virtually all DOC₁ concentrations are higher than observations. Exceptions are within the euphotic zone (above ~50 m), which includes the Bosporus Strait (an end-member), where autotrophic production is evidenced by elevated oxygen and depleted nitrate concentrations (Fig. 3).

Overall, differences between observed DOC and DOC₁ demonstrate a net removal of up to ~50 μmol kg⁻¹ (Fig. 8), in agreement with Ducklow et al. (2007). This removal is further explored by predicting DOC using mixing scenario #2, which estimates DOC concentrations that are imported into the AOL.

4.2.2. Predicting DOC with mixing scenario #2

Following mixing scenario #1, DOC end-members for the CIL are established for mixing scenario #2. The CIL sampled during the cruise had an average concentration of 139 μmol kg⁻¹ and Sₚ of 19.166 (Section 3), while the Bosporus end-member was previously defined for mixing scenario #1 as 71 μmol kg⁻¹ and 36.25. Using the Bosporus and CIL end-members, the relationship between DOC and Sₚ in the AOL is:

\[
\text{DOC}_2 = 215 - 3.98 \times S_p.
\]

where DOC₂ is predicted DOC in the AOL, represented by the blue line in Fig. 8. DOC₂ is always lower than DOC₁, suggesting that there is loss of DOC once waters mix down into the AOL. In the BBL, DOC₂ is essentially identical to observations in the BBL, meaning that DOC may be conserved within that layer, or perhaps that the BBL’s DOC sources and sinks are balanced (i.e., the DOC pool is dynamic, but no net change in concentration is observed). The difference between DOC₂ and observations increases above the BBL, through the DAOL and into the UAOL, showing a net removal of up to ~20 μmol kg⁻¹ in the AOL. Observations between the UAOL and CIL appear to be linearly related (Fig. 8), which may suggest conservative mixing, leading to the possibility that a portion of the net removal identified in the OL is imported from below.

The ~20 μmol kg⁻¹ difference between UAOL observations and mixing scenario #2 is unlikely to result from the layer’s ~0.25 Sₚ offset in predicted Sₚ (Fig. 7), because this offset only explains ~1 μmol kg⁻¹ of the difference (Eq. 7). Since observed temperatures are warmer than predicted in the UAOL (Fig. 7), it’s possible that this layer is formed seasonally (i.e., in the summer). However, there wasn’t
an obvious seasonal pattern in Bosporus DOC concentrations (Polat and Tugrul, 1995), so it is unlikely that the difference between DOCc and observations in the UAOL would be significantly different if seasonal variations were addressed. Considering both mixing scenarios, the majority of observations (with exceptions in the euphotic zone and near the end-members) are lower than predicted values (Fig. 8). We find that there is net removal of DOC within and below the CIL, and that further removal occurs under anoxic conditions.

4.3. Distributions of net DOC deficits

The Black Sea’s net DOC deficits (ΔDOCx) are calculated by subtracting observations from predicted concentrations:

$$\Delta \text{DOC}_x = \text{DOC}_x - \text{DOC}. \quad (8)$$

based on mixing scenario #x (i.e., #1 or #2). The basin’s DOC deficit that is subsequent to mixing between the river and Bosporus waters (ΔDOC1) is calculated using DOC1, while the deficit that is subsequent to mixing between the Bosporus and CIL waters (ΔDOC2) is calculated using DOC2. ΔDOCx is the fraction of ΔDOC1 removed within the AOL. These DOC deficits are shown as basin-wide sections in Figs. 9 and 10, respectively.

4.3.1. Net DOC deficit - ΔDOC1

ΔDOC1 is the DOC deficit observed given conserved mixing of DOC from the two major inputs to the Black Sea (river and Bosporus waters). In the OL, ΔDOC1 ranges from about −10 μmol kg⁻¹ at the surface to 41 ± 28 μmol kg⁻¹ (n = 12) in the CIL near the OL-CIL boundary (Fig. 9a, Table 3). There is net production of autochthonous DOC by phytoplankton, as evidenced by the slightly negative ΔDOC1 (Fig. 9a) and elevated oxygen concentrations (Fig. 3). This production suggests that ΔDOC1 may underestimate the net DOC deficit, since ΔDOC1 does not account for autochthonous inputs; the model used here assumes that autochthonous DOC is short-lived relative to water column mixing, which the vast majority of it is (Hansell, 2013). In the sub-euphotic SOL, where ΔDOC1 is 46 ± 7 μmol kg⁻¹ (n = 22), the net deficit is slightly larger than in the OL, suggesting a further −5 μmol kg⁻¹ removal in the SOL (Fig. 9a, Table 3).

In the AOL, ΔDOC1 is 45 ± 9 μmol kg⁻¹ (2σ, n = 158) (Fig. 9b), with the BBL, DAOL and UAOL having respective deficits of 37 ± 2 μmol kg⁻¹ (n = 21), 42 ± 6 μmol kg⁻¹ (n = 56) and 48 ± 4 μmol kg⁻¹ (n = 81) (Table 3). The deficit identified in the UAOL constitutes the maximum net removal of DOC within the Black Sea, equivalent to −29% removal with respect to conserved UAOL concentrations of 165 ± 4 μmol kg⁻¹ (n = 324) (Fig. 8). Within the AOL and its sub-layers, ΔDOC1 distributions suggest that there is a gradient (i.e., net removal) of up to 17 μmol kg⁻¹ under anoxic conditions (Fig. 9b).

4.3.2. Net DOC deficit #2 - ΔDOC2

DOC removal subsequent to the formation of the AOL and its sub-layers is isolated using ΔDOC2. Since ΔDOC2 is a component of ΔDOC1, their difference in the AOL represents the deficit that is imported from the OL based on mixing scenario #2, which is 34 ± 12 μmol kg⁻¹, compared with 41 ± 28 μmol kg⁻¹ from ΔDOC1 (Table 3). These results suggest that maximum net removal in the OL is 34–41 μmol kg⁻¹, and that further removal of −5–12 μmol kg⁻¹ occurs within the SOL given the OL range (Table 3), assuming that these deficits are locally formed and not imported from the UAOL.

ΔDOC2 in the AOL is 11 ± 8 μmol kg⁻¹ (2σ, n = 158), increasing from a minimum of 4 ± 2 μmol kg⁻¹ (n = 21) in the BBL to 10 ± 5 μmol kg⁻¹ (n = 56) in the >1000 m-thick DAOL, with a maximum of 13 ± 5 μmol kg⁻¹ (n = 81) in the overlying UAOL (Fig. 10, Table 3). Since ΔDOC2 is close to zero in the BBL (i.e., DOC is apparently conserved subsequent to Bosporus-CIL mixing), and there is a ΔDOC2 gradient from the BBL to the UAOL, perhaps the BBL had been more recently ventilated than the rest of the AOL. Recent ventilation of the BBL is, however, not supported by CFC data (Lee et al., 2002). An alternative explanation for the ΔDOC2 distribution is that additional DOC sources exist in the BBL, such as from sediments, returning levels to apparent conservation (discussed further below). Overall, ΔDOC2 in the UAOL shows that −10% of the DOC imported into the AOL from the OL is removed.
under anoxic conditions, based on conserved UAOL concentrations of 130 ± 2 μmol kg⁻¹ (n = 324). This requires ~19% removal in the OL’s CIL since the maximum net removal for the basin is ~29%, identified above with ΔDOC1.

### 4.4. Processes responsible for DOC distributions

The autochthonous production of DOC is evidenced by a net surplus of up to ~10 μmol kg⁻¹ in the euphotic zone (i.e., ΔDOC1 is about ~10 μmol kg⁻¹ at the surface) (Fig. 9a). The average primary productivity in the Black Sea is 349 mg C m⁻² d⁻¹ (Yuney et al., 2002). Perhaps 50% of this daily production is released as DOC (Ducklow and Carlson, 1992; Nagata, 2000), resulting in the daily net production of ~0.3 μM DOC in a 50 m euphotic zone. Much of this DOC will be removed on a daily basis, while a small fraction will persist long enough to accumulate (Hansell, 2013), likely explaining the ~10 μmol kg⁻¹ surplus in the euphotic zone (Fig. 9a).

There are also processes responsible for DOC removal near the surface. Estuarine particle flocculation removes 3-11% of riverine DOC across salinity gradients from 0-20, with most flocculation occurring at salinities <15 (Sholkovitz, 1976; Sholkovitz et al., 1978). Since the Danube River holds ~300 μmol kg⁻¹ DOC, flocculation would remove ~9-33 μmol kg⁻¹ of this carbon, explaining the net deficits found in the OL (Fig. 9a). Additionally, photo-oxidation can remove ~46% of terrigenous DOC (Smith and Benner, 2005; Spencer et al., 2009), which would result in the removal of ~138 μmol kg⁻¹ on the shelf, which could be balanced by seasonal accumulation (Cauwet et al., 2002). Despite these large removals, there is net production of autochthonous DOC on the shelf (Ducklow et al., 2007), requiring additional removal mechanisms in the OL off the shelf, and further removal in the SOL and AOL based on ΔDOC2 distributions (Fig. 9). Before addressing removal processes in the deeper waters, the export of autochthonous DOC production must first be explored.

In the modern ocean, the global DOC export rate is estimated to be ~4% of primary production (Hansell et al., 2009), equivalent to a net DOC production rate of 14 μg C m⁻² d⁻¹ in the Black Sea, given the primary productivity above. If constant over the year, this rate would support export of ~5 g C m⁻² yr⁻¹ from the euphotic zone, contributing ~8.5 μmol kg⁻¹ to the observed deep concentrations. Thus, export of autochthonous DOC, if fully conserved, represents up to ~7% of AOL DOC concentrations (given average concentrations, Fig. 5b), suggesting that the majority of deep DOC is from other sources. Since ΔDOC2 does not consider autochthonous production, the 11 ± 8 μmol kg⁻¹ net deficit identified in the AOL could in fact be 8.5 μmol kg⁻¹ larger, implying that there are appreciable removal mechanisms in the sub-layers of the AOL.

In the UAOL, dissolved iron concentrations are high (Lewis and Landing, 1991), promoting the formation of particulate iron sulfides that sink out of the water column (Dyrssen, 1986; Muramoto et al., 1991). DOC may co-precipitate with or be scavenged by these particles, drawing down concentrations in the UAOL. In the anoxic Framvaren Fjord, Yao and Milicer (1995) estimated that ~30% of the sulfide was removed from the oxic-anoxic interface; they suggested incorporation into organic matter and the formation of iron sulfides as removal mechanisms, possibly leading to the removal of DOC. Rutenburg and Sulak (2011) found that dissolved organic matter containing phosphorus adsorbs onto iron oxide particles, suggesting that DOC may be scavenged from the water column. German et al. (2015) also found that dissolved iron plumes from hydrothermal vents scavange DOC, subsequently delivering particulate organic carbon to the seafloor. Perhaps DOC scavenging occurs within the UAOL, where iron sulfides are available to transport carbon to the layers below.

In the open ocean where oxygen is present and iron is scarce, bacteria dominate the removal of DOC via heterotrophic respiration (i.e., bacterial production) (Carlson and Hansell, 2015), and they are likely responsible for any remaining net deficit in the Black Sea’s OL not accounted for by flocculation and photo-oxidation. Bacteria are most abundant in the euphotic zone and are significantly more active on the oligotrophic shelf, based on conserved UAOL concentrations of 130 ± 2 μmol kg⁻¹ (n = 324). This requires ~19% removal in the OL’s CIL since the maximum net removal for the basin is ~29%, identified above with ΔDOC1.
the northwest shelf than in the basin interior (Becquevort et al., 2002; Morgan et al., 2006). Since rivers deliver high concentrations of new, potentially labile DOC to the shelf, this delivery may stimulate bacteria and enhance removal on the shelf.

In the basin interior, bacterial abundance increases near the SOL-UAOL interface (Sorokin, 1972; Jorgensen et al., 1991) and within the UAOL (Bird and Karl, 1991; Sorokin et al., 1995), with similar features observed in the anoxic Cariaco Basin (Taylor et al., 2001). Elevated bacterial and chemooautotrophic production have also been observed near the SOL-UAOL interface (Sorokin et al., 1995; Yilmaz et al., 2006), suggesting active transformation of organic matter near this boundary. DOC concentrations are low near the SOL-UAOL interface, especially within the UAOL (Fig. 5; Ducklow et al., 2007), suggesting that the net effect of chemooautotrophic addition of DOC to the UAOL is small, where the deficits are largest (Figs. 9b, 10). Profiles of bacterial and chemooautotrophic production in the Black Sea are similar to those in the Cariaco Basin (Taylor et al., 2001), where bacterial activity transforms organic matter near the redox transition zone (i.e., near the SOL-UAOL interface). DOC concentrations in the Cariaco Basin are also lowest within the region of elevated chemooautotrophic production (Lorenzoni et al., 2013), reaffirming that chemooautotrophy contributes little to the DOC pool.

A specific bacterial process that transforms organic matter to CO₂ (and CH₄) is fermentation, yielding acetate and other carboxylates as intermediate products (Thauer et al., 1989). Formate, acetate and lactate were observed in the AOL (Mopper and Kieber, 1991; Albert et al., 1994), showing concentration spikes of ~30–80 μM within the BBL at some stations, which are not reflected in the rather uniform DOC distributions (Fig. 5; Tugrul, 1993; Ducklow et al., 2007). Similar to acetate concentrations in the BBL, Ho et al. (2002) found acetate concentrations of ~30 μM at one station in the deep Cariaco Basin, while DOC was not elevated at this depth (Lorenzoni et al., 2013). It is unclear why these spikes in carboxylates are not reflected in DOC observations in either the Cariaco Basin or Black Sea. However, if carboxylates are produced in the BBL (or Cariaco's deep water), as suggested by Mopper and Kieber (1991), DOC removal may be underestimated in or near this layer, affecting the vertical deficit gradient (Figs. 9b, 10). It’s also possible that the deficit in the BBL is altered by DOC that is imported into the layer from the margins, sediments, or from the dissolution of sinking particles.

4.5. Is the Black Sea analogous to an anoxic ocean?

The deep Black Sea receives at least ~40% of its water from rivers (Fig. 6), and with that water, it receives high concentrations (~300 μmol kg⁻¹) of terrigenous DOC (Cauwet et al., 2002; Saliot et al., 2002). It also receives moderate concentrations (~71 μmol kg⁻¹) of marine DOC via the Bosporus Strait (Polat and Tugrul, 1995), which is likely to be reduced via mineralization subsequent to export. Autochthonous production of DOC is estimated to contribute a maximum of 8.5 μmol kg⁻¹ to the deep DOC pool, assuming no mineralization after export, which is ~7% of deep concentrations (~117 μmol kg⁻¹, Fig. 5b, Section 3); the remaining 108.5 μmol kg⁻¹ likely originates from allochthonous sources (i.e., rivers and marine). Considering that the present-day deep ocean has DOC concentrations of ~40 μmol kg⁻¹ (Hansell et al., 2009), it is plausible that the fraction of marine DOC in the deep Black Sea (~60%, Fig. 6b) also decreases to ~40 μmol kg⁻¹ over time (i.e., equivalent to 24 μmol kg⁻¹, or ~21% of deep concentrations). This results in the deep water terrigenous fraction (normalized to S tours = 0) having a concentration of ~211 μmol kg⁻¹ (i.e., 84.5 μmol kg⁻¹, or ~72%); Alternatively, if marine DOC is conserved in the deep Black Sea (i.e., ~43 μmol kg⁻¹, or ~37%), it would result in the terrigenous fraction having a concentration of ~164 μmol kg⁻¹ (i.e., 65.5 μmol kg⁻¹, or ~56%). Regardless of marine DOC being conserved and considering the inputs from primary production export, we find that terrigenous organic matter is likely an important component of the DOC pool, stable isotopes from sediment cores and fluorescence data from the AOL suggest the importance of terrigenous material (Arthur et al., 1994; Coble, 1996).

When considering the anoxic abyssal Eocene ocean, Sexton et al. (2011) postulated that anoxia allowed DOC to accumulate, creating a massive reduced carbon reservoir that was periodically oxidized and released from the ocean as CO₂, causing warm (hyperthermal) climate events. This postulation of DOC-sourced hyperthermal events also explained shifts in carbon isotopes found in the sedimentary record; elevated DOC found in the anoxic Black Sea rationalized the idea. However, the Black Sea’s elevated DOC is not due to anoxia-induced accumulation; it is instead the result of external inputs. This result leaves an alternative explanation for elevated DOC in anoxic oceans: that the Eocene ocean contained elevated terrigenous DOC from enhanced river input, thus making the Black Sea’s DOC pool analogous to the ocean during the Eocene. Periodic releases of this elevated terrigenous DOC pool may explain the hyperthermal events and sedimentary isopic shifts (Ridgwell and Arndt, 2015).

5. Summary

Across the Black Sea, DOC concentrations were >180 μmol kg⁻¹ near the surface, decreasing to 116 ± 6 μmol kg⁻¹ in the UAOL (~150–500 m) and then gradually increasing to 122 ± 2 μmol kg⁻¹ in the BBL (~1775 m). Near the surface there is a net production of up to ~10 μmol kg⁻¹ DOC. In the OL below the euphotic zone (~50 m), there is net removal (i.e., deficits) of up to ~34–41 μmol kg⁻¹ in the CIL and further ~5–12 μmol kg⁻¹ removal in the SOL, estimated to be removed in ~5 years time. DOC removal continues in the AOL, ranging from a minimum deficit of 4 ± 2 μmol kg⁻¹ in the BBL to a maximum of 13 ± 5 μmol kg⁻¹ in the UAOL, where removal is estimated to occur over ~300–600 years. The vertical gradient in the AOL’s DOC deficit may be due to greatest net removal in the UAOL (e.g., via particle scavenging), while sources in the BBL (e.g., fermentation or particle solubilization) may cause the gross deficit to be underestimated in the deeper AOL. Since there are DOC sources in the AOL and export production is not included, the net deficit of 13 ± 5 μmol kg⁻¹ is a conservative estimate of removal under anoxic conditions. We find no evidence for anoxia-induced DOC accumulation, however we find evidence to suggest that concentrations are elevated relative to the ocean due to the large terrigenous input (>50% of observed deep concentrations), which may have implications for explaining DOC concentrations in the anoxic Eocene ocean. Overall, 48 ± 4 μmol kg⁻¹ (or ~29%) of allochthonous DOC is removed in the Black Sea with respect to predicted concentrations, of which ~10% is removed under anoxic conditions, requiring only ~15% net removal in the OL. Unresolved questions include the composition and origin of the Black Sea’s persistent DOC pool (e.g., marine vs. terrigenous; autochthonous vs. allochthonous), its reactivity under oxygenated conditions, seasonal DOC variability in the Bosporus Strait, and whether or not the UAOL is seasonally formed.

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