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 $>180 \mu\text{mol kg}^{-1}$ at the surface, decreasing to $\sim 125 \mu\text{mol kg}^{-1}$ at the base of the oxic layer and reaching a minimum of $\sim 113 \mu\text{mol kg}^{-1}$ in the upper anoxic layer between ~150 and 500 m. At greater depths the concentrations increased; maximum anoxic layer concentrations of $122 \mu\text{mol kg}^{-1}$ 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 $\sim 10 \mu\text{mol kg}^{-1}$ was identified at the surface, likely due to local primary production. DOC exported to depth was non-conservative: up to $\sim 34\text{--}41 \mu\text{mol kg}^{-1}$ was removed from the basin's oxic layer in <5 years, and an additional $13 \pm 5 \mu\text{mol kg}^{-1}$ was removed from the anoxic layer during its ~300-600 years

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 $48 \mu\text{mol kg}^{-1}$ (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.

Keywords: Black Sea; DOC; dissolved organic carbon; GEOTRACES

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 Bosphorus 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 Bosphorus 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). In the OL below the euphotic zone, aerobic mineralization of organic matter forces the loss of oxygen and the regeneration of inorganic nutrients (Hiscock and Millero, 2006). Between ~100 and 150 m is the suboxic layer (SOL); 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).

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; Oguz 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 are either near or below the detection limit in the underlying water (Lee et al., 2002; Stanev 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 Bosphorus Strait (Unluata et al., 1990; Murray et al., 1991); the resulting dense water sinks to form the AOL (Ozsoy et al., 1993; Oguz 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 (S_p) 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 S_p 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 (Oguz et al., 2004).

Deep Black Sea residence time estimates are wide ranging (Ostlund, 1974; Top and Clarke, 1983; Dyrssen, 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 Bosphorus 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 64PE373, 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 x 24.4-L polyvinylidene fluoride (PVDF) bottles housed in a titanium frame (Rijkenberg et al., 2015), equipped with a Sea-Bird Electronic, Inc. (SBE) 9plus CTD sensor package. Temperature was calibrated with a high-accuracy reference thermometer (SBE 35) and S_P (Lewis and Perkin, 1978) was calibrated using a Guildline Model 8400B Laboratory Salinometer with Ocean Scientific International Ltd. (OSIL) salinity standard, batch P155. The temperature had an accuracy of $<0.001^\circ\text{C}$ when compared to the SBE 35 and the S_P 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 (σ_θ) were calculated using the 2010 Thermodynamic Equation Of Seawater (TEOS-10) with the Gibbs-SeaWater (GSW) Toolbox (version 3.04; McDougall and Barker, 2011) for MATLAB (R2014a) and plotted using Ocean Data View (Schlitzer, 2014).

Dissolved oxygen (DO) 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 $\pm 0.1 \mu\text{M}$ (Winkler, 1888; Reinthaler et al., 2006). H_2S was measured following the procedures of Grasshoff (1969) with an estimated precision of $\pm 0.263 \mu\text{M}$. Nitrate was calculated by subtracting measured nitrite concentrations (did not exceed $0.22 \mu\text{M}$) from measured nitrate plus nitrite concentrations; both were measured on board following the procedures of Grasshoff et al. (1983) with a propagated precision of $\pm 0.018 \mu\text{M}$. Photosynthetically active radiation (PAR) was measured using a Satlantic PAR-sensor to estimate the base of the euphotic zone ($<3\text{-}10\%$ cosine error), in conjunction with oxygen measurements.

Water for DOC analysis was collected from the PVDF bottles by filtering through Sartorius Sartobran[®] P $0.2 \mu\text{m}$ pore size, 300 cm^2 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 hours 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 CO_2 (Dickson et al., 2007). Analysis was verified with a precision of $\pm 1.5 \mu\text{M}$ 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 S_p , representing mixing

between the Bosphorus Strait and Danube River waters (end-members external to the Black Sea). AOL formation is modeled with mixing scenario #2 by the mixing of Bosphorus Strait water with the CIL [an external and an internal (CIL) end-members] (Fig. 2). Hydrographic variables that behave conservatively at depth, such as θ and S_p , trace subsurface mixing, offering insights on the basin's hydrographic distributions and the biogeochemical processes that occur within.

Mixing scenarios #1 and #2 (Fig. 2) are employed to predict DOC concentrations with respect to conservative tracers, such as θ and S_p . Since we take S_p to behave more conservatively than θ at the surface and in the basin's deep layers (i.e., due to geothermal input), it is employed for predicting DOC concentrations. DOC is first predicted throughout the full water column by employing mixing scenario #1. Subsequent to this generalized mixing, DOC is predicted using mixing scenario #2, representing the pool of DOC that is imported into the AOL (after loss of DOC in the overlying OL). Concentrations predicted from both mixing scenarios are then compared with observations to identify DOC's behavior in the basin's oxic, suboxic and anoxic waters.

3. Results

Samples were collected in the western gyre, central basin eddy, eastern gyre and Batumi eddy, along with the Bosphorus 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 $> \sigma_\theta \approx 14 \text{ kg m}^{-3}$, with concentrations increasing to a

maximum of $4.6 \mu\text{mol kg}^{-1}$ just above the OL-SOL interface (Fig. 3). The upper σ_θ boundary of the SOL was $15.64 \pm 0.24 \text{ kg m}^{-3}$ (2σ , $n = 12$) where oxygen concentrations were $20 \pm 4 \mu\text{mol kg}^{-1}$, while its lower σ_θ boundary was $16.20 \pm 0.10 \text{ kg m}^{-3}$ ($n = 7$) where H_2S concentrations reached $1.0 \pm 0.9 \mu\text{mol kg}^{-1}$. 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 $\sim 450 \mu\text{mol kg}^{-1}$ at the bottom of the basin (Fig. 3).

Temperature was $\sim 25^\circ\text{C}$ at the surface, then decreased with depth to the water column minimum of 7.663°C at $\sigma_\theta = 14.690 \text{ kg m}^{-3}$ near the center of the CIL (Fig. 3, showing $<8^\circ\text{C}$). The CIL spanned from $\sigma_\theta = 14.250 \text{ kg m}^{-3}$ to 15.185 kg m^{-3} , having a θ of $7.853 \pm 0.174^\circ\text{C}$ and a S_p of 19.166 ± 0.632 (2σ , $n = 58$). The upper boundary of the CIL was approximately coincident with the lower boundary of the euphotic zone. Below the CIL, θ increased to a local maximum of 8.85°C at stations 3, 4 and 9 in the central basin at $\sim 500 \text{ m}$, corresponding to the θ anomalies identified by Murray et al. (1991) and Ozsoy et al. (1991), and here representing the UAOL-DAOL interface at $\sigma_\theta = 17.04 \text{ kg m}^{-3}$. Below this local maximum, θ increased to a maximum of $8.9012 \pm 0.0012^\circ\text{C}$ ($n = 53$) at depths $>1775 \text{ m}$, i.e., within the BBL (Fig. 4a). S_p generally increased from ~ 18 at the surface to 22.3482 ± 0.0016 ($n = 53$) in the BBL (Fig. 4b), with the highest observed S_p being 36.515 at the bottom of station 12 near the Bosphorus Strait. Since σ_θ is primarily controlled by S_p in the Black Sea, σ_θ also increased with depth, ranging from $\sim 10 \text{ kg m}^{-3}$ at the surface to $17.2441 \pm 0.0012 \text{ kg m}^{-3}$ ($n = 53$) in the BBL (Figs. 3, 4c), with a maximum σ_θ of 27.059 kg m^{-3} at the bottom of station 12.

DOC concentrations (Fig. 5a) exceeded $180 \mu\text{mol kg}^{-1}$ at the surface, with the highest concentration of $205 \mu\text{mol kg}^{-1}$ at station 12 near the Bosphorus Strait (Table 1), likely containing a strong terrigenous signal from coastal water leaving the Black Sea. Concentrations decreased

with depth to $\sim 175 \mu\text{mol kg}^{-1}$ near the base of the euphotic zone, $139 \pm 28 \mu\text{mol kg}^{-1}$ (2σ , $n = 13$) in the CIL and $\sim 125 \mu\text{mol kg}^{-1}$ at the bottom of the OL (Fig. 5a). Overall, OL concentrations were $162 \pm 49 \mu\text{mol kg}^{-1}$ ($n = 59$), excluding three samples with strong Bosporus influence (low DOC) at station 12 (Table 1), with concentrations of $85 \pm 12 \mu\text{mol kg}^{-1}$. In the SOL, DOC decreased only slightly with depth, having concentrations of $124 \pm 9 \mu\text{mol kg}^{-1}$ ($n = 22$). Concentrations in the AOL ranged from a minimum of $\sim 113 \mu\text{mol kg}^{-1}$ in the UAOL to a maximum of $122 \mu\text{mol kg}^{-1}$ near the bottom (Fig. 5b). The average DOC concentration throughout the AOL was $117 \pm 7 \mu\text{mol kg}^{-1}$ ($n = 158$); mean concentrations were $116 \pm 6 \mu\text{mol kg}^{-1}$ ($n = 81$) in the UAOL, $117 \pm 5 \mu\text{mol kg}^{-1}$ ($n = 56$) in the DAOL, and $122 \pm 2 \mu\text{mol kg}^{-1}$ ($n = 21$) in the BBL.

4. Discussion

4.1. Mixing scenarios in θ - S_p space

4.1.1. Mixing scenario #1

The Black Sea's marine source is the Mediterranean Sea via the Bosporus Strait while rivers are the major source of freshwater to the basin (Oguz et al., 2004; Efimov et al., 2012). The contrasting salinities of the basin's two primary source waters make S_p an appropriate tracer for mixing within the basin (represented by mixing scenario #1 in Fig. 2), assuming changes from net evaporation are inconsequential. On the other hand, θ does not behave conservatively near the surface since insolation varies seasonally. The Bosporus and river waters also hold distinctly different DOC concentrations (Pulat and Tugrul, 1995; Cauwet et al., 2002; Raymond and Spencer, 2015).

To better understand the marine and freshwater contributions, the distribution of freshwater in the Black Sea (as % freshwater) is calculated using the average S_P of the inflowing Bosphorus water (36.25 ± 1.25 from Unluata et al., 1990) and observed S_P :

$$\% \text{ Freshwater} = (1 - S_P / 36.25) * 100. \quad (1)$$

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 θ 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 θ of $13.49 \pm 1.0^\circ\text{C}$) and S_P used in Eq. 1. Mean θ (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:

$$\theta_2 = 0.330 * S_P + 1.529 \quad (2)$$

$$S_{P2} = 3.031 * \theta - 4.634. \quad (3)$$

These equations for mixing scenario #2 predict θ and S_P (θ_2 and S_{P2}) in the AOL (blue line in Fig. 7), with overall root mean square errors (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 θ_2 and S_{P2} 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 θ_2 and 0.261 for S_P .

For θ and S_P exclusive to the UAOL, linear regressions from the observed data are employed:

$$\theta_{UAOL} = 0.301 * S_P + 2.239 \quad (4)$$

$$S_{P-UAOL} = 3.261 * \theta - 6.884. \quad (5)$$

UAOL θ and S_P regressions (θ_{UAOL} and S_{P-UAOL}), both having R^2 values of 0.98, and RMSEs of 0.014°C and 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 Bosphorus 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 Bosphorus 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 S_P 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 - S_P curvature 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 S_P 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 Bosphorus and Danube DOC end-members for mixing scenario #1. Inflowing Bosphorus seawater has an annual average concentration of $71 \pm 8 \mu\text{mol kg}^{-1}$ (here converted from μM reported by Polat and Tugrul, 1995), while the S_P of 36.25 from Unluata et al. (1990) is used for consistency with Eqs. 2 and 3. The concentration of $300 \mu\text{mol kg}^{-1}$ and S_P 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 S_P end-members is described by:

$$\text{DOC}_1 = 300 - 6.32 * S_P, \quad (6)$$

where DOC_1 is the predicted concentrations from S_P , represented by the red line in Fig. 8. Virtually all DOC_1 concentrations are higher than observations. Exceptions are within the euphotic zone (above ~50 m), which includes the Bosphorus Strait (an end-member), where autochthonous production is evidenced by elevated oxygen and depleted nitrate concentrations (Fig. 3).

Overall, differences between observed DOC and DOC_1 demonstrate a net removal of up to $\sim 50 \mu\text{mol kg}^{-1}$ (Fig. 8), in agreement with Ducklow et al. (2007). This removal is further explored by predicting DOC using mix 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 $139 \mu\text{mol kg}^{-1}$

and S_P of 19.166 (Section 3), while the Bosphorus end-member was previously defined for mixing scenario #1 as $71 \mu\text{mol kg}^{-1}$ and 36.25. Using the Bosphorus and CIL end-members, the relationship between DOC and S_P in the AOL is:

$$\text{DOC}_2 = 215 - 3.98 * S_P, \quad (7)$$

where DOC_2 is predicted DOC in the AOL, represented by the blue line in Fig. 8. DOC_2 is always lower than DOC_1 , suggesting that there is loss of DOC once waters mix down into the AOL. In the BBL, DOC_2 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 DOC_2 and observations increases above the BBL, through the DAOL and into the UAOL, showing a net removal of up to $\sim 20 \mu\text{mol kg}^{-1}$ 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 $\sim 20 \mu\text{mol kg}^{-1}$ difference between UAOL observations and mixing scenario #2 in Fig. 8 is unlikely to result from the layer's $\sim 0.25 S_P$ offset in predicted S_P (Fig. 7), because this offset only explains $\sim 1 \mu\text{mol kg}^{-1}$ 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 Bosphorus DOC concentrations (Polat and Tugrul, 1995), so it is unlikely that the difference between DOC_2 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 (ΔDOC_X) 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 Bosphorus waters (ΔDOC_1) is calculated using DOC_1 , while the deficit that is subsequent to mixing between the Bosphorus and CIL waters (ΔDOC_2) is calculated using DOC_2 . ΔDOC_2 is the fraction of ΔDOC_1 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 - ΔDOC_1

ΔDOC_1 is the DOC deficit observed given conserved mixing of DOC from the two major inputs to the Black Sea (river and Bosphorus waters). In the OL, ΔDOC_1 ranges from about -10 $\mu\text{mol kg}^{-1}$ at the surface to $41 \pm 28 \mu\text{mol kg}^{-1}$ ($n = 13$) in the CIL near the OL-SOL boundary (Fig. 9a, Table 3). There is net production of autochthonous DOC by phytoplankton, as evidenced by the slightly negative ΔDOC_1 (Fig. 9a) and elevated oxygen concentrations (Fig. 3). This production suggests that ΔDOC_1 may underestimate the net DOC deficit, since ΔDOC_1 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 ΔDOC_1 is $46 \pm 7 \mu\text{mol kg}^{-1}$ ($n = 22$), the net deficit is slightly larger than in the OL, suggesting a further $\sim 5 \mu\text{mol kg}^{-1}$ removal in the SOL (Fig. 9a, Table 3).

In the AOL, ΔDOC_1 is $45 \pm 9 \mu\text{mol kg}^{-1}$ (2σ , $n = 158$) (Fig. 9b), with the BBL, DAOL and UAOL having respective deficits of $37 \pm 2 \mu\text{mol kg}^{-1}$ ($n = 21$), $42 \pm 6 \mu\text{mol kg}^{-1}$ ($n = 56$) and $48 \pm 4 \mu\text{mol kg}^{-1}$ ($n = 81$) (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 $165 \pm 4 \mu\text{mol kg}^{-1}$ ($n = 324$) (Fig. 8). Within the AOL and its sub-layers, ΔDOC_1 distributions suggest that there is a gradient (i.e., removal) of up to $17 \mu\text{mol kg}^{-1}$ under anoxic conditions (Fig. 9b).

4.3.2. Net DOC deficit #2 - ΔDOC_2

DOC removal subsequent to the formation of the AOL and its sub-layers is isolated using ΔDOC_2 . Since ΔDOC_2 is a component of ΔDOC_1 , their difference in the AOL represents the deficit that is imported from the OL based on mixing scenario #2, which is $34 \pm 12 \mu\text{mol kg}^{-1}$, compared with $41 \pm 28 \mu\text{mol kg}^{-1}$ from ΔDOC_1 (Table 3). These results suggests that maximum net removal in the OL is ~34-41 $\mu\text{mol kg}^{-1}$, and that further removal of ~5-12 $\mu\text{mol kg}^{-1}$ occurs within the SOL given the OL range (Table 3), assuming that these deficits are locally formed and not imported from the UAOL.

ΔDOC_2 in the AOL is $11 \pm 8 \mu\text{mol kg}^{-1}$ (2σ , $n = 158$), increasing from a minimum of $4 \pm 2 \mu\text{mol kg}^{-1}$ ($n = 21$) in the BBL, to $10 \pm 5 \mu\text{mol kg}^{-1}$ ($n = 56$) in the >1000 m-thick DAOL, with a maximum of $13 \pm 5 \mu\text{mol kg}^{-1}$ ($n = 81$) in the overlying UAOL (Fig. 10, Table 3). Since ΔDOC_2 is close to zero in the BBL (i.e., DOC is apparently conserved subsequent to Bosphorus-CIL mixing), and there is a ΔDOC_2 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 ΔDOC_2 distributions is that additional DOC sources exist in the BBL, such as from sediments,

returning levels to apparent conservation (discussed further below). Overall, ΔDOC_2 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 $130 \pm 2 \mu\text{mol kg}^{-1}$ ($n = 324$). This requires ~19% removal in the OL's CIL since the maximum net removal for the basin is ~29%, identified above with ΔDOC_1 .

4.4. Processes responsible for DOC distributions

The autochthonous production of DOC is evidenced by a net surplus of up to $\sim 10 \mu\text{mol kg}^{-1}$ in the euphotic zone (i.e., ΔDOC_1 is about $-10 \mu\text{mol kg}^{-1}$ at the surface) (Fig. 9a). The average primary productivity in the Black Sea is $349 \text{ mg C m}^{-2}\text{d}^{-1}$ (Yunev 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 $\sim 0.3 \mu\text{M DOC}$ 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 $\sim 10 \mu\text{mol kg}^{-1}$ 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 $\sim 300 \mu\text{mol kg}^{-1}$ DOC, flocculation would remove $\sim 9\text{-}33 \mu\text{mol kg}^{-1}$ 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 $\sim 138 \mu\text{mol kg}^{-1}$ 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 ΔDOC_1 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 $14 \text{ mg C m}^{-2}\text{d}^{-1}$ in the Black Sea, given the primary productivity above. If constant over the year, this rate would support export of $\sim 5 \text{ g C m}^{-2}\text{yr}^{-1}$ from the euphotic zone, contributing $\sim 8.5 \text{ } \mu\text{mol kg}^{-1}$ 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 ΔDOC_2 does not consider autochthonous production, the $11 \pm 8 \text{ } \mu\text{mol kg}^{-1}$ net deficit identified in the AOL could in fact be $8.5 \text{ } \mu\text{mol kg}^{-1}$ 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 Millero (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. Ruttenberg 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 scavenge 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 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 chemoautotrophic 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 chemoautotrophic addition of DOC to the UAOL is small, where the deficits are largest (Figs. 9b, 10). Profiles of bacterial and chemoautotrophic 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 chemoautotrophic production (Lorenzoni et al., 2013), reaffirming that chemoautotrophy 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., 1995), 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 Bosphorus 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 $\sim 40 \mu\text{mol kg}^{-1}$ (Hansell et al., 2009), it is plausible that the fraction of marine DOC in the deep Black Sea ($\sim 60\%$, Fig 6b) also decreases to $40 \mu\text{mol kg}^{-1}$ over time (i.e., equivalent to $24 \mu\text{mol kg}^{-1}$, or $\sim 21\%$ of deep concentrations). This results in the deep water terrigenous fraction (normalized to $S_p = 0$) having a concentration of $\sim 211 \mu\text{mol kg}^{-1}$ (i.e., $84.5 \mu\text{mol kg}^{-1}$, or $\sim 72\%$). Alternatively, if marine DOC is conserved in the deep Black Sea (i.e., $\sim 43 \mu\text{mol kg}^{-1}$, or $\sim 37\%$), it would result in the terrigenous fraction having a concentration of $\sim 164 \mu\text{mol kg}^{-1}$ (i.e., $65.5 \mu\text{mol kg}^{-1}$, or $\sim 56\%$). Regardless of marine DOC being conserved and considering the input 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 CO_2 , 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 isotopic shifts (Ridgwell and Arndt, 2015).

5. Summary

Across the Black Sea, DOC concentrations were $>180 \mu\text{mol kg}^{-1}$ near the surface, decreasing to $116 \pm 6 \mu\text{mol kg}^{-1}$ in the UAOL ($\sim 150\text{-}500 \text{ m}$) and then gradually increasing to $122 \pm 2 \mu\text{mol kg}^{-1}$ in the BBL ($>1775 \text{ m}$). Near the surface there is a net production of up to $\sim 10 \mu\text{mol kg}^{-1}$ DOC. In the OL below the euphotic zone ($>50 \text{ m}$), there is net removal (i.e., deficits) of up to $\sim 34\text{-}41 \mu\text{mol kg}^{-1}$ in the CIL and further $\sim 5\text{-}12 \mu\text{mol kg}^{-1}$ removal in the SOL, estimated to be removed in ~ 5 years time. DOC removal continues in the AOL, ranging from a minimum deficit of $4 \pm 2 \mu\text{mol kg}^{-1}$ in the BBL to a maximum of $13 \pm 5 \mu\text{mol kg}^{-1}$ in the UAOL, where removal is estimated to occur over $\sim 300\text{-}600$ 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 $13 \pm 5 \mu\text{mol kg}^{-1}$ 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, $48 \pm 4 \mu\text{mol kg}^{-1}$ (or $\sim 29\%$) of allochthonous DOC is removed in the Black Sea with respect to predicted concentrations, of which $\sim 10\%$ is removed under anoxic conditions, requiring only $\sim 19\%$ 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 Bosphorus Strait, and whether or not the UAOL is seasonally formed.

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Table 1. Stations sampled during cruise 64PE373 in the Black Sea, given in the sequence from east to west.

Region and Station	Date	Position	Depth
<i>Bosporus Strait</i>			
12	July 23, 2013	41° 13.44'N, 29° 07.55'E	59 m
<i>Bosporus Plume</i>			
11	July 23, 2013	41° 34.31'N, 29° 08.80'E	576 m
<i>Western Gyre</i>			
1	July 14, 2013	42° 15.96'N, 30° 00.94'E	2081 m
2	July 14-15, 2013	42° 31.29'N, 31° 24.11'E	2120 m
10	July 22, 2013	42° 44.33'N, 32° 30.31'E	2133 m
3	July 16, 2013	43° 01.65'N, 33° 43.85'E	2164 m
<i>Central Basin Eddy</i>			
9	July 21, 2013	43° 12.01'N, 34° 46.21'E	2157 m
<i>Eastern Gyre</i>			
4	July 17, 2013	43° 08.55'N, 35° 13.78'E	2136 m
8	July 20, 2013	42° 48.67'N, 37° 34.03'E	2105 m
5	July 18, 2013	42° 20.93'N, 38° 41.03'E	2040 m
<i>Batumi Eddy</i>			
7	July 19, 2013	41° 56.23'N, 39° 40.45'E	1942 m
6	July 19, 2013	41° 30.70'N, 40° 37.18'E	1645 m

Table 2. Biogeochemical and hydrographic layers of the Black Sea, and definitions of upper and lower boundaries.

Layer	Upper Boundary	Lower Boundary
<i>Oxic Layer</i>	Surface	$\sigma_\theta = 15.64 \text{ kg m}^{-3}$
<i>Euphotic Zone</i>	Surface	Depth $\approx 50 \text{ m}$
<i>Cold Intermediate Layer</i>	Temperature = 8°C	Temperature = 8°C
<i>Suboxic Layer</i>	$\sigma_\theta = 15.64 \text{ kg m}^{-3}$	$\sigma_\theta = 16.20 \text{ kg m}^{-3}$
<i>Anoxic Layer</i>	$\sigma_\theta = 16.20 \text{ kg m}^{-3}$	Seafloor
<i>Upper Anoxic Layer</i>	$\sigma_\theta = 16.20 \text{ kg m}^{-3}$	$\sigma_\theta = 17.04 \text{ kg m}^{-3}$
<i>Deep Anoxic Layer</i>	$\sigma_\theta = 17.04 \text{ kg m}^{-3}$	Depth = 1775 m
<i>Benthic Bottom Layer</i>	Depth = 1775 m	Seafloor

Table 3. Layer-specific net DOC deficits. ΔDOC_1 is the deficit that is subsequent to mixing between the Danube River and Bosporus Strait waters, while ΔDOC_2 is the fraction of ΔDOC_1 removed within the AOL, representing the deficit that is subsequent to mixing between the Bosporus and CIL waters. The difference between ΔDOC_1 and ΔDOC_2 ($\Delta\text{DOC}_1 - \Delta\text{DOC}_2$) in the AOL represents the deficit imported from the OL's CIL, based on mixing scenario #2, and the SOL deficit is inferred from subtracting range in the OL from the SOL's ΔDOC_1 .

Layer	ΔDOC_1	ΔDOC_2	$\Delta\text{DOC}_1 - \Delta\text{DOC}_2$
<i>Oxic Layer</i>	-10-41 $\mu\text{mol kg}^{-1}$	NA	$\leq 34 \pm 12 \mu\text{mol kg}^{-1}$
Surface	-10 $\mu\text{mol kg}^{-1}$	NA	NA
<i>Cold Intermediate Layer</i>	$41 \pm 28 \mu\text{mol kg}^{-1}$	NA	$34 \pm 12 \mu\text{mol kg}^{-1}$
<i>Suboxic Layer</i>	$46 \pm 7 \mu\text{mol kg}^{-1}$	NA	$\sim 5-12 \mu\text{mol kg}^{-1}$
<i>Anoxic Layer</i>	$45 \pm 9 \mu\text{mol kg}^{-1}$	$11 \pm 8 \mu\text{mol kg}^{-1}$	$34 \pm 12 \mu\text{mol kg}^{-1}$
Upper Anoxic Layer	$48 \pm 4 \mu\text{mol kg}^{-1}$	$13 \pm 5 \mu\text{mol kg}^{-1}$	$35 \pm 6 \mu\text{mol kg}^{-1}$
Deep Anoxic Layer	$42 \pm 6 \mu\text{mol kg}^{-1}$	$10 \pm 5 \mu\text{mol kg}^{-1}$	$32 \pm 8 \mu\text{mol kg}^{-1}$
Benthic Bottom Layer	$37 \pm 2 \mu\text{mol kg}^{-1}$	$4 \pm 2 \mu\text{mol kg}^{-1}$	$33 \pm 3 \mu\text{mol kg}^{-1}$

Figure Captions

Figure 1. Distributions of chlorophyll *a* ($\mu\text{g L}^{-1}$) and stations occupied during the cruise. The generalized upper layer circulation of the Black Sea is added with grey 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 “X” 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/.

Figure 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 Bosphorus Strait.

Figure 3. Vertical profiles of oxygen, nitrate, hydrogen sulfide, and temperature ($<8^{\circ}\text{C}$, defining the CIL) 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 σ_{θ} . Approximate layer boundary depths are marked on the right side of the y-axis.

Figure 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.

Figure 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. Section plotted using Ocean Data View (Schlitzer, 2014).

Figure 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.

Figure 7. Potential temperature versus practical salinity. Black dots are observations, while colored lines represent conservative end-member mixing discussed in text. Gray lines are potential density contours.

Figure 8. DOC plotted against practical salinity observed during the cruise. Observations are marked by black dots. DOC mixing curves are plotted, where the red line represents mixing between the Bosphorus and Danube and the blue line represents mixing between the Bosphorus and CIL.

Figure 9. DOC deficits (ΔDOC_1) across the Black Sea according to mixing scenario #1, spanning depths (a) 0-200 m and (b) 0-2250 m. 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.

Figure 10. DOC deficits (ΔDOC_2) across the AOL of the Black Sea according to mixing scenario #2. 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.

Figures

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.