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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.

1. Introduction

The Black Sea is the world's largest anoxic basin and inland sea (Fig. 1). With a volume of 547,000 km^3 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

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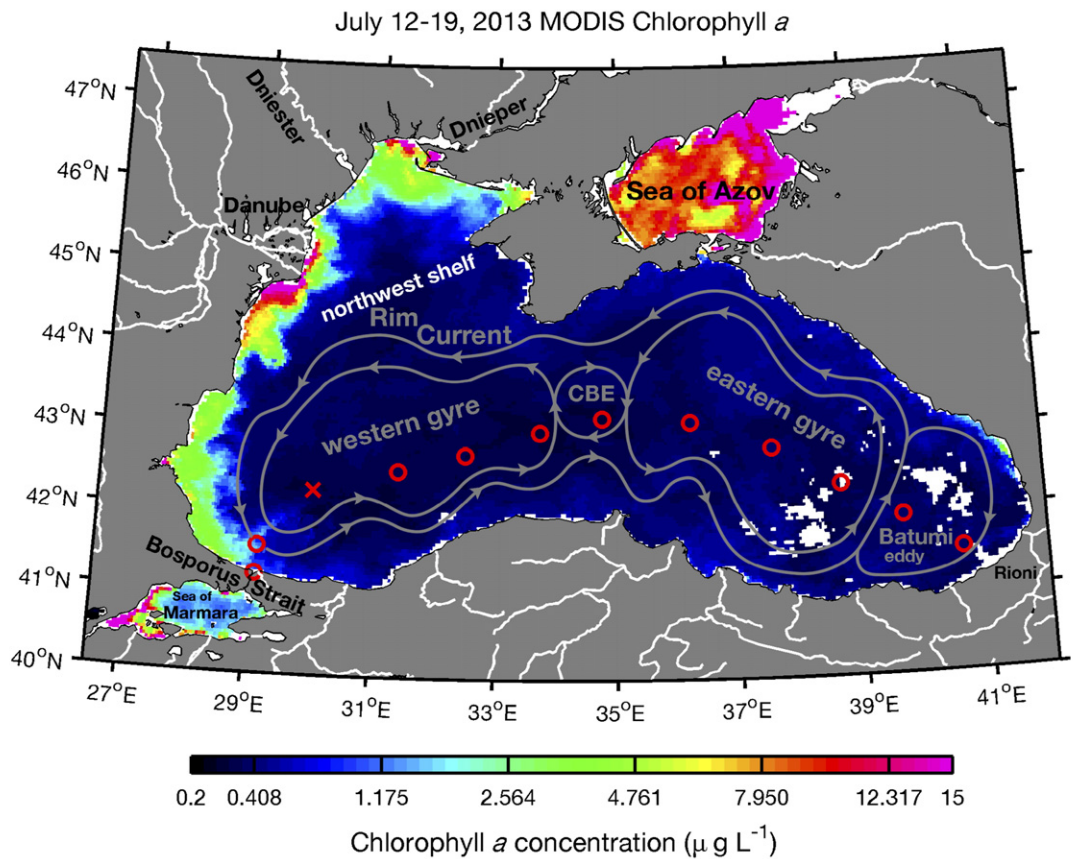

Fig. 1. Distributions of chlorophyll *a* (μg L^{-1}) and stations occupied during the cruise. The generalized upper layer circulation of the Black Sea is added with gray arrows adapted from Oguz et al., 1993. Chlorophyll *a* is from July 12–19, 2013 and stations were occupied from July 14–23, 2013. CBE 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/.

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). 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 (H_2S) 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 H_2S increasing with depth due to sulfate reduction (Dyrssen, 1986).