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Biogeochemical relationships between ultrafiltered dissolved organic matter and picoplankton activity in the Eastern Mediterranean Sea

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ABSTRACT

We targeted the warm, subsurface waters of the Eastern Mediterranean Sea (EMS) to investigate processes that are linked to the chemical composition and cycling of dissolved organic carbon (DOC) in seawater. The apparent respiration of semi-labile DOC accounted for 27 $\pm$ 18% of oxygen consumption in EMS mesopelagic and bathypelagic waters; this value is higher than that observed in the bathypelagic open ocean, so the chemical signals that accompany remineralization of DOC may thus be more pronounced in this region. Ultrafiltered dissolved organic matter (UDOM) collected from four deep basins at depths ranging from 2 to 4350 m exhibited bulk chemical (^{1}H-NMR) and molecular level (amino acid and monosaccharide) abundances, composition, and spatial distribution that were similar to previous reports, except for a sample collected in the deep waters of the N. Aegean Sea that had been isolated for over a decade. The amino acid component of UDOM was tightly correlated with apparent oxygen utilization and prokaryotic activity, indicating its relationship with remineralization processes that occur over a large range of timescales. Principal component analyses of relative mole percentages of monomers revealed that oxygen consumption and prokaryotic activity were correlated with variability in amino acid distributions but not well correlated with monosaccharide distributions. Taken together, this study elucidates key relationships between the chemical composition of DOM and heterotrophic metabolism.

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1. Introduction

1.1. Dissolved organic matter (DOM) cycling

Oceanic dissolved organic carbon (DOC) is one of the largest reservoirs of carbon on Earth, and its potential for exchange with other carbon reservoirs has brought it within the focus of global carbon-cycle research (Williams and Druffel, 1988; Toggweiler, 1989; Hedges, 1992; Hansell, 2002). The euphotic zone is the principal site of organic matter production in the open ocean. The magnitude and composition of DOM produced during bloom events vary considerably and are controlled by a number of biological, chemical and physical parameters (Carlson, 2002). In the surface ocean, DOC stocks exceeding the deep refractory pool are composed of 'labile' and 'semi-labile' DOC (Hansell and Carlson, 1998a). Because labile DOC concentrations represent a very small fraction of bulk DOC (0-6%), the vertical gradient of the bulk DOC observed in stratified systems is mostly comprised of 'semi-labile' DOM (Carlson and Ducklow, 1995; Cherrier et al., 1996). The labile component of DOC arising from autotrophic production in the surface ocean is thought to support production of heterotrophic bacterioplankton (i.e. the microbial loop; Azam et al., 1983), and is either repackaged into bacterial organisms and passed to higher trophic levels or remineralized. Semi-labile DOC escapes rapid degradation by marine heterotrophs in surface ocean waters and is available for export to the ocean's interior by convective mixing (Copin-Montegut and Avril, 1993; Carlson

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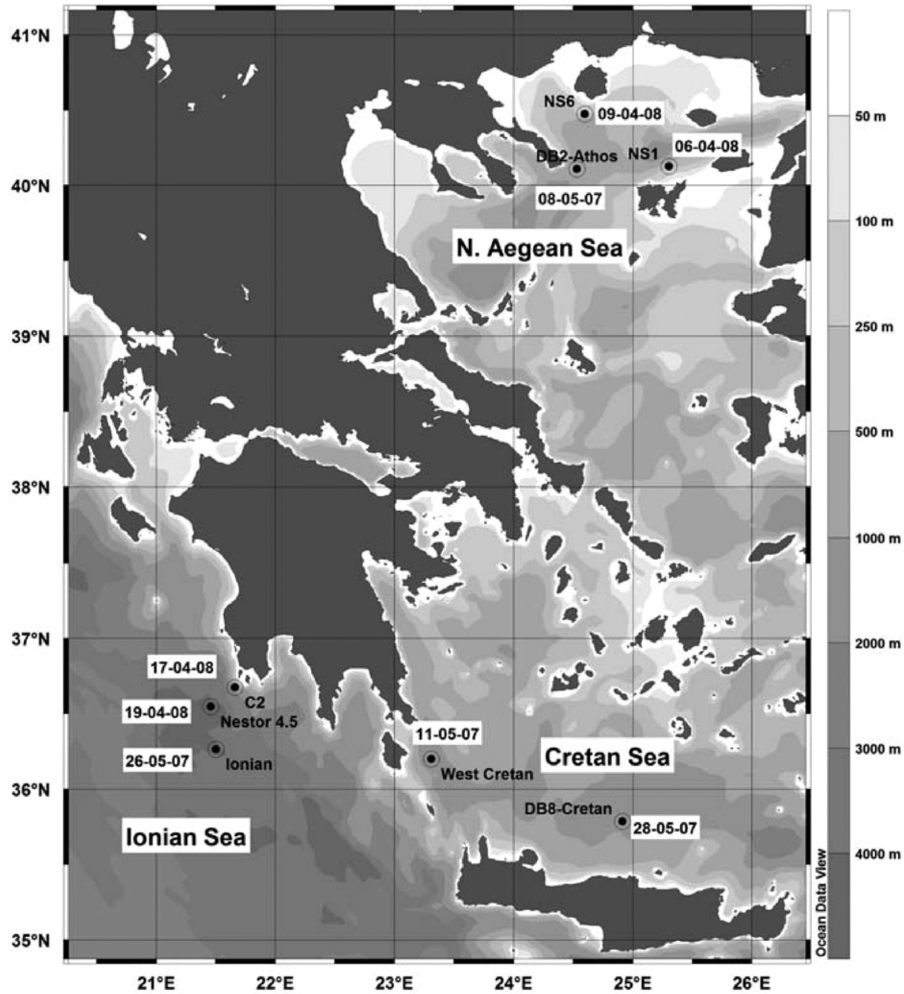

Fig. 1. UDOM sampling stations (circles) collected during POSEIDON, SESAME, and KM3NET cruises in May 2007 and April 2008. Sampling dates are provided adjacent to the location.

et al., 1994), advection along isopycnals surfaces (Hansell and Carlson, 2001), or sorption onto sinking particles (Keil and Kirchman, 1994; Druffel et al., 1996). This fraction can amount to 1.2 Gt C yr^{-1}, or 17% of global new production (Hansell and Carlson, 1998b) and provides a carbon source that fuels production by deep-sea free-living prokaryotes (Karner and Herndl, 1992; Smith et al., 1992; Nagata et al., 2000, 2010).

1.2. Oceanographic setting

The Mediterranean Sea has often been described as a small ocean as it encompasses all oceanic processes at much smaller time and space scales (Béthoux et al., 2002). Its thermohaline cell is forced by deep-water formation at the northern coasts of the Mediterranean during winter, and the formation of Levantine Intermediate waters in the northern part of the Eastern Mediterranean. In its eastern part, the Eastern Mediterranean Sea (EMS) is an ultra-oligotrophic environment characterized by extremely low dissolved nutrient concentrations, chlorophyll-a concentrations, and phytoplankton biomass in surface waters (Krom et al., 2003). The EMS is unique among the oligotrophic oceans because the ratio between dissolved nitrate and phosphate is higher than 20 in all sub-thermocline water masses (Krom et al.,1992; Béthoux et al., 2002). Its annual primary productivity is 60-80 g C m^{-2} y^{-1} (Ignatiades, 1998; Psarra et al., 2000), approximately half that determined in the oligotrophic Sargasso Sea (e.g., 157 $\pm$ 7 g C m^{-2} y^{-1}, Brix et al., 2006).

The area under investigation in this study extends throughout the Aegean Sea and into the Cretan and Ionian Seas (Fig. 1). Complex sea-bed topography together with Black Sea Waters (BSW) entering through the Dardanelles Straits and highly saline waters of Levantine origin determine the structure of the water column in the Aegean and, partly, the Ionian Seas. The surface layer of the north – northwest Aegean is covered by a light, thin layer of (BSW) of salinity as low as 30-35. The depths between 70 and 400 m in the North Aegean are waters with southeast Aegean / Levantine origin and are identified as the Levantine Intermediate Water (LIW; Lascaratos, 1993; Tzipperman and Speer, 1994), the most voluminous water mass of the Mediterranean (estimated at 2-3.5 $\times$ 10^{13} m^3; Myers and Haines, 2000).

Below the LIW, the deep basins of the North Aegean are filled with locally formed North Aegean Deep Water (NAeDW). These waters form at infrequent intervals, as their high density hinders renewal and ventilation. The current NAeDW was formed during two major dense water formation events in the winters of 1992 and 1993 (Zervakis et al., 2000). Since then, the properties have evolved as a result of turbulent vertical mixing with the overlying LIW (Zervakis et al., 2003). During mild winters, LIW in the northeastern Aegean can be further subducted in an annual process that contributes to the formation Cretan Deep Water (CDW) (Zervakis et al., 2004; Gertman et al., 2006). The latter water mass thus contains higher dissolved

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