



Particle sources over the Danube River delta, Black Sea based on distribution, composition and size using optics, imaging and bulk analyses



A.P. Karageorgis^{a,*}, W.D. Gardner^b, O.A. Mikkelsen^c, D. Georgopoulos^a, A.S. Ogston^d, G. Assimakopoulou^a, E. Krasakopoulou^a, Gh. Oaie^e, D. Secrieru^e, Th.D. Kanellopoulos^a, K. Pagou^a, Ch. Anagnostou^a, E. Papatthassiou^a

^a Hellenic Centre for Marine Research, Institute of Oceanography, 46.7 km Athens-Sounio Avenue, 19013 Anavyssos, Greece

^b Department of Oceanography, Texas A&M University, College Station, TX, USA

^c Sequoia Scientific, Inc., 2700 Richards Road, Suite 107, Bellevue, WA 98005, USA

^d University of Washington, School of Oceanography, Box 357940, Seattle, WA 98195, USA

^e National Institute of Marine Geology and Geocology, 23-25, Dimitrie Onciul Street, RO 024053 Bucharest, Romania

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ABSTRACT

Optical measurements provide substantial information on the dynamics and composition of particulate matter in the open ocean and coastal waters. When calibrated with the analysis of simultaneously collected discrete bottle samples, (particulate matter concentration: PMC, particulate organic carbon concentration: POC, chlorophyll α concentration: chl α , particle volume concentration and particle size distribution measured *in situ*), optical proxies increase the vertical resolution of changes in particle properties in the water column. We report relationships of inherent optical properties (beam attenuation at 2 wavelengths, fluorescence) and bulk particle properties obtained in the NW Black Sea during October 2007. The Danube River delta area was heavily stratified at that time, mainly due to a sharp thermocline at 17–27 m. Beam c_p and fluorescence were significantly correlated and showed highest values near the coast, with a decreasing trend offshore. *In situ* measured particle size distributions were characterized by modes at ~40 μm , 20 μm and 5 μm . PMC, POC, and chl α exhibited wide ranges of spatial variation, a common feature being the gradual decrease in concentrations from the coast to offshore. The POC:PMC and POC:chl α ratios suggested a general predominance of biogenic material over terrigenous particles throughout the study area. The commonly accepted sequence of large phytoplanktonic species transitioning to smaller ones during summer–autumn was confirmed by light microscopy and SEM observations. Detritus of *Chaetoceros* sp. and other diatoms was the dominant component of particulate matter. The small percentage of terrigenous particles was surprising given the high riverine sediment loads suggesting that most of the sediment load flocculated and was deposited before reaching the delta. Given the lack of previous data in this area, our study may serve as a baseline or background to look for changes in future bio-optical and/or biogeochemical measurements.

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1. Introduction

The northwestern sector of the Black Sea has attracted the interest of many scientific groups and large scale projects during past decades. The area receives 80% of the basin's total freshwater discharge, originating in the rivers Danube (208 $\text{km}^3 \text{yr}^{-1}$), Dnieper (43.4 $\text{km}^3 \text{yr}^{-1}$), and Dniester (9.1 $\text{km}^3 \text{yr}^{-1}$) (Mikhailov and Mikhailova, 2008). The Danube

River is the major contributor in terms of freshwater and sediment inputs, forming the second largest delta in Europe. The evolution of the delta over the last 12000 years has been studied in detail (e.g. Dan et al., 2007, 2009; Panin, 1996, 1997; Panin and Jipa, 2002).

One of the most severe environmental issues in the Black Sea is related to eutrophication, which resulted, directly or indirectly, in ecosystem degradation, including the frequent occurrence of harmful algal blooms (Moncheva et al., 2001). In the 1970s, the seaweed population of *Phyllophora* was substantially reduced due to light limitation and hypoxia (Zaitsev, 1992). The cumulative impact of enhanced riverine nutrients and over-enrichment of the jellyfish *Aurelia*, coinciding with the abundance of the exotic ctenophore (comb jelly) *Mnemiopsis leidyi* (e.g., Shiganova, 1998; Weisse et al., 2002) feeding on zooplankton and crustaceans, was probably the

* Corresponding author. Tel.: +30 22910 76369; fax: +30 22910 76347.

E-mail addresses: ak@hcmr.gr (A.P. Karageorgis), wgardner@tamu.edu (W.D. Gardner), ole.mikkelsen@sequoiasci.com (O.A. Mikkelsen), dgeor@hcmr.gr (D. Georgopoulos), ogston@ocean.washington.edu (A.S. Ogston), gogo@hcmr.gr (G. Assimakopoulou), ekras@hcmr.gr (E. Krasakopoulou), goaie@geoecomar.ro (G. Oaie), dsecrieru@yahoo.com (D. Secrieru), thkan@hcmr.gr (T.D. Kanellopoulos), popi@hcmr.gr (K. Pagou), chanag@hcmr.gr (C. Anagnostou), vpapath@hcmr.gr (E. Papatthassiou).

main cause of the collapse of the anchovy fishery (*Engraulis encrasicolus*) in the late 1980s (Kideys, 1994), with profound economic consequences (Knowler, 2005).

The EROS-2000 and EROS-21 European Union (EU) projects, between 1994 and 1998, focused their research in the NW Black Sea in order to understand the complex interactions among human activities and the marine environment (Lancelot et al., 2002), the relationship between phytoplankton communities and nutrient availability (Ragueneau et al., 2002), nutrient exchanges at the sediment–water interface (Friedrich et al., 2002), assessment of metal pollution (Guieu and Martin, 2002), as well as sedimentation rates (Friedrich et al., 2002). The nature of organic matter associated with suspended matter and its imprint on sediment was studied by Reschke et al. (2002); the authors identified distinct zones of low organic carbon (C_{org}) along the coast and the shelf, and high C_{org} in the abyssal plains. Moreover, hydrodynamic process studies and modeling were carried out by Beckers et al. (2002).

The daNubs EU project focused mainly on the relation of nutrient management in the Danube Basin to emission and instream loads in and into the river system of the Danube Basin, and the influence of nutrient discharges on the NW Black Sea coastal area (Behrendt and Schreiber, 2004; Kroiss et al., 2006). During two oceanographic cruises in 2002 and 2004, the river plume dynamics were investigated (Karageorgis et al., 2009). Previous studies on river plume dynamics and associated hydrological patterns were published by Kourafalou and Stanev (2001), Yankovsky et al. (2004), and Kourafalou et al. (2005).

So far, most studies in the NW Black Sea have dealt with nutrient dynamics, phytoplankton, zooplankton, and fisheries management and consequences, as well as general hydrological features and modeling of circulation. Basin-wide beam transmission and spectral measurements are summarized briefly by Mankovsky et al. (1998), whereas hydro-optical studies of the Black Sea in relation to intense eutrophication (1986–1992) are given by Vladimirov et al. (1999).

Apart from the recent work of Karageorgis et al. (2009), very little is yet known about the optical properties of suspended particulates, their particle size distribution, and the composition in this area. This work aims to bring together standard CTD data, optical data (inherent optical properties, IOPs) acquired by transmissometers (two wavelengths) and fluorometers, as well as a variety of bulk particle analyses on water bottle samples such as particulate matter and particulate organic carbon concentrations, and chlorophyll α concentrations in different size fractions. Data on *in situ* particle size distribution obtained by LISST (Laser In Situ Scattering and Transmissometry) are presented for the first time for the region. Potential anomalies in LISST size measurements in high density gradients and particle populations are also examined. This unique data set may serve as a baseline for future marine optics studies in the NW Black Sea.

2. Regional setting

2.1. Morphology and hydrology

The Danube River's catchment area is 817 000 km² and its delta covers 5800 km² (Panin, 1999). The Danube River mouth area belongs to the open deltaic type and is the largest river delta in the Black Sea (Mikhailov and Mikhailova, 2008). At the head of the delta, also referred to as 'Mile 44' the Danube River splits into Chilia (length 116 km) and Tulcea branches, and the latter bifurcates ~17 km downstream into the Sulina, and Sfantu Gheorghe branches, 63, and 109 km in length, respectively (Fig. 1).

Continuous sediment discharge during the Holocene has created an extensive delta plain and, on the continental shelf, a delta front and a prodelta (Panin, 1999) with gentle seafloor gradients (Dan et al., 2009, and references therein). The deepest station occupied during this study was within 40 km from the coast, at 52 m water depth (slope: 0.001°). The continental slope of the basin is roughly the boundary of

the Black Sea's dominant circulation feature known as the Rim Current, which creates a cyclonic basin-wide circulation; western and eastern cyclonic gyres are developed in the open sea, and nearshore anticyclonic eddies between boundaries of the Rim Current and the shore (Oğuz et al., 1993; Poullain et al., 2005; Stanev, 1990; Titov, 1999; Zatsepin et al., 2003). The Black Sea's hydrodynamic structure is characterized by a permanent pycnocline developed between 100 and 150 m, which inhibits exchanges between surface and deep waters. This results from riverine freshwater, which overlies more saline water of Mediterranean origin. Consequently, waters below 150 m are anoxic, making the Black Sea the largest anoxic basin in the world. According to Kourafalou et al. (2005), the circulation on the northwestern Black Sea shelf is governed by buoyancy-driven flows due to river input (dominated by Danube runoff), subject to wind-driven advection in the upper layers and topographic controls. Recently, Karageorgis et al. (2009) have shown that coastal waters during late summer/autumn are characterized by a sharp thermocline, with warm, low salinity waters occupying the upper 20–30 m (September 2002 and 2004). They also demonstrated that plume dynamics are effectively controlled by the wind regime and the freshwater discharge.

2.2. Wind regime

Basin scale, monthly mean wind speeds are typically 5 m s⁻¹ during summer, increasing to 8 m s⁻¹ during winter, with northerlies dominating in the western sector of the Black Sea (Oğuz and Malanotte-Rizzoli, 1996, and references therein). In winter northeastern winds are more frequent in the western basin, but northwest gales may occur as well (Özsoy and Ünlüata, 1997).

Prior to the cruise, winds were from the northeast at 5–8 m s⁻¹. When sampling began, winds turned to southerlies, and then again to northerlies, which prevailed during sampling at the Danube front area (Fig. 2a). By the end of the cruise, the light northeastern winds shifted again to light southerlies. As shown by Kourafalou and Stanev (2001) and Karageorgis et al. (2009), the southerly or southeasterly wind forcing compresses the Danube River plume near the coast and a coastal current with south-southwestern direction develops.

2.3. Danube River discharge

The Danube River contributes 60% of the freshwater discharge entering the NW Black Sea. The total Danube discharge entering the delta splits into Chilia branch (53–57%), Sulina branch (19–22%), and Sf. Gheorghe branch (~23%; Sommerwerk et al., 2009). Freshwater and suspended solids (SS) average monthly data for 2007 were obtained from the Fluvial Administration of the Lower Danube (Romania) at station 'Mile 44', which represents the beginning of the delta area (Fig. 2b). During the October 2007 cruise, water discharge was 4980 m³ s⁻¹ and SS load 197 kg s⁻¹, the latter corresponding to SS concentration of ~40 g m⁻³. Available data for March 2007, a month representative of high discharges, were available to examine water discharge and suspended sediment load along the river beginning at the Iron Gates I reservoir, ~950 km inland, to the downstream point at which the river separates into three branches that discharge into the Black Sea (Fig. 2c). Water discharge varied between 6000 and 8000 m³ s⁻¹ in the main stream out to the delta area, where water discharge separates unequally into three branches (Fig. 2c). The case is not the same for suspended solids load, which shows a large reduction from Drencova toward the Iron Gates I & II reservoirs. Downstream, SS load increases again, until the beginning of the delta area (Mile 44; Fig. 1), where the river experiences two bifurcations. In the three distributaries, suspended solid loads decrease abruptly as the total load is divided within three branches.

Suspended solids load for October 2007 at the beginning of the delta area (Mile 44) was 197 kg s⁻¹ and close to the Chilia (22 km), Sulina (4 km), and Sf. Gheorghe (8 km) branch mouths were 98, 38, and

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