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

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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 c2, 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 km3 yr−1), Dniester (43.4 km3 yr−1), and Dniester (9.1 km3 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
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 (Guieuan 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 into and in 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., 2005). Previous studies on river plume dynamics and associated hydrological patterns were published by Kourafalou and Stanev (2001), Yankovsly 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 817000 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 Sfântu 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 cycloic basin-wide circulation; western and eastern cycloic gyres are developed in the open sea, and nearshore anticyclic eddies between boundaries of the Rim Current and the shore (Oğuz et al., 1993; Poulain et al., 2005; Staney, 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%; Sommerwelk 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...
49 kg s$^{-1}$, respectively (C. Bondar-GEOECOMAR, pers. comm.), while suspended sediments concentrations were around 40 g m$^{-3}$ for all stations. Likewise, water discharge data at the same locations were 2490, 961, and 1235 m$^3$ s$^{-1}$, respectively. These data indicate that Chilia is the largest branch in terms of both discharge and SS load, followed by Sf. Gheorghe and Sulina. Dan et al. (2009) reported that human interventions (dams, water usage, etc.) over the last 150 years have diminished the quantity of sediment reaching the coast and, consequently, led to a severe retreat of the shoreline, especially in the Sulina-Sf. Gheorghe coastal sector. Only the Chilia secondary delta is prograding, favored by the relatively large supply of sediment, which is more than 50% of the total sediment discharge of the Danube River (Bondar and Panin, 2001).

3. Methodology

3.1. Field work, sampling and analytical methods

Measurements derive from a cruise of the R/V Aegaeo in the Danube delta (NW Black Sea), during 5–12 October 2007. In total, 18 stations were occupied (Fig. 1). Apart from station STRAP, where a sediment trap array was deployed (water depth: 2075 m), all other stations were located in shallow depths (10–53 m) in the Danube delta area (Fig. 1). Due to bad weather conditions (strong northeasterlies) a number of offshore stations were not occupied.

Standard CTD measurements were obtained with a Sea-Bird Electronics 11+ CTD interfaced with a General Oceanics rosette with twelve 10-liter Niskin bottles. Profiling speed was ~0.7 m s$^{-1}$. Light transmission was measured by two 0.25-m path-length transmissometers emitting at 470 nm-blue (Chelsea ALPHAtracka MKII) and 660 nm-red (WET Labs C-Star), and fluorescence by a fluorometer (Chelsea AQUAttracta III; excitation: 430 nm, emission: 685 nm).

Particle volume concentration, and particle size distribution in 32 classes, in the range of 1.5–250 μm, were determined with an autonomous LISST-Deep type B (Laser In Situ Scattering and Transmissometry), which also measured beam attenuation, c (Agrawal and Pottsmith, 2000). The major difference of LISST-Deep and the more widely used LISST-100X (e.g. Durrieu de Madron et al., 2005; Karp-Boss et al., 2007; Mikkelsen et al., 2008) is the special aluminium housing, which allows deployment to 3000 m depth, whereas the 100X is limited to sampling down to 300 m depth. LISST measurements were made at coastal stations (in total 17).

Finally, a sonar altimeter was coupled with the CTD, providing accurate distance from the bottom, and thus enabling measurements to within 1–2 m of the seabed. Sensors were factory calibrated prior to the cruise; optical windows were rinsed with MilliQ water and wiped carefully prior to each cast. All data were routinely binned into 1-dbar intervals after quality control of raw data. Subsequently, all metadata, profile, and bottle data were input to Ocean Data View software v4.3.6 (Schlitzer, 2010); DIVA gridding (data-interpolating variational analysis; http://modb.oci.ulg.ac.be/projects/1/diva) was applied.

The particulate matter concentration (PMC, in mg m$^{-3}$) was determined by on board water filtration of 0.7 to 5 l of seawater passed through pre-weighted Millipore isopore membrane polycarbonate filters
Filter blanks were pre-combusted (67 samples) were corrected on the basis of blank with a CHNS FLASH 200 Thermo Scienti -1991; Verardo et al., 1990), and POC was subsequently determined at 450 °C. The filters were dried at −20 °C until analysis in the laboratory according to the fluorometric method of Holm-Hansen et al. (1965) as developed by Welschmeyer (1994) and evaluated by USEPA Method 445 in a TURNER 00-AU-10 fluorometer, which provides a procedure for determination of low level chlorophyll α and its magnesium-free derivative, pheopigment α, in marine and freshwater phytoplankton using fluorescence detection. Pheopigments present in the sample are determined collectively as pheopigment α by measuring fluorescence before and after acidification.

Water-column integrated values of chlorophyll α were calculated from the surface down to the last sampled depth through trapezoidal integration (O’Reilly and Evans-Zetlin, 1998).

For cell counting, species identification, and enumeration, water samples were taken from surface, mid-waters, and near-bottom as stations RST2, SGT3 and KT and fixed with Lugol’s iodine solution. Microscopic counts were conducted according to the sedimentation chamber (10 and 25 ml) technique (Utermöhl, 1958), using an Olympus IX70 inverted microscope (200 or 400× magnification). The Utermöhl technique is restricted to larger phytoplankton cells (>10 μm), therefore only identification and enumeration of diatoms, dinoflagellates, and autotrophic nanoflagellates species was performed, according to Tomas (1997).

### 3.2. Particulate beam attenuation \( c_p \)

Light transmission readings of two transmissometers (\( \lambda = 660 \)) and 470 nm) were converted to beam attenuation coefficient (\( c, \text{m}^{-1} \)), according to the equation:

\[
c = -\frac{1}{z} \ln(Tr/100),
\]

where \( z \) is the transmissometers’ path length (m) and \( Tr \) is light transmission in percent units. Beam \( c_{660} \) and beam \( c_{470} \) correspond to the beam attenuation coefficient of a 660-nm WET Labs transmissometer and 470-nm Chelsea transmissometer, respectively.

In general, beam \( c \) is given by the equation:

\[
c = c_p + c_w + c_{CDOM},
\]

where \( c_p \) (\( \text{m}^{-1} \)) is the attenuation due to particles, \( c_w \) (\( \text{m}^{-1} \)) is the attenuation due to particle-free water and \( c_{CDOM} \) (\( \text{m}^{-1} \)) is the attenuation due to colored dissolved organic matter.

In order to calculate the beam attenuation due to particles for the WET Labs transmissometer (\( c_{660} \)) the minimum beam \( c \) (particle free water value) of the deep cast (station STRAP) was subtracted from beam \( c_{660} \) (Gardner et al., 2006; Karageorgis et al., 2008). Attenuation due to CDOM at red wavelengths is assumed negligible (Boss et al., 2009; Bricaud et al., 1981; Jerlov, 1968). To calculate attenuation due to particles for the Chelsea transmissometer (\( c_{470} \)), the minimum beam \( c \) of the same deep station was subtracted from \( c_{470} \). However, CDOM causes increasing absorption of light with decreasing wavelength; therefore the term \( c_{470} \) potentially includes information both about particles, and CDOM. Sometimes, CDOM is

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measured at a wavelength of 440 nm because it corresponds, approximately, to the peak absorption by phytoplankton (Bowers and Brett, 2008). However, CDOM adsorption can vary with CDOM composition/source (Nelson and Siegel, 2002) and has been reported at several other wavelengths in the literature (D'Sa and DiMarco, 2009; Stedmon et al., 2000).

3.3. Scattering and absorption coefficients from LISST-Deep data

Agrawal (2005) showed how the volume scattering function (VSF) from 0.1 to 20° could be derived from the raw light scattering data from a LISST-100 type B. By integrating this part of the VSF, one obtains an estimate of the in situ forward scattering coefficient covering the angular range from 0.1 to 20°, \( b_f \). By subtracting \( b_f \) from the LISST-Deep beam attenuation measurement \( c \) an estimate of the in situ absorption coefficient \( a \) can be obtained. Because the forward scattering coefficient obtained from the LISST-Deep only covers light scattered from 0.1 to 20° it is a minimum estimate of the total forward scattering coefficient. Consequently the measure of \( a \) obtained in this manner is a maximum estimate.

3.4. PMC vs. beam \( c_p \)

Transmissometer beam attenuation measurements have been commonly used to estimate the mass or volume concentration of particles in natural waters, but a linear relationship will occur only when the effects of variations in size, shape, and index of refraction are negligible or mutually compensating (Baker and Lavelle, 1984, and references therein). A regression of PMC vs. \( c_p(470) \) and \( c_p(660) \) exhibited strong correlations, for both transmissometers (Fig. 3a). Since particle size is the most influential variable next to particle mass (Baker and Lavelle, 1984), the strong correlations could be attributed to relatively homogeneous particle size and composition distribution in the Danube delta area during the specific sampling period. This argument will be further examined in the LISST particle size data analysis section. It is noteworthy that the values of \( c_p(470) \) are almost double than those of \( c_p(660) \). While most of the difference is due to the greater particle absorption at blue wavelengths, additional absorption in the blue spectrum is likely due to CDOM. The ratio of \( c_p(470) / c_p(660) \) is 1.65, falling between the reported ratios of 1.8 for the ratio of \( c_p(380) / c_p(655) \) (Jerlov, 1976) and 1.4 for \( c_p(400) / c_p(650) \) (Chung, 1996; Kitchen, 1978). The ratio also depends on the types of particles present.

3.5. POC vs. beam \( c_p \)

Previous studies have shown that \( c_p \) is well correlated with both PMC and POC (Bishop, 1999; Bishop et al., 1999; Gardner et al., 1993, 1995, 2001, 2003, 2006; Gunder sen et al., 1998; Holser et al., 2011; Karageorgis and Anagnostou, 2003; Karageorgis et al., 2008; Son et al., 2012). Gardner et al. (2001) divided data in surface, near bottom, and mid-waters and established different relationships between beam \( c_p \) and POC. More recently, Son et al. (2009) based the correlation on the percentage of POC relative to PMC according to the formula:

\[
\%\text{POC} = (\text{POC} / \text{PMC}) \times 100
\]

Data were divided in two sets: (i) \( \%\text{POC} < 25 \); and (ii) \( \%\text{POC} > 25 \), representing particle populations with higher, and lower relative proportion of mineral material, respectively. For our data the regression of beam \( c_p(660) \) to all POC data and subsets (< and >25% POC) revealed linear correlations (Fig. 3b). Squared correlation coefficients for all data and \( \%\text{POC} > 25 \) are fairly similar, while \( R^2 \) for samples with \( \%\text{POC} < 25 \) was higher. The latter strongly linear correlation suggests that particles with higher inorganic component contribution scatter light more uniformly than biogenic particles. Samples with <25% POC were mostly obtained from the benthic nepheloid layer (BNL), making sediment resuspension a likely source. The greater scatter characterizing the \( \%\text{POC} > 25 \) population suggests either greater diversity and patchiness in the organic carbon content of the particulate material or differences in the optical signature of the particles which induce variation in \( c_p(660) \) (Gundersen et al., 1998). Interestingly, the intercept values are much higher than those reported for different regions of the world ocean (e.g. Gardner et al., 2006), indicating the presence of small sized particles (e.g. viruses and heterotrophic bacteria) not retained by the GF/F filters and yet contrib-ute to the attenuation of light (Bishop et al., 1999). Absorption by such organic matter may be notable in more productive waters and eutrophic coastal areas. Furthermore, relatively high dissolved organic carbon concentrations were recorded throughout the northwestern shelf of the Black Sea (mean mixed layer DOC concentrations ranged between 233 and 272 µM; Ducklow et al., 2008), which also potentially contrib-ute to the attenuation of light. Similar linear correlations were obtained for \( c_p(470) \) vs. POC regressions, indicating that POC variability can be successfully monitored by transmissometers at different wavelengths (600 and 470 nm).

In the open ocean, \( c_p \) may be better correlated with POC than PMC because most particulate matter is of biogenic origin. Organic matter attenuates more light per unit mass than terrigenous material because of increased absorption (Baker and Lavelle, 1984; Bunt et al., 1999), which affects the relative contribution of inorganic terrigenous particles.

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versus organic matter. If inorganic matter dominates the particle load from river input or resuspension, the beam $c_p/PMC$ correlation is likely to be better than the $c_p/POC$ correlation (e.g. Gardner et al., 2001). If resuspended sediments are present in the water it is possible to have a poor correlation between $c_p$ and POC, but very good $c_p/PMC$ correlations. The presence of abundant CDOM in coastal waters further complicates the $c_p/PMC$ and $c_p/POC$ correlation because the CDOM concentration is usually inversely correlated with salinity, which also increases with depth and distance from the river mouth (D’sa and DiMarco, 2009).

Beam attenuation at a single wavelength cannot alone reveal anything about the composition of the particles present. Even using two wavelengths has not been used to determine particle composition. At least two inherent optical properties are needed to determine relative composition of particles (organic versus inorganic) e.g. absorption, fluorescence and backscattering (Holser et al., 2011; Roesler and Perry, 1995), backscatter and total scatter (Loisel et al., 2007; Nencioli et al., 2010), backscatter and attenuation (Boss et al., 2009).

3.5. Scanning electron microscopy

Small pieces from filter samples used for the determination of PMC (Millipore HTTP04700) were gold-coated using a Baltec SCD-005 sputter coater and observed under a Philips XL-20 scanning electron microscope (SEM) equipped with an EDAX energy dispersive X-ray fluorescence analyzer. The filters’ isopore membrane is composed of polycarbonate film, which has a smooth, glass-like surface for optimized SEM observation.

4. Results and discussion

4.1. Hydrography

During October 2007, surface temperature and salinity patterns off the Danube delta (Fig. 4a,b) showed a narrow belt of cooler ($\leq 19^\circ$C) and less saline ($\leq 16$) water at shallow water depths. The river influence is most prominent off the Sf. Gheorghe and Chilia distributaries mouths. The northernmost (Chilia) transect shows the greatest extent of freshwater, but is oriented largely along bathymetric contours towards the northeast and may reflect both northward dispersal of river water or southward advection of freshwater associated with the Dniester and Dniester rivers from the region west of the Crimean Peninsula.

Offshore of the river mouth, the coastal water-column structure is characterized by two pycnoclines (Fig. 5), one largely associated with the surface temperature gradient in the northwestern Black Sea and the other with the salinity gradient associated with recent freshwater input from the Danube River. The warmer Black Sea surface layer (19.2–20.4°C) was approximately 20–30 m thick, and overlies cooler, more saline waters characteristic of the cold intermediate waters of the Black Sea (Özsoy and Ünlüata, 1997). At the deep STRAP site, the seasonal warm Black Sea surface water (temperature 20.2°C; salinity 17.4) is seen to approximately 25 m depth. In addition, the freshwater input from the Danube River creates a thin low-density layer of
approximately 10 m thickness that gradually diminishes with distance offshore. The shallowest station (Stn. RNT-1, south of Sulina; Figs. 1, 4b) located in 11 m of water showed surface salinity of 8.5. At even this water depth, the plume was not bottom-attached indicating that nearbed estuarine processes (e.g., the estuarine turbidity maximum) were likely located within the distributaries channels, not over the delta. The shallow freshwater layer was strongly stratified close to shore, becoming more mixed with distance offshore and away from the river distributaries.

The sections of temperature and salinity leading away from the Chilia transect (Fig. 6a,b) show little variability in the temperature and salinity structure except very close to the mouth, reflecting recent discharge of river water. The source of the plume water towards the north is unclear, but subtle change in the mixing relationship suggests an alternate source to the Danube River. The sections of temperature and salinity off the St. Gheorghe branch (Fig. 6c,d) indicate an upward bulging of isopycnals near the coast, suggesting upwelling conditions. Wind conditions in the days prior to the sampling of this section (7–9 October) were upwelling favorable (Fig. 2a). Throughout much of the rest of the sampling, the winds turned to downwelling favorable conditions, and the change in wind conditions may be the cause of some of the variability observed in the surface layer patterns.

4.2. Transmissometry and fluorescence

The spatial distribution of beam $c_{p(660)}$ in the surface nepheloid layer (SNL, 3-m depth) shows particle-rich waters occupying a narrow zone parallel to the coastline, with turbidity maxima occurring near the Danube branch mouths, as well as SW of the St. Gheorghe branch, westwards of the 17 km-elongate Sakhalin spit island (Fig. 7a; 44.80°N, 29.53°E). Offshore, the optical signal of particulates decreases rapidly to low values. In the benthic nepheloid layer (BNL, measurements ~1 m above bottom) values are much lower, indicating that resuspension from the seabed is limited and confined mostly to the coastal stations (Fig. 7b). A single station, RST1 (10 m depth), westwards of the Sakhalin spit island, deviates from the general pattern, as increased turbidity is observed near the seabed (2.2 m$^{-1}$). Given that SNL is also pronounced at the same location (3.7 m$^{-1}$), the local BNL maximum could result from increased productivity and terrestrial particulate input. In the rest of the sampling area beam $c_{p(660)}$ and beam $c_{p(470)}$ vertical profiles show high values near the surface (3–6 m), followed by a sharp decrease towards the bottom (10 m), and very low nearbed suspension. Karageorgis et al. (2009) have shown similar patterns in the RST1 area during September 2002 and 2004, accompanied by high chl $\alpha$ values in the surface waters, thus providing evidence of phytoplankton growth.

Noteworthy are the almost double values of beam $c_{p(470)}$ over $c_{p(660)}$ in the SNL and the BNL. Since $c_{p(470)}$ is an expression of scattering and absorption of both particles and CDOM, whereas $c_{p(660)}$ represents scattering and absorption due to particles only, their difference could give a semi-quantitative measure of the absorption coefficient of CDOM, in m$^{-1}$: $\alpha_{CDOM} = c_{p(470)} - c_{p(660)}$. Greater CDOM absorption at 532 nm than at 660 nm was previously reported by Behrenfeld and Boss (2006). Ferrari and Dowell (1998) comment that CDOM is the main contributor to light absorption in the blue region of the spectrum in the Baltic Sea, and noted a significant inverse dependency of $\alpha_{CDOM}$ with salinity in surface waters. A regression plot of our calculated $\alpha_{CDOM}$ vs. salinity shows a very high correlation, which is further improved, when stations RNT1 and SGT1 were excluded (Fig. 8). Data from stations very near river mouths often include scatter in the correlations, as rivers are typically major sources of CDOM and the presence of terrigenous particles contributes to the water color (Bowers and Brett, 2008). In the Danube front area, our estimate of CDOM ranges from 0.06 to 2.36 m$^{-1}$ (mean: 0.46 ± 0.45 m$^{-1}$). Its spatial distribution at the SNL (not shown) follows closely the spatial distribution of salinity (as would be expected from the strong correlation in Fig. 8) therefore the semi-conservative nature of CDOM with respect to salinity...
et al. (2009) described similar relationships between pension throughout the water column during October 2007. Karageorgis particulates, i.e. living phytoplankton, are the prevailing particles in sus-
al speed, machinery. The strong correlations imply that chlorophyll-containing α was 52 m, the same distribution patterns as our data (Fig. 9b). A linear regression of with the Giovanni online data system; Acker and Leptoukh, 2007) show the 2007 MODIS satellite composite of chlorophyll α distribution patterns as beam size using optics, imaging and bulk..., J. Mar. Syst. (2013), http://dx.doi.org/10.1016/j.jmarsys.2013.11.013 supports its use as a tracer of fresh water input (Ferrari and Dowell, 1998). It should be noted however, that CDOM is subject to photo-
oxidation, so it may not be conservative on weeks–months time scales (Coble, 2007; Estapa et al., 2012; Nelson and Siegel, 2002). Over time the CDOM/salinity correlation will decline or change due to mixing and photo-oxidation, but it was well correlated within the time and space scales of this study (8 days, 10’s of kilometers).

The spatial distribution of fluorescence at the SNL (Fig. 9a) shows highest values (15.3) at station RST1, westwards of Sakhalin spit island. Secondary maxima appear near the Chilia branch. Fluorescence decreases offshore to minimum values, exhibiting largely the same distribution patterns as beam cp(660) (Fig. 7a). The 8-day (8–14 October, 2007) MODIS satellite composite of chlorophyll α distribution (produced with the Giovanni online data system; Acker and Leptoukh, 2007) shows the same distribution patterns as our data (Fig. 9b). A linear regression of fluorescence vs. beam cp(660) from all water depths (max. sample depth was 52 m, n = 660), yields a coefficient R² = 0.864, and the regression of fluorescence vs. beam cp(470) an R² = 0.863 (both significant at α = 0.1%). The strong correlations imply that chlorophyll-containing particulates, i.e. living phytoplankton, are the prevailing particles in suspension throughout the water column during October 2007. Karageorgis et al. (2009) described similar relationships between fluorescence and beam c during September 2002 and 2004 that were attributed to abundance of phytoplankton, and closely matched near-surface chl α distribution patterns revealed by SeaWiFS satellite imagery composites. Mean fluorescence values at the SNL were estimated at 0.8, 0.9, and 5.6 (arbitrary units), for 2002, 2004, and 2007 respectively, suggesting that, in 2007, primary productivity was much higher. It should be noted, however, that during the 2004 cruise a Dr. Haardt fluorescence sensor was used, whereas a Chelsea AQUAtracka III fluorometer was used in 2002 and 2007.

A beam cp(660) transect SW–NE of the Chilia branch (Fig. 10a) shows clearly that highest turbidity is recorded in the upper 3–7 m nearest to the branch mouth. PMC at station KILNT1 (3.6 g m⁻³) is one of the highest values recorded in the study area, and POC measured here was our maximum value (1350 mg m⁻³). Below 10-m depth, values decrease substantially. The overall distribution patterns seem to follow that of salinity as well as density, and to a lesser extent temperature (Fig. 5). In the NE direction, beam cp(660) values exhibit generally a decreasing trend. Fluorescence values are highest in the upper waters of the station closest to the branch mouth, and the overall pattern is almost identical to the beam cp(470) (Fig. 10b).

A transect NW–SE of beam cp(660) and fluorescence offshore the St. Gheorghe branch (Fig. 10c, d), illustrates that both cp(660) and fluorescence exhibit their highest values in the upper 10 m, decreasing rapidly with depth. However, the signal near the river branch mouth is not very pronounced, compared to the Chilia section. Nevertheless, the close relationship of beam cp(660), and fluorescence is demonstrated again along this transect, suggesting a common source of particles in the water.

4.3. Particle size distribution patterns

At Stn. KT, south of the river mouth, the mixed layer extends down to 27 m (Fig. 11a). The sharp decrease in temperature from ~26 to 37 m and stable temperatures above causes strong density gradients which produce schlieren optical effects that may influence the LISST measurements (Mikkelsen et al., 2008).

Beam attenuation is measured directly by the LISST (Fig. 11b). The beam attenuation c increases between depths of ~23 and 35 m. However, this is not due to a strong increase in the forward scattering coefficient, b. Rather, it is related to a strong increase in the absorption coefficient, a, indicating the presence of absorbing particles in this region.

A relatively high value of b/c shows that beam attenuation is dominated by scattering, whereas a high value of a/c shows that beam...
attenuation is dominated by absorption (Fig. 11c). Below ~25–27 m depth, the beam attenuation becomes more and more dominated by absorption, not scattering.

Particle size distributions from the downcast of Stn. KT from surface to 42 m depth and binned at 1-m intervals show maximum volume concentration of ~30 mm m$^{-3}$ (Fig. 12a). The size distribution of particles from depths <27 m and deeper than 37 m (small, low concentrations curves in the middle) shows much lower volume concentrations (Fig. 12b). Note that the maximum apparent volume concentration for particles outside the 27–37 m depth is 0.3 mm m$^{-3}$; i.e. 2 orders of magnitude smaller than particles within the band. The median particle size is the same in upper and lower waters; around 40 μm, but the size spectra from <27 m shows a lot more variation, and has 3 modes. Interestingly, the smallest mode is at 5 μm, which could be related to chl α concentration peak for <5 μm particles. In the schlieren regions the size distributions have peak concentrations of ~30 mm m$^{-3}$ and a median size of 150–180 μm (Fig. 12c), resulting from false estimates due to increased beam c in the schlieren regions (Mikkelsen et al., 2008). Schlieren effects have been recorded at all stations where pycnoclines occurred (e.g. Stns. KILNT1, KILNT3, KILST1, SUL1, SUL2.

Fig. 9. Spatial distribution of (a) fluorescence (arbitrary units) at the surface nepheloid layer, SNL (3-m depth); and (b) 8-day (8–14 October, 2007) MODIS satellite composite of chlorophyll α (mg m$^{-3}$).

Fig. 10. Distribution of (a) beam $c_{\text{top}}$ (m$^{-1}$); and (b) fluorescence (arbitrary units) along the Chilia SW–NE transect; (c) beam $c_{\text{top}}$ (m$^{-1}$); and (d) fluorescence (arbitrary units) along the St. Gheorghe NW–SE transect. Refer to Fig. 1 for section locations.

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RNT2, SGT1, SGT2). Thus, in the highly stratified Danube delta, LISST profiles of particle volume concentration and particle size distributions need to be carefully interpreted.

4.4. Particulate matter distribution patterns

Particulate matter concentration derived from all bottle data in the delta region (Stn. STRAP excluded) varied from 0.3 to 4.8 g m\(^{-3}\). Lower values were recorded at 100 m at Stn. STRAP. At Stn. STRAP, PMCs varied from surface values of 0.3–0.4 g m\(^{-3}\) (3–20 m), to very low values <0.1 g m\(^{-3}\) (50–150 m), below which PMCs increased slightly down to 2023 m (0.1–0.3 g m\(^{-3}\)). The SNL exhibited PMCs in a pattern of decreasing values offshore, and parallel to the coastline similar to beam absorption (Fig. 7a). The maximum value was recorded at the surface of a shallow station (RNT1; 10 m depth) in front of the Danube subaerial delta, whereas much lower values were observed at

Fig. 11. Station KT profiles: (a) temperature (°C) and salinity; (b) beam attenuation (m\(^{-1}\)), forward scattering (m\(^{-1}\)) and absorption (m\(^{-1}\)) from LISST; and (c) forward scattering and absorption ratios to beam attenuation.

Fig. 12. Particle size distributions at Stn. KT (a) all size spectra; (b) size distribution of particles from depths less than 27 m and deeper than 37 m; and (c) size distribution of particles from depths between 27 m and 37 m, representing the schlieren region. Similar particle size distribution patterns were observed at all stations exhibiting sharp thermocline.

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the easternmost (SULT3; 1 g m\(^{-3}\)) and southernmost (KT; 0.5 g m\(^{-3}\)) stations. A secondary surface local maximum value was observed westwards of the Sakhalin spit island. In the bottom nepheloid layer, PMCs decrease substantially over the region (range 0.3–4.4, mean 1.1 ± 1.0 g m\(^{-3}\)), and relatively higher PMCs were observed in a narrow band near the coastline. Similar to the surface distribution, the station near the Sakhalin spit island showed high PMC (Stn. RST1; 4.4 g m\(^{-3}\)).

4.5. Particulate organic carbon distribution

Concentrations of particulate organic carbon exhibited the lowest values in the deep layer at the offshore Stn. STRAP (90 mg m\(^{-3}\) at depths 500–2023 m). Highest POC values were found close to the coast in the surface layer of Stns. KILNT1 (1360 mg m\(^{-3}\)) and RST1 (1220 mg m\(^{-3}\)) while a third maximum (1160 mg m\(^{-3}\)) was recorded at the surface of Stn. KILNT4. The concentration range is consistent with results previously obtained in the NW Black Sea (Maldonado et al., 1999; Saliot et al., 2002); these average POC concentrations in the euphotic zone (380 mg m\(^{-3}\)) are ~4 times higher of those recorded in the Southern Black Sea in Sept–Oct 1995 (Yilmaz et al., 1998) but comparable to the upper limit of the depth-averaged concentrations measured in the same area (343 mg m\(^{-3}\)) during 1990–1998 (Coban-Yildiz et al., 2000).

The high (>1000 mg m\(^{-3}\)) POC content at the SNL decreases markedly with distance offshore (Fig. 13a). However, Stn. KILNT2 at the northern edge of the study area and the southernmost Stn. KT deviate from this general pattern exhibiting almost uniform POC concentrations throughout the water column (Fig. 14). At the BNL, POC concentration with relatively high values (from 210 to 930 mg m\(^{-3}\)) is observed in a very narrow band along the coastline, decreasing gradually offshore (Fig. 13b).

The distribution of the surface concentrations of PMC, POC, and chl\(\alpha\) might be expected to vary as a function of distance from the river source as water mixes, particles settle and primary production increases in clearer, more stratified water. Given that there are three distributaries flowing into the area, we have chosen salinity as the best “proxy” for distance from the source, although we realize that the paths followed may not be linear, and properties of the water (nutrients, salinity) and particles (PMC, POC, chl\(\alpha\)) may vary slightly between sources. Although surface POC, in general, is better correlated with PMC (\(R^2 = 0.413\)) than chl\(\alpha\) (\(R^2 = 0.245\)), the POC distribution in some areas is decoupled from that of PMC, whereas it appears to follow more closely the chl\(\alpha\) distribution (Fig. 15).

In the low salinity (8.25) surface waters of Stn. RNT1, the high concentration of bulk particulate matter (4.8 g m\(^{-3}\)) observed is not associated with respectively high POC, and chl\(\alpha\) values indicating that biogenic debris and mineral particles largely contribute to the particulate pool. In the salinity gradient between 12 and 16, the relatively high POC content of Stns. RST1 and SGT3 coincides with high chl\(\alpha\) values, whereas at Stns. KILNT1 and KILNT4 corresponds to low chl\(\alpha\) values, implying the presence of detrital and/or non-pigmented organic matter in the latter case. On the other hand, the elevated phytoplanktonic biomass of Stn. SGT1 (Fig. 16a) is not high in either PMC or POC and probably could be attributed to the diversity and patchiness of the sampled particulate material.

4.6. Chlorophyll \(\alpha\) and phytoplankton

4.6.1. Size-fractionated chlorophyll \(\alpha\)

Chlorophyll \(\alpha\) concentration indicates the trophic level of the pelagic ecosystem. It is also a measure of the phytoplankton production potential. The size distribution of phytoplankton assemblages is a major biological factor that governs the functioning of pelagic food-webs and
consequently affects the rate of carbon export from the upper to deep layers (Legendre and Le Fèvre, 1991; Malone, 1980). The small phytoplankton cells (<5 μm) are important in the pelagic food web and pico- and nanophytoplankton cells contain more chlorophyll per mass unit than larger phytoplankton cells, which increases their photosynthetic activity and correspondingly growth rate (Marañón et al., 2007; Roy et al., 2011). Microplankton (<5 μm) includes mostly diatoms and dinoflagellates. Nanophytoplankton includes, among others, coccolithophores and silicoflagellates.

Highest depth-integrated chl α concentrations were recorded in the southern sector at Stns. RST1 (98.7 mg m⁻³), SGT1 (42.3 mg m⁻³), and RNT3 (20.2 mg m⁻³) (Fig. 16a). In the Chilia sector, the highest chl α concentrations were recorded at Stns. KILNT1 (14.1 mg m⁻³) and KILST1 (14.2 mg m⁻³). In the Sulina sector, the highest chl α concentration was observed at Stn. SULT1 (5.8 mg m⁻³). Maximum chl α concentrations were observed at water depths between 2 and 20 m, as below these depths, light is significantly attenuated. Overall, the data on total and fractionated chl α in the study area clearly show a progressive increase from the north to the south at near-shore stations, whereas chl α concentrations generally decrease at offshore stations; similar patterns have been reported by Yunev et al. (2007). Vasiliu et al. (2010) observed high chl α concentrations during May and September 2009 in the area west of Sakhalin Isl. (Portita), attributed to local hydrodynamic conditions (weak winds, currents) favoring phytoplankton growth, rather than elevated nutrient inputs.

The integrated <5 μm chl α size fraction, corresponding to the pico- and nanoplanktonic autotrophs, contributed the majority (54–99%) to the total chl α concentration. The microplankton contributed an average percentage of ~21% of the total chl α (Fig. 16b). At stations where elevated chl α concentrations were recorded, picophytoplankton represented the most important contributor (~60%), while microplankton, usually contributed a smaller proportion (~40%).

The vertical distribution of phytoplankton biomass at three selected stations is shown in Fig. 17. The vertical patterns of chl α are linked to the hydrological regime of the study area during autumn 2007. The surface layers at Stns. SGT3 and RST2 are characterized by a gradual decrease of chl α concentrations from 20 to 15 mg m⁻³. Near the pycnocline (~20 m), chl α values decrease further, and reach lowest concentrations towards the bottom. The maximum chl α of microplankton was found at Stn. SGT3, with values ~10 mg m⁻³.

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4.6.2. Phytoplankton community structure and relation to environmental factors

The phytoplankton populations were studied at stations SGT-3 and KT. The phytoplankton community was dominated by diatoms (Cerataulina pelagia, Hemiaulus hauckii, Thalassiothrix mediterranea, Leptocylindrus danicus, Leptocylindrus minimus, Proboscia alata, Chaetoceros decipiens, Nitzschia longissima, Pseudonitzschia seriata, Dactylosolen fragilissimus, Skeletonema costatum), dinoflagellates (Gonyaulax spinifera, Gymnodinium sp., Proteropinum excentricum), autotrophic nanoflagellates (Coccolithus sp., Chlamydomonas sp., Teleaulax acuta).

In the Black Sea the autumn phytoplankton peak, along with the winter/spring bloom, is mainly driven by mixing processes. Physically driven (wind-induced, fronts, upwelling) water mixing drives seasonal nutrient supply to the euphotic zone, and in turn enhances the primary production. The two phytoplankton maxima (winter/spring and autumn) and one minimum in the summer are generally recognized as a natural pattern of the phytoplankton annual cycle in middle latitudes (Longhurst, 1995). Öğüz et al. (2000, 2003) pointed out that the autumn bloom is governed not only by physical processes but also by biological interactions (autumn rebounds in gelatinous carnivore populations and decreases in mesozooplankton stocks).

The general structure of the succession cycle of phytoplankton in the Black Sea could be divided into four seasonal phases; early winter (low activity), winter–spring maximum (covering the onset of and spring bloom maximum), summer, and less intensive autumn peak proliferation (Bologa et al., 1984; Mikaelyan, 1997). These periods show characteristic species composition, abundance, and production. During the winter phase (November to mid-March) the dominant phytoplankton group is diatoms, often a mix of pennate and centric forms. Onset of the spring bloom varies from year to year and coincides with the onset of stratification. It may start early, peaking at the end of March, or later peaking in May or even as late as early June, during which period there is a substantial increase in the phytoplankton biomass. The spring bloom (April and May) is dependent also upon the Danube River flow, when nutrient-rich shelf waters are sufficiently warm for phytoplankton growth (Cociasu and Popa, 2005; Yunev et al., 2007). The decline of the spring bloom on the shelf is most likely a combination of nutrient depletion and increased zooplankton grazing pressure (Chu et al., 2005). The dominant phytoplankton groups during this period are naked flagellates, coccolithophores, and small diatoms. Pseudonitzschia pseudodelicatissima often starts the annual diatom succession.

As the community enters the summer phase (June to the end of August), phytoplankton abundance is reduced and shifts to Chaetoceros, then larger diatoms, and later to dinoflagellates from the genus Proteropinum, Scrippsiella trochoidea, Heterocapsa triqueta, Prorococentrum minimum. As during spring, this summer-autumn period of the Black Sea planktonic life often begins with the proliferation of the smallest diatoms (Pseudonitzschia) and/or coccolithophores. The most pronounced and prolonged autumn phytoplankton peak occurs in August–September. With the autumn cooling, phytoplankton concentration decreases, and November storms terminate the annual cycle of the phytoplankton succession in the Black Sea (Bodeanu, 1989).

The phytoplankton assemblages during this study (October 2007) consisted of ~40 phytoplankton taxa from three phytoplankton classes. Most of these taxa (ca. 85%) were composed of diatoms, and dinoflagellates. The ‘other’ (Cyanophyta, Chrysophyta, Dictyochophyta, Euglenophyta, and Prasinophyceae) formed only ca. 10% of the whole population. Our findings support also the normal sequence of phytoplankton growth in summer–autumn, as partly decomposed Chaetoceros fragments were very abundant, and diatom’s autumn peak proliferation was evidenced.

4.7. Estimates of particulate matter composition and particle size

The POC:PMC ratio provides some qualitative information on the composition of particulate matter, in terms of relative contributions of organic and inorganic (non-algal) particles to total particulate matter (e.g. Gardner et al., 2001; Loisel et al., 2007; Stramski et al., 2008). In the SNL, POC:PMC ratio ranged from about 0.15 to 0.70 (mean 0.30 ± 0.14). Assuming that doubling POC roughly equals total organic material concentration, the general dominance of organic matter is a plausible notion. Plotting POC:PMC ratio against salinity, we observe that many coastal (low salinity) stations exhibit relatively low POC:PMC ratios, thus suggesting increased contribution of mineral particles (Fig. 18a). Near the bottom, POC:PMC ratios vary between 0.13 and 0.48 (mean 0.32 ± 0.11), while no clear spatial trend can be identified (Fig. 18b). Similar mean ratios at surface and near-bottom waters indicate that the respective proportion of organic and inorganic particles remains fairly constant.

Changes in the POC:Chl α ratio are related to phytoplanktonic community variations, proportions of living phytoplankton and detrital organic matter, and changes in particle size distribution (Loisel and Morel, 1998; Stramski et al., 2008). POC comprises autotrophic organisms, bacteria, small size zooplankton, and detritus, thus decreasing ratios are due to an increase of autotrophic particles and vice versa. In the SNL, POC:Chl α varies between 10 and 263 (mean 84 ± 78), without any marked trend relative to salinity, and thus the distance from the Danube River branches (Fig. 18c). In contrast, near the bottom the POC:Chl α ratio is one order of magnitude higher than those in the
Fig. 18. Ratio of particulate organic carbon concentration (POC), to particulate matter concentration (PMC) as a function of salinity for (a) the surface nepheloid layer, SNL; and (b) the bottom nepheloid layer, BNL. Ratio of POC to total chlorophyll α concentration, chl α, versus salinity for (c) the SNL; and (d) BNL.

Fig. 19. SEM images of particulate matter filtered onto isopore membrane polycarbonate filters. (a) Ceratium furca, Prorocentrum sp., and Protoperidinium sp. on a dense matrix of biogenic fragments; (b) Chaetoceros sp. and Thalassionema sp. on fragments of Chaetoceros sp.; (c) Hemiaulus sp. and diatoms fragments; (d) Dinophysis caudata and Pseudonitzschia sp.; (e) Stephanodiscus sp. on diatom fragments and clay minerals; (f) Thalassiosira sp. and Pseudonitzschia sp. on clay minerals.
SNL, where the ratio reaches up to 2000 (mean: 601 ± 669) (Fig. 18d). The highest values were measured at Stns. RNT2, RST2, and SGT2 with salinities in the range 18–19. This pattern suggests that near the bottom the autotrophic fraction of particulate organic carbon is quite negligible and organic particles are mainly dominated by detrital material and heterotrophic organisms.

SEM images clearly reveal the predominance of biogenic material in all samples (Fig. 19a–f). It is striking that biogenic frustules and their fragments are scattered on a dense matrix of biogenic origin (Fig. 19a–d); Chaetoceros sp., Hemiaulus sp., and Pseudonitzschia sp. can be identified. Individual phytoplanktonic particles in good condition represent diatoms and dinoflagellates species (Fig. 19a–f). Clay minerals are rare (Fig. 19e, f). Particles sizes are highly variable: diatoms fragments (e.g. Chaetoceros sp.) may be larger than 150 μm, some dinoflagellates (e.g. Ceratium sp.) may reach 200–300 μm, while other species are smaller than 5 μm in diameter.

The large size variation complicates optical measurements and makes it difficult to assess particle composition without the use of direct observation methods. In fact, the co-existence of living (fluorescent) and nonliving populations further complicates the in-depth analysis of inherent optical properties such as fluorescence, and light transmission, which are used in this work as proxies for particle composition estimates.

On the other hand, in situ collected size spectra provide reliable information on particle size distributions. It should be noted however, that a major discrepancy stems from the different methods applied to determine particle size. Whereas LISST shows 3 distinct median particle diameters at 40, 20, and 5 μm, phytoplankton analysis suggests that the biomass is dominated by pico- and nano-phytoplankton autrophs, i.e. particles <5 μm in diameter. That brings into question how size distributions are estimated in vitro and what are the consequences of sample preparation prior to analysis. For example, filtration breaks-up aggregates, shifting mean particle size distribution towards smaller diameters for SEM and chl α size fractionation. Likewise, size-filtration for the determination of chl α concentration certainly destroys fragile aggregates. Among the methods used in this study to determine particle size, we regard in situ LISST measurements as closest to reality outside of the schlieren zone. Comparison of images from visual examination of filters suggests that the 40 μm mode may be attributed to (a) microflocs, i.e. aggregates smaller than 100 μm; and (b) to nonliving phytoplankton diatom fragments. Similarly, the 20 and 5 μm modes are probably related to smaller diatoms and dinoflagellates, the terrigenous inorganic particles remaining as a minor proportion and most likely being smaller than 5 μm.

4.8. Fate of riverine sediment

Although the Danube carries a substantial load of sediment, analysis of particulate matter a short distance seaward of the river mouth supports the view that particulate matter is dominated by phytoplankton, with terrigenous sediments being a minor proportion: e.g. (1) spatial distribution patterns of beam cp(660) and fluorescence along the Chilia (Fig. 10a, b) and SF. Gheorghe transsects (Fig. 10c, d) show similar characteristics; (2) a regression analysis of beam cp(660) and fluorescence yields a high correlation coefficient R² = 0.861 (n = 3110); (3) there is little evidence of resuspended sediment from the sea floor (Figs. 7b, 10a, 16a); (4) scanning electron microscope images show that phytoplankton cells and detritus are abundant, whereas few clay mineral assemblages appear on the polycarbonate filters examined (Fig. 19e, f). This suggests that most of the sediment load settles out before leaving the estuarine portion of the river as is seen in many river systems and suggested by Geyer et al. (2004). Fig. 2c shows that much of the sediment in the river settles out by Mle 44 where the river splits into three branches. More sediment is probably lost through flocculation and settling as saline water is encountered before the river empties into the Black Sea. Flocculation, taking place in the lower reaches of rivers and estuaries is a common process (Eisma, 1986). Milligan et al. (2007) reported that during normal discharge, flocculated fine-grained sediment from the Po River settles close to the mouth, leaving only a small amount of material in suspension in the plume for direct deposition onto the prodelta. However, the very low PMCs observed, and the extremely limited presence of terrigenous PM in front of the Danube River mouth, is rather striking.

5. Summary and conclusions

We have combined inherent optical properties (light transmission, fluorescence), and several bulk measurements from discrete water samples (particle size, chl α, particulate matter, and organic carbon concentrations) to gain better insight into the distribution patterns and composition of particulate matter in the NW Black Sea. The experiments were carried out during a single cruise in October 2007, a period of relatively low water and suspended solids discharge of the Danube River.

The marine sector of the delta was heavily stratified due to the development of a near surface halocline and a strong mid-water thermocline. The river plume followed a typical anticlockwise circulation, with low salinity waters confined near the coast. Transmissometry proved to be efficient in capturing the particulate matter spatial distribution patterns, which exhibited highest values in a narrow band close to the coast, fading progressively in an offshore direction. A remarkable correlation of particle beam cp and fluorescence implied a predominance of phytoplankton over non-algal particles, which was confirmed after visual observation of filtered particulates via SEM methods. The simultaneous use of transmissometers emitting at red and blue wavelengths (670 nm and 470 nm) provided an indirect, though reliable method to estimate CDOM abundance; in the Danube front area, our estimate of CDOM ranged between 0.06 and 2.36 m⁻¹.

In situ measured particle size distributions showed modes at 40, 20, and 5 μm. LISST readings were substantially biased by schlieren between 17 and 27-meter depth, concomitant with the pronounced temperature-controlled pycnocline. At the schlieren region, the beam attenuation becomes dominated by absorption, than scattering.

Particulate matter concentrations peaked at 4.76 g m⁻³ at Chilia, the central branch of the Danube River, and POC maxima (1160–1360 mg m⁻³) were also consistently found at the shallowest stations. Similarly, total and size-fractionated chl α concentrations exhibited a decreasing trend from the coast towards offshore stations; pico- and nanophytoplankton (<5 μm) were the dominant component groups.

Relationships between beam cp, PMC and POC were established revealing good correlation between parameters, thus suggesting particle homogeneity in terms of quality and particle size. Ratios of POC to PMC and chl α were used to assess indirectly particulate matter composition. We identified a prevalence of organic over terrigenous matter concentration, particularly in surface waters, whereas near the bottom, a deviation in ratios sometimes was observed due to sediment suspension in the BNL.

Findings of SEM analysis confirmed the above notions and also revealed the presence of a remarkably dense matrix of Chaetoceros sp. fragments, which was by far the most prominent biogenic component of particulate matter throughout the study area. The occurrence of fragments of this latter species confirms the previously documented summer–autumn transition from large to smaller diatoms. Such assemblages resemble inorganic, non-algal particles, thus complicating the interpretation of optical measurements. Finally, the contribution of terrigenous particles is surprisingly small and is attributed to rapid settling of riverine sediments through flocculation/aggregation processes in the lower reaches of the river. Our multi-proxy dataset may serve as a baseline in future bio-optical and or biogeochemical experiments and models of the area, since the NW Black Sea is poorly studied in that respect.
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