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ScienceDirect
Estuarine, Coastal and Shelf Science 74 (2007) 493–514
ESTUARINE COASTAL AND SHELF SCIENCE
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Nitrogen cycling in the offshore waters of the Black Sea

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Received 16 July 2006; accepted 3 May 2007

Abstract

The purpose of this study was to measure directly the rates of several of the processes responsible for the production and utilization of nitrogenous nutrients, and to use these rates and other data to generate an annual nitrogen budget for the Black Sea. Water column samples and experimentation with ^{15}N labeled nutrients in the offshore waters of the Black Sea reveal strong seasonal cycles in the utilization of different forms of N, the regeneration of NH_4^+ and the production of NO_2^- in and below the surface mixed layer. There was no opportunity to sample during winter, but historical data and contemporary satellite ocean color data for the study period allow us to make extrapolations to a full annual cycle for the Black Sea N budget. The processes supplying N to, and the microbial processes within, the Cold Intermediate Layer (CIL), which lies below the surface mixed layer, figure prominently in determining the sources of N available for primary production. The uptake of NO_3^- by phytoplankton in this system was less sensitive to NH_4^+ concentration than has been observed in many oceanic waters. The seasonal shift in nutrient uptake kinetics was consistent with seasonality of nutrient availability. Rates of *in situ* NO_2^- production (and inferred nitrification) for the offshore waters was 1.6×10^{11} mol y^{-1}, three times the published estimates for NO_3^- supplied from the NW Shelf (NWS) region, which originates from riverine discharges. Measured rates of nitrification in the CIL are about 60% of phytoplankton $NO_3^- + NO_2^-$ uptake (2.8×10^{11} mol y^{-1}). Remineralization is about 25% of the NH_4^+ phytoplankton utilization rate (3.8×10^{11} mol y^{-1}). Within the CIL NH_4^+ is utilized in NO_2^- production (and implied nitrification) at a rate that is similar to the rate of NH_4^+ remineralization from organic matter. By preserving the rates that are determined with the most confidence, and making adjustments to the rates least confidently determined, nitrification (+60%, which is within the range of published values) and ammonium remineralization (+13%), the Black Sea N budget can be brought into balance. A balanced annual budget for N cycling in the offshore waters of the Black Sea estimates a particle export rate from the oxygenated surface layer to the deep anoxic waters equivalent to 8% of the total N production. We extrapolate an annual mean *f*-ratio of 0.38 by the conventional formulation (NO_3^- uptake: total N uptake). However, the balanced N budget permits a direct comparison of allochthonous sources of N to total N production in this unusual aquatic ecosystem, resulting in an *f*-ratio of 0.17, which is reconciled with particulate export when the budgeted losses due to anammox and denitrification are included. The NO_3^- content of the CIL is sensitive to year-to-year fluctuations in the source of N from the NWS. These processes plus the intensity of winter mixing, which supplies new N for the fall-winter bloom, are influenced by climate. Oscillations in winter temperature over the past few decades allow inference as to how the Black Sea N budget may be affected by future warmer conditions for this region.

Keywords: phytoplankton; nitrogen uptake; new production; nitrogen cycling; remineralization; nitrogen export; Danube; Black Sea

1. Introduction

The purpose of this study was to ascertain through direct measurement the relative importance of different processes in the supply and retention of nitrogenous nutrients in the near-surface offshore waters of the Black Sea (>200 m bottom depth for the purposes of this study),

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0272-7714/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.ecss.2007.05.005

and to construct a quantitative summary of these ecosystem processes.

The Black Sea is a dilution basin with a positive water balance resulting from an excess of precipitation and runoff over evaporation (Unluata et al., 1989). The drainage basin of this sea is over five times the area of the sea itself, delivering the industrial, domestic, and agricultural runoff of a population of more than 162 million people, primarily via three major rivers in the northwestern sector (Mee, 1992; Revenga et al., 1998). Riverine outflows, dominated by the Danube, clearly affect N and other biogeochemical cycling in the Black Sea, and historical changes in flow regimes, sediment, and nutrient loading have influenced the biota of the Black Sea in dramatic ways (e.g. Mee, 1992; Bologa et al., 1995; Humborg et al., 1997; Van Eeckhourt and Lancelot, 1997; Jaoshvili, 2002; Lancelot et al., 2002).

A surface outflow of brackish water (salinity 18–20) exits the Black Sea via the Turkish Straits connecting to the Aegean and Mediterranean Seas. In return, denser Mediterranean water (salinity 36–38) enters the Black Sea as an undercurrent through the same channel and flows over the continental shelf into the deep central basin of the Black Sea, maintaining the salinity of the intermediate and deep water masses at a consistently higher value ($\sim$22) than the overlying surface waters. The resulting permanent pycnocline impedes exchanges of dissolved constituents between the surface mixed layer and deeper waters, setting up a multilayer system, with oxic, oxyclinic, sub-oxic, and anoxic layers (e.g. Oguz et al., 2000). The persistent sub-oxic layer (SOL) at the oxic-anoxic interface in the Black Sea is of particular importance in nutrient cycling. In this layer the concentrations of oxygen and sulfide are both extremely low, $<5\ \mu\text{mol kg}^{-1}$ and $<1\ \mu\text{mol kg}^{-1}$ respectively (Tugrul et al., 1992; Buesseler et al., 1994; Murray et al., 1995).

Basin-scale circulation in the Black Sea is characterized by large cyclonic gyres in the eastern and western portions of the central basin. A cyclonic boundary current along the narrow continental slope circumscribes the central gyre region, spawning a chain of permanent and semi-permanent anticyclones along the sea's margin (Fig. 1, after Korotaev et al., 2003). This so-called "Rim Current" derives its energy from wind stress and is strongly modified by topography at the edge of the continental slope, resulting in a ribbon-like pattern that widens and narrows according to slope width, attaining speeds of up to $40\ \text{cm s}^{-1}$ (Oguz et al., 1992). Divergence results from cyclonic circulation in the central gyre region, with characteristic doming of isopycnals towards the center of the gyres, while convergence is prevalent along the chain of coastal gyres, setting up a large-scale transverse circulation system subducting coastal waters into the deepest regions of the sea. This circulation system has important implications for the export and fate of coastal accumulations of plankton, detritus, nutrients, and pollutants into the central basin (Ovchinnikov et al., 1994).

A Black Sea water mass known as the Cold Intermediate Layer (CIL) is also important in the supply, fate, and recycling of nutrients (e.g. Oguz et al., 1993; Ozsoy et al., 1993). The CIL is characterized as a sub-surface temperature minimum bounded by $T = 8\ ^\circ\text{C}$, whose thickness varies regionally and seasonally from 25 m to $\sim$100 m (e.g. Fig. 2). The upper boundary lies at 20–30 m in the core of the central gyres, and deepens to 60–100 m towards the outer edges of these features, and in the rim current and coastal waters. The processes responsible for maintaining the CIL have been the subject of considerable study and debate, and this continues to be the focus of active research (Sorokin, 2002). Once thought to be replenished primarily by advective transport of winter-cooled NW shelf (NWS) waters, it now appears that both advective and convective processes, distributed over several regions of the basin during the winter months, contribute to varying degrees and are subject to regional inter-annual climatic variability (Stanev et al., 2003; Titov, 2003, 2004;

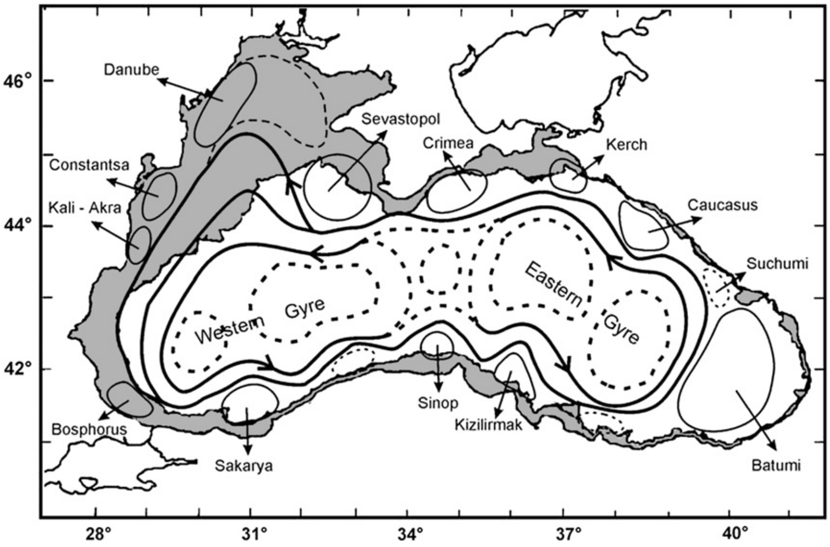

Fig. 1. Schematic map describing quasi-permanent and recurrent features of the Black Sea upper layer circulation system (from Korotaev et al., 2003). (Area < 200 m bottom depth shaded.)

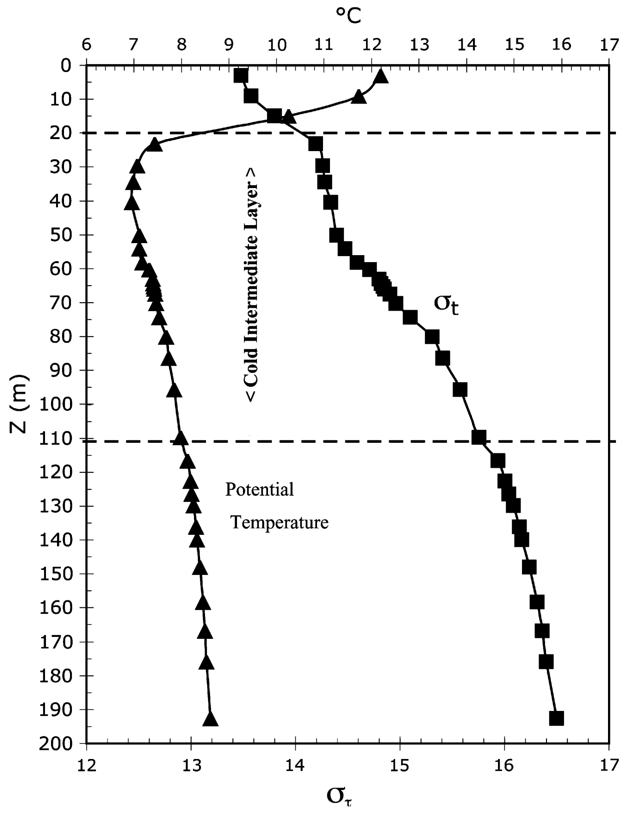

Fig. 2. Characteristic Cold Intermediate Layer signature, bounded by 8 °C, in a profile from the eastern central gyre, station M30V45, April 1998.

Gregg and Yakushev, 2005). The origin of the CIL has implications for the availability of nitrogenous nutrients in the central basin. Recently, Stanev et al. (2003) have estimated that, on average, the origins of the CIL are: the continental slope in the NW region, 42%; the central gyre region, 28%; the NW shelf, 20%; and waters along the eastern margin, 10%. The CIL turnover time is estimated to be ~5.5 years. It is capped by a spring/summer thermocline. Below the permanent pycnocline, temperature and salinity gradually increase with depth to maxima of 9 °C and 22, respectively, in the deepest waters of the Black Sea (Oguz et al., 1995).

The euphotic zone in the Black Sea typically extends to a depth of about 20–35 m. Wintertime surface NO_3^- concentrations of 1.0 and 2.5 μmol N kg^{-1} have been observed in the central gyre and coastal regions respectively (Cokacar, 1996). Under stratified conditions during late spring, summer and autumn, euphotic zone NO_3^- concentrations are maintained at <0.1 μmol N kg^{-1} by phytoplankton uptake, and are often reported at or below typical analytical detection limits of 0.02–0.05 μmol N kg^{-1}. A few meters below the euphotic zone, NO_3^- concentrations increase sharply with depth to 6–8 μmol N kg^{-1}. Below this nitracline, suboxic conditions prevail (<5 μmol kg^{-1} dissolved O_2), favoring heterotrophic denitrification processes that result in decreasing NO_3^- concentration with depth. The net effect of these competing processes is a persistent NO_3^- maximum underlying the euphotic zone throughout the central Black Sea. Deeper than 100–130 m, hydrogen sulfide concentrations increase, and combined inorganic N occurs almost exclusively as NH_4^+.

Major changes in nutrient concentrations, phytoplankton productivity, and food chain dynamics throughout the Black Sea have been documented over the last several decades (Bologa, 1985/1986; Moncheva and Krastev, 1997; Bologa et al., 1999; Shtereva et al., 1999; Cociasu and Popa, 2002; Yunev et al., 2002). The most affected area is the northwestern Black Sea (Tolmazin, 1985; Zaitsev, 1993), especially the Romanian coastal shelf zone (Bologa, 1985/1986; Cociasu et al., 1996; Humborg et al., 1997; Bologa et al., 1999; Petranu et al., 1999), where the direct effects of riverine discharges are most apparent. Enhanced nutrient loading in the major rivers along the northwest coast is considered as the likely cause of the increasing frequency of localized anoxic events and dense coastal algal blooms in the shallow, normally oxygenated coastal waters of the NWS region in 1980s up to the mid-1990s (GESAMP, 1990).

Starting about 1992, a decline in economic activity in eastern Europe resulted in a trend towards reduced nutrient loading in the Danube River (LeMarchand and Le Guidec, 1997; Masaryk and Varley, 1997; Moncheva and Krastev, 1997; Shtereva et al., 1999; Somlyódy et al., 1999). Data for chlorophyll-*a* (Chl-*a*) and primary production in the offshore waters of the Black Sea during the 1960s–1990s also show a decline in the second half of the 1990s (Yunev et al., 2002).

Other substantial changes occurred in the Black Sea ecosystem over the last four decades, including extensive commercial fishing and the introduction of two alien ctenophore species, *Mnemiopsis leidyi* and *Beroe ovata* (Vinogradov et al., 1989; Kideys, 2002). By the late 1990s, when the fieldwork described in this paper began, abundances of both ctenophore species had declined (Kideys, 2002, 2005; Shiganova et al., 2004). The higher trophic level processing of primary production by different groups of organisms, such as ctenophores, crustaceans, or teleosts, can lead to different patterns of nutrient recycling and retention in the mixed layer. Ctenophores, for example, are less likely to be consumed by predators, and hence a larger fraction of their biomass is ultimately processed by microbial decomposition pathways. This would have direct bearing on the relative importance of new and regenerated nutrients in Black Sea phytoplankton productivity.

The coastal waters of the Black Sea are clearly sensitive to variations in both anthropogenic and climatological forcing (Oguz, 2005a,b), with strong implications for N cycling and plankton community dynamics. Offshore transport integrates these processes, resulting in a cumulative record in the central gyre waters that is accessible through direct observation, modeling and remote sensing (e.g. Yunev et al., 2002). Future natural and anthropogenic changes in regional climate along with evolving industrial and agricultural uses of the riverine systems that drain into the Black Sea will result in still different rates of N cycling and primary production in the offshore waters of the Black Sea.

The Black Sea has been an increasingly successful study site for multidisciplinary ecosystem modeling and many of these models are N based (e.g. Oguz et al., 1995, 1996, 1997, 1998, 1999, 2000, 2001a; Gregoire and Lacroix, 2002; Lancelot et al., 2002). However, direct measurements of nitrogenous nutrient utilization by phytoplankton to compare with the results of these models have been lacking. Only two other studies have employed direct measurements of N uptake and recycling rates in the offshore regions of the Black Sea; that of Ward and Kilpatrick (1991) was confined to nitrification/denitrification processes in the upper water column, and that of Krivenko et al. (1998) reported on seasonal NO_3^- and NH_4^+ uptake rates in the euphotic zone at 7 stations concentrated in the north-central offshore waters SE of the Crimea during 1988–93 (data from 5 stations located in the Sevastapol Gyre are also reported). In addition, ^{15}N uptake rates in coastal waters adjacent to the Crimea have been reported by Krivenko and Lukjanova (1994) and Krivenko and Stel'makh (2003), and in the Danube/NWS mixing zone by Ragueneau et al. (2002).

In this paper, we present the results of experiments designed to assess euphotic and suboxic zone N uptake and recycling rates for NO_2^-, NO_3^-, and NH_4^+, and interpret these data in terms of new and regenerated N productivity and particulate export in the offshore waters of the Black Sea. This study was set within the context of ongoing, basin-scale Turkish oceanographic investigations, including aspects of the physics, chemistry and biology of the Black Sea, which provide important ancillary data for nutrients, primary productivity, particulate elemental composition, plankton enumeration, and biomass, etc.

Due to ship scheduling constraints and weather restrictions on ship operation we did not have the opportunity to sample in the winter. We use literature values and contemporary satellite ocean color data to extrapolate our findings to a full annual cycle.

2. Materials and methods

2.1. Study area and hydrographic methods

This research was conducted during the course of three cruises aboard the Turkish vessel R/V *Bilim*, under the aegis of the Middle East Technical University (METU), Institute of Marine Sciences (IMS), Erdemli, Icel, Turkey, (April 1998, September 1998, and September/October 1999), and Leg 1 of the R/V *Knorr* Black Sea cruise in late May of 2001 (Murray, 2006). Stations were concentrated in the southern half of the Black Sea, in the eastern and western central gyres, and the adjacent Rim Current (Fig. 3, Table 1). All stations are offshore, i.e. >200 m bottom depth. The area of this region is 1.3×10^5 km^2 (Sorokin, 2002) and this value is used throughout our study to extrapolate experimental results to basin scale rates with units of mol N y^{-1}. IMS station designations are provided for cross-reference to other publications, databases and ongoing Black Sea monitoring studies.

A light attenuation profile was obtained daily at each station using a Li-Cor (Lincoln, NE) LI-1000 data logger and LI-192SA underwater PAR sensor. Water samples were obtained with a General Oceanics (Miami, FL) rosette sampler equipped with 12 × 5 L Niskin bottles fitted with silicone rubber closure springs. The rosette frame carried a Sea Bird Electronics (Bellevue, WA) Model 9 CTD probe. The water column was sampled at specific euphotic zone light depths (60%, 36%, 22%, 8%, 3%, 1% I_o). Sampling was extended down to the 0.1% light depth at some stations. Samples were also obtained at several deeper depths into the SOL for nitrification determinations. With the exception of the May 2001 cruise, ambient NH_4^+ concentrations were determined colorimetrically using a solid phase extraction protocol derived from the high sensitivity method ($\pm$ 2–3 nmol kg^{-1}) of Brzezinski (Brzezinski, 1988; McCarthy et al., 1996). Ambient NO_2^- and NO_3^- (and NH_4^+ in May 2001) concentrations were obtained from the shipboard autoanalyzer system following protocols similar to those described by Strickland and Parsons (1972) and Grassoff et al. (1983). Dissolved oxygen (DO) was determined by conventional Winkler and iodometric titration (Basturk et al., 1994). Hydrogen sulfide concentrations were determined by the colorimetric method (Cline, 1969).

Chl-*a* and net primary productivity data used in this study were obtained from samplings and incubations contemporaneous with the ^{15}N experiments as described by Yayla et al. (2001) and Yilmaz et al. (2006).

2.2. Nitrogen uptake studies

Nitrogen uptake and recycling rates were determined with ^{15}N tracer techniques to obtain rates of NO_2^-, NO_3^-, and NH_4^+ uptake, NH_4^+ remineralization, and NH_4^+ oxidation. Details of these methods are given elsewhere (McCarthy et al., 1984, 1999; McCarthy and Nevins, 1986; Horrigan et al., 1990). At a few stations N_2 fixation was determined by the method of Montoya et al. (1996).

^{15}N labeled substrates (99 atom-%) were added to the samples collected from the water column at a minimum level equivalent to the analytical detection limit of the ambient nutrient, or 10% of ambient concentration, whichever was greater (McCarthy et al., 1992). Euphotic zone samples were placed in 1.2-L transparent polycarbonate bottles and incubated on deck in clear acrylic tanks supplied with flowing surface sea water (to prevent solar heating) under simulated *in situ* (SIS) light conditions obtained by neutral density screens.

Suboxic samples were incubated in replicate, gas tight 320 ml (brim full) borosilicate glass incubation bottles (Wheaton Science Products, Millville, NJ), equipped with butyl rubber septum caps and rendered opaque with tightly wrapped black vinyl electrical tape. These samples were transferred from the Niskin sampler to the incubation bottles using hydrographic gas sampling techniques. A silicone rubber tube connected to the sampler was inserted into the bottom of the incubation bottle and the sample water was allowed to fill and overflow while the incubation bottle was rotated and the tube gently tapped to dislodge gas bubbles. The septum cap was then fitted and additional sample water was flushed through the bottle via a tube terminated with a syringe needle and a second needle inserted into the septum to release the overflow and vent any headspace. The ^{15}N additions were

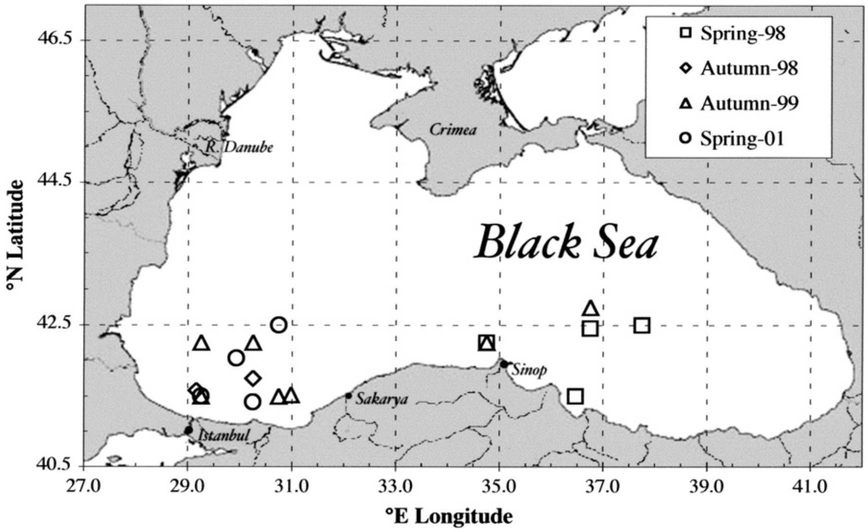

Fig. 3. Station positions and sampling periods for this study. Further details are provided in Tables 1 and 2.

introduced through the septum in microliter volumes via a gastight syringe and the samples were incubated in the dark at near ambient temperatures (±1.5 °C) in a laboratory incubator.

Samples for N_2 fixation were handled similarly but incubated under SIS conditions in the deck-board incubators (in the case of euphotic samples) or in the dark laboratory incubator (in the case of suboxic samples). The isotope addition consisted of 250 μl $^{15}N_2$ (99 atom-%).

The ^{15}N incubations were terminated after a period of 5 h by filtration onto pre-combusted (1 h at 450 °C) 25 mm Whatman GF/F glass fiber filters. The filters were dried at 60 °C and stored in a desiccator for post-cruise ^{15}N analyses. In some cases, the filtrate from ^{15}N enriched incubations was retained for recovery of ^{15}N labeled NO_2^- (the product of $^{15}NH_4^+$ oxidation) and ^{15}N labeled NH_4^+ (to determine NH_4^+ remineralization within the NH_4^+ labeled experiments by isotope dilution) by solid phase extraction protocols (Horrigan et al., 1990; McCarthy et al., 1996).

^{15}N enrichment and elemental N concentration in particulate material and extracted dissolved fractions for these tracer experiments were determined with a Europa Scientific 20/20 mass spectrometer equipped with an automated Dumas combustion sample preparation system (ANCA nt) in a continuous flow configuration (Preston and Owens, 1983; Barrie and Workman, 1984). Details of our mass spectrometric and rate calculation methods are provided in McCarthy et al. (1999).

At "long" stations, occupied for a minimum of 24 h, samples were collected and incubated for three periods in a diel cycle: morning (first half light day), afternoon (second half light day), and nighttime. Daily rate calculations have been obtained by integrating the results of these three samplings on a 6, 6, and 12 h basis respectively. In prior studies, we have observed distinct diel patterns in N uptake rates and nutrient depletion effects that would have been masked by single 24 h incubations (McCarthy et al., 1996). On "short" stations, with limited time available on station, one sampling/incubation was conducted during the daylight hours and the daily rates have been adjusted on the basis of the mean day:night uptake ratios observed at the longer stations.

3. Results

3.1. Hydrography

Profiles for σ_t, H_2S, dissolved oxygen, NH_4^+, NO_3^-, and NO_2^- at station M30V45 in spring-98 in the east central gyre (Fig. 4) are typical of offshore stations in the Black Sea during the late spring - early summer period. While the depth of specific hydrographic features may vary regionally and temporally, their tight correlation with density is a distinctive characteristic of the Black Sea system (Codispoti et al., 1991; Tugrul et al., 1992) with a 0.2–0.3 difference in σ_t between cyclonic and anticyclonic regions (Basturk et al., 1997; Oguz et al., 2002). The near-surface oxic layer, which includes the euphotic zone, has dissolved oxygen concentrations >300 μmol kg^{-1}. Beneath this, the gradient in the oxyclinic layer is influenced by respiration and nitrification associated with organic matter degradation. At the base of this layer, near 130 m, the dissolved oxygen concentration is about 10 μmol kg^{-1}. Within the oxyclinic layer NO_3^- concentrations reach maximum levels (5–7.5 μmol kg^{-1} at $\sigma_t = 15.5$ in this study), and decrease with depth to trace levels (<0.1 μmol kg^{-1}) due to denitrification in the SOL. The underlying anoxic layer is characterized by high H_2S and NH_4^+.

3.2. Nitrogen uptake rates

A representative diel series of N uptake profiles from the same station (M30V45 spring 1998; Fig. 5) illustrates significantly lower uptake rates for NO_2^-, NO_3^- and NH_4^+ occurring during the nighttime relative to the morning and afternoon periods, and a decline in uptake rates with depth in the euphotic zone. The ratios of nighttime to daytime N uptake rates (mean for total 17 stations ± 1 s.d.) were 0.6 ± 0.4 for NO_2^- and

Table 1
Daily integrated euphotic zone N reservoirs, uptake rates, turnover times, summed reservoirs and rates, and *f*-ratios for the stations sampled

Season	Station (°N Lat)	Station (°E Lon)	IMS Station[a]	$\int[NO_2^-]$ (mmol m^{-2})	$\int\rho\ NO_2^-$ (mmol $m^{-2}\ d^{-1}$)	$\tau\ NO_2^-$ (d)	$\int[NO_3^-]$ (mmol m^{-2})	$\int\rho\ NO_3^-$ (mmol $m^{-2}\ d^{-1}$)	$\tau\ NO_3$ (d)	$\int[NH_4^+]$ (mmol m^{-2})	$\int\rho\ NH_4^+$ (mmol $m^{-2}\ d^{-1}$)	$\tau\ NH_4^+$ (d)	*f*-ratio
Apr 1998	42.250	34.750	M15R45	1.8	0.68	2.6	1.6	1.3	1.2	2.1	5.3	0.39	0.18
	41.500	36.467	M27T45	2.2	0.95	2.3	1.2	1.8	0.66	1.1	2.9	0.39	0.32
	42.450	36.750	M30V45	2.4	1.8	1.3	1.1	2.2	0.51	1.2	5.3	0.23	0.23
	42.500	37.750	L30T28	1.3	0.74	1.8	0.6	1.4	0.43	0.50	2.4	0.21	0.31
Sep 1998	41.583	29.167	L35L10	1.3	0.23	5.4	1.4	1.6	0.88	3.0	2.6	1.15	0.36
	41.750	31.250	L45M15	2.3	0.47	4.9	7.7	3.9	1.9	3.2	5.9	0.54	0.38
Sep 1999	41.517	30.983	L31M59	0.56	0.57	0.98	1.6	3.1	0.53	0.27	1.7	0.16	0.58
	42.250	34.750	M45T45	0.70	0.40	1.8	2.9	2.8	1.1	1.4	5.3	0.27	0.33
Oct 1999	41.500	30.750	M15R45	1.1	0.83	1.3	8.9	2.2	4.0	1.1	3.4	0.34	0.34
	42.750	36.750	M15L15	1.4	1.1	1.2	3.3	4.0	0.83	0.9	3.2	0.27	0.48
	42.250	29.250	L30M45	0.50	2.3	0.22	1.4	7.3	0.19	1.0	4.7	0.21	0.51
	41.500	29.250	L30L15	0.50	0.88	0.57	1.2	3.5	0.34	1.3	5.5	0.23	0.35
	42.250	30.250	M15M15	0.50	1.4	0.36	1.2	5.2	0.23	0.89	5.1	0.18	0.45
May 2001	41.500	29.250	L30L15 (3)	0.36	0.09	4.0	1.1	0.50	2.2	0.90	1.4	0.64	0.25
	42.033	29.933	M02L56 (5)	0.40	0.06	6.7	1.6	0.36	4.4	1.0	1.3	0.76	0.21
	42.500	30.750	M30M45 (6)	0.80	0.35	2.3	0.40	0.80	0.50	1.0	2.1	0.48	0.25
	41.417	30.250	L25M15 (10)	0.36	0.06	6.0	0.36	0.33	1.1	0.90	1.6	0.55	0.16
		Monthly mean values	**Apr**	**1.9**	**1.05**	**2.0**	**1.1**	**1.67**	**0.71**	**1.2**	**4.0**	**0.30**	**0.25**
			May	**0.48**	**0.14**	**4.7**	**0.86**	**0.50**	**2.0**	**1.0**	**1.6**	**0.61**	**0.22**
			Sep	**1.2**	**0.42**	**3.3**	**3.4**	**2.9**	**1.1**	**2.0**	**3.9**	**0.53**	**0.40**
			Oct	**0.80**	**1.3**	**0.74**	**3.2**	**4.4**	**1.1**	**1.0**	**4.4**	**0.24**	**0.44**
			Apr−Oct	**1.1**	**0.76**	**2.6**	**2.2**	**2.5**	**1.2**	**1.3**	**3.5**	**0.41**	**0.33**

[a] R/V *Knorr* station numbers (May 2001) noted in parentheses.

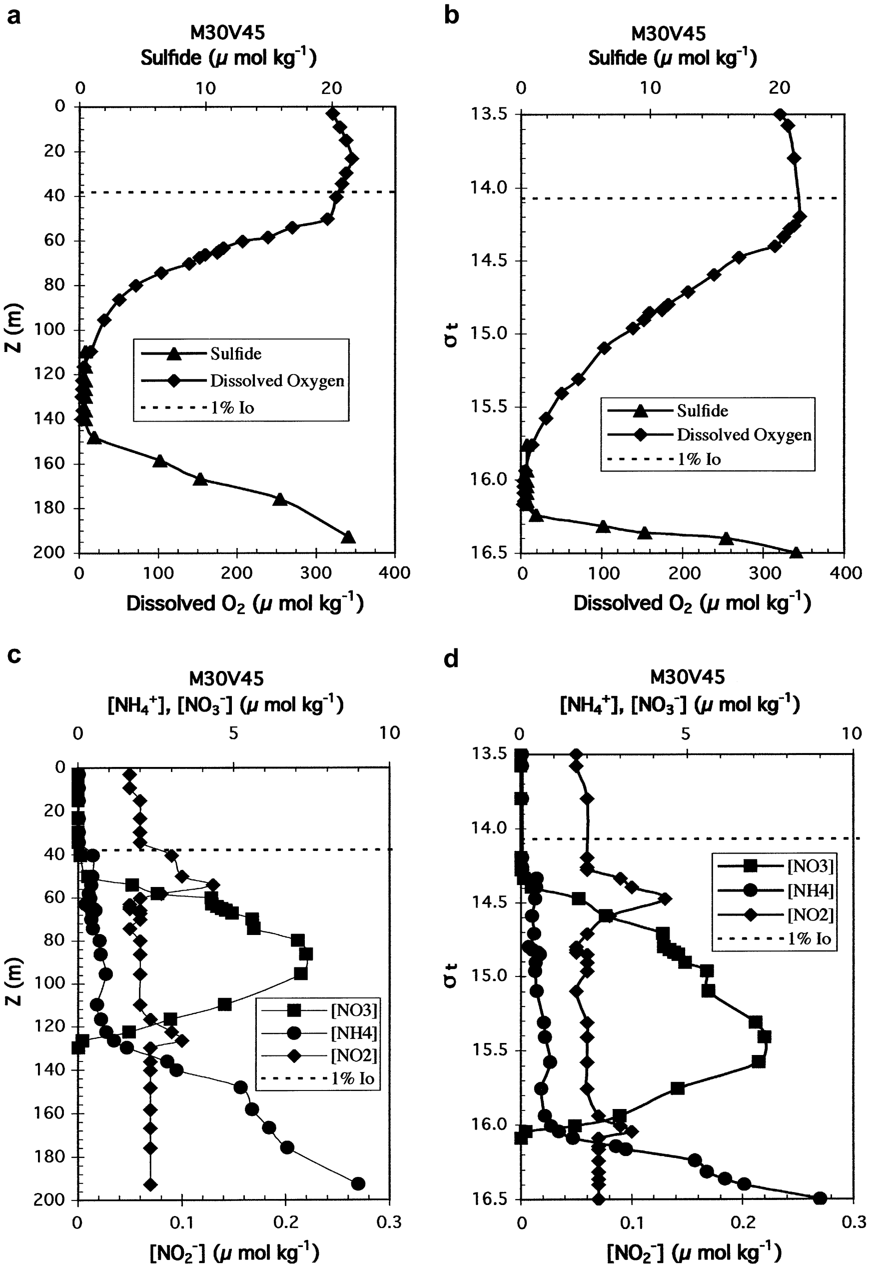

Fig. 4. Characteristic hydrographic properties (upper 200 m) from the eastern central gyre, Station M30V45, April 1998.

0.7 ± 0.4 for both NO_3^- and NH_4^+. Turnover or replacement times for these nutrient pools, computed from utilization rates/ambient concentration, are also plotted in Fig. 5. In Fig. 6 the daily uptake rates for six representative spring and fall stations over the three years of the study are shown.

At two Rim Current stations on the spring-98 cruise (M15R45 and L30T28) secondary *in vivo* fluorescence maxima were observed as further described by (Eker-Develi and Kideys, 2003). Concentrations of NO_3^- at these depths (50–85 m) were 0.5–1.0 μmol N kg^{-1}; and counter to expectations, NO_3^- uptake persisted at depth, well within the nitracline and fluorescence maximum, at rates 0.4–2.0 times the euphotic zone uptake rates (Fig. 6b,c). Samples obtained from these fluorescence maxima and incubated at surface light levels yielded C fixation rates comparable to shallow euphotic zone samples, indicating that these sub-euphotic phytoplankton populations are well adapted to higher light levels (Yayla et al., 2001). Interpretation of the *in situ* fluorescence data showed that these secondary fluorescence maxima exhibit diel changes, with broader peaks at shallower depths during the dark period (Eker-Develi and Kideys, 2003). The diatom *Proboscia alata* was found to be a characteristic constituent of these deeper assemblages (Eker-Develi and Kideys, 2003).

Dinitrogen fixation experiments were conducted on a few stations on the autumn 1999 cruise. Samples were collected from two depths in the euphotic zone on two occasions in the vicinity of station M15M15. The average rate of fixation was 75 nmol N kg^{-1} d^{-1}, roughly equivalent to NO_2^- uptake

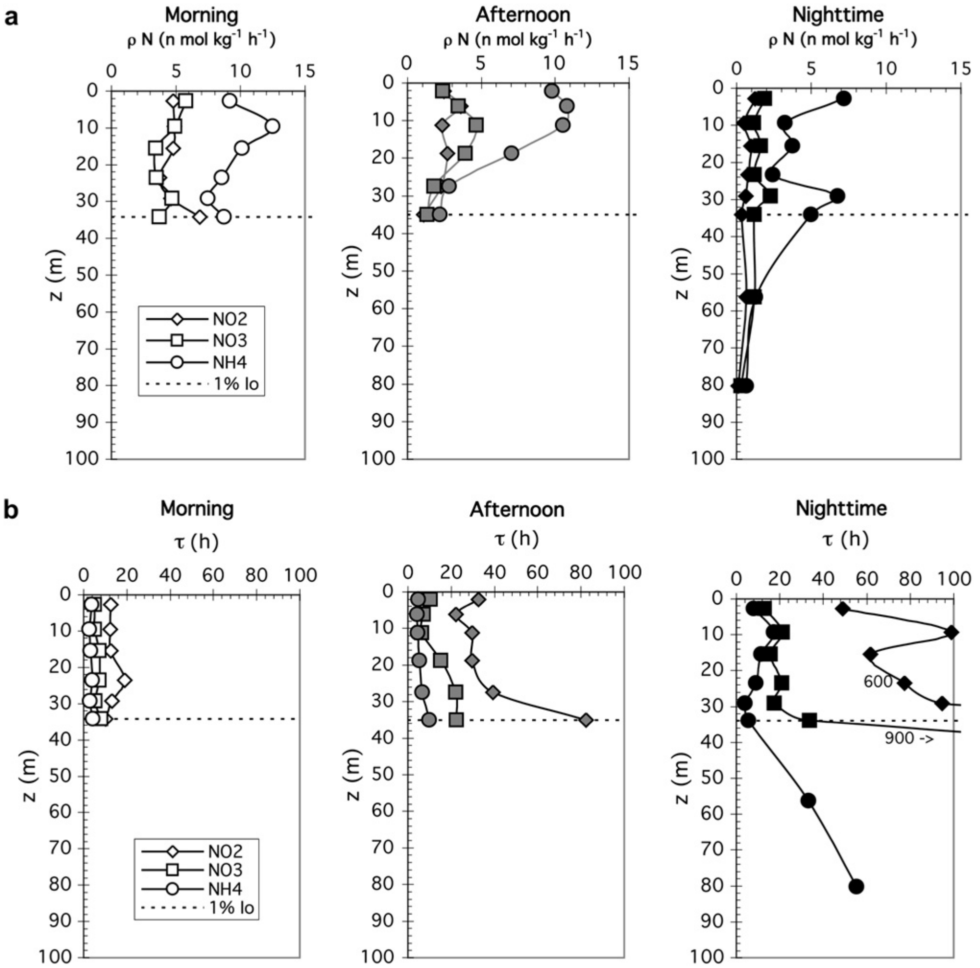

Fig. 5. Characteristic diel pattern in N uptake (ρ) and turnover (τ) profiles from the eastern central gyre sampled during the first half light day (Morning), second half light day (Afternoon) and the dark period (Nighttime). Station M30V45, April 1998.

in these euphotic samples. Logistical problems prevented delivery of the $^{15}N_2$ gas cylinder to the ship earlier in the cruise; however, 4-L samples were collected at several stations and stored in the deck incubators under SIS conditions for a period of 2–6 days prior to the delivery of the gas. Dinitrogen fixation experiments on sub-samples from these bottles yielded rates 4–10 times higher than the short-term incubations just described. Chl-*a* had increased 3–6 fold in the stored samples, indicating significant phytoplankton growth during the storage period, and the increase in N_2 fixation rates could indicate that the biomass of N_2 fixing organisms increased similarly. While not representative of *in situ* rates, these experiments further substantiate N_2 fixing activity in the Black Sea microbial assemblage.

Dinitrogen fixation experiments were also conducted in May 2001, but discernible rates were not observed in any of the euphotic zone samples assayed. However, two profiles at stations that extended into the SOL were positive for N_2 fixation (Fig. 6f) with a maximum rate of 54 nmol N kg^{-1} d^{-1} and an average integrated rate of 0.8 μmol N m^{-2} d^{-1} in the SOL for profiles on two consecutive days.

Table 1 summarizes the daily integrated euphotic zone N reservoirs, uptake rates and turnover times for the three dissolved N species studied, their summed reservoirs and rates, and *f*-ratios (fraction of total nitrogenous nutrient uptake as NO_3^-). Additional properties of the stations sampled, standing stocks, and indices of community productivity are summarized in Table 2.

Results of NH_4^+ and NO_3^- uptake kinetics experiments are shown in Fig. 7, and the kinetic parameters are summarized in Table 3. The parameters are similar for the two spring periods, but K_s and V_{max} were considerably higher for both N nutrients during the autumn 1999 period.

The potential suppressive effect of ambient NH_4^+ concentration on NO_3^- utilization was assessed on both the spring 1998 and autumn 1999 cruises (Fig. 8), and these data indicate that NH_4^+ concentrations as low as 0.1 μmol N kg^{-1} could suppress NO_3^- uptake discernibly. However, the suppressive effect was not as severe as has been reported for some oceanic regions (McCarthy et al., 1996, 1999).

3.3. Ammonium oxidation and remineralization rates

Ammonium oxidation rates (Fig. 9a,b) and remineralization rates (Fig. 9c,d) at three stations during the spring 1998 and autumn 1999 cruises are plotted against depth and density.

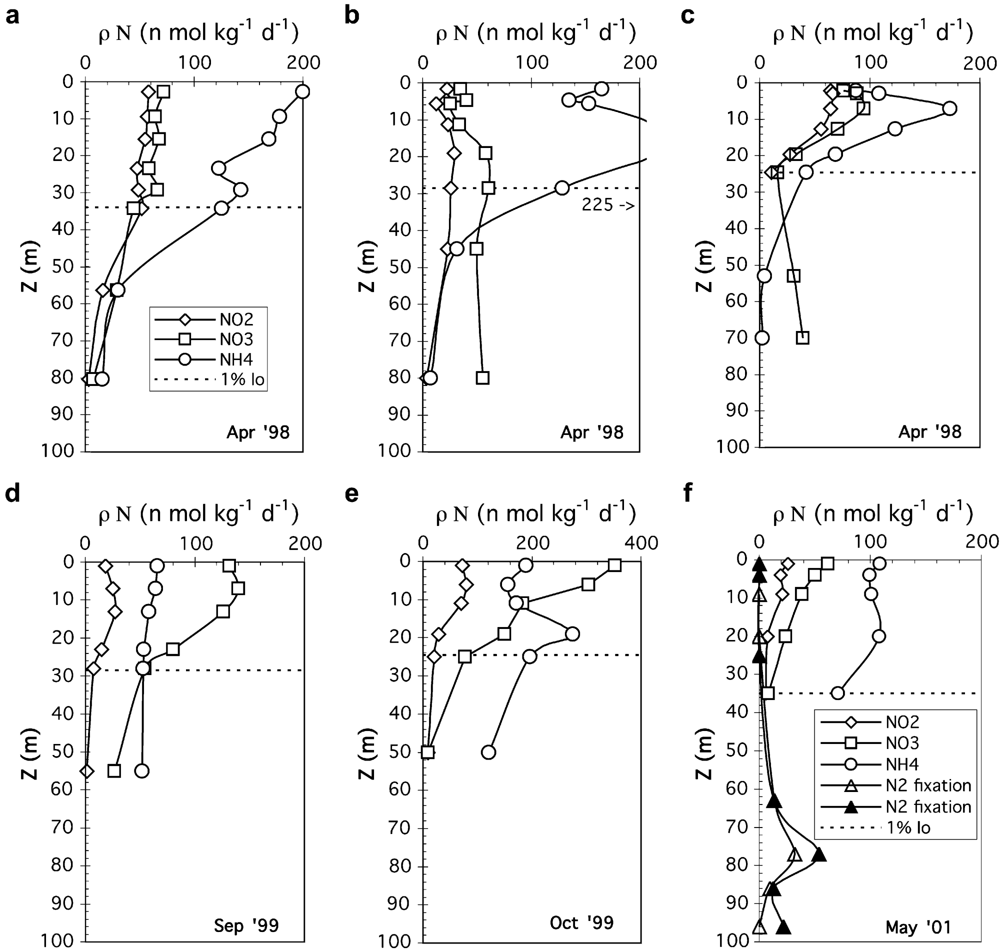

Fig. 6. Daily N uptake (ρ) profiles for six representative eastern and western basin stations. IMS station numbers: (a) M30V45; (b) M15R45; (c) L30T28; (d) L31M59; (e) M15M15; (f) M30M45. Dinitrogen fixation rates are also included for station M30M45 (replicate profiles 26 and 28 May 2001). (Note: different abscissal scale in 6e.)

Inter-station variability is small when the data are plotted against density. Oxygen levels were approximately 11 μmol kg^{-1} at $\sigma_t = 15.5$ and about 3 μmol kg^{-1} at $\sigma_t = 16.1$ and 16.2 in contrast to 260 μmol kg^{-1} in the mixed layer. The euphotic zone integral for NH_4^+ oxidation is 0.1 mmol N m^{-2} d^{-1}; however, maximal rates of NH_4^+ oxidation occurred in the NO_2^- maximum near the base of the euphotic zone, resulting in an integral of 1.3 mmol N m^{-2} d^{-1} for the entire profile.

3.4. Chl-a, primary productivity and C:N uptake rates

From primary productivity data obtained during this study (1998–2001) an average net primary production (April–October) was estimated as 40 mmol C m^{-2} d^{-1} (Table 2). Average total Chl-*a* concentration was 12 mg m^{-2} for the euphotic zone and the lowest Chl-*a* concentrations and primary production rates occurred during the May 2001 sampling period (Table 2).

The mean C:N uptake ratio (molar) observed in this study, 6.8, is close to the Redfield ratio (Redfield, 1958) (Table 2). In both autumn period cruises, primary productivity, PON, and Chl-*a* concentrations were higher than published historical means, most notably in the central gyre waters, while in May 2001 conditions resembled a post-bloom or unproductive period, with high PON/CHL ratios (Table 2) and (Coban-Yildez, 2003; Coban-Yildez et al., 2006a).

4. Discussion

4.1. The phytoplankton bloom cycle in the Black Sea

A number of studies have described the annual bloom cycle in the Black Sea through synthesis and analysis of historical field observations of Chl-*a* concentrations [(1964–91) Vedernikov and Demidov, 1993; (1978–92) Vedernikov and Demidov, 1997; (1986–92) Yunev et al., 2002; (1980–95) Chu et al., 2005; (1980–2004) Finenko et al., 2005]. The general pattern resolved in these studies indicates a winter-early spring (Nov–Mar) bloom period with peak Chl-*a* concentration ~2 mg m^{-3}. During the balance of the year, Chl-*a* concentration in the euphotic zone is more typically ~0.3 mg m^{-3}. The analysis of Chu et al. (2005) suggests a bimodal cycle, with

Table 2
Standing stocks and indices of community productivity at the stations sampled

Season	Station (°N Lat)	Station (°E Lon)	IMS Station[a]	NO_3^- max (m)	EZ[b] (m)	SML[c] (m)	PON (mmol m^{-2})	$\int$Chl-*a*[d] (mg m^{-2})	$\int$N[e] (mmol m^{-2})	$\int$pN[f] (mmol m^{-2} d^{-1})	C-prod[g] (mmol m^{-2} d^{-1})	C:N uptake	PP:Chl-*a*[h] (g C·g Chl-*a* d^{-1})
Apr 1998	42.250	34.750	M15R45	123	29	15	35	13	5.6	7.3	30	4.1	28
	42.450	36.750	M27T45	70	35	18	42	20	4.6	5.6	*24*	*4.3*	
	42.500	37.750	M30V45	86	35	15	39	15	4.7	9.3	42	4.5	
	41.500	36.467	L30T28	125	25	13	46	11	2.4	4.6	34	7.4	37
Sep 1998	41.583	29.167	L35L10	88	35	25	35	14	5.7	4.5	31	6.9	26
	41.750	30.250	L45M15	81	33	30	29	23	13	10	*73*	*7.1*	
Sep 1999	41.517	30.983	L31M59	80	28	18	38	14	2.5	5.3	40	7.5	35
	42.750	36.750	M45T45	75	35	12	42	10	5.1	8.4	27	3.1	31
Oct 1999	42.250	34.750	M15R45	97	30	18	45	18	11	6.4	61	9.5	41
	42.250	29.250	M15L15	80	30	23	41	9.1	5.5	8.3	25	3.0	32
	41.500	30.750	L30M45	97	25	30	58	25	2.9	14	*89*	*6.3*	
	41.500	29.250	L30L15	110	25	30	42	8.9	3.0	9.9	*62*	*6.3*	
	42.250	30.250	M15M15	80	25	25	49	4.3	2.6	12	*73*	*6.3*	
May 2001	41.500	29.250	L30L15 (3)	110	18	20	68	2.6	2.3	2.0	30	15	137
	42.033	29.933	M02L56 (5)	85	20	24	72	3.3	3.0	1.7	27	15	97
	42.500	30.750	M30M45 (6)	80	20	15	51	2.2	2.2	3.2	12	3.8	66
	41.417	30.250	L25M15 (10)	shallow	18	10	89	4.8	1.6	2.0	9.9	4.9	25
		Monthly mean values	**Apr**	**101**	**31**	**15**	**41**	**15**	**4.3**	**6.7**	**32**	**5.1**	**32**
			May	**92**	**19**	**17**	**70**	**3.2**	**2.3**	**2.2**	**20**	**9.7**	**81**
			Sep	**81**	**33**	**21**	**36**	**15**	**6.6**	**7.1**	**43**	**6.2**	**31**
			Oct	**93**	**27**	**25**	**47**	**13**	**5.0**	**10**	**62**	**6.3**	**37**
			Apr−Oct	**92**	**27**	**20**	**48**	**12**	**4.6**	**6.8**	**40**	**6.8**	**50**

[a] R/V *Knorr* station numbers (May 2001) noted in parentheses.
[b] EZ: Euphotic zone, the depth at which 1% of surface light intensity reaches.
[c] SML: Surface mixed layer, determined by seasonal thermocline.
[d] $\int$Chl-*a*: Active Chl-*a*.
[e] $\int$N: Total dissolved inorganic nitrogen (NO_2^-, NO_3^- and NH_4^+) concentration.
[f] $\int$pN: Uptake rate of total dissolved inorganic nitrogen (NO_2^-, NO_3^- and NH_4^+).
[g] Net Primary Production Rate determined by ^{14}C-labeled inorganic C uptake. (Italics: stations not sampled for PP estimated from average C:N uptake from sampled stations on the same cruise).
[h] Daily assimilation ratio (g C · g Chl-*a* d^{-1}).

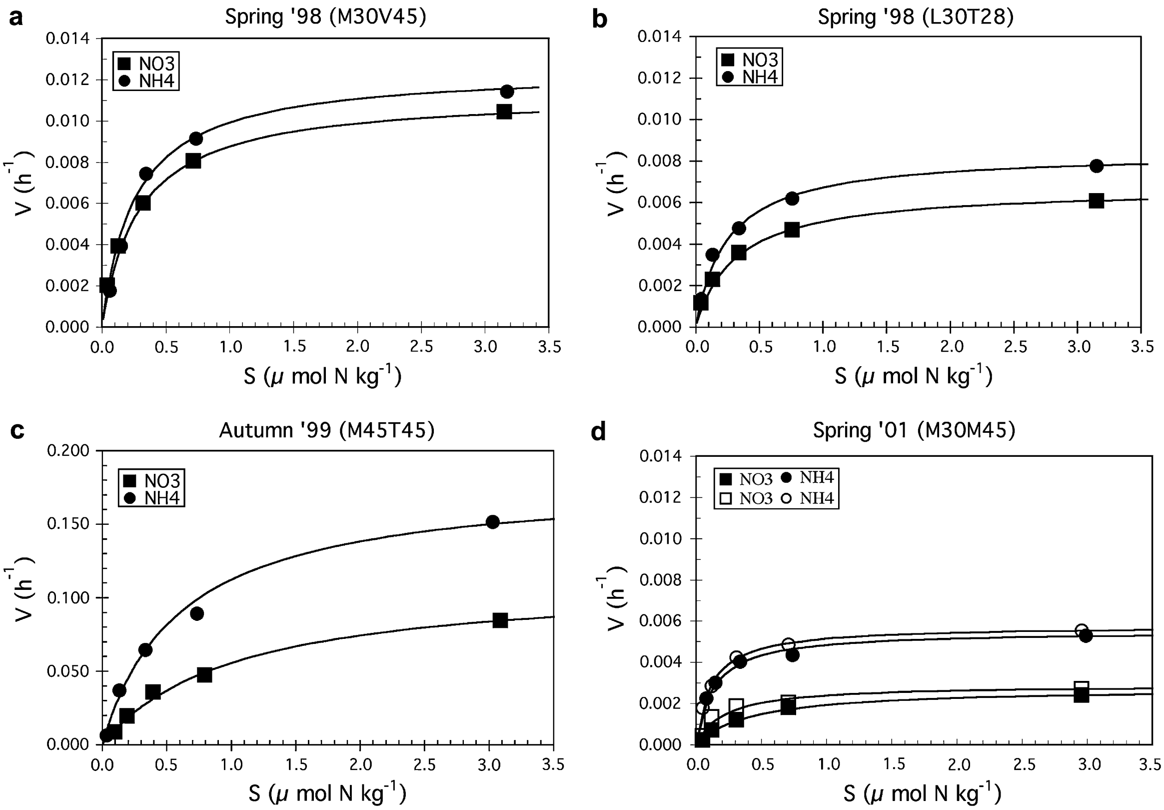

Fig. 7. Characteristic NO_3^- and NH_4^+ uptake kinetic curves (v vs. substrate concentration). (Note: different abscissal scale in 7c.)

a secondary autumn bloom (September–October) about half the magnitude of the winter-early spring bloom.

It is important to note that the rates and possibly the seasonality of primary production in the Black Sea over the last four decades would have been influenced by changes in riverine nutrient loading, plankton community structure, and regional climate. The winter-early spring bloom event is indicative of a release of nutrient limitation by convective mixing or enhanced transport of nutrients primarily from riverine source regions by the mechanisms discussed in Section 1.

During the warmer months, a sub-surface Chl-*a* maximum typically develops at, or just below, the euphotic depth in the offshore waters of the Black Sea (cf. Vedernikov and Demidov, 1997; Yilmaz et al., 1998; Yayla et al., 2001; Finenko et al., 2005). This Chl-*a* maximum is due to elevated pigment levels, rather than elevated phytoplankton biomass as some authors have suggested. The high Chl-*a* concentrations were not accompanied by high PON values (Yilmaz et al., 1998; Yayla et al., 2001), i.e., the Chl-*a* maximum was coincident with a PON:Chl-*a* minimum. Since the mixing depth is typically similar to, or shallower than, the euphotic depth during these months (Table 2), it is unlikely that these deep, low light-adapted populations contribute discernibly to net production in the Black Sea, unless they are capable of substantial daily vertical migration (see Section 4.4).

Table 3
Mean uptake kinetic parameters per season

Cruise	V_{max} NO_3^- (h^{-1})	K_s NO_3^- (μmol kg^{-1})	V_{max} NH_4^+ (h^{-1})	K_s NH_4^+ (μmol kg^{-1})
Spring 1998	0.009	0.31	0.011	0.26
Autumn 1999	0.112	1.03	0.18	0.61
Spring 2001	0.0029	0.33	0.0057	0.13

Beginning in 1978, remote sensing of sea surface plant pigment concentration in the surface waters of the Black Sea with the Costal Zone Color Scanner (CZCS) and subsequently with the Seaviewing Wide Field-of-view Sensor (SeaWiFS) radiometers has provided opportunities for improved characterizations of the annual bloom cycle in the Black Sea (e.g. Longhurst, 1998; Nezlin et al., 1999, 2002; Oguz et al., 2002, 2003). The bloom cycle evident in remotely sensed data for the offshore waters of the Black Sea has similarities to the seasonal pattern observed in subtropical ocean systems since it lacks the distinct spring bloom commonly associated with oceanic waters at the latitudes of the Black Sea (Longhurst et al., 1995; Nezlin et al., 2002). The satellite data also indicate a more sharply defined bloom onset (September–October) and earlier peak (November–December) than is evident in syntheses of historical field data sets [(1964–91) Vedernikov and Demidov, 1993; (1978–92) Vedernikov and Demidov, 1997; (1986–92) Yunev et al., 2002; (1980–95) Chu et al., 2005; (1980–2004) Finenko et al., 2005].

Nezlin et al. (2002) and Oguz et al. (2003) analyzed monthly SeaWiFS data covering the period of the present study (1998–2001). The pigment signature of the bloom

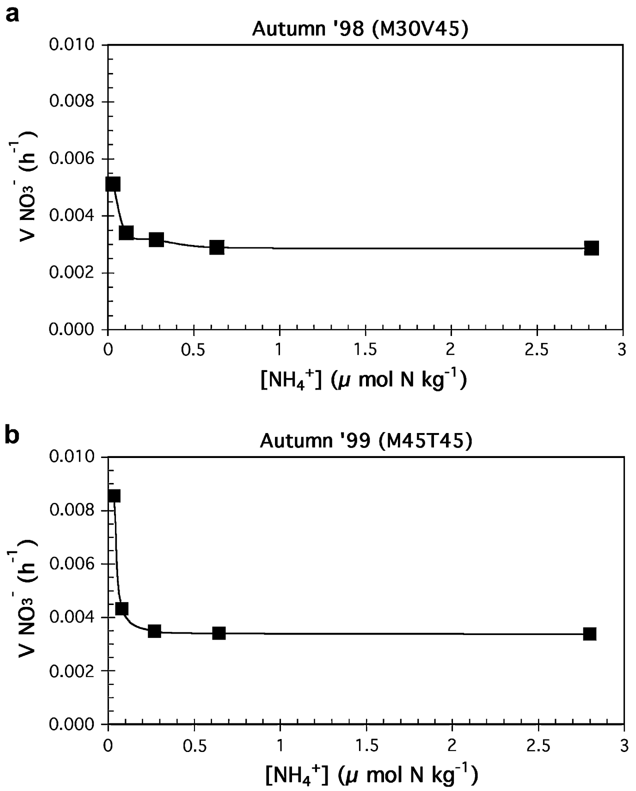

Fig. 8. Characteristic NO_3^- uptake (v) vs. NH_4^+ concentration response (NO_3^- uptake suppression).

onsets sharply in September–October, peaks in November–January, then decays over a five- to six-month period, reaching an annual minimum in April–May. The character and magnitude of the bloom appear to be sensitive to relatively small interannual climatic variations (air temp. anomaly, SST anomaly, salinity anomaly (reflecting Danube watershed precipitation), wind stress etc.) that can affect winter mixing depths (Nezlin et al., 2002). There is also an apparent bloom cycle response to a recent regional climatic warming trend (Oguz et al., 2003). Coincident with this warming trend there has been a steady decrease in the volume of the CIL throughout the Black Sea (Krivosheya et al., 2002; Staneva and Stanev, 2002; Oguz et al., 2003).

Photosynthetic efficiency may be characterized by an "assimilation ratio" (g C · g Chl-a^{-1} d^{-1}). In the data analyzed by Vedernikov and Demidov (1997) from 16 Black Sea cruises for the period 1978–92, daily euphotic zone assimilation ratios averaged 15.5 g C · g Chl-a^{-1} d^{-1} for May–October, and 8.3 g C · g Chl-a^{-1} d^{-1} for November–April, a 46% reduction in winter. Analysis of data summarized by Sorokin (2002, table 6.18) yields 19.9 and 12.4 g C · g Chl-a^{-1} d^{-1} summer vs. winter, a 38% reduction in this ratio for offshore waters during the colder months. In our synthesis of an annual productivity and N cycle we use the average of these two values (42%).

Assimilation ratios in this study (April–October) averaged 33.3 g C · g Chl-a^{-1} d^{-1} (excluding the apparent outlier value of 81.0 observed during the May 2001 samplings). This mean is similar to that found by Eppley et al. (1973) for North Pacific mixed layer data ($x = 32$ g C · g Chl-a^{-1} d^{-1}), and is lower than the value of 44 (12 h light day) expected for optimal light conditions in coastal waters and cultures (Ryther and Yentsch, 1957).

Oguz et al. (2003) provide climatology of SeaWiFS-derived Chl-*a* for the 1993–2001 period using a 50% Black Sea-specific correction factor to compensate for overestimation by the standard SeaWiFS algorithm (Suetin et al., 2002, 2004; Sancak et al., 2005). Though limited in number, "ground truth" analysis of our *in situ* station observations (exclusive of the May 2001 data) for the SeaWiFS climatology also yields an order of 50% correction factor. However, our *in situ* data in May 2001 (R/V *Knorr* Leg 1) are only 10% of the SeaWiFS climatology value for May, and the analysis of Oguz and Ediger (2006) on the more extensive data set for May–June 2001 (R/V *Knorr* Legs 1 and 2, and R/V *Bilim*) averaged only 25% of the SeaWiFS values.

As noted in Section 2.4, biological conditions at the stations sampled during the late May 2001 period (Leg 1 of the R/V *Knorr* cruise) were anomalous with respect to N uptake rates, C:N ratios, and assimilation ratios. SeaWiFS images suggest that a major bloom developed along the western margin of the Black Sea earlier in May of 2001 and was advected south and east along the Anatolian coast and into the western offshore waters. Unsupported by sufficient upwelling or recycling of nutrients in the central region, patches of senescent cells, accumulating detritus, and degradation products may have prevailed during our sampling period. The elevated detrital component implied by abnormally high POC:Chl-*a* ratios indicates that this period had enhanced heterotrophic, relative to autotrophic, processes (Coban-Yildez et al., 2006a). Additional confirmation of this comes from high lipid to protein and carbohydrate to Chl-*a* ratios derived from pyrolysis/GC/MS (Coban-Yildez et al., 2006b). Accumulation of chromophoric DOM during this period may have contributed to elevated radiometer signal levels reflected in the SeaWiFS-derived Chl-*a* values following the bloom. We conclude the May 2001 period was anomalous with respect to the relationship of remotely sensed radiometry and Chl-*a* concentration. A correction factor of 50% applied to the SeaWiFS climatology remains widely applicable under typical Black Sea conditions and we have retained this correction factor in the analysis that follows. Moreover, the following analysis does not use the May 2001 or the SeaWiFS climatology from the spring and summer months.

Regressions of N and C uptake on *in situ* Chl-*a* determined from shipboard samples during this study (Fig. 10) permit extrapolation of uptake rates from the SeaWiFS Chl-*a* climatology for a four-year period (1998–2001) (Oguz et al., 2003). Using an average Chl-*a* concentration of 0.63 mg m^{-3} from the SeaWiFS data for the winter bloom period (November–April) and a 42% reduction for assimilation ratio during the winter (the mean of the Vedernikov and Demidov (1997) and Sorokin (2002) data discussed previously) yields average uptake rates of 5.5 and 31.5 mmol m^{-2} d^{-1} for N and C respectively for the winter months. By combining these values with those obtained during our study (Fig. 11) we extrapolated

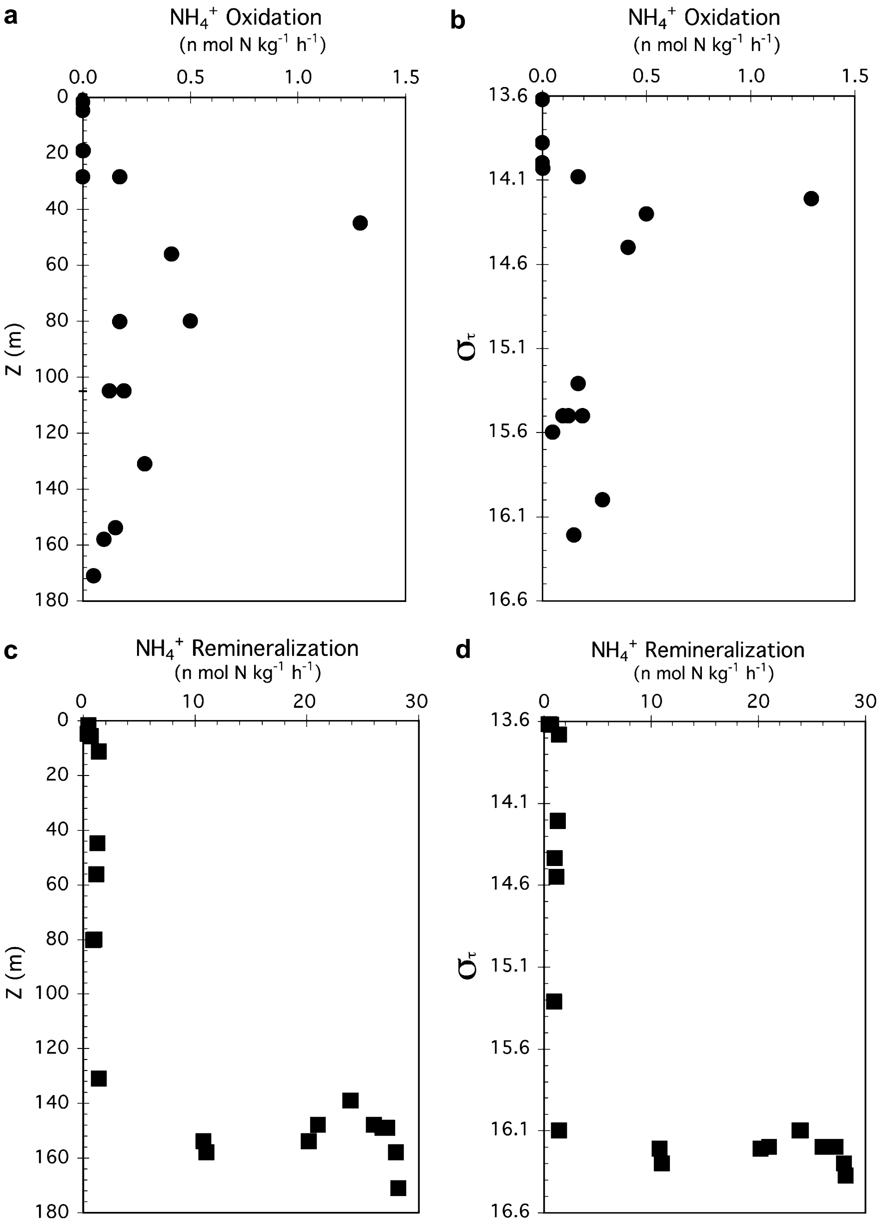

Fig. 9. Composite profiles of NH_4^+ oxidation and remineralization rates from three stations (M30V45, M15R45, L30T28) plotted against depth (a,c) and density (σ_t) (b,d), respectively.

average annual uptake rates of 5.6 and 34 mmol m^{-2} d^{-1} for N and C respectively (C:N molar uptake = 6.1). The corresponding annual C uptake, 150 g C m^{-2} y^{-1}, is similar to that of Vedernikov and Demidov (1993, 1997), based on historical field data. Assuming that the observed *f*-ratio for October (0.44) approximates the prevalent *f*-ratio throughout the winter bloom period (November–April), we have extrapolated a NO_3^- uptake rate of 2.4 mmol m^{-2} d^{-1} through the winter bloom period (Fig. 11), and an average annual rate of 2.2 mmol m^{-2} d^{-1}.

Total N uptake rates ($n = 3$) for January–February (1988–93) sampled by Krivenko et al. (1998, and unpublished data) SW of the Crimea and in the Eastern Central Basin average 2.1 mmol N m^{-2} d^{-1} (including a 12% increase to account for the average NO_2^- uptake as obtained in our study) which is about 38% of the winter rate we show in Fig. 11. There were a number of differences in our respective experimental methods, including the duration of incubation experiments and sensitivity of nutrient analyses, especially for NH_4^+. Perhaps of greater importance, however, is the question of similarity in overall ecosystem structure and productivity from one decade to the other.

Surface Chl-*a* concentrations at stations sampled by Krivenko et al. (1998, and unpublished data) averaged 1.5 mg m^{-3}, consistent with historical data sets covering the same period (e.g. Vedernikov and Demidov, 1997; Finenko et al., 2005). From these data we have estimated a mean euphotic zone Chl-*a* concentration of 0.9 mg m^{-3} for their study period. Converting the winter N productivity data of Krivenko et al. (1998, and unpublished data) to C with a factor

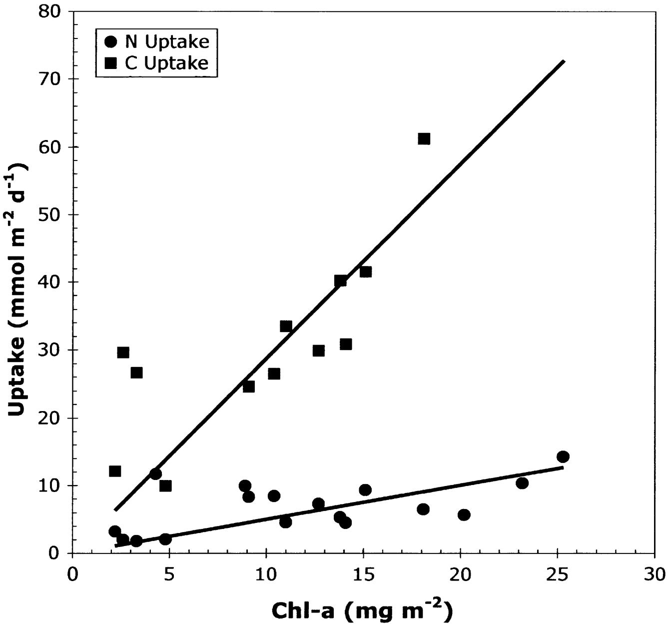

Fig. 10. Regressions of euphotic zone rates of N uptake and primary production vs. euphotic zone Chl-*a* concentration, with regressions forced through the origin.

of 6.7 (Redfield, 1958) yields 13.8 mmol C m^{-2} d^{-1} and an assimilation ratio of 6.1 for these winter months. The average Jan–Feb (1978–92) primary productivity presented by Vedernikov and Demidov (1997) is equivalent to 7.0 mmol N m^{-2} d^{-1} (applying the Redfield ratio of 6.7), and is similar to our estimate derived from SeaWiFS data. Thus, if our data and Krivenko's are fully comparable, it appears that typical wintertime Chl-*a* concentrations were lower and assimilation ratios were higher throughout all seasons in the late 1990s–2001 period relative to the 1980s–early 1990s period.

Nitrogen productivity extrapolated from the SeaWiFS data as described above for the full period analyzed by Oguz et al. (2003) with our *in situ* observations superimposed is presented in Fig. 12a. Annual averages of the SeaWiFS derived N productivity rates are presented in Fig. 12b. The mean annual N productivity is 6.3 mmol m^{-2} d^{-1} for 1997–2001. For comparison, the annual composite assembled for our field study yielded a mean annual N productivity of 5.6 mmol m^{-2} d^{-1} (Fig. 11).

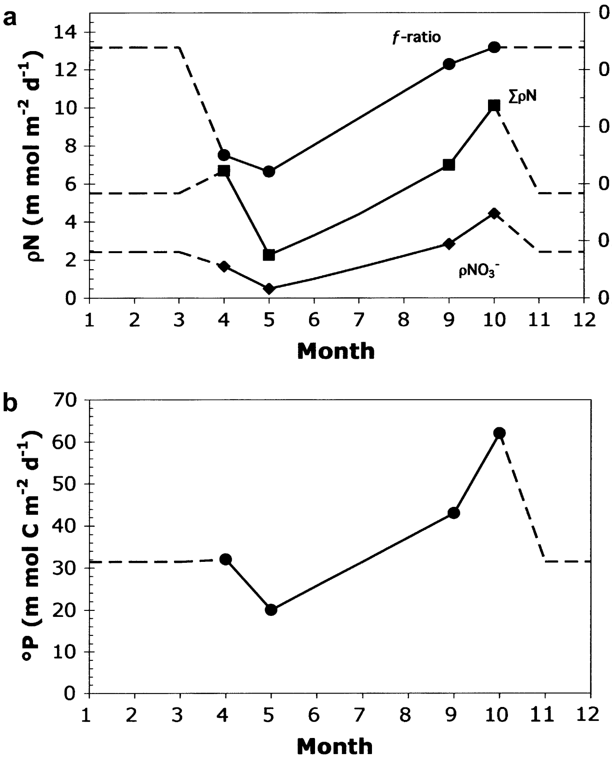

Fig. 11. Observed mean monthly NO_3^- uptake, total N uptake and *f*-ratio (a), and Primary Productivity (b) (solid lines and symbols), combined with extrapolated monthly data for the Nov–Apr winter bloom period (dashed lines) derived from SeaWiFS Chl-*a* data as described in the text.

4.2. Autochthonous Sources of NO_3^- within the CIL

Nitrification processes are strongly inferred from persistent NO_2^- and NO_3^- maxima at intermediate depths in the CIL between the lower boundary of the euphotic zone and the upper boundary of SOL (Fig. 4c,d and 9 a,b; and Ward and Kilpatrick, 1991). Karl and Knauer (1991) estimated that 95% of euphotic zone particle export flux is remineralized in this layer, and our calculations confirm that remineralization and oxidation of NH_4^+ derived from particulate matter sinking into the CIL and implied nitrification is an important source of NO_3^- in the Black Sea. In the near-surface oxic/euphotic

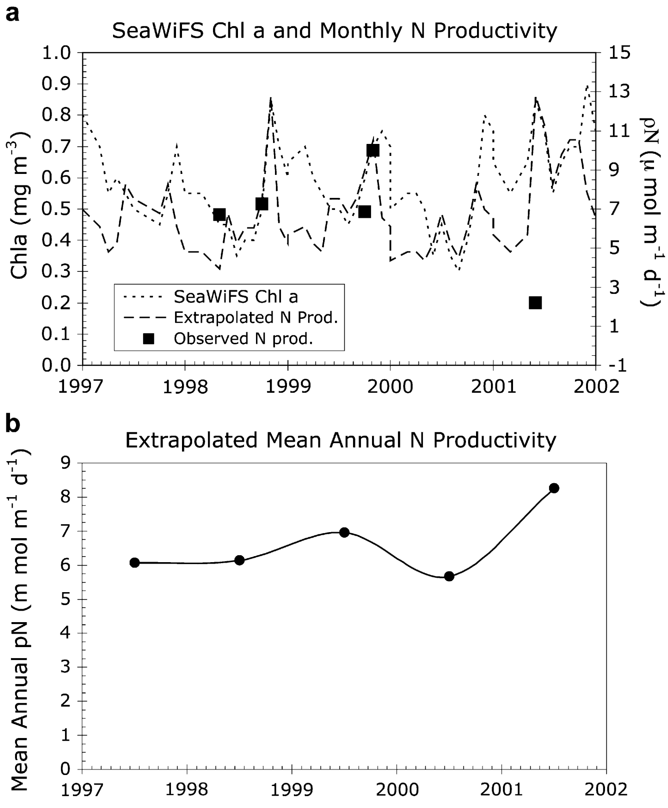

Fig. 12. (a) Chlorophyll *a* concentration from the 1997–2001 SeaWiFS climatology data by Oguz et al. (2003), and our extrapolated N productivity (Section 4.1) and *in situ* observations superimposed; and (b) the extrapolated N productivity data on an average annual basis.

layer (integrated from Fig. 9), observed rates of NH_4^+ oxidation to NO_2^- are relatively low, 0.1 mmol N m^{-2} d^{-1}. This is only about 6% of the rate that NO_3^- is incorporated directly into phytoplankton production. Deeper within the CIL/SOL, nitrification, inferred from our NO_2^- production measurements (1.3 mmol N m^{-2} d^{-1}, integrated from Fig. 9), could provide 72% of the NO_3^- incorporated directly into phytoplankton production. This rate of nitrification is 40% of the rate we measured for NH_4^+ produced by remineralization/respiration processes. Ward and Kilpatrick (1991) also measured rates of nitrification in the Black Sea as NH_4^+ oxidation and as NO_2^- oxidation. They noted a tight coupling of these processes with higher potential for oxidation of NO_2^-, which would tend to keep NO_2^- at low concentrations in the CIL. They do not provide CIL integrals for these rates, but from their Fig. 4 we calculate an approximate rate of 0.29 mmol N m^{-2} d^{-1}, which is about 22% the rate we determined. Yakushev and Neretin (1997) used a model for Black Sea N cycling to compute a nitrification rate of 2.4 mmol N m^{-2} d^{-1}, twice our measured rate. With extrapolated rates of nitrification, 1.6×10^{11} mol N y^{-1} for the offshore waters of the Black Sea as inferred from our NO_2^- production measurements, the NO_3^- reservoir in the CIL (on the order of 1.1×10^{11} mol N at the time of this study) could be replaced in 250 days by *in situ* processes.

4.3. Allochthonous sources of N to the CIL

The seasonal formation and distribution of the CIL throughout the central Black Sea facilitates the export of riverine nutrients from coastal waters which sustain the NO_3^- maximum layer in the offshore waters. Satellite imagery reveals frequent 100 km-scale excursions of the Rim Current from the NWS into the central western basin, along with a ubiquitous array of filaments, meanders, off-shore jets, and other forms of mesoscale and sub-mesoscale structures along the Anatolian coast (Oguz et al., 2002).

The annual DIN outflow of the Danube River (>90% as NO_3^-) is about $5.0 \pm 0.7 \times 10^{10}$ mol N y^{-1} for the period 1988–92 (Cociasu et al., 1996). Garnier et al. (2002), citing Cociasu et al. (1996), present nutrient discharge rates up to 1995 (their Fig. 4). A leveling-off or reversal of the early 1990s downward trend in DIN discharge is evident for the 1993–95 period. There do not appear to be more current published data on Danube DIN, and thus we assume that the estimate of 5.0×10^{10} mol N y^{-1} remains a reasonable value for the purposes of this analysis.

Along with the input of riverine DIN to the NWS system, an additional 9.3×10^{10} and 1.2×10^{10} mol N y^{-1} arises from remineralization and nitrification processes in the NWS water column and sediments respectively, as estimated by Gregoire and Lacroix (2002). These authors further estimate that about one third, 5.4×10^{10} mol N y^{-1}, of these three N sources is exported to the open sea, primarily as NO_3^-.

At 2.9×10^9 mol N y^{-1}, the DIN outflow from Turkish rivers is about 5% of the Danube's (Tuncer et al., 1998); however, the proximity of these rivers to the Rim Current and enhanced transport processes east of Sakarya along the Anatolian coast (Sur et al., 1994, 1996) might lead to a proportionally greater contribution of these nutrient sources to offshore waters.

During the period 1969–1988, the magnitude of the sub-euphotic zone NO_3^- maximum in the off-shore waters of the Black Sea more than doubled, increasing from 2–3 μmol N kg^{-1} in 1969 to 7–8 μmol N kg^{-1} in 1988. It then decreased to 5–6 μmol N kg^{-1} in the second half of the 1990s (Codispoti et al., 1991; Tugrul et al., 1992; Oguz and Salihoglu, 2000; Konovalov and Murray, 2001). This change has been attributed to decreased Danube nutrient loading during the 1990s. From these data we calculate that the Danube source of N to offshore waters can replace the entire CIL NO_3^- reservoir in ~2 years. Thus, a change in NO_3^- content of the CIL could occur over a relatively short period as a result of changes in Danube nutrient discharge.

Another source of new N to the Black Sea, which has been enhanced anthropogenically, is wet and dry atmospheric deposition. Drawing on several studies (Afinogenova et al., 1992; Erdman et al., 1994; Kubilay et al., 1995) and one with annual estimates spanning the twelve-year period from 1985 to 1996 (Tsyro and Innes, 1996), we can infer an average total N deposition rate ($NO_2^- + NO_3^- + NH_4^+$) on the order of 1.3 x $\pm 0.4 \times 10^{10}$ mol N y^{-1} (1 s.d.), approximately 60% of which is NH_4^+· This rate of deposition is equivalent to about 18% of the estimated NWS exports (Gregoire and Lacroix, 2002). Episodic, near-shore wet deposition events at a remote sampling station near Amasra on the southwestern Black Sea coast contained N concentrations as much as 10 times greater than the basin-wide deposit averages (Alagha and Tuncel, 2003; Karakas et al., 2004). This nitrogenous deposition is thought to originate with sources in Europe and industries around Istanbul (Alagha and Tuncel, 2003). Since the aggregate magnitude of these local events along the Anatolian coast has not been assessed, the estimate of aeolian N deposition noted above may be conservative.

Richardson et al. (1998) have pointed out that vertically migrating phytoplankton like *Proboscia (Rhizosolenia)* spp., which take up sub-euphotic NO_3^-, may also be an important aspect of new production in the open ocean. Their model, parameterized with published estimates of *Proboscia* spp. oceanic abundance, indicates that new production by migrating *Proboscia* spp. could be equivalent to as much as 17% of the new production supplied by turbulent mixing processes. *Proboscia calcar-avis* and *Proboscia alata* occur in the Black Sea, and they were present in the secondary fluorescence maxima within the nitracline at two stations in spring 1998 (Eker et al., 1999; Eker-Develi and Kideys, 2003). We observed significant NO_3^- uptake in sub-euphotic samples in proximity to these maxima (Fig. 6b,c), and the same samples exhibited full photosynthetic activity when exposed to near-surface irradiance (Yayla et al., 2001). These two stations were in the Rim Current, where both lateral offshore transport and downwelling are prevalent. Historical data of METU/IMS do not, however, indicate common occurrence of sub-euphotic fluorescence maxima. Thus, although some studies point to evidence for diel migration of certain phytoplankton species in the Black Sea (Sorokin, 2002 and references cited therein), the possible contribution of migrating phytoplankton to new productivity in the Black Sea remains uncertain, but most likely it is small.

Zehr et al. (1998) have identified a genetic potential for N_2 fixation in a number of free-living cyanobacteria and members of the class *Proteobacteria*. It is not known whether these organisms are active in the Black Sea, but this is worth examining, especially given their phylogenetic proximity to sulfate reducing microbes (Zehr et al., 1998). Dinitrogen-fixing endosymbiotic cyanobacteria such as *Richelia intracellularis* have not been detected thus far in Black Sea diatom samples microscopically examined by Turkish investigators (A. Kideys, personal communication).

Our limited data from ^{15}N studies confirm that N_2 fixation in the euphotic zone of the Black Sea may at times be a relevant source of new production. However, as noted above (Section 2.2), euphotic zone N_2 fixation was not detected under post-bloom conditions in spring 2001. The N_2 fixation we observed in the SOL in May 2001 would contribute to microbial biomass and N recycling within this layer, but would constitute only a small source of new N to the euphotic zone.

Studies of Black Sea N_2 fixation by microbial heterotrophs have recently been summarized by Sorokin (Sorokin, 2002). Dinitrogen-fixing microbes (*Azotobacter, Clostridium, Vibrio, Pseudomonas, Spirillum* and *Treponema)* were isolated from western Black Sea (Ukrainian coastal) waters and cultured on N-free media (Pshenin 1965, 1966, 1978, 1980, in Russian, as cited by Sorokin, 2002). The capability of these isolates to fix N_2 was also demonstrated with ^{15}N. Seasonality in N_2 fixation rates was correlated with phytoplankton bloom cycles in these studies and N_2 fixation supplied the N requirement for 10–20% of bacterial biomass production. If the bacterial production:phytoplankton production ratio for the Black Sea is similar to that for oceanic waters, 0.3 (Cole et al., 1988), then the value cited by Sorokin (2002) would suggest that the equivalent of 5% of primary production, i.e. 0.33×10^{11} mol N y^{-1}, could be supported by N_2 fixation. *In situ* N_2 fixation rates were not determined with direct measurement in their studies, and the study region did not include the central basin waters; however, until more data are available, this value appears to be a the best available estimate for annual rates of N_2 fixation in the Black Sea.

Decadal changes in phytoplankton biomass and primary production mirror the observed trends in allochthonous nutrient sources for the Black Sea. For example, during the 1960s, 1970s, and the first half of the 1980s the offshore Chl-*a* concentrations were 0.15 ± 0.04 mg m^{-3}. Earlier in the 1990s, concentrations increased steadily to 1.0 ± 0.7 mg m^{-3}, then after 1994 they decreased to 0.26 ± 0.08 mg m^{-3} (Mikaelyan, 1997; Yunev et al., 2002). As noted above, shifts in the food web caused by other factors during this period, such as the introduction of non-native ctenophores, could also have influenced the partitioning of biomass among different trophic levels and hence the partitioning of N among various nutrient and biomass pools.

4.4. New and regenerated production and *f*-ratios

In most publications on aquatic N studies the calculation of *f*-ratio values departs from the full formulation: $f =$ new:total production ratio suggested by Eppley and Peterson (1979). A simplified version of the *f*-ratio commonly used includes only NO_3^- and NH_4^+, and thus assumes that N_2 fixation and aeolian deposition are small contributions to new production and that NO_2^-, urea, and amino N are small contributions to recycled production. The overriding concept of the *f*-ratio, however, is the comparison between allochthonous or new and autochthonous or recycled sources of N. The importance of this distinction was broadened with the paradigm advanced by Eppley and Peterson (1979) suggesting that globally averaged new production supported by allochthonous N should be equivalent to globally averaged particulate organic flux of N to the deep ocean.

For typical pelagic oceanic waters NO_3^- is the dominant source of N supporting new production and NH_4^+ is the dominant source of N supporting recycled production, and comparison of uptake rates for these two forms of N is sufficient for most *f*-ratio generalizations. In the course of this study we have used this more general simplified formulation of the *f*-ratio. From our balanced budget values in Section 4.5 it is evident, however, that with respect to sources of NO_3^-, only about 20% (riverine plus atmospheric deposition) of the NO_3^- taken up by plankton (or consumed via anammox) is truly allochthonous. In other words, about 80% of the NO_3^- taken up by plankton is generated locally by nitrification. Unlike the typical condition for a central ocean basin, where NO_3^- below the thermocline may be of remote deep ocean origin, 90% of the NO_3^- within the CIL below the euphotic zone results from the remineralization of particulate and dissolved organic N that either settled from or was mixed downward from the euphotic zone.

The annual integrals of data presented in Fig. 11 demonstrate that more than one third of the annual N production in the Black Sea is supported by NO_3^- uptake. The preferential use of NH_4^+ over NO_3^- in these Black Sea studies (Fig. 8) is less dramatic than has been observed in many marine regions (McCarthy, 2002). This may be an inherent characteristic of the constituent phytoplankton. A diminished suppression of NO_3^- utilization by the presence of NH_4^+ plus the typically low Black Sea NH_4^+ concentrations (Fig. 4) in the oxic/euphotic layer (Fig. 5) would tend to elevate the *f*-ratio for the Black Sea.

The autumn increase in *f*-ratio (Table 1, Fig. 11) is commensurate with the onset of the autumn-winter bloom. At this time the species assemblage N uptake kinetics shifted (Table 3). Half saturation constants increased three-fold relative to the prior spring values, and maximum rates for population doubling time from daytime nutrient uptake rates ($0.69/V_{max}$) decreased from 70 h to 5 h.

While there is merit in calculating a conventional *f*-ratio for the Black Sea, a fundamental difference between the Black Sea and offshore ocean waters is that the strong density gradient underlying the CIL of the Black Sea is a substantial barrier to upward flux of N from deep water (NH_4^+ for the Black Sea). The best estimate of this flux rate for the Black Sea is 1.2×10^{-1} mol m^{-2} y^{-1} (Kuypers et al., 2003), which is a minuscule fraction of N used in primary production.

A more thorough new production:total production analysis for the Black Sea would compare the N delivered by riverine discharge, atmospheric deposition, N_2 fixation, and the small upward flux term for NH_4^+ from the anoxic layer to total N production. These allochthonous N terms sum to 1.1×10^{11} mol y^{-1}, which is 17% of the N used in primary production, or an *f*-ratio of 0.17.

In the central Black Sea, diffusive flux plus seasonal and storm induced mixing processes are the dominant means by which NO_3^- in the underlying CIL replenishes NO_3^- in the overlying surface layer. At our annual rate of $NO_3^- + NO_2^-$ utilization, 2.8×10^{11} mol N y^{-1} (extrapolated from data in Fig. 11), Black Sea phytoplankton would be capable of consuming the full NO_3^- content of the CIL (on the order of 1.1×10^{11} mol N at the time of this study) in 140 days.

4.5. Balancing the Black Sea N budget

The NO_3^- reduction data of Ward and Kilpatrick (1991), from a single station, are apparently the only published direct measurements for Black Sea denitrification. Several N based modeling studies have used these data to parameterize model simulations (e.g. Oguz et al., 2000; Gregoire et al., 2004). Integration (30–130 m) of these data (Fig. 5, Ward and Kilpatrick, 1991) yields a rate of 4.8 x10^{-2} mmol m^{-2} d^{-1}. The modeling work of Yakushev and Neretin (1997) and Gregoire and Lacroix (2002) produced estimates of 5.6×10^{-1} and 2.8×10^{-1} mmol m^{-2} d^{-1}, respectively. While these rates are small relative to other terms in the Black Sea N budget, Gregoire et al. (2004) have argued from model calculations that steady state solutions for this system require denitrification of this magnitude in order to prevent the progressive accumulation of riverine NO_3^- in the CIL.

It has been suggested that NH_4^+ diffusing upward to the SOL may be reduced to N_2 via reactions with MnO_2 (Murray et al., 1995; Luther et al., 1997; Yakushev and Neretin, 1997; Oguz et al., 2000, 2001b); however, there are no published estimates for the rates of these reactions.

Kuypers et al. (2003) have recently reported the discovery of free-living anaerobic NH_4^+ oxidizers in the Black Sea capable of the ‘‘anammox’’ reaction in the SOL lying between the CIL and the deeper anoxic water. They estimate that these microbes are oxidizing NH_4^+ to N_2 using NO_2^- as an electron acceptor in a 1:1 molar ratio to produce N_2 at a rate of about 2.0×10^{-1} mmol N m^2 d^{-1}. This rate of NH_4^+ oxidation is slightly more than their estimated upward flux of NH_4^+ from the deep anoxic reservoir (1.2×10^{-1} mmol N m^2 d^{-1}).

We have constructed a schematic representation of the processes that supply and remove N as $NO_2^- + NO_3^-$, NH_4^+ and N_2 in the upper oxygenated waters of the Black Sea (Fig. 13) and the resulting budget summary (Table 4). Units were standardized to mol y^{-1} for the offshore waters using an area of 3.1×10^5 km^2 (Sorokin, 2002) and appropriate depth ranges for integration. Values are from our measurements, unless otherwise noted with literature citations, extrapolated to a full year. Some of these annual extrapolations were detailed in the presentation and discussion of results above.

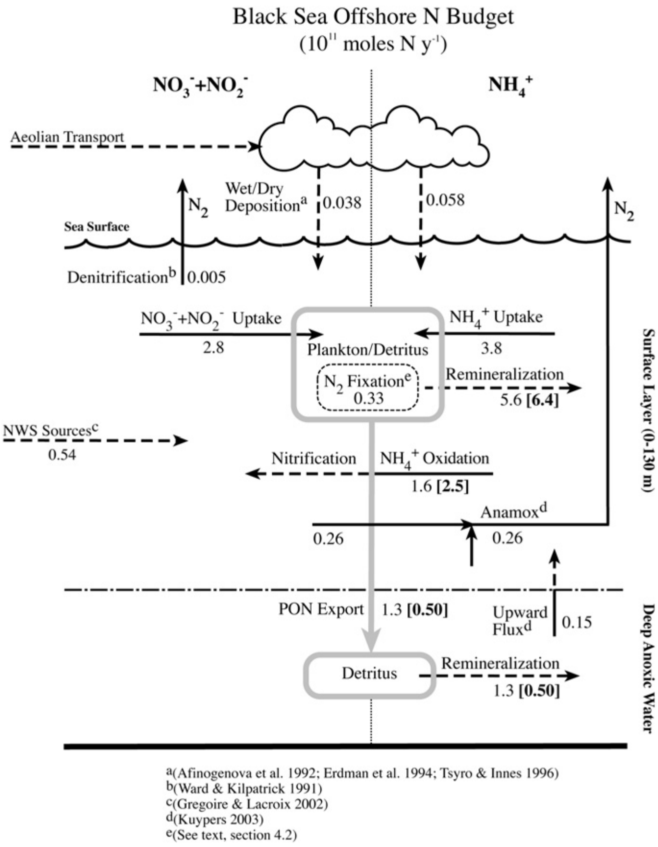

Fig. 13. Schematic representation of the Black Sea offshore annual N budget (Section 4.5). Dashed arrows are input terms and solid arrows are output terms. Brackets indicate values adjusted to conserve N, assuming steady state PON concentration over an annual period. See text for further explanation.

We further refined the budget shown in Fig. 13 to include partitioning the 130 m surface layer into a 30 m euphotic layer and the underlying CIL. While this allowed for a more detailed examination of fluxes within and between these layers, the simpler version presented here is sufficient for ascertaining broad balances and imbalances among our observations and published rates for important processes in the N budget.

Phytoplankton uptake of NH_4^+ and NO_3^-, remineralization of NH_4^+, and nitrification dominate this budget. Among these values, the more limited data for nitrification result in higher uncertainty for the extrapolation of this rate to an annual value for the entire Black Sea. The turnover time for the NO_3^- content of the CIL

Table 4
Black Sea offshore N budget summary for the upper water column (0–130 m). Brackets indicate values adjusted to balance budget (see text for explanation)

	$NO_2^- + NO_3^-$		NH_4^+		PON	
	Initial	Adjusted	Initial	Adjusted	Initial	Adjusted
Supply	2.2	[3.1]	5.8	[6.6]	6.9	6.9
Consumption	3.1	3.1	5.7	6.6	5.6	6.4
Δ	−0.9	0.0	0.1	0.0	1.3	0.50[a]

[a] Export to deep water.

mentioned above points to the potentially large significance of an imbalance for NO_3^-, such as indicated in this budget. Rates of nitrification will be influenced by the particle size and composition of sinking detrital material. Large and dense particles are more likely to sink out of the oxygenated waters before their organic N contents can be remineralized. Thus there are definitive food web linkages and feedbacks in the nitrification process.

Source and consumption terms for NH_4^+ are more nearly in balance (Table 4, Fig. 13). The phytoplankton uptake rate for NH_4^+ is the best known of these process rates. Nitrification also appears as a significant loss term for NH_4^+ in the budget, and it is comparable to about half the total remineralization term for NH_4^+. As with the discussion above regarding extrapolations of annual rates of nitrification, we also have lower confidence in the annual extrapolations of NH_4^+ remineralization relative to the phytoplankton NH_4^+ uptake rates.

Assuming steady state for the PON concentration (plankton plus detritus) in the oxygenated waters over an annual period, our compilations of observed and literature values extrapolated for this period (Table 4, Fig. 13) have NH_4^+ consumption comparable to supply, NO_3^- consumed in excess of supply (-0.9×10^{11} mol y^{-1}). Such an imbalance in NO_3^- is unlikely, and two adjustments in this budget (Table 4, Fig. 13) bring NO_3^- consumption and supply into balance, maintain balance for NH_4^+, and result in a smaller calculated particle flux to depth.

As stated above, one of the major processes in this budget least well known with precision is the rate of NH_4^+ oxidation, or nitrification. Our observed value is greater than the value observed by Ward and Kilpatrick (1991) and half the value estimated from model studies by Yakushev and Neretin (1997). Increasing our value by 60% to 2.5×10^{11} mol y^{-1} (midway to the Yakushev and Neretin value) would increase NO_3^- supply to meet the extrapolated consumption value. To maintain budget balance for NH_4^+, our extrapolated remineralization rate would then need to increase by only 13% to 6.4×10^{11} mol y^{-1}. A combined effect of these two adjustments is a reduction in estimated flux of PON to deep anoxic waters to 0.50×10^{11} mol y^{-1}, 8% of the total plankton N production rate. Little is known about the rates of particle flux into the deep anoxic waters of the Black Sea; however, this result is consistent with one published study which reported that 95% of the euphotic zone particle flux is remineralized in the CIL, based on sediment trap experiments conducted in May 1988 (Karl and Knauer, 1991).

Consideration of the new production vs. particle flux paradigm (Eppley and Peterson, 1979) requires elaboration in the context of the Black Sea system. Under equilibrium conditions (Fig. 13) the sum of allochthonous sources of N – riverine (NO_3^-), N_2 fixation, atmospheric deposition ($NO_3^- + NH_4^+$), and upward flux (NH_4^+) – equals 1.1×10^{11} y^{-1} and is comparable to the estimated particle export rate plus losses due to anammox and denitrification (1.0×10^{11} y^{-1}).

4.6. Climate change effects on the Black Sea ecosystem

An interpretation of long-term hydrographic data in the Black Sea reveals that, in addition to long-term changes in the inputs from land-based sources, climate fluctuations have also influenced this ecosystem (Oguz et al., 2003). The 1970s and 1980s had relatively warm winters, and thus less winter convective mixing. During the first half of the 1990s (especially in the years of 1992 and 1993) the coldest winters in the last four decades occurred. This resulted in greater winter mixing, enhanced nutrient transport from nutrient rich deeper layers, and more production in the surface layer of the Black Sea (Mikaelyan, 1997; Yunev et al., 2002). Since 1993, a milder climate has returned to the region and average sea surface temperatures increased by as much as 3 °C in the central surface waters (Oguz et al., submitted). This increase in temperature together with changes in nutrient input are thought to have contributed to changes in lower trophic level plankton abundance and composition (Mikaelyan, 1997; Bologa et al., 1999; Bodeanu et al., 2003; Oguz et al., 2003).

Responses of the Black Sea ecosystem to variations in temperature over the past few decades suggest strong sensitivity of this system to shifts in regional climate. Climate models forced by IPCC emission scenario B2 project about 2 °C warmer for the land surrounding the Black Sea by year 2050 (Kundzewicz and Parry, 2001). If inter-decadal temperature variations such as those experienced over the last three decades were to be superimposed upon the projected regional warming, more persistent stratification during future warmer periods could result in greater N limitation of planktonic production. If riverine input of N to the Black Sea were unchanged, this increased stratification and reduced plankton utilization could result in an increase in the CIL NO_3^- content.

These climate scenarios also project warmer conditions and diminished precipitation for the entire watershed of the Danube. Climate change is, however, only one of several factors that could influence the discharge of riverine N to the Black Sea over the next few decades. The CIL residence time calculations discussed in Section 4.5 demonstrate tight coupling between riverine input and plankton consumption processes for NO_3^- in the Black Sea. A dramatic increase or decrease in riverine N input, even without a shift in climate, would ripple throughout the Black Sea ecosystem within a few years.

5. Conclusions

Allochthonous processes that supply N to the Cold Intermediate Layer (CIL), which lies below the surface mixed layer, and microbial processes within the CIL strongly influence the availability of N for primary production in the Black Sea. Multiple unique aspects of the Black Sea N cycle, and perhaps the unusual food web of the Black Sea as well, give rise to a relatively high *f*-ratio for this planktonic ecosystem. It ranges from 0.25 in spring following the fall-winter bloom to 0.46 in the autumn at the onset of the bloom. We extrapolate an annual mean *f*-ratio of 0.38. The uptake of NO_3^- by phytoplankton in this system was less sensitive to NH_4^+ concentration than has been observed in many oceanic waters. The seasonal shift in nutrient uptake kinetics was consistent with the seasonality of nutrient availability.

The rate of *in situ* NO_2^- production (and inferred nitrification) for the offshore waters was 1.6×10^{11} mol y^{-1}, three times the published estimates for NO_3^- supply from the NW Shelf (NWS) region, which results largely from riverine discharges of N. This rate of nitrification implies a 250-day turnover time for NO_3^- content of the CIL. Phytoplankton $NO_3^- + NO_2^-$ uptake, 2.8×10^{11} mol y^{-1}, implies turnover of the CIL NO_3^- content in about 140 days.

Remineralization of NH_4^+ within the mixed layer occurs at 25% the rate of NH_4^+ utilization by phytoplankton, 3.8×10^{11} mol y^{-1}, implying phytoplankton dependence on NH_4^+ flux from below. Within the CIL NH_4^+ is consumed by NO_2^- production (and implied nitrification) at a rate that is similar to the rate of NH_4^+ remineralization from organic matter.

The most uncertain of our measured values are the rates of NH_4^+ remineralization and oxidation (nitrification). By using the mean of our measured rate for the NH_4^+ oxidation and a published value from a modeling study (a 60% increase over our value) and by making a modest (+13%) adjustment in our value for NH_4^+ remineralization our N budget for the oxygenated waters of the Black Sea can be brought into equilibration. The balanced budget implies an annual export of 8% of primary production to the deep anoxic waters of the Black Sea and permits a direct comparison of allochthonous sources of N to total N production in this unusual aquatic ecosystem, resulting in an adjusted *f*-ratio of 0.17, which is reconciled with particulate export when the budgeted loses due to anammox and denitrification are included.

Recent interest in the anammox reaction will likely stimulate new research on these processes, and clearly more work is needed to refine estimates of the N_2 fixation rate. However, both of these rates are likely to remain of minor importance to the overall N budget of the Black Sea. The most important terms to know with greater precision are the NH_4^+ remineralization and oxidation (nitrification) rates and the riverine supply term. The *in situ* supply and consumption terms for NH_4^+ will be influenced by changes in the food web of the Black Sea. Riverine discharge of N is sensitive to regional climate and anthropogenic processes within the watershed. The intensity of winter mixing within the basin, which supplies new N for the fall-winter blooms, also responds to climate. Oscillations in winter temperature over the past few decades allow some inference as to how the Black Sea N budget may be affected by warmer conditions projected for this region.

Acknowledgments

NSF Support (J.J. McCarthy.): OCE-9729793, OCE-9731232. NSF Support (J.W. Murray): OCE-0081118. NATO Science for Peace Programme (METU, IMS), TUBITAK National Oceanographic Programme (METU, IMS). We thank the captains and crews of R/V *Bilim* and R/V *Knorr*, Dr. S. Tugrul and IMS technicians for nutrient analyses and assistance with deck operations on both vessels, Dr. O. Krivenko (IBSS, Ukraine) for valuable unpublished data, Dr. J.W. Murray for providing the opportunity to join his 2001 study aboard R/V *Knorr*, and Drs. S. Besiktepe (director, IMS) and T. Oguz (IMS) for their support throughout the project.

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