Nitrogen cycling in the off-shore waters of the Southern Black Sea

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Abstract- Planktonic nitrogen productivity and relative importance of NO_3, NO_2 and NH_4 on productivity in the Black Sea were estimated by direct measurements. 1998 – 2001 period was characterised by more intense N-productivity in autumn then in spring. Concentrations of dissolved inorganic nitrogen species in the euphotic zone were low and their turnover rates were less than a day. Though the main nitrogen source utilised by phytoplankton was NH_4, annual 'f-ratio' was unexpectedly high, which could not be compensated by the estimated budget of new nitrogen input.

Keywords- New production, f-ratio, nitrogen cycle, Black Sea

Introduction

Due to the loss of nitrogen via denitrification in the suboxic layer, primary productivity at the off-shore waters of the Black Sea is thought to be limited by nitrogen. Many of the models regarding variations in the ecosystem of the Black Sea, therefore, have generally been based on nitrogen (Oğuz et al., 2001 and references cited therein). However, until now, direct measurements on nitrogen dynamics were limited to a couple of studies (Krivenko et al., 1998; Ward and Kilpatrick, 1991). This study focuses on filling some of the existing gaps on the direct measurements of nitrogenous nutrient utilisation by phytoplankton, especially on the relative importance of new and regenerated nutrients. A co-operative research entitled as 'New Production and Nitrogen Cycling In The Off-shore Regions of The Black Sea', was conducted between Museum of Comparative Zoology, Harvard University (USA) and Institute of Marine Sciences, METU (TURKEY). The main purpose of the study was to investigate the relative importance of NO_3, NO_2 and NH_4 in planktonic nitrogen productivity in the euphotic zone of the Black Sea. NH_4 oxidation/ remineralisation rates, NO_3 and NH_4 uptake kinetics, potential for nitrogen fixation were also studied.

Sampling and Analytical Methods

The experiments were performed at a total 17 stations in April and September 1998 and in September-October-99 aboard R/V BİLİM and in May-01 aboard R/V KNORR, covering both central Black Sea and its shelf-break regions on rim-current

(Fig. 1). Daily cycle of nitrogen uptake rates was followed as first light (FL), mid-day (MD) and night-time (NT) measurements. The measurements for NO_3, NO_2, NH_4 (together called dissolved inorganic nitrogen, DIN) uptake rate, as well as NH_4 remineralisation and oxidation rate measurements were done by using isotope tracer methods (McCarthy et al., 1999 and references cited therein). As accurate measurement of low NH_4 concentration in the euphotic zone is important to precisely measure rate of NH_4 uptake, high sensitivity NH_4 measurements (± 3 nM) were carried out (Brzezinsky, 1988) by applying solid phase extraction (McCarthy et al., 1996), except for May 2001. Nitrogen fixation was determined at a few stations in September-October 1999 and May 2001 by the method of Montoya et al., 1996.

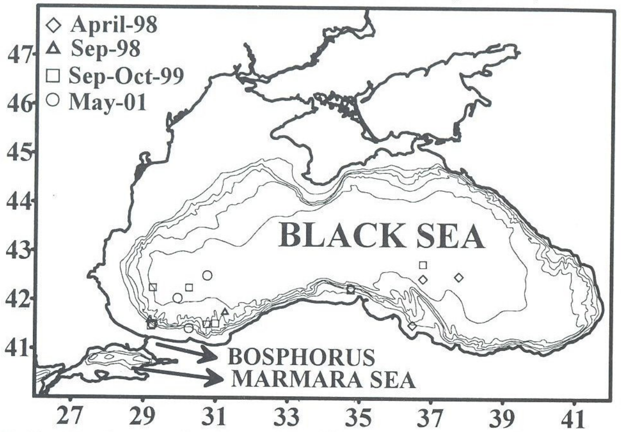

Fig. 1. Station location map for this study. Different cruises are represented by different symbols

Results and Discussion

Results of this study are discussed in detail in McCarthy et al. (manuscript in preparation), and only a brief summary is given here (Table 1). Seasonall averaged integrated nitrogen production rate for the euphotic zone ranged between 2 and 9 $mmolm^{-2}d^{-1}$. In May-01, both nitrogen and carbon productivity was significantly reduced (Table 1), representing heterogenous composition of euphotic zone SPOM pool, post-bloom conditions and/or mixotrophy, as discussed in more detail in Çoban-Yıldız et al., 2003 a,b. Nutrient concentrations in the euphotic zone were low and the residence time of DIN was a day or less (Table 1). NH_4 measurements carried out by solid-phase extraction technique yielded euphotic zone average concentrations less than 0.05 μM except for September-98 (Table 1). The pie charts (Fig. 2) show the relative contribution of the three nitrogen species to N-productivity. NH_4 was the main N source utilised, yielding f-ratios ranging between 0.22 and 0.43 (Table 1).

Table 1. Euphotic zone integrated total nitrogen ($\rho NO_3+\rho NO_2+\rho NH_4$) and carbon productivity, turnover rate of total dissolved inorganic nitrogen ($NO_3+NO_2+NO_3$), f-ratio and NH_4 concentrations for the euphotic zone of the Black Sea (cruise mean ± standard deviation where standard deviation represents regional variation).

Season	Σ N-prod. ($mmolNm^{-2}d^{-1}$)	Net C-prod. ($mmolCm^{-2}d^{-1}$)	DIN turnover rate (day)	f-ratio ($\rho NO_3/\rho DIN$)	NH_4 (μM)
April-98	6.7 ± 2.1	35.0±5.9	0.7 ± 0.2	0.26 ± 0.07	0.039 ± 0.024
Sep-98	7.4 ± 4.1	30.8	1.3 ± 0.0	0.37 ± 0.01	0.091 ± 0.007
Sep-Oct-99	9.2 ± 3.1	38.1±16.9	0.6 ± 0.5	0.43 ± 0.10	0.035 ± 0.013
May-01	2.3 ± 0.7	20.7±9.1	1.1 ± 0.5	0.22 ± 0.04	0.049 ± 0.003

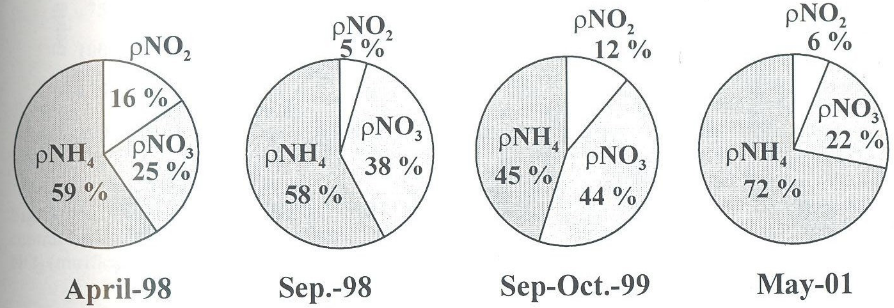

Fig. 2. Relative contribution of NH_4, NO_3 and NO_2 to total nitrogen productivity in the Black Sea

As clearly depicted in Fig. 3, seasonal nitrogen productivity suggests more intense autumn and less pronounced spring blooms for 1998 – 2001 period, being in very good agreement with the recent ecological and climatological alterations reported (Oğuz et al., 2002, Oğuz et al., 2003). Higher f-ratios calculated for autumn blooms indicate substantial contribution of NO_3 to nitrogen productivity. High autumn productivity, therefore, was not only as a result of intense regeneration after mezozooplankton growth (Oğuz et al., 2003), but also due to shelf-off shore interaction due to mezoscale processes and lateral transports (Oğuz et al., 2002).

Although the number of measurements is insufficient to calculate an annual N-productivity, combined with the data of Krivenko et al. (1998) and by using a polynomial fit (Fig. 4), a rough annual nitrogen productivity was estimated. We should note the decadal gap between the two data sets and flexibility of the polynomial fit, which would decrease the accuracy of the estimation. According to this, NO_3 based productivity of the Black Sea (0.83 $molNm^{-2}yr^{-1}$ or 4.9 x 10^6 tons Ny^{-1}) corresponds to 46 % of total nitrogen productivity (1.8 $molNm^{-2}yr^{-1}$ or 11 x 10^6 tons Ny^{-1}). For comparison, direct calculation from the average of 4 cruises yields slightly higher annual production rate (2.3 molNm^{-2}y^{-1}) and lower f-ratio (0.32).

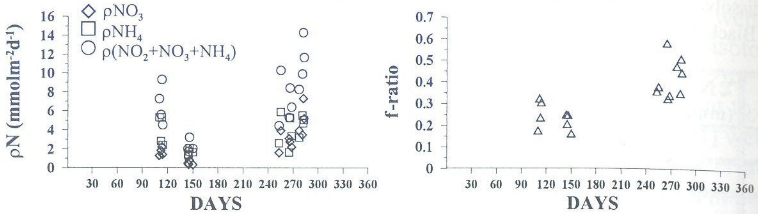

Fig. 3. Seasonal variations in nitrogen productivity and corresponding f-ratio during 1998-2001

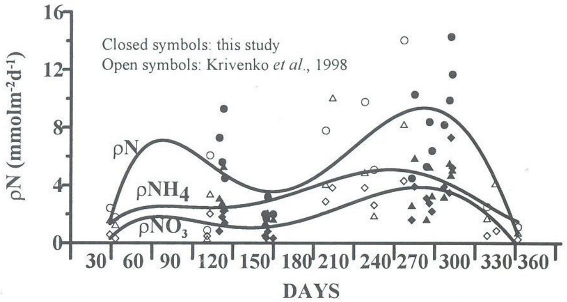

Fig. 4. Seasonality in annual nitrogen productivity estimated by direct measurements

Potential main sources of new nitrogen to the Black Sea include export of Danube River DIN to the open sea, atmospheric deposition, and input from depth by physical processes. Annual nitrogen budget for the Black Sea is estimated referring to several studies, which considered these sources. Export of Danube DIN to the open sea and annual DIN input from depth by physical processes have been estimated to be 7.6 x 10^5 tons Ny^{-1} and 4.4 x 10^5 tons Ny^{-1} respectively, by a modelling study (Gregoire & Lacroix, 2002). Atmospheric deposition has been calculated as ~ 5 x 10^5 tons Ny^{-1} based on measurements (Kubilay et al., 1995; Omar el Agha, 2000) and as ~ 1.8 x 10^5 tons Ny^{-1}, based on modelling studies (Erdman et al., 1994; Tsyro and Innes, 1996). These new nitrogen sources correspond roughly to 8, 2-3 and 4 % (together being less than 20 %) of total annual N-productivity of 11 x10^6 tons Ny^{-1} estimated by this study and can not compensate for the annual f-ratio of 0.46 or cruise means of 0.33. Our limited data on N_2 fixation compensate for 0 % (in May 2001) to 15 % (in September – October 1999) of total nitrogen production rate of corresponding seasons.

It should be noted that the f-ratio was obtained by dividing NO_3-based annual production rate by total annual N-productivity as it has been applied for open-ocean, where new production is regulated by the supply of NO_3 from depth. In the Black

Sea,on the other hand, deep-ocean reservoir is NH_4, which has been lost from the system as N_2 due to denitrification processes. Very active nitrification zone at the bottom of the euphotic layer forms a strong nitracline close to the euphotic zone, especially in central region (Fig. 5). The residence time of NO_3 at the bottom of the euphotic zone, therefore seems to be too short to be considered as 'new nitrogen' and caution is required in applying 'f-ratio' to the Black Sea.

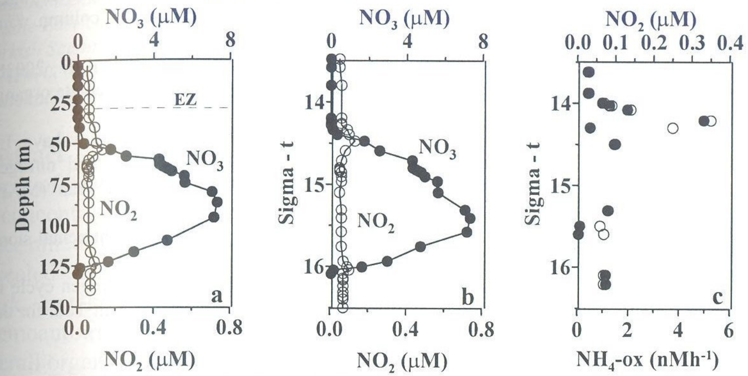

Fig. 5. Vertical distribution of NO_2 and NO_2 concentrations against (a) depth and (b) density at eastern central basin and (c) composite profiles of NO_2 concentrations (open symbols) and NH_4 oxidation rates to NO_2 (nitrification rate, solid symbols) in spring 1998.

Conclusion

1- In recent years, rate of nitrogen production in the Black Sea was more intense in autumn and less pronounced in spring.
2- In the Black Sea, the main source of nitrogen utilised is NH_4, while contribution of NO_3 increased in autumn.
3- Residence time of dissolved nitrogen in the euphotic zone during studied period was less than a day.
4- Available estimations on new nitrogen input to the euphotic zone of the Black Sea corresponds to less than 20 % of annual N-production rate estimated by this study.
5- N_2 fixation seems to play a role in nitrogen supply and their potential contribution in supplying new nitrogen to the euphotic zone should be clarified.
6- Application of 'f-ratio' to the Black Sea needs special consideration.

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