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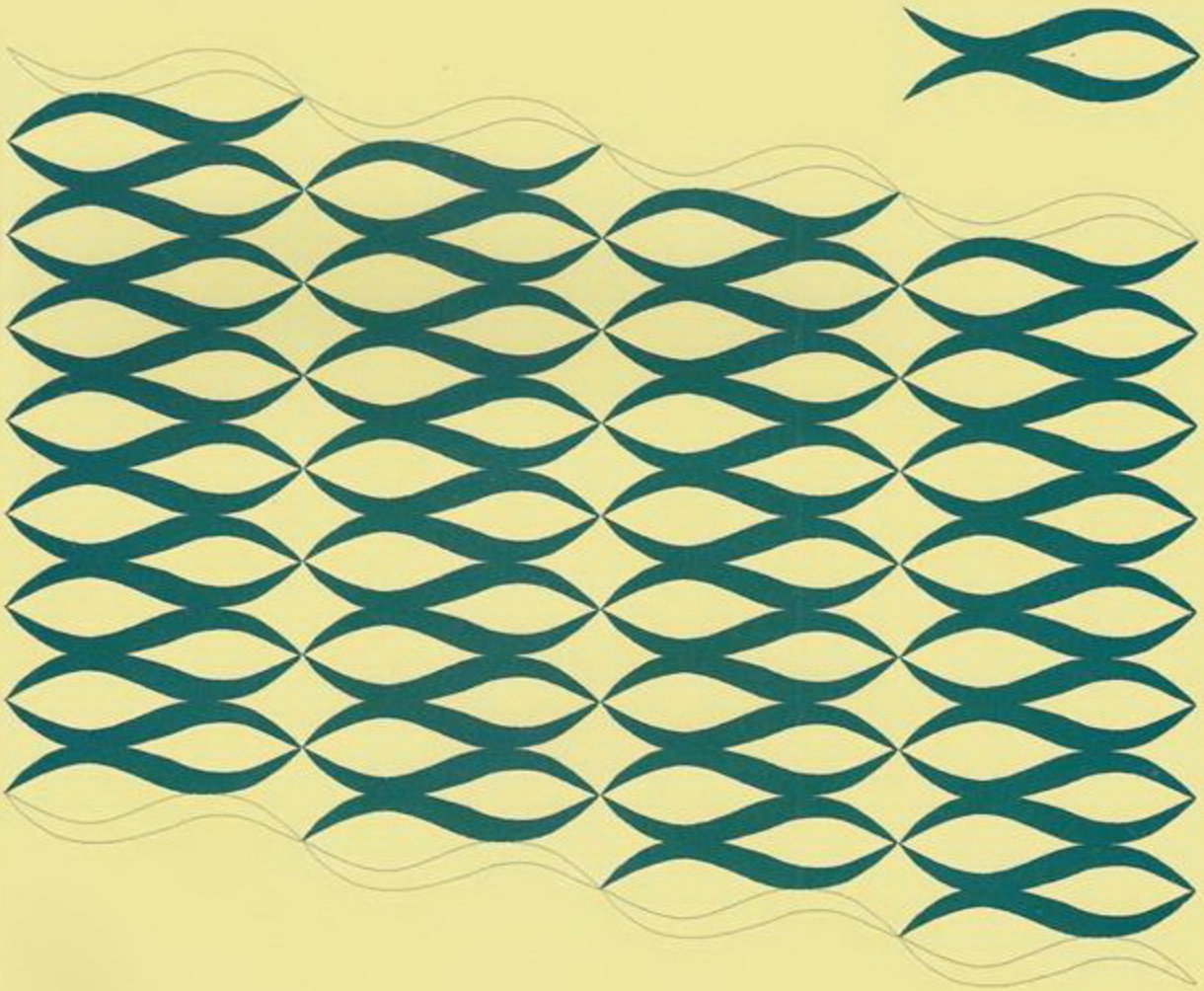

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The Black Sea Nitrogen Budget Revision in Accordance with Recent Atmospheric Deposition Study

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Abstract

To date, most of published nitrogen (N) budget assessments for marine ecosystems (particularly, the Black Sea) are, unfortunately, rather general and incomprehensive due to regular atmospheric load underestimation and frequent neglecting of some relevant N cycling constituents (e.g., N_2 fixation rate, dumping, shipping, gaseous emission, chemo denitrification). In this study it has been argued that atmospheric input was systematically underestimated in most of previous assessments of, since organic N constituents were not included. It has been experimentally found that organic part in atmospheric deposition was dominant (~66% or 1777 ± 678 kg N km^{-2}) N pollutant constituent, while DIN was ~34% (907 ± 361 kg N km^{-2}) only during 2011–2012 campaign. Besides, contributions of water soluble (24.3%) and particulate (28.3%) organic N were distributed approximately equally in atmospheric deposition. Overall, an important role of atmospheric N organic pollutants in deposition, which was neglected before, has been proved. As a results, an average annual atmospheric bulk deposition rate of total N (TN) has been calculated as 2684±316 kg N km^{-2} based on long-term experimental dataset, thus atmospheric TN load for the whole Black Sea area has been estimated as 1159 ± 136 Gg N.

During this study N budget for the Black Sea has been revised and its constituents have been amended. According to presented estimation of N balance the Black Sea is under strong pressure of anthropogenic N load (approximately 798-1692 Gg N y^{-1}), mainly from atmosphere and the north-western rivers. Weak understudied points and uncertainties, to which the Black Sea countries' research community should pay attention and focus its efforts immediately, have been highlighted.

Keywords:Black Sea, atmospheric deposition, N budget, TN, TON, DIN, WSON.

Introduction

Nitrogen (N) is a key nutritional element for any living form both on land and in sea, but only reactive N (N_r) is ubiquitously bio-available for the most of organisms (Galloway *et al.*, 2008), except those that can directly fixate di-nitrogen (N_2). It is understood that terrestrial and marine N cycles are linked closely. Since the globe population grew up dramatically and huge amount of N_r was already used (fossil and anthropogenic synthesized) to achieve food production demands during last century, the N use consequences have been becoming more important and urgent over the years (Gruber and Galloway, 2008; ENA, 2011). Many efforts of scientific society in past decades were made to investigate N cycling with peculiarities of different ecosystems around the globe, determinate main sources, sinks, crucial N species, label main threats to develop basic ways to mitigate impact of N on the environment and humans (ENA, 2011). The main outputs of N policy regulation were documented in International conventions and protocols (see ENA, 2011 for full list), including those connected to the Black Sea environment (*e.g.* 1979 UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP), 1988 Sofia protocol on Nitrogen oxide (NO_x) emissions, 1992 Bucharest Convention on the Protection of the Black Sea Against Pollution, 1992 Convention on transboundary Waters and International Lakes, 1994 UN Framework Convention on Climate Change (UNFCCC), 1997 Kyoto Protocol, 1999 Gothenburg Protocol on acidification, eutrophication and ground-level ozone). Growing interest and concern for numerous potential short-term and long-term threats, caused by N, have recently led to the first European Nitrogen Assessment (ENA, 2011), highlighting N problem in different ecosystems world widely.

N is the limiting factor for primary productivity, i.e. phytoplankton growth in marine ecosystem. (Capone *et al.*, 2008; Gruber, 2008). Due to stratification, which prevents mixing of nutrients

between water layers, an abundant N could be stored in certain layer at certain depth (Voss *et al.*, 2011). Unfortunately most of previous assessments regarding N impact on marine ecosystem are rather general and not comprehensive. Previously estimated N budgets for the offshore (Gregoire and Lacroix, 2002; McCarthy *et al.*, 2007), the north-western part (Gregoire and Friedrich, 2004; Gregoire and Beckers, 2004) and the whole area (Teodoru *et al.*, 2007) of the Black Sea were underestimated at least related to atmospheric load and did not often consider relevant processes (e.g., N_2 fixation rate, dumping, shipping, gaseous emission (NH_3, N_2O, organic N), chemodenitrification). Further complex investigations with modern approaches are urgently needed to re-consider N budget in each concrete marine ecosystem, since atmospheric input has been increasing significantly in past decades and nowadays is the dominant source of N_r for open sea regions (Medinets and Medinets, 2012; Moore *et al.*, 2013). Thus, for instance, peculiarities of N exchange in the Black Sea demand study due to periodical eutrophication events, which occur on huge areas (Capone *et al.*, 2008; Medinets and Medinets, 2012; Moore *et al.*, 2013). The driver of such harmful occurrences is likely the excess of atmospheric deposited N, which could be presented by both organic and inorganic forms. However no long-term measurements, consequently no qualitative assessment of the total organic N (TON) input, as well as total N (TN) load, from the atmosphere to the Black Sea surface has been made up to date.

The aim of this work is to highlight the significant role of TON constituent, as well as estimate its contribution, which is usually neglected, to TN atmospheric deposition fluxes onto the sea surface and revise N budget for the Black Sea according to this experimental data. Moreover, in the framework of this study an advanced scheme of the Black Sea N budget has been proposed, where weak understudied points and uncertainties, to which the Black Sea countries' research community should pay attention and focus its efforts, have been identified.

Materials and Methods

Study Area

Experimental part of this study has been carried out on Marine Research Station (MRS) "Zmiinyi Island" of the Odessa National I.I. Mechnikov University (ONU), which is located on the Zmiinyi Island (45°15'22.0" N and 30°12'03.8" E) in the north-western part of the Black Sea (NWBS) about 35-40 km far from the Danube Delta and being due to the distance from the anthropogenic sources of atmospheric pollution a representative site for atmospheric background monitoring (Medinets *et al.*, 2008; Medinets and Medinets, 2010, 2012).

Sampling and Analysis

Atmospheric monitoring programme of the MRS "Zmiinyi Island" included sampling and chemical analysis of atmospheric precipitation and depositions, as well as obligatory meteorological observations during sampling events. These studies were based on standard methods and recommendations from the EMEP manual (EMEP, 2001). Passive bulk deposition sampler, recommended by the EMEP (EMEP, 2001), was used (Medinets and Medinets, 2012) to collect atmospheric bulk deposition. As a collector for aerosol particles we used the special hermetic bag, previously washed by de-ionised water (DI-H_2O), exposed during a fortnight or a month. Bulk atmospheric depositions and precipitation on the island were usually sampled from May to December in 2011 and 2012. Monthly bulk depositions were calculated as a sum of 2 fortnightly or as single monthly deposition, accurately recalculated into appropriate calendar month period. The basic methods applied during this study for N compounds determination has been previously described by Medinets and Medinets (2012) in detail. Ionic chromatograph Personal IC 790 (Metrohm Ltd, Switzerland) was used for measurements of dissolved inorganic N compounds (DIN) such as ammonium, nitrate and nitrite. Appropriate ISO standards were used for all the above analyses. TN in unfiltered and water soluble TN (WSTN) in filtered deposition samples were determined using persulphate oxidation method (RD, 2007). Water insoluble TN (WITN) (presumably consists of particulate organic N (PON)) has been calculated as difference between TN - WSTN. TON in the samples was calculated as a difference between TN and DIN, while water soluble organic N (WSON) was derived as a difference between WSTN and DIN. WSON in atmospheric deposition is an equivalent to dissolved organic N (DON) in sea water.

Statistical Analysis

Standard statistical approaches including correlation analysis ($P<0.05$) have been applied to find interrelationships between studied constitutes. Significance tests for comparison of the average values using Student t-test (normal distribution) have been performed. All the analyses have been carried out with STATISTICA (version 6.1 for Windows, StatSoft, Inc., 1984-2004). Graphical visualisation has been drawn using MS Excel 2010.

Results and Discussion

Atmospheric N Bulk Deposition (Field Measurements)

Firstly we have carried out long-term (8 months per year) measurements of TN deposition with

assessment of inorganic and organic constituents during 2011-2012. Monthly average TN deposition was 224±162 kg N km^{-2} for the entire investigated period with maximum of 571 kg N km^{-2} in May 2012 and minimum of 54 kg N km^{-2} in August 2012 (Figure 1). No statistically significant correlation between TN and precipitation amount has been found for whole period. However, strong correlations with those variables have been shown both for 2011 ($r=0.86$; $P<0.01$) and 2012 ($r=0.85$; $P<0.05$). It is noteworthy that in 2012 only 6 months period (July - December) has been used for correlation analysis since total precipitation amounts for May and June were very approximate due to failure of equipment.

Deposited DIN monthly average rate made 76±65 kg N km^{-2} for the study period; maximum (232 kg N km^{-2}) was observed in June 2012, minimum value (5.6 kg N km^{-2}) - in August 2012 (Figure 1). The average contribution of NH_4^+ to DIN was a bit less (46.2±32.6%) than that of NO3- (53.3±32.9%). Maximum NH_4^+ inputs (86.7-88.3%) were registered in May 2011 and 2012 as well as in October 2011, minimum (1.0-1.4%) - in November 2011 and 2012. Strong correlation ($r=0.74$; $P<0.05$) has been found between DIN and amount of precipitation for 2011-2012, mainly due to significant correlation between ammonium and precipitation ($r=0.73$; $P<0.01$). The latter has confirmed previous findings (Medinets and Medinets, 2012) that scavenging within rain is important way for NH_4^+ deposition. Meanwhile no statistically significant correlation between nitrate and rainfall was demonstrated.

Water soluble constituents of TN (i.e. WSTN) had strong correlation coefficient ($r=0.86$; $P<0.05$) with precipitation (Figure 1) for July–December 2012 period. However, such strong relationship is likely to be attributed to DIN constituent (mainly due to NH_4^+, which demonstrated strong correlation ($r=0.83$; $P<0.05$) with rain water amount), rather than WSON constituent, which showed no statistically significant correlation with precipitation. Inasmuch as WITN (presumably presented by PON) had also no significant correlation with precipitation as well as WSON, it seems to be suggested that dry deposition can be important process for organic constituents scavenging from atmosphere. Though more experimental data are needed to argue the latter suggestion.

It has been found that annual bulk deposition of TN on the Black Sea surface was 2908 kg N km^{-2} for 2011 and 2460 kg N km^{-2} for 2012, including DIN contribution of 652 kg N km^{-2} and 1163 kg N km^{-2}, respectively (Figure 2). The average value of TN bulk deposition for 2011-2012 made 2684±316 kg N km^{-2}, including 907±361 kg N km^{-2} of DIN. Hence all previous datasets including recent estimations for 2003-2007 (Medinets and Medinets, 2008) and 2004-2010 (Medinets and Medinets, 2012) consisted only of DIN data, consequently underestimated the real atmospheric N load into the sea. Moreover, aerosol removing by dry deposition from atmosphere has been recently shown as a prevailing way for the Black Sea open waters (Medinets and Medinets, 2012). They have found that for ammonium (dominant N species in atmospheric deposition) both dry (51%) and wet (49%) pathways of removing were important, but for nitrate wet scavenging was the prevalent one (59%). It has been confirmed that for inorganic bulk deposition about 99% of ammonium and nitrate are transported into the near-water atmosphere around the Zmiinyi Island from the natural and anthropogenic continental sources and there was no significant inorganic N emission over the open sea (Medinets and Medinets, 2012).

Furthermore, the share of TON in atmospheric deposition for 2011-2012 has been *ca.* 66%

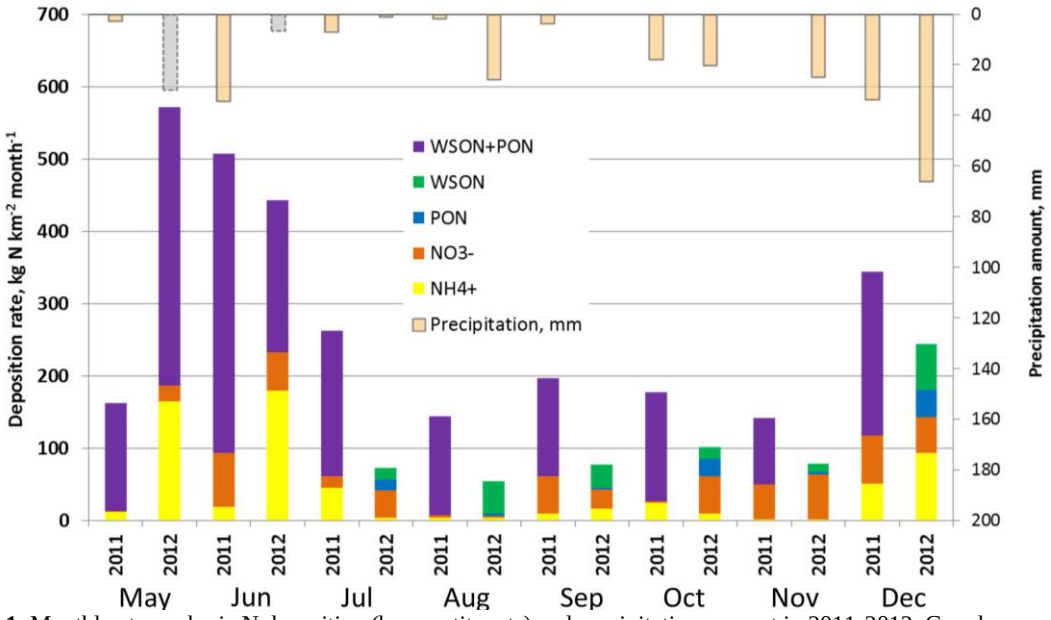

Figure 1. Monthly atmospheric N deposition (by constituents) and precipitation amount in 2011-2012. Grey bars mean approximate precipitation amount in May and June 2012 (due to equipment failure).

(1777±678 kg N km^{-2}), which agreed very well with recent preliminary finding by Medinets and Medinets (2012) and were comparable to literature data by Crockford *et al.* (1996), Cornell *et al.* (2003) and Miyazaki *et al.* (2011) for open sea regions. The results being presented have shown that TON (water soluble and insoluble) exceeded DIN of atmospheric deposition in absolute value by factor of 2-3 ($P<0.05$), which enables us to conclude that the estimated fluxes of N compounds into the Black Sea through atmosphere made before were rather underestimated. It has been stated that even recently both measured (Medinets *et al.*, 2008; Medinets and Medinets, 2010, 2012) and modelled (Bartnicki and Fagerli, 2008; EMEP, 2010; Im *et al.*, 2013) values regarding deposited TN to the sea surface were significantly underestimated without taking TON load into account or possibly due to use of irrelevant data. It has been shown that using of those outdated data (Afinogenova *et al.*, 1992; Erdman *et al.*, 1994; Kubilay *et al.*, 1995; Tsyro and Innes, 1996) seems to be unacceptable for any further estimating and modelling issues, leading to large underestimation of atmospheric scavenging influence on marine ecosystem.

Measurements of WSTN together with TN and DIN have been started in summer 2012, thus estimations of WSON (water soluble) and WITN (water insoluble) constituent contributions in TN became possible and have been done (Figure 3). According to preliminary results of 6 month long experiment, *ca.* 66% of WSTN was DIN and the rest was considered as WSON (~34%). Using these data I have estimated that WSON could total to *ca.* 24.4% of TN, hence WITN, which is likely to be presented by PON mainly, could make *ca.* 28.3%.

It is likely that various constituents of TN atmospheric deposition can have different impacts on ecosystem. For example, easy available water soluble N (both WSON and DIN) deposited on sea surface obviously increases primary productivity (triggering phytoplankton growth) and may also lead to eutrophication events. Meanwhile most of water insoluble N (presumably presented by PON mainly) can be settled out and stored/buried in anoxic sediments. However, the later assumption needs to be investigated further.

Budget of N in the Black Sea

Undoubtedly, to compose the detailed Black Sea N budget peculiarities of N turnover in both shallow water (oxic and OMZ layers) with depth up to 80-100 m (*ca.* 10% of the whole Black Sea area) and deep water part (sulfidic layer), where biogeochemical processes are different because of a presence of H_2S zone below productive layer, should be considered separately. However we have tried to concentrate on main players only, which means that to produce N budget scheme I have proposed and considered only basic input and output fluxes. Those available flux

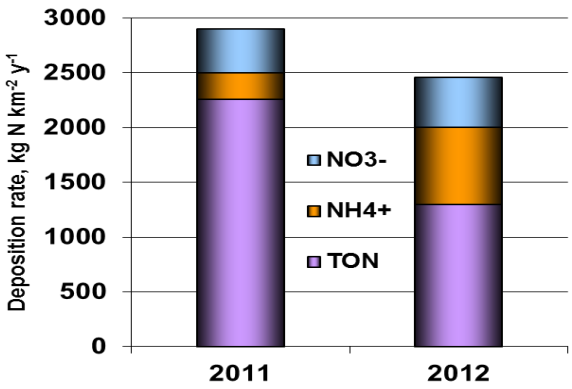

Figure 2. Atmospheric N deposition in 2011-2012.

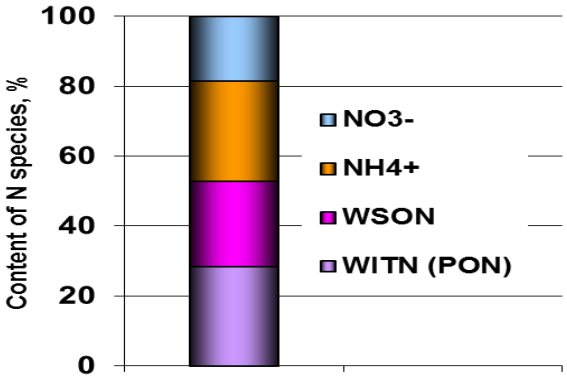

Figure 3. Contribution of N species into atmospheric N deposition in 2012.

data, measured or estimated for the Black Sea area have been recalculated for the whole sea area of 432,000 km^2 (BSC, 2012) per year period to identify and show significance of each source. Other un-available flux data have been mentioned and their possible importance has been discussed.

Incoming N Fluxes to the Sea

Atmospheric Input

Aerosols Bulk Deposition

For balance the average TN bulk deposition value for 2011-2012 (this study data) has been used, which made 2684±316 kg N km^{-2} or 1159±136 Gg N for the whole sea area, including 1777±678 kg N km^{-2} or 767±293 Gg N for the whole sea area of TON and only 907±361 kg N km^{-2} or 392±156 Gg N for the whole sea area of DIN. Thus it has been shown that deposited TN consisted of 66.2% of TON and 33.8% of DIN, i.e. average annual TON flux onto sea surface exceeded DIN flux two times. Relying on these results it is suggested that previous N deposition load assessments, that included DIN only, have been underestimated by *ca.* 66%.

Gases Scavenging

Up to date there were no direct measurements of N gases deposition, both inorganic (HNO_2, HNO_3, NO_x, NH_3) and organic (MPAN, PAN, PPN etc), to the Black Sea surface, but potential importance of such a way of N scavenging is known (Duce *et al.*, 1991; Capone *et al.*, 2008; Fowler *et al*., 2009). It was stated by Duce *et al.* (1991) that global ocean surface is a sink for tropospheric NO_x by way of both dry and wet deposition with globally estimated rate about 40 Gg N y^{-1}, excluding emission from ships. The highly reactive and soluble HNO_3 in gas form having high deposition velocity leads to large rates of deposition (Fowler *et al.*, 2009), *i. e.* is immediately absorbed by sea surface. Only limited data are available regarding NH_3 exchange in atmosphere-ocean system, Duce *et al.* (1991) roughly assessed NH_3 deposition rate as 16.7 Tg N y^{-1} for global ocean.

Riverine Input

Fluvial input has a huge effect on coastal waters ecosystems and is one of the strongest external pollution sources in the NWBS, where three big rivers join the sea. For balance scheme we used available data regarding riverine DIN load of the Danube (362.55 Gg N y^{-1}) into the Black Sea reported by TDA (2007) for the period 2003-2005. Inputs of TN from the Dnieper (11.2 Gg N y^{-1}) and the Dniester (22.8 Gg N y^{-1}) river basins to the sea were derived using UNDP (2003) and BSEP (1999) report data, covering 1996-2000 measurement period. Unfortunately there is no available datasets or evidence of direct measurements connected to organic N load from the Danube River into the Black Sea. Recently Oguz *et al.* (2008) proposed and used available data of biochemical oxygen demand of wastewater during decomposition occurring over a 5-day period (BOD5) for indirect estimation of DON input from rivers (Danube, Dniester, Dnieper and Bug), which was made for the BSC (2008). They assumed, based on Diego-McGlone *et al.* (2000) ratio of DON/BOD5 = ~0.3, that DON input from north-western rivers could be ~300 Gg N y^{-1} for 1997-1999 and 150 Gg N y^{-1} for 2000-2005. DON value is strongly connected with N pollution sources and their intensity in river basins and may vary dramatically (Oguz *et al.*, 2008). We have suggested that a mean value of high and low polluted periods (~225 Gg N y^{-1}) should be used, however we do not exclude that this value could have been underestimated. It is known that the Danube contribution to BOD5 load accounts for 80%. Since the Dnieper and the Dniester estimation was already made for TN (incl. DON) by UNDP (2003) and BSEP (1999), we had to increase the Danube N load 180 Gg N y^{-1} only. Thus we have assumed that total riverine input of TN from the main north-western rivers into the Black Sea was *ca.* 577 Gg N y^{-1}.

Coastal Input

Magnitudes of N pollutants input from land-bases sources (incl. small rivers) located near shore into the sea basin are available for period of 1996-2000 for each Black Sea riparian country (BSEP, 1999; UNDP, 2003). It was reported by UNDP (2003) and BSEP (1999) that TN loads were 75.5 Gg N y^{-1} for Bulgaria, 45.4 Gg N y^{-1} for Romania, 42.8 Gg N y^{-1} for Ukraine, 38.0 Gg N y^{-1} for Turkey, 13.5 Gg N y^{-1} for Russia and 1.6 Gg N y^{-1} for Georgia. Summarized N input from coastal sources was estimated as 217 Gg N y^{-1}.

Biological N_2 Fixation (BNF)

BNF activity was found globally in the entire water column: in pelagic zone, including upper euphotic (Foster *et al.*, 2006, 2007; Hewson *et al.*, 2007) and lower sub-oxic layer (McCarthy *et al.*, 2007), as well as in benthic zone (Capone, 1988, 2008), including seagrass (Smith *et al.*, 2004) and deep sea sediment habitants (d'Hondt *et al.*, 2004). Direct representative measurements of BNF *in situ* for the Black Sea are not available and the significance and rate of such process is still under debate. Only episodic results of experiments *in vitro* describing potential N_2 fixation rate and discovering abundance of N_2 fixating heterotrophs was reviewed by Sorokin (2002). He argued that N, which is needed for 10-20% of bacterial biomass production, can be supplied by N_2 fixation. Recently McCarthy *et al.* (2007), based

on ratio of bacterial production to phytoplankton production for ocean waters (~0.3) reported by Cole *et al.* (1998), have suggested that 10-20% of bacterial production is approximately 5% of primary production, thus roughly estimated N_2 fixation rate could be $0.33x10^{11}$ mol N y^{-1} or 462 Gg N y^{-1}. This estimation is still considered as the most precise one for the whole Black Sea.

Shipping

Shipping and recreation activity constituents are still understudied, but ought to be paid attention to and investigated in near future. For instance, average number of ships passing through Bosporus was already *ca.* 45,000 per year by 2000 (EIA, 2000), unsurprisingly nowadays this number could be much higher. Basically shipping is associated with NO_x, which increased dramatically in past decades from 2.2 Tg N in 1950 to 9.4 Tg N in 2001 for the global ocean (Eyring *et al.*, 2005). In view of the fact that NO_x is very short-living gas, it and/or its products are normally immediately deposited to the sea surface (Bange, 2008).

Dumping

It is known that dumping of dredged materials and pollutants into marine environment causes in the vicinity of dumpsites accumulation of pollutants in bottom sediments and secondary pollution of sea water. While almost all the dumping sites are located in the NWBS's shallow part with depth of under 30 m, it is quite natural that dredged spoils dumping by 15 main ports in the NWBS causes re-suspension of nutrients, DIN and DON in particular, and pollutants deposited in the dredged material increas the content of suspended matter in water, as well as stimulate the processes of secondary pollution of marine environment. For instance, Ukraine has constantly functioning sea dump sites in Odessa, Ilyichivsk, Kerch, Yuzhniy, Feodosiya, Sevastopol ports and site in the Danube River Delta (Dem`yanovskaya and Yangolenko, 2006). It was reported that in the last years volume of dredged spoils dumped in Ukrainian sea ports had tendency to increase (BSC, 2009). The data regarding N content in dredged materials and pollutants, which are dumped into the sea, are not reported for all the Black Sea countries, therefore the total volume of dredged materials and pollutants and accordingly the total volume of dumped N compounds are unknown (BSC, 2009).

Recently assessed percentage distribution of external N pollution sources, reported as 50% for atmospheric, 40% for riverine and 10% for coastal constituents for the whole Black Sea using data collected in the zone 40 km from the cost (Medinets and Medinets, 2010, 2012), was underestimated related to atmospheric load, since no TON was taken into account. This study data has shown (Table 1) that 59.4% of N came into sea from atmosphere, 29.5% from fluvial and 11.1% from coastal sources, which agreed very well with Moore *et al.* (2013) reviewed data, who demonstrated that 60.9% of N came from atmosphere to the global ocean area (after Duce *et al.*, 2008) and only 38.9%, including 26.7% of dissolved and 12.2% of particulate, were from fluvial sources (Seitzinger *et al.*, 2010).

Outgoing N Fluxes from the Sea

Anaerobic Ammonium Oxidation (Anammox)

This process in the Black Sea was discovered by Kuypers *et al.* (2003) in OMZ between cool intermediate layer and deeper anoxic water, where concentrations of downward NO_3^- and NO_2^- and upward NH_4^+ reach zero. They found there abundant free-living anaerobic ammonium oxidizers, which were responsible for combining of NO_2^- and NH_4^+ with producing N_2. It is noteworthy that NO_2^- serves as electron acceptor (via NO formation) for the NH_4^+ oxidation, as well as electron donor in the reaction with bicarbonate (HCO_3^-) for biomass formation, producing also NO_3^- as a by-product (Strous *et al.*, 2006; Medinets *et al.*, 2015 and reference there in).

Assuming that molar ratio of NH_4^+ to NO_2^- was equal (1:1), Kuypers *et al.* (2003) assessed anammox rate as 0.2 mmol N m^{-2} d^{-1}. It is likely that this estimation was rough enough, since it has been stated that total consumption rates of substrates for anammox were 1.27 moles of NO_2^- (including 0.27 mole for carbon fixation and 1 mole (via NO) for NH_4^+ oxidation) and 1 mole of NH4+ per 0.066 mole with production of 1 mole of N_2 (via hydrazine formation) (Strous *et al.*, 2006; Medinets *et al.*, 2015 and reference there in). It is known (Murray and Yakushev, 2006) that NO_2^- and NH_4^+ concentrations are depleted up to zero somewhere at depth of around 80 m (δ_θ=15.95), *i.e.* sea area with the depth >80 m appears to be relevant for high anammox activity. Therefore during recalculation of anammox rate for the Black Sea basin only area deeper than 80 m (338 000 km^2 by GEBCO, 2012) has been taken into account. Estimated N_2 emission by anammox was 345 Gg N y^{-1} for the whole Black Sea.

Denitrification

Scarce short-term data by Ward and Kilpatrick (1991) regarding direct measurement of denitrification in the Black Sea are only available up to date. They measured denitrification rate in one station with the rate of 0.048 mmol m^{-2} d^{-1}. Last decades several modelling studies with estimations of higher denitrification rate in the Black Sea for whole basin with depth >90 m (0.56 mmol N m^{-2} d^{-1} or 1000 Gg N y^{-1}) by Yakushev and Neretin (1997), for shelf and continental slope (0.28 mmol N m^{-2} d^{-1}) by Gregoire and Lacroix (2002), for NWBS in summer

Table 1. Incoming and outgoing fluxes of N species, which were used in N balance scheme

Source/process	Flux, Gg N y^{-1}	Year of measurement/ estimation	Measured/ estimated	Reference
In-flux				
Atmospheric input	1159±136	2011-2012 (TN)	Meas. and estim.	This study
Fluvial input				
- Danube	362.6	2003-2005 (DIN)	Measured	TDA, 2007; BSC, 2008
	180	1997-2005 (DON)	Estimated	Oguz *et al.* (2008)
- Dnieper	11.2	1996-2000 (TN)	Measured	UNDP, 2003; BSEP, 1999
- Dniester	22.8	1996-2000 (TN)	Measured	UNDP, 2003; BSEP, 1999
Coastal input	217	1996-2000	Meas. and estim.	UNDP, 2003; BSEP, 1999
Flow to the Black Sea *via* Bosporus	60	1986-1992 (TN)	Meas. and estim.	Polat and Tugrul, 1995
Biological N_2 fixation	462	1965-1980	Estimated	McCarthy *et al.* (2007) after Sorokin, 2002 and Cole, 1998
Out-flux				
Anammox	345*	[2000-2002]	Meas. and estim.	Kuypers *et al.* (2003)
Denitrification	106[a]	[1988-1990]	Meas. and est.	[a]Ward and Kilpatrick, 1991
	1000[b]	1991-1996	Estimated	[b]Yakushev and Neretin, 1997
Sedimentation	142	1995-1998	Meas. and estim.	Teodoru *et al.* (2007)
Flow to the Marmara Sea *via* Bosporus	190	1986-1992 (TN)	Meas. and estim.	Polat and Tugrul, 1995

* - estimated for sea area with depth >80 m; [ ] - approximate period

period (1-2 mmol N m^{-2} d^{-1}) by Friedrich *et al.* (2002) and for NWBS for full year period (1.27 mmol N m^{-2} d^{-1}) by Gregoire and Friedrich (2004) were published. It was also evaluated that 60% of PON deposited on sea sediments in NWBS could be lost via denitrification (Gregoire and Friedrich, 2004). It is likely that this common ubiquitous process in anoxic basin of the Black Sea is understudied, *i.e.* extreme lack of relevant information. Moreover, peculiarities of the Black Sea condition, where denitrification can be suppressed by S^{2-} presence (Joye, 2002; Senga *et al.*, 2006) and peak rate is observed at depth of 80-130 m (Yakushev and Neretin, 1997; Murray and Yakushev, 2006), ought to be considered. That is why in that study two variants of N balance were composed, the first based on direct measurements data, the other one - on assessment previously carried out for the whole sea, since denitrification activity seems to be very important for anoxic basins. Thus first value of rough denitrification rate was assessed as 106 Gg N y^{-1} (after Ward and Kilpatrick, 1991) for the whole sea area including shallow water, since this process occurs in anoxic sediments of shelf and slope (Rysgaard *et al.*, 1994; Hartnett and Devol, 2003; Reimers *et al.*, 1992) and the possibility of aerobic denitrification in water column was also found (Lloyd, 1993; Yoshinari and Koike, 1994; Rysgaard *et al.*, 1994). Second value (1000 Gg N y^{-1}) was taken from Yakushev and Neretin (1997), who assessed the nitrification rate for water column at depth >80 m.

Chemodenitrification

Mentions of importance of chemodenitrification, *i. e.* process of NH_4^+ reduction to N_2 at presence of MnO_2, in OMZ of the Black Sea have been found (Murray *et al.*, 1995; Yakushev and Neretin, 1997; Oguz *et al.*, 2001), but no rate assessment has been described yet.

Sedimentation

Teodoru *et al.* (2007) sampled and analysed 10 sediment cores totally in two transects (W-E and N-S) during 1995-1998. They evaluated the rate of TN burial in the Black Sea sediments. Different rates of sedimentation intensity were demonstrated for various zones of sea bed. The zone with the highest accumulation rate appeared to be continental shelf (3580 g cm^{-2} y^{-1}), mainly exposed by allochtonous river-born N, followed by zones of shelf break (230 g cm^{-2} y^{-1}), slope (from 123 till 60 g cm^{-2} y^{-1}) with the lowest accumulation rate in abyssal basin (52 g cm^{-2} y^{-1}). The mass accumulation rates per appropriate area were assessed as 89 Gg y^{-1} for continental shelf, 24 Gg y^{-1} for slopes and 29 Gg y^{-1} for abyssal plain, hence an overall sedimentation flux for the whole Black Sea bed was estimated as 142 Gg y^{-1} (Teodoru *et al.*, 2007).

Water Mass Exchange

Polat and Tugrul (1995) found that annual flows of TN into the Sea of Marmara from the Black Sea was approximately three times higher than those backward, mainly due to riverine N load from NWBS coast. Accordingly the value of N exchange *via* Bosporus from the Black Sea into the Sea of Marmara was 190 Gg N y^{-1} and only 60 Gg N y^{-1} backward for the 1986-1992 (Polat and Tugrul, 1995). Unfortunately N flows between the Sea of Azov and the Black Sea via Kerch Strait has not been assessed,

as no data has been found in published literature.

NH_3 and N_2O Emission

Scarce data are available regarding oceanic NH_3 emission, but Bouwman *et al.* (1997) suggested that ocean is one of the major sources of atmospheric NH_3 (8.2 Tg N y^{-1}) and assessed that its contribution was *ca*. 15% of global sources. Thus despite the real rate of NH_3 emission from the Black Sea has never been measured, it is likely to be important for N budget. It was stated (IPCC, 2001) that oceanic N_2O emission (open water only) has an important influence on N_2O global budget, contributing *ca.* 17% of total sources and *ca*. 31% of all natural sources. Later on Bange *et al.* (1996) argued the significance of coastal areas, which could contribute up to 61% (*ca.* 7.6 Tg N y^{-1}) of global oceanic N_2O emission (*ca*. 12.5 Tg N y^{-1}).

Emission of Organic N (ON)

Recently it has been indicated (Dahl *et al.*, 2003; Facchini *et al.*, 2008; Miyazaki *et al.*, 2010; Jickells *et al.*, 2013) that open waters are the source of WSON emission (*e.g.*, amino acids, urea, peptides, amines, alkyl nitrates), which could be important constituents of aerosol (O'Down *et al.*, 2004; Ceburnis *et al.*, 2011). Data regarding ON emission are very limited, hence estimation of rates is possible neither for global ocean nor for the Black Sea.

Insomuch, anammox seems to be prevailing and 'ecosystem harmless' (with N_2 production) pathway of N loss (345 Gg N y^{-1}) from the Black Sea, while N loss by denitrification might be equall or higher in an anoxic basin, but the approximate rate of this process is hard to define due to scarce and controversial data (varying from 106 to 1000 Gg N y^{-1}).

N budget Pattern and Calculation

Despite of the fact that all the data presented here were measured/estimated in/for different year periods (but still during last decades) sometimes based on scarce short-term data, I suppose that it could be acceptable to calculate N budget (Figure 4; Table 1) focusing on external anthropogenic inputs influence and demonstrating the importance of atmospheric constituent in regional scale in the past decades.

Budget of N for the Black Sea has been calculated as a difference between the sum of incoming fluxes, which enrich the sea water with N (atmospheric deposition, fluvial load, coastal pollution, influx *via* Bosporus, BNF) and the sum of outgoing fluxes, which eliminate N from the basin (anammox, denitrification, outflow *via* Bosporus to the Marmara Sea) or make it unavailable for a long time (burial in sediments).

N budget for the Black Sea (Figure 4; Table 1) (1159+577+217+60+462)–(345+[from 106 to 1000] +190+142) = [from 1692 to 798] Gg N y^{-1}

Influence and the rate of BNF are still under debate, but we decided to use that estimate since it could be crucial for huge area of the sea basin. It seems that one of the most important and fundamental process in anoxic water reservoir is denitrification, but in the Black Sea basin such process has not been studied systematically yet, and hence only rare sporadic data are available. That is why we decided to calculate N budget using two marginal values, derived from field data measurements and modelling estimation. Basically rough N budget indicates that overload of N enters the Black Sea basin persistently with a range of 798-1692 Gg N y^{-1}.

It should be noted that presented N budget is rather approximate, since many constituents were measured in different year periods (Table 1). Some constituents are understudied and were estimated only using either short-term sporadic (BNF) or even single measurements (denitrification). Other constituents, which were just mentioned but not estimated at all (atmospheric deposition of gases, emission of NH_3, N_2O and ON, chemodenitrification), unmonitored or not reported (dumping and shipping), have unknown

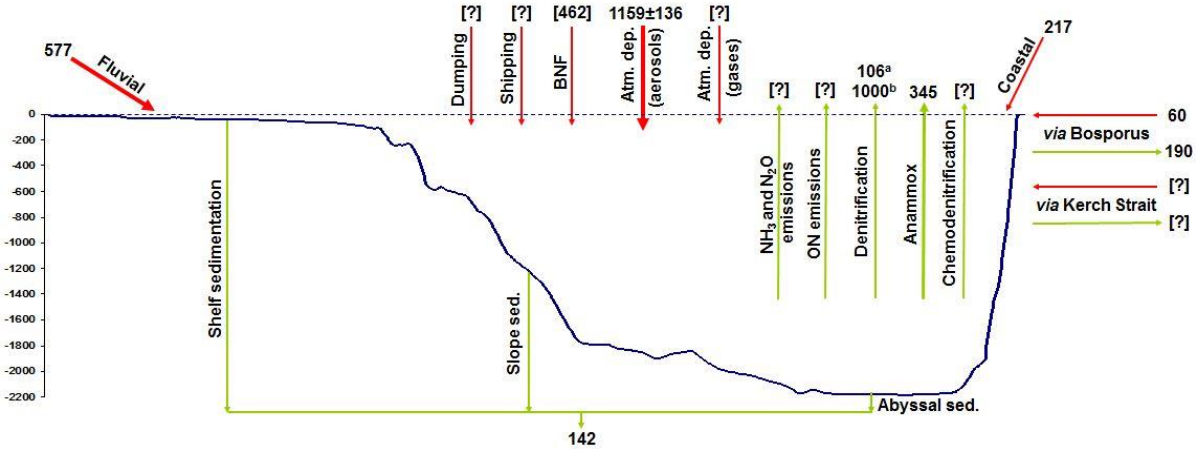

Figure 4. Budget of N (in Gg N y^{-1}) for the Black Sea ecosystem (explanations and references are listed in Table 1).

rates.

Regular investigations of significant processes affecting N balance are urgently needed.

Conclusion

It has been stated that all previous assessments of atmospheric input were underestimated, since TON constituents were not included. Recent (2011-2012) average annual atmospheric bulk deposition rate of TN has been quantitatively assessed as 2684±316 kg N km^{-2} based on direct long-term measurements, thus atmospheric N load for the whole Black Sea area has made 1159±136 Gg N. Important role of atmospheric TON pollutants in deposition, which was usually neglected, has been proved. Organic part in atmospheric aerosol deposition was the dominant (66.2% or 1777±678 kg N km^{-2}) N pollutant constituent, while DIN made 33.8% (907±361 kg N km^{-2}) only. Contributions of water soluble (24.3%) and particulate (28.3%) organic N were distributed approximately equally in atmospheric deposition. Prevailing role (59.4%) of atmospheric N input compared to other main external N pollution sources (fluvial and coastal) into the Black Sea has been proved.

According to present estimation of N budget the Black Sea is under strong pressure of anthropogenic N load (approximately from 798 to 1692 Gg N y^{-1}), mainly from atmosphere and north-western rivers, whilst rates of many processes are often far from representative or under strong debate. Weak understudied points and uncertainities still exist in the Black Sea N budget because of absence (e.g., deposition of gases, chemodenitrification, NO_x, NH_3 and ON emission) and lacking of available measured data (e.g., BNF, deinitrification), as well as because there is no proper monitoring data or those scarce data are unavailable for public.

To protect and enhance the Black Sea ecosystem full implementation of the existing regulations related to N is urgently needed, in addition to an efficient environmental monitoring. Also integration of sectoral policies and enhancing of interdisciplinarity in the research, supporting of regional assessments and pollution swapping evaluations in particular, should be developed. Basic measures for mitigation of N harmful effect on the Black Sea ecosystem have to be developed and applied, paying more attention to those un-monitored anthropogenic activities and understudied processes, which ought to be investigated and estimated in near future.

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