www.trjfas.org
ISSN 1303-2712
Turkish Journal of Fisheries and Aquatic Sciences 12: 497-505 (2012) DOI: 10.4194/1303-2712-v12_2_42

Investigations of Atmospheric Wet and Dry Nutrient Deposition to Marine Surface in Western Part of the Black Sea

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Received
Accepted

Abstract

The Black Sea ecosystem has three main sources of nutrient pollution: coastal, riverine and atmospheric inputs. Anthropogenically produced N transported to the coastal and open sea zones is closely connected with excess of nutrients supply that can result at acidification, eutrophication, excessive oxygen consumption and hypoxia. The aim of our work was to estimate the quantities and tendencies of atmospheric wet and dry depositions of nutrients (N and P) of different origin to the Zmiinyi Island surface during 2004 - 2010. Our study has confirmed previous findings that there was practically no N and P emission over the open sea and the main source of transportation (91-99% of NH_4^+, NO_3^- and PO_4^{3-}) was atmospheric run-off from the continent. We have shown that aerosol removing over the sea occurs for the most part by means of dry deposition (40-80% of bulk deposition). We have assessed that in 2004 - 2010 average annual atmospheric bulk depositions of inorganic N and P made 694±45 kg N km^{-2} (in the form of NH_4^+, NO_3^- and NO_2^-) and 100±11 kg P km^{-2} (in the form of PO_4^{3-}). Important direction was the study of organic N in bulk deposition, which exceeds mineral N part about 1.6 times.

Keywords: pollution, aerosol, precipitation, Zmiinyi Island, organic nitrogen.

Introduction

The first European Nitrogen Assessment (ENA, 2011) was made and the significance, importance and threats of N dilemma to our environment and health were accented. After humans disturbed the N cycle significantly by the production of artificial fertilizers, fossil fuel combustion or animal husbandry, the man-made sources of fixed/reactive N are at present time greater than the quantity produced by natural N fixation (Gruber and Galloway, 2008; Voss *et al.*, 2011). Terrestrial and marine N cycles are closely linked. Anthropogenically produced N transported to the coastal and open sea zones is closely connected with excess of nutrients supply that can result at acidification, eutrophication, excessive oxygen consumption and hypoxia (Seitzinger *et al.*, 2005; Diaz and Rosenberg, 2008; Voss *et al.*, 2011). Amount and availability of nutrient elements and their compounds are usually limiting factors for organism healthy growth until they are in excess and impact the ecosystem (Gruber and Galloway, 2008). In open sea stratification prevents from exchange of dissolved substances between layers of water, so surplus of nutrients may accumulate at certain depth (Voss *et al.*, 2011). Nutrients can be a limiting factor for aquatic ecosystem, for instance phosphorus (P) is a limiting factor for coastal water of the Black Sea and nitrogen (N) for open water (Cociasu *et al.*, 1998; DaNUbs, 2005). The Black Sea ecosystem has three main sources of pollution especially with nutrients: coastal, riverine and atmospheric inputs (BSC, 2008). Atmospheric fluxes to the sea surface are the results of long-range atmospheric transport of pollutants from the regions of Europe and the Black Sea countries sources. As there are very little experimental data on nutrients deposition to the Black Sea surface, it is very difficult to make the precise assessment of nutrients balance in the Black Sea. Short assessment of the amount of N compounds coming from atmosphere into the Black Sea ecosystem carried out by the BSC (2008) using inter alia our data for 2004-2007 (Medinets *et al.*, 2008; Medinets and Medinets, 2010) showed that it is close to the input of the Danube River (BSC, 2008). Overview of the EMEP modelling data of inorganic N compounds depositions for 1995-2005 by Bartnicki and Fagerli (2008) presented annual average loads of N into the Black Sea for 1995-2005. Besides, it should be noted that practically all the assessments of

N fluxes to the Black Sea ecosystem mentioned above have been made only for the dissolved inorganic N (DIN) compounds. In the past decade the attention of researchers has been attracted by the question of organic N (ON) compounds' content in marine aerosol and atmospheric dry and wet depositions (Spokeset *et al*., 2000; Cape *et al.,* 2001, 2010; Cornel *et al*., 2003; Mace *et al.,* 2003; Krom *et al*., 2004; Markaki *at el.,* 2010; Miyazaki *et al.,* 2011). For the Black Sea no assessment of the ON input into atmospheric deposition of total N (TN) has been made until now.

This work tries to fill existing gaps in assessments of N and P atmospheric fluxes into the Black Sea ecosystem. At this study we presented the results of analysis of our experimental data and assessed the quantities and tendencies during 2004-2010 of atmospheric wet and dry depositions of nutrients (N and P compounds) of different origin to the surface of the Zmiinyi Island located in the north-western part of the Black Sea (NWBS). Estimations of basic/prevalent way of dry or wet depositions for each compound from the atmosphere to the marine surface (firstly for this region) and the origin of nutrients depositions (marine or continental-anthropogenic) are described too. Thereafter firstly in 2010 we have started to study the content of total organic N (TON) and DIN in bulk atmospheric deposition, which are usually neglected, and tried to estimate their significance especially for this area of the Black Sea.

Materials and Methods

Study Area

Atmospheric deposition sampling site on the Zmiinyi Island is located in the NWBS (45°15'22.0" N and 30°12'03.8" E) 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), especially as there is Marine Research Station (MRS) "Zmiinyi Island" of the Odessa National I. I. Mechnikov University (ONU).

Sampling and Analysis

Atmospheric monitoring programme of the MRS "Zmiiniy 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). For determination of bulk atmospheric depositions we used plate bulk deposition sampler described in details in our previous studies (Medinets *et al.,* 1993, 1990, 2008; Medinets and Medinets, 2010). As a collector for aerosol particles we used the special filter tissue FPP-15-1.5 exposed during every 5 days. Bulk atmospheric depositions and precipitations on the island were sampled in the following periods: May-November 2004, April-December 2005, January-December 2006, May-December 2007, May-December 2008, April-December 2009, June-December 2010. Precipitation samples were conserved and analysed after each rain. Altogether 182 samples of atmospheric precipitation and 304 samples of bulk depositions were taken. During June-December 2010 we have used additional bulk deposition sampler recommended by the EMEP (EMEP, 2001). Monthly wet depositions were calculated by multiplying average monthly ion concentration by sum of monthly precipitation. Monthly bulk depositions were calculated as a sum of all 5 day depositions during the appropriate month. For conductivity and pH measurements we used conductivity meter MC226 (Mettler Toledo, USA) and pH-meter Hydrus 400 (Fisherbrand, UK). For measurements of ionic composition of samples was used ionic chromatograph Personal IC 790 (Metrohm Ltd, Switzerland). Appropriate ISO standards were used for all the analyses above. TN in unfiltered deposition samples was determined using persulphate oxidation method (RD, 2007). This means that we have defined the sum of all N compounds (water soluble and water insoluble). TON in the samples was calculated as a difference between TN and DIN.

Meteorological observations

Meteorological observations have been carried out 3 times per day using standard WMO methods (WMO, 2008) and equipment: bulk precipitation quantity (Tretiakov rain gauge, Ukraine), wind direction and velocity (vane and anemometer MC-13, EPMGGO, Russia), temperature (aspirated psychrometer MB-4M, NIKI MLT-Povolzhie, Russia).

Statistical Analysis

Statistical methods including correlation analysis ($P<0.05$) were applied to investigate relationships between studied ions in atmospheric deposition of different species and meteorological data. We also calculated significance tests for comparison of the average values using Student t-test (normal distribution). All the analyses were carried out with STATISTICA (version 6.1 for Windows, StatSoft, Inc., 1984-2004). Diagrams and trends were built using MS Excel 2003.

Results

Meteorological Data Variations

Basic meteorological parameters have been

observed during sampling campaigns in 2004-2010. Monthly average observations of wind speed, air temperature and sum of precipitation are presented on Figure 1. During 2004-2010 monthly average wind speed fluctuated from 2.7±2.2 m s^{-1} (May 2009) to 8.5±3.9 m s^{-1} (November 2007) with average value of 5.4±1.4 m s^{-1}. Average air temperature during sampling campaigns was 17.3 ±7.7ºC. The warmest month of sampling was August 2010 (28.4±3.2ºC), the coldest-January 2006 (-0.3±3.2ºC). Average amount of precipitation while we have performed our sampling campaigns was 27.2±27.2 mm $month^{-1}$. We have registered strong rainfalls (104 mm $month^{-1}$) in August 2006, which are not typical for the relatively dry (ca. 280 mm $year^{-1}$) Zmiinyi Island climate. Opposite to the abovementioned, in August 2008 we have observed no rain. To calculate average annual wet deposition we have used annual precipitation data, comprising our own data and the data kindly provided by meteorological station "Zmiinyi Island" of the State Meteorological Service of Ukraine for the periods when we have performed no observations.

Atmospheric Bulk Deposition

The annual average estimations of DIN bulk deposition as sum of NH_4^+, NO_3^- and NO_2^- were made during 2004-2010 (Figure 2). Average DIN bulk deposition value for the period of sampling campaigns was 693±74 kg N km^{-2} $year^{-1}$. The maximum of DIN deposition intensity (947±111 kg N km^{-2} $year^{-1}$) has been observed for 2009, the minimum rate (272±47 kg N km^{-2} $year^{-1}$)-in 2008. During 2004-2010 average contribution of different DIN compounds made 64.4±9.2% of NH_4^+, 35.3±9.1% of NO_3^- and only 1.7±0.1% of NO_2^-. The maximum ammonium contribution to DIN (76.8%) has been observed in 2008 and its minimal input (50.2%) has occurred in 2006.

Average annual bulk deposition of dissolved inorganic phosphorus (DIP) in form of PO_4^{3-} during our 2004-2010 studies was 100±11 kg P km^{-2} $year^{-1}$ (Figure 2). The extremely high rate (223±20 kg P km^{-2} $year^{-1}$) of deposited DIP has been found in 2006. Relatively low deposition intensities of DIP have been registered in 2008 (26±5 kg P km^{-2} $year^{-1}$) and 2010 (37±5 kg P km^{-2} $year^{-1}$).

Atmospheric Wet Deposition

Studies of precipitation rates, pH and conductivity in rain water samples (Figure 3) have revealed the following. Average annual pH level of atmospheric wet deposition made 5.4±0.8 during the whole period of observations with the maximum of 6.5±0.1 in 2010 and the minimum of 4.5±0.1 in 2005. Annual conductivity of atmospheric precipitation varied from 50±4 µS cm^{-1} (in 2004) to 301±50 µS cm^{-1} (in 2009) with average value of 132±84 µS cm^{-1} during the field campaigns.

Calculation of DIN (as sum of NH_4^+, NO_3^- and NO_2^-) deposited with rain water was carried out for

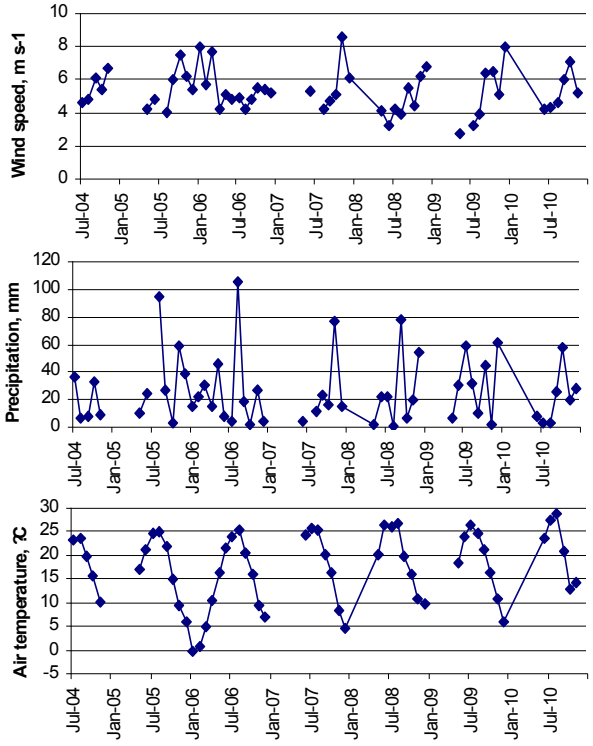

Figure 1. Temporal variations of monthly average main meteorological parameters during sampling campaigns in 2004-2010.

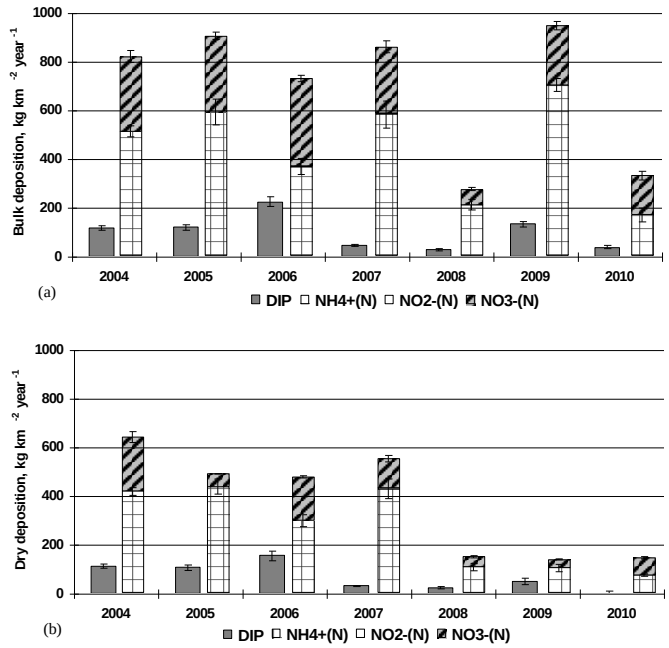

Figure 2. Variations of annual average values of DIN (by its ionic constituents) and DIP in bulk deposition (a) and dry deposition (b) in 2004-2010

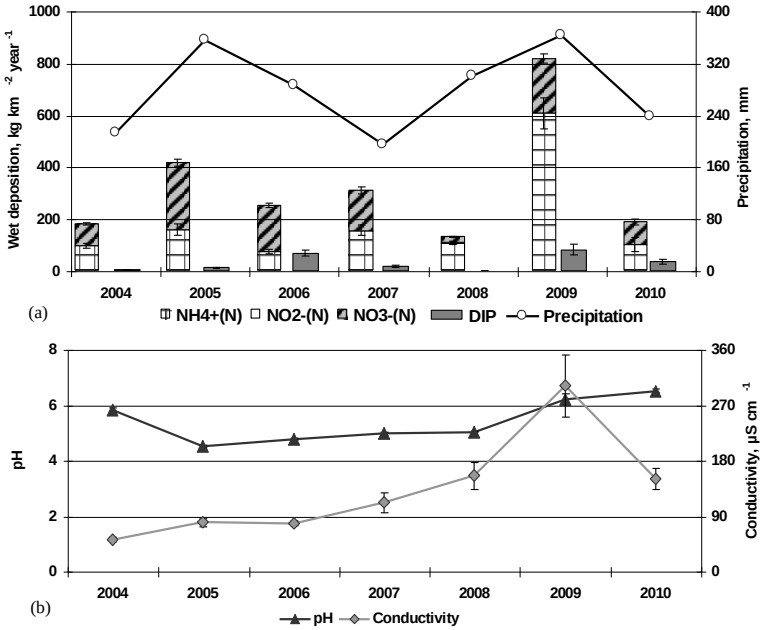

Figure 3. Variations of annual average values of wet deposited DIN (by its ionic constituents) and DIP with precipitation rates (a), pH and conductivity of rain water samples (b) for 2004-2010.

each year of study periods (Figure 3). Analysis of results of wet deposition ionic composition has shown that annual average value for the whole period of field campaigns made 325±43 kg N km^{-2} $year^{-1}$ with the maximum wet deposition rate of DIN (812±148 kg N km^{-2} $year^{-1}$) in 2009 and with the minimum (127±11 kg N km^{-2} $year^{-1}$) in 2008. Average contribution of different inorganic N ions in DIN wet deposition was 46.0±15.3% for nitrate, 53.9±15.3% for ammonium and less than 0.2% for nitrite during 2004-2010. The maximum nitrate input has been observed in 2006 and made 72%. The minimum part of wet deposited NO_3^- (17.8%) in DIN was found in 2008.

There was 32±7 kg P km^{-2} $year^{-1}$ wet deposited annually with precipitations in the form of PO_4^{3-} for the whole investigation period (Figure 3). The maximum rate (82±21 kg P km^{-2} $year^{-1}$) of DIP wet deposition has been found in 2009 and the lowest-in 2008 and made only 1.6±0.4 P km^{-2} $year^{-1}$.

Investigations of TON

We have been studying TON (as a sum of water soluble organic N (WSON) and water insoluble organic N (WION) compounds) in TN deposition from June to December 2010. Here we have demonstrated our first results regarding the distribution of mineral and organic N compounds in bulk deposition. For the better demonstrativeness reflecting purpose of our investigation we have presented results in relative units (%) as a part of TN deposition (Figure 4). The average contribution of TON for the study period was 63±13%. The maximum (81%) of TON deposition has been observed in September and the minimum (48%) in August.

Discussion

As it is known (Medinets *et al.*, 2007; 2008; BSC, 2008; Bartnicki and Fagerli, 2008), about 30-40% water soluble N and P compounds enter marine ecosystem from the atmosphere. At that, the main mechanisms of their entering marine surface during air masses transport are wet (scavenging with precipitation) and dry (as the result of aerosol particles falling out) depositions. Marine aerosols generated by sea surface as the result of wind-caused interaction between atmosphere and marine surface are the additional factor strengthening deposition of gaseous and aerosol particles of anthropogenic origin in the near-water atmosphere (Buat-Menard, 1983; Tuncel, 2001). Thus, we could assume that the speed of wind over the sea and precipitation are the main meteorological factors that determine the speed of physical processes of atmosphere purification over the sea.

Analysis of the results we have received about intensity of nutrients (N and P) deposition to the Black Sea surface in the Zmiinyi Island area (Figure 2, 3) showed that NH_4^+ was dominant N compound in DIN of bulk deposition with input 64±10%. There was no single dominant compound (neither NH_4^+ nor NO_3^-) in DIN of wet deposition for all field campaign periods: 54±15% for nitrate and 46±15% for ammonium. For dry deposited N compounds (Figure 2) average input for NH_4^+ and NO_3^- made 70±13% and 30±13% respectively. This means that NO_3^- deposited mainly during wet scavenging processes and NH_4^+-during dry processes.

We have also found that bulk deposition of NO_3^- strongly correlated with sulfates ($r=0.53$; $P<0.01$) and less strongly with sodium ($r=0.39$; $P<0.05$). Ammonium statistically significant ($r=0.76$; $P<0.001$) correlated with phosphate. No significant correlations were revealed between bulk deposition rates of others ions and meteorological parameters (wind speed, temperature and precipitation rate). We found that wet deposition of some ions (continental or partially continental origin) had significantly ($P<0.001$, $n = 52$) strong correlation with amount of precipitation ($r = 0.68$ for SO_4^{2-}, $r = 0.67$ for NO_3^-). At that, strong correlation interconnection was observed for NH_4^+ with Na^+ ($r=0.76$) and SO_4^{2-} ($r=0.71$) at $P<0.001$. Nitrate also strongly correlated with sulfate ($r = 0.72$; $P<0.001$). For NH_4^+ deposited by dry deposition we have registered strong correlation with NO_3^- ($r = 0.59$) and PO_4^+ ($r=0.77$) at $P<0.001$. Thus, correlation analysis proved our conclusion that atmospheric precipitation influenced NO_3^- washing-out from atmosphere.

Important issue for this study was determination of basic/prevalent way of removing (dry or wet) of each species of investigated aerosols from the atmosphere. We have calculated the average annual input of wet and dry deposition for certain ions for the period of 2004-2010 (Figure 5), from the analysis of which it followed that input of each ion into the total deposition was different due to the mechanisms of wet and dry deposition. Wet deposition share made: for NO_3^- (56.2%), NH_4^+ (40.6%), PO_4^- (34.9%), NO_2^- (28.7%) and minimal (21-30%) for marine-origin ions (such as Na^+, K^+, Cl^- etc). Inverse relationship was observed for dry deposition. Such distribution of different ions input into wet and dry deposition could be explained with different forms of precursors of the

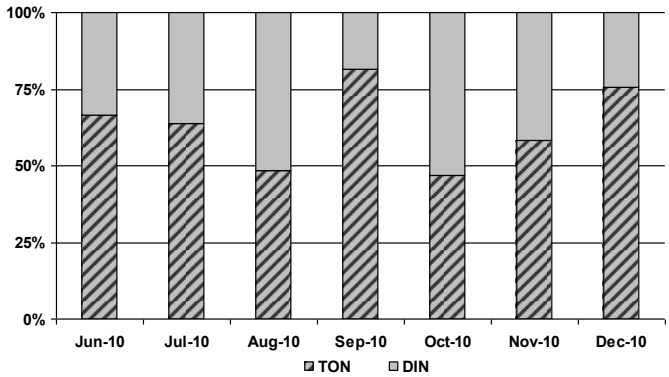

Figure 4. Temporal variations of input (%) of TON and DIN to TN bulk deposition in the Zmiinyi Island area during 2010 sampling campaign.

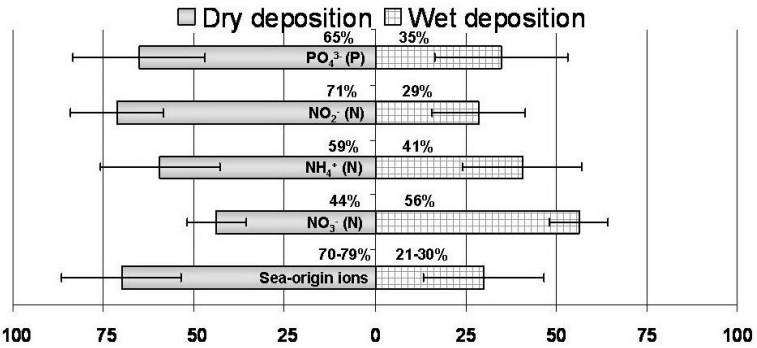

Figure 5. Average input (%) of dry and wet deposition for certain nutrients ions for 2004 – 2010 in the Zmiinyi Island area of the Black Sea.

studied ions, as well as mechanisms of their entering the near-water atmosphere. The ions like NH_4^+ and NO_3^- are largely originating from gas admixtures (NH_3 and NO_x), which enter the atmosphere over the continent from anthropogenic and natural sources and reach significant height and clouds, react in the process of long-range transport with cloud moisture and chemically transform into ions of NH_4^+ and NO_3^-. That is why the mechanism of their scavenging would be preferably with precipitation, which was confirmed by our data. Largely dry deposition of phosphate and ions of marine origin, which has been registered by us, could be explained by the fact that the sources of those ions are the marine (for the ions Na^+, K^+, Cl^-) and continental surface (for PO_4^{3-}) and transport of those ions happens only in the lower atmospheric layer. Significant correlation coefficient between PO_4^{3-} and NH_4^+ in dry deposition ($r = 0.77$; $P<0.001$), as well as high level of NH_4^+ removal through dry deposition (59%) could evidence that both of them have the same area of sources. Predominant removal of phosphates from the near-water layer of atmosphere due to dry deposition was caused by the fact that PO_4^{3-} could be transported into the Zmiinyi Island area only as the result of agro-economic activities during/after input of fertilizers in the rural regions of Ukraine, Romania and Bulgaria. Assumption about transport of PO_4^{3-} from rural fields with coarse dust particles accords well with the conclusion by Tuncel (2001) that, unlike the continental areas, dry deposition dominates over marine areas.

Based on the data received about N and P atmospheric fluxes intensity to the island surface we have quantitatively assessed the rate of the ions deposition on the sea surface in the region of the Zmiinyi Island (Table 1). We have shown that for 2004-2010 average annual atmospheric bulk deposition of inorganic N and P compounds to the sea surface made 694±45 kg N km^{-2} (as sum of NH_4^+, NO_3^- and NO_2^-) and 100±11 kg P km^{-2} (in the form of PO_4^{3-}). Comparison of our recent results (2008-2010) with the previous data of studies has shown that DIN bulk deposition in the area of the Zmiinyi Island was 1.6 and 1.3 times less that the corresponding values for the same region in 2004-2007 (by amended data of Medinets and Medinets, 2010) and for the NWBS was in 1990-1992 (Medinets *et al.*, 1993) respectively. The main relative input to DIN bulk deposition for 1990-1992 (Medinets *et al*, 1993) was made by ammonium the flux of which was 87%, further on, during 2004-2007, its input went down to 62% and increased again reaching 70% during 2008-2010. Atmospheric flux of NO_3^- to the sea surface in the period from 1992-1993 to 2004-2010 increased from 91 kg N km^{-2} to 245±17 kg N km^{-2} (2004-2010) or in percentage to DIN from 14% to 35% respectively. The amount of deposited P in 2008-2010 decreased 2 times compared to 2004-2007 data.

Based on the data (Table 2) we have found that average annual inorganic wet deposition rate was 2.3 and 1.3 times higher ($P<0.001$) for NH_4^+ and DIN respectively in 2008-2010 compared to the data for 2004-2007. The contribution of ammonium to the wet deposition of DIN was 72% for 2008-2010 as set-off to 41% only in 2004-2007. There were no significant changes in wet deposition rates of PO_4^{3-} for those periods.

Comparison of N average depositions with the published data (BSC, 2008; Bartnicki and Fagerli, 2008) has shown that they agreed well (Table 1), exceedance of our experimental data for the Zmiinyi Island area made only 1.7 (2004-2007) and 1.1 times (2008-2010) compared with the modeled values of deposition intensity for the entire Black Sea for the years 2005 and 2010 (Bartnicki and Fagerli, 2008). Taking into account the fact that the Zmiinyi Island is located 40 km far from the Danube Delta this enabled us to conclude that the results of atmospheric chemistry investigations made on the island are representative for the western Black Sea part which is influenced by western transport of air masses from the European continent.

We have estimated input of ions entering the near-water atmosphere of the NWBS in the Zmiinyi Island area due to the transport from continental sources, i.e. the input of non-marine origin. Our study has confirmed previous finding (Medinets, 1983; Medinets *et al.*, 1993, 2008; Medinets and Medinets, 2010) that for inorganic bulk deposition about 91% to

Table 1. Comparison of average intensities of N and P bulk deposition (kg km^{-2} $year^{-1}$) of authors' and published data

Area, (years), [source of data]	NH_4^+(N)	NO_3^-(N)	NO_2^-(N)	DIN	PO_4^{3-}(P)
Western Black Sea, the Zmiinyi Island (2004-2010)	447±30	245±15	1.7±0.2	694±45	100±11
Western Black Sea, the Zmiinyi Island (2008-2010)	360±31	155±15	0.6±0.1	516 ±54	66±8
Western Black Sea, the Zmiinyi Island (2004-2007)	512±36	312±17	2.5±0.3	827±53	129±10
NWBS (1990-1992) [Medinets *et al.,* 1993]	584	91	-	675	-
Whole Black Sea (1990-1992) [Medinets *et al*., 1993]	450	125	-	575	-
Whole Black Sea (2005) [Bartnicki and Fagerli, 2008]	~210	~264		474	
Whole Black Sea (2010) [Bartnicki and Fagerli, 2008]	~230	~244		474	

Table 2. Comparison of average intensities of N and P wet deposition (kg km^{-2} $year^{-1}$) for recent studied period (2008 - 2010) and literature data

Area, (year), [source of data]	NH_4^+(N)	NO_3^-(N)	NO_2^-(N)	DIN	PO_4^{3-}(P)
Western Black sea, the Zmiinyi Island (2004-2010)	182±35	143±16	0.3±0.4	325±45	31±7
Western Black sea, the Zmiinyi Island (2008-2010)	268±54	102±13	0.4±0.6	375±47	40±11
Western Black sea, the Zmiinyi Island (2004-2007)	118±14	169±10	0.3±0.1	287±24	25±4
Whole Black Sea (2005) [Bartnicki and Fagerly, 2008]				284	

99% of ammonium, nitrate and phosphate are transported into the near-water atmosphere of the Zmiinyi Island from the natural and anthropogenic continental sources and there was no significant inorganic N and P emission over the open sea. Thus sea surface is the sink for nutrients' atmospheric run-off from the continent (Medinets *et al.,* 2008; Medinets and Medinets 2010). For atmospheric wet deposition input of continental sources was the following: about 99% for ions of ammonium and nitrate and ca. 62% for phosphate.

Recent reviews have reported that WSON input to wet deposition may be up to 30% of the TN in terrestrial region (Cape *et al.,* 2001; Neff *et al.,* 2002; Cornell *et al.,* 2003) and 67-83% in open oceans (Crockford *et al.,* 1996; Cornell *et al.,* 2003; Miayazaki *et al,* 2011), but we still knew a little about chemical composition and form of this 'unknown' origin substances (Cornell *et al.,* 2003; Cape and Gonzalez, 2010). Only in few sources (e.g. Miyazaki *et al.*, 2011) we have found the information about content of TON (including WION and WSON), which can reach in marine aerosol ca. 67% of the TN (with 55% of WION and 12% of WSON).

To investigate organic N compounds deposition for western part of the Black Sea from June 2010 we have started monthly sampling and analysis for assessment of TN in bulk deposition, including DIN and TON. We have found (Figure 4) that average TON rate for June-December 2010 was 63±13% of TN. Our data was comparable to literature data by Crockford *et al.* (1996), Cornell *et al.* (2003) and the recent one by Miyazaki *et al.* (2011) for open sea regions. Our first result has shown that organic N (water soluble and insoluble) could exceed DIN of atmospheric depositions in absolute magnitude at least twice, which enables us to conclude that the estimated fluxes of N compounds into the Black Sea through atmosphere made before were underestimated at least in factor of 2. We plan to continue studies of organic N input into the total N flux to the sea surface, as it could significantly change the balance assessments of N entering marine ecosystem and give a start to reconsideration of nature conservation priorities in the Black Sea basin.

Conclusion

We have quantitatively assessed the average annual bulk deposition of DIN (694±45 kg N km^{-2} $year^{-1}$) and DIP (100±11 kg P km^{-2} $year^{-1}$) to the marine surface for whole period of 2004-2010.

It has been demonstrated that NH_4^+ was dominant inorganic N compound and made significant input to dry (70±13%) and consequently to bulk (64±10%) DIN deposition. We have registered approximately equal wet scavenging rate for both NH_4^+ (56±15%) and NO_3^- (44±15%). Also strong correlation between amount of precipitation and wet deposited SO_4^{2-} ($r=0.68$) and NO_3^- ($r=0.67$) with significance at $P<0.001$ has been found. For dry deposited NH_4^+ strong correlation with NO_3^- ($r=0.59$) and PO_4^+ ($r=0.77$) at $P<0.001$ was registered.

Input of dry and wet ways to bulk deposition for N, P and sea-origin ions has been quantitatively estimated for 2004-2010. It was found that for ammonium both dry (51%) and wet (49%) ways of removing were important, but for nitrate wet scavenging could be the prevalent one (59%). Dry sedimentation was more important for phosphates (76%) and sea-origin ions (70-79%) than washing-out with rain water.

We have confirmed that for inorganic bulk deposition about 91% to 99% of ammonium, nitrate and phosphate are transported into the near-water atmosphere of the Zmiinyi Island from the natural and

anthropogenic continental sources and there was no significant inorganic N and P emission over the open sea.

Our first result of ON investigations has shown that average TON rate was 63±13% of TN for June-December 2010. It was found that TON (WSON and WION) could exceed DIN of atmospheric bulk depositions in absolute magnitude at least twice for the western part of the Black Sea. We have suggested that past and current estimation of atmospheric N fluxes into the Black Sea (published and our previous) obviously was underestimated at least in factor of 2. The continuation of studies of ON inputs into the TN flux to the sea surface is important and timely issue, as it could significantly change the N balance assessments for the Black Sea ecosystem and give a start to reconsideration of nature conservation priorities in the Black Sea basin.

Due to unique location of the Zmiinyi Island isolated from continent pollutants sources and is located 40 km far from the Danube Delta, this enabled us to conclude that the results of atmospheric chemistry investigations made on the island are representative for the western Black Sea part which is influenced by western transport of air masses from the European continent. Therefore the MRS "Zmiinyi Island" (ZMN_UA site) can be used as representative site for different kinds of observations and investigations in the Black Sea. We are ready and opened for collaboration in the framework of national and international projects and activities focusing on the Black Sea environmental state.

Acknowledgements

The studies of ONU were carried out in the framework of the National Programme of the Zmiinyi Island research and infrastructure development in 2009-2010 funded by the Ministry of Education and Science of Ukraine (2003-2010) and as a contribution to the European FP7 project (2009-2013) No. 226740 EnviroGrids (Building Capacity for a Black Sea Catchment Observation and Assessment System supporting Sustainable Development). Authors would like to express their gratitude to all the staff of the RMS "Zmiinyi Island" and Regional Centre for Integrated Environmental Monitoring and Ecological Studies of ONU for their efforts during 2004-2010.

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