Estimation of Nutrient Flux Input to the Crimean Southern Coast (Katsiveli) Supplied by the Atmospheric Precipitation in 2010–2015

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The results of evaluation of the dissolved inorganic nitrogen (nitrate, nitrite and ammonium), dissolved inorganic phosphorus (phosphate) and silicon fluxes to the region of Katsiveli (Southern coast of the Crimea) supplied via atmospheric precipitations in 2010–2015 are discussed in this paper; their seasonal and inter-annual changes are also studied. The obtained data indicated that the main forms of nitrogen in atmospheric depositions are nitrates and ammonium. The increase of nutrients content in warm period of the year in intra-annual change is observed for all elements. It can be explained both by inverse dependence of elements concentration on precipitation amount and by features of their migration and input sources. It has been also revealed that the six-year average flux of the nutrients consists of 30.4 mmol/m^2·year of inorganic nitrogen and 0.118 and 0.315 mmol/m^2·year of phosphorus and silicon, respectively. It has been noted that atmospheric deposition of inorganic nitrogen can lead to increase of primary production in the Black Sea on to 2.5%, while annual inorganic phosphorus input with atmospheric depositions contribution to primary production formation makes up 0.5 %. Additional contribution of inorganic silicon atmospheric input to primary production formation made up 0.02 % of its annual value in the Black Sea open part.

Keywords: inorganic nitrogen, phosphorus, silicon, atmospheric depositions, the Black Sea.

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Introduction. An active use of the Crimean coastal regions for recreational, agricultural and industrial purposes has led to the fact that an additional amount of nutrients have begun to get into the marine environment. Though nutrients do not cause direct harm themselves as they are ecosystem components, when the volume of their input exceeds the one of their consumption an ecosystem becomes oversaturated. Correspondingly, a problem of eutrophication arises.

An atmosphere is a significant source of nutrients. Nitrogen compounds (ammonium and nitrogen oxide), phosphorus and silicon get into the Earth atmosphere due to the effect of natural and anthropogenic processes. Then, these nutrients are forced out with atmospheric depositions [1] and they get into a catchment area or a sea.

It is assumed [2] that the contribution of nutrients atmospheric input in the open parts of the seas during the intensive creation of primary production is insignificant due to the mixing of waters. On the other hand, during the summer and early autumn, the stratification of the water column makes the atmospheric contribution significant, and in some cases it becomes the main source of "new" nutrients in the euphotic layer of the deep-sea areas.

The main aim of the given research is to estimate the input of nutrients (inorganic nitrogen, phosphorus, silicon) with atmospheric depositions at the Black Sea coast.

Methods and materials. Samples of bulk atmospheric depositions were taken at the Southern coast of the Crimea (Katsiveli, Black Sea Hydrophysical Proving Ground of RAS) during 2010 – 2015 (Fig. 1). During the observational period 284 samples were taken and analyzed for the content of nitrogen inorganic forms (nitrate, nitrite, ammonum) and 232 samples – for inorganic phosphorus and silicon content. Atmospheric deposition laboratory analysis was carried out in Marine Hydrophysical Institute (Sevastopol). Statistical data processing was performed by descriptive statistics methods and "Data analysis" add-on in *Excel*.

Fig. 1. Monitoring point of nutrient content in atmospheric depositions (Katsiveli)

39 % of taken and analyzed atmospheric deposition samples were collected during warm period (April – September) and 61% – during cold period (October – March) of the year. Annual nutrient flux was calculated according to the data on their content in atmospheric depositions. Processed samples made up 71 % of the total amount of precipitation events in the given observation point.

Results and discussion. Nitrogen compounds. The obtained data indicated that in atmospheric depositions prevailed acid-forming components of the nitrogen forms. NH_4:NO_3:NO_2 percentage ratio in atmospheric precipitation samples made up 33:66:1. Apparently, such low nitrite content may be explained by the fact that they are intermediate product of ammonium oxidation to nitrates. These results perfectly match the available data on nitrogen form ratio in atmospheric precipitation samples [2 – 5].

The maximum inorganic nitrogen concentration (596.55 µmol/l) was indicated in the sample taken in June 2015. Inorganic nitrogen concentration dropped to its minimum (21.45 µmol/l) in January 2014.

Annual input of sum of nitrogen inorganic forms with atmospheric depositions varied from 22.4 µmol/m^2·year (2014) to 38.8 µmol/m^2·year (2011) (Fig. 2).

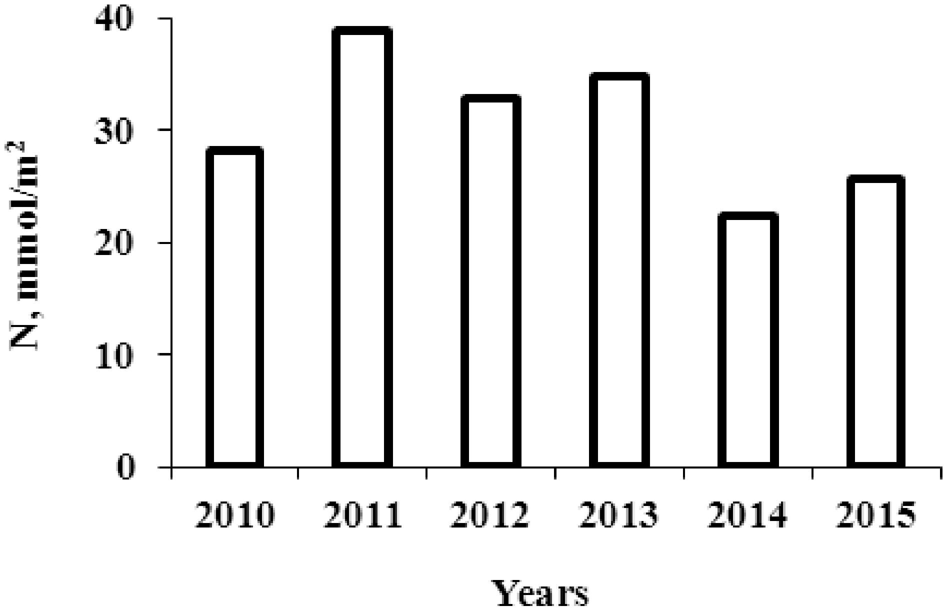
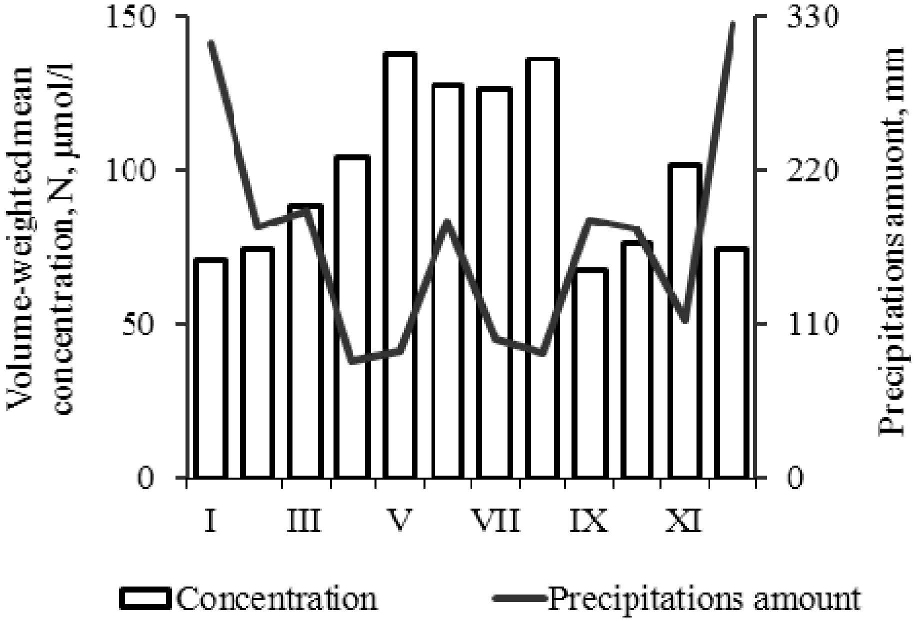


Fig. 2. Inorganic nitrogen flux with atmospheric depositions in 2010 – 2015 (nitrogen flux in 2015 has been calculated using the data for January – July)

In intra-annual change of inorganic nitrogen (which gets with the atmospheric depositions) volume weighted mean concentration an increase from March to August and decrease in cold period of year are observed (Fig. 3, *a*). The change of concentration and the sum of precipitation amount are in antiphase. Probably, such result may be explained by inorganic nitrogen concentration decrease as precipitation amount increases (Fig 3, *b*). This corresponds to the known literature data [6, 7].

At the same time, the cases of high inorganic nitrogen concentration presence in the samples at high amount of precipitation fallen in warm period of the year were observed. This also contributed to the increase in the total nitrogen flow.

In interannual variation of weighted mean concentration volume of inorganic nitrogen in atmospheric depositions (Fig. 4) we may point out some statistically insignificant concentration increase in 2011 with its further decrease by 2013. Also, inorganic nitrogen concentration peaks in May 2013 and 2015 and in August 2014 are observed. These peaks are characteristic of single precipitation events (one case in May 2013, two in August 2014 and two in May 2015). These precipitations were characterized by small amount (1 – 5 mm) and high nitrogen content.



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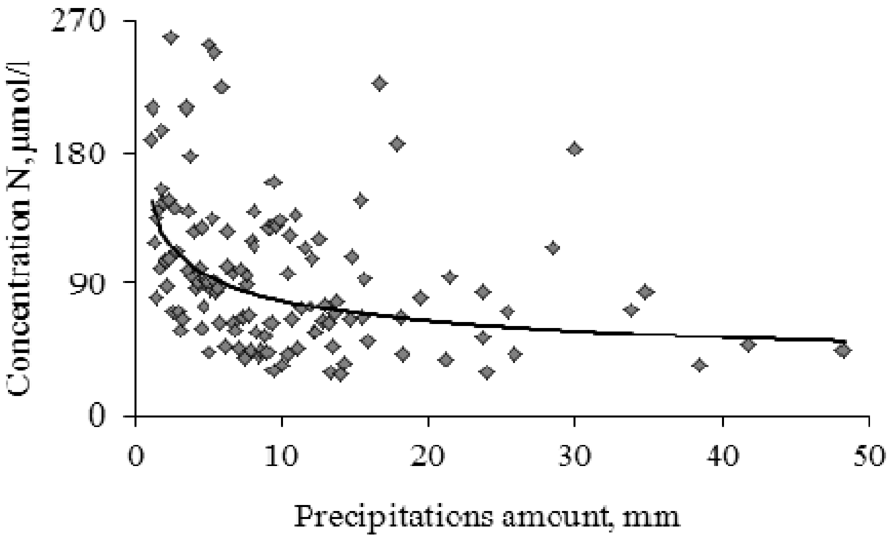

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Fig. 3. Intra-annual variation of inorganic nitrogen weighted mean concentration in atmospheric depositions and sum of precipitation amounts (*a*); variation of inorganic nitrogen concentration depending on precipitation amount (*b*)

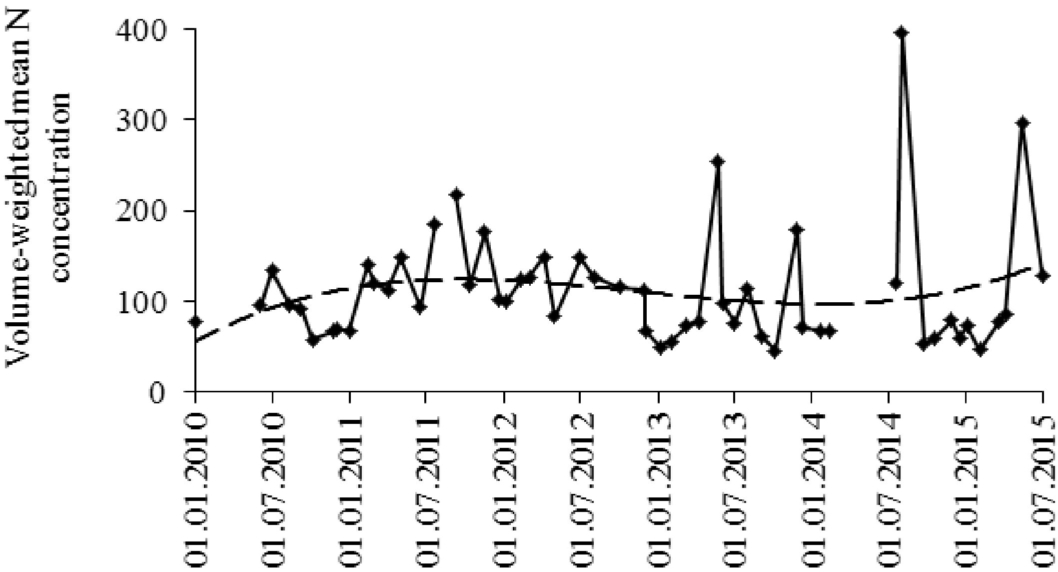
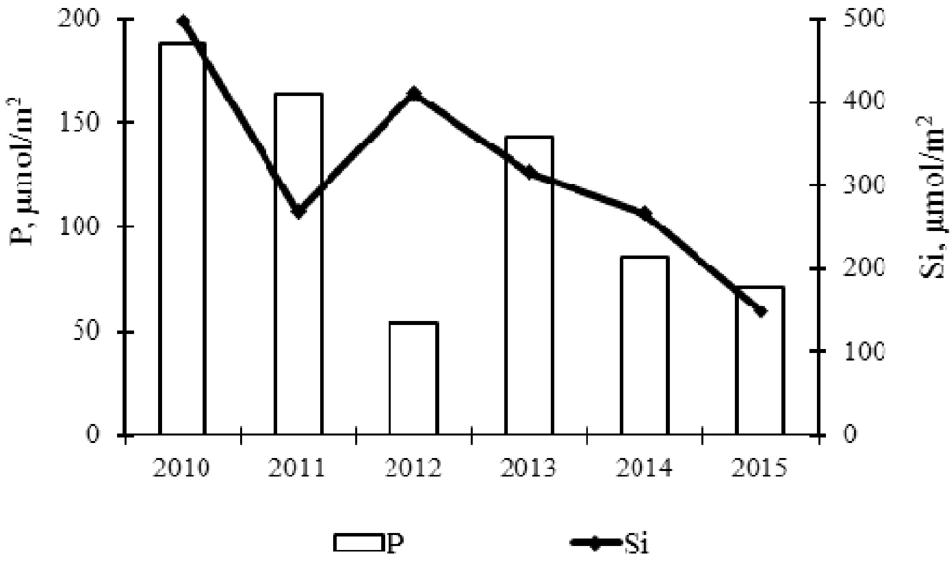


Fig. 4. Inerannual variation of inorganic nitrogen weighted mean concentration in atmospheric depositions

Inorganic phosphorus and silicon. During the period under investigation, phosphate and silicon fluxes with atmospheric depositions were significantly lower than inorganic nitrogen flux (Fig. 5, *a*). However, under certain conditions phosphorus may also be a limiting nutrient element. According to [8], more intensive anthropogenic nitrogen input to the marine ecosystem may cause a situation when some sea regions will become phosphorus-limited ones.

The minimum phosphorus flux was in 2012 (Fig. 5, a) and this can be explained by the absence of data on its concentration in depositions during the period from May to September, i.e in those months when in other years the maximum concentrations of this element in atmospheric depositions were observed. However, under the same condition the silicon flow in 2012 was higher than the one in other years (except for 2010). If one consider the change of this element concentration in the atmospheric depositions during this period (Fig. 5, *b*), it can be seen that its concentration reached the maximum in 2012. Apparently, it was the factor determining a high silicon flux.

In intra-annual change of inorganic phosphorus volume weighted mean concentration (Fig. 6, a) its significant increase in warm period of the year is observed. This can be explained (in the same way as for inorganic nitrogen) by decrease of precipitation events during this period. Besides, such intra-annual distribution can be explained by the features of phosphorus migration in biosphere which is also connected with input of its mineral forms with the dust particles formed under erosion of soil and rocks.



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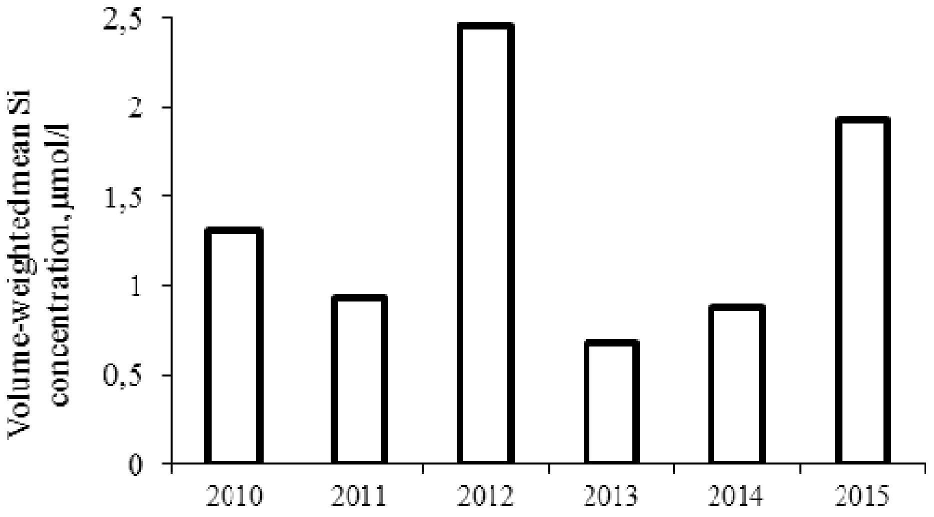


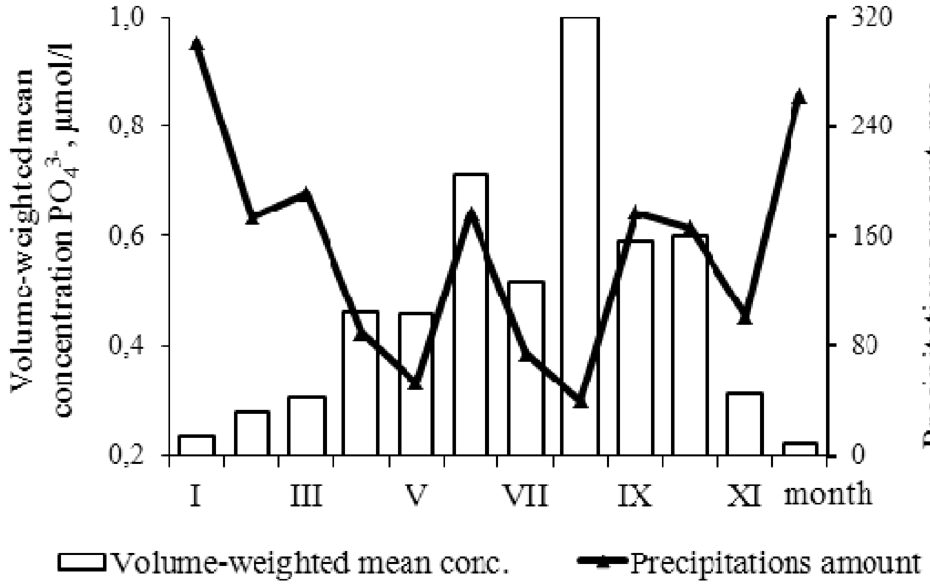
b

Fig. 5. Inorganic phosphorus and silicon flux with atmospheric depositions (*a*) and silicon weighted mean concentration variation (*b*)

Silicon (Fig. 6, *b*) is also characterized by a certain increase of volume weighted mean concentration during the period from April to August. This may be related to the decrease of precipitation event number and, as a consequence, to terrigenous silicon accumulation in the atmosphere in aerosol form.

Interannual variation of inorganic phosphorus (Fig. 7, *a*) and silicon (Fig. 7, *b*) content in atmospheric depositions is characterized by a decrease by 2015.

Phosphates volume weighted mean concentration in 2010 – 2011 was 1.5 times higher than in 2012 – 2015 at that.



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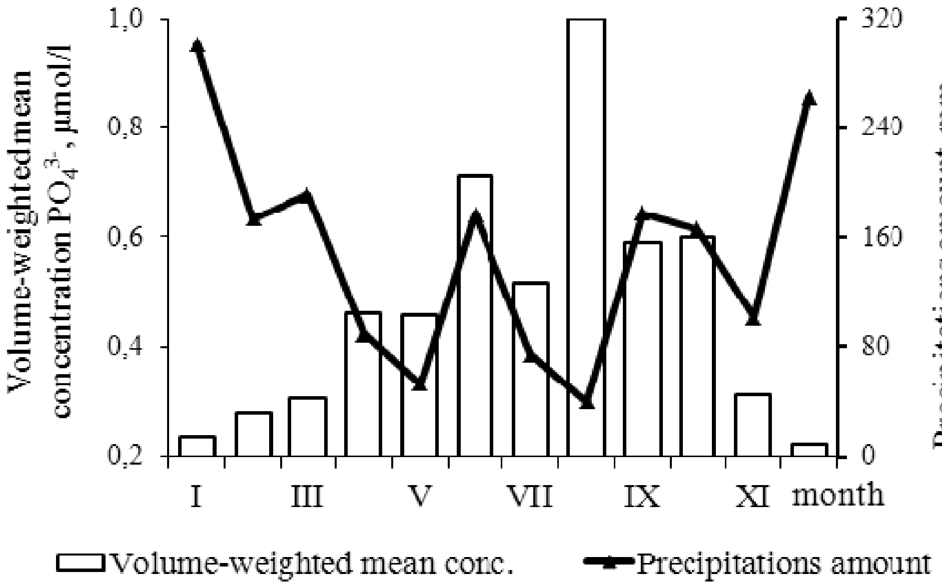

b

Fig. 6. Intra-annual variation of precipitation amount sum and inorganic phosphorus weighted mean concentration (*a*), the one of precipitation amount sum and silicon weighted mean concentration (*b*) in atmospheric depositions

Silicon concentration maximum values were observed in April 2012 and in August 2014 when high concentrations of the element in depositions with small precipitation amount were determined.

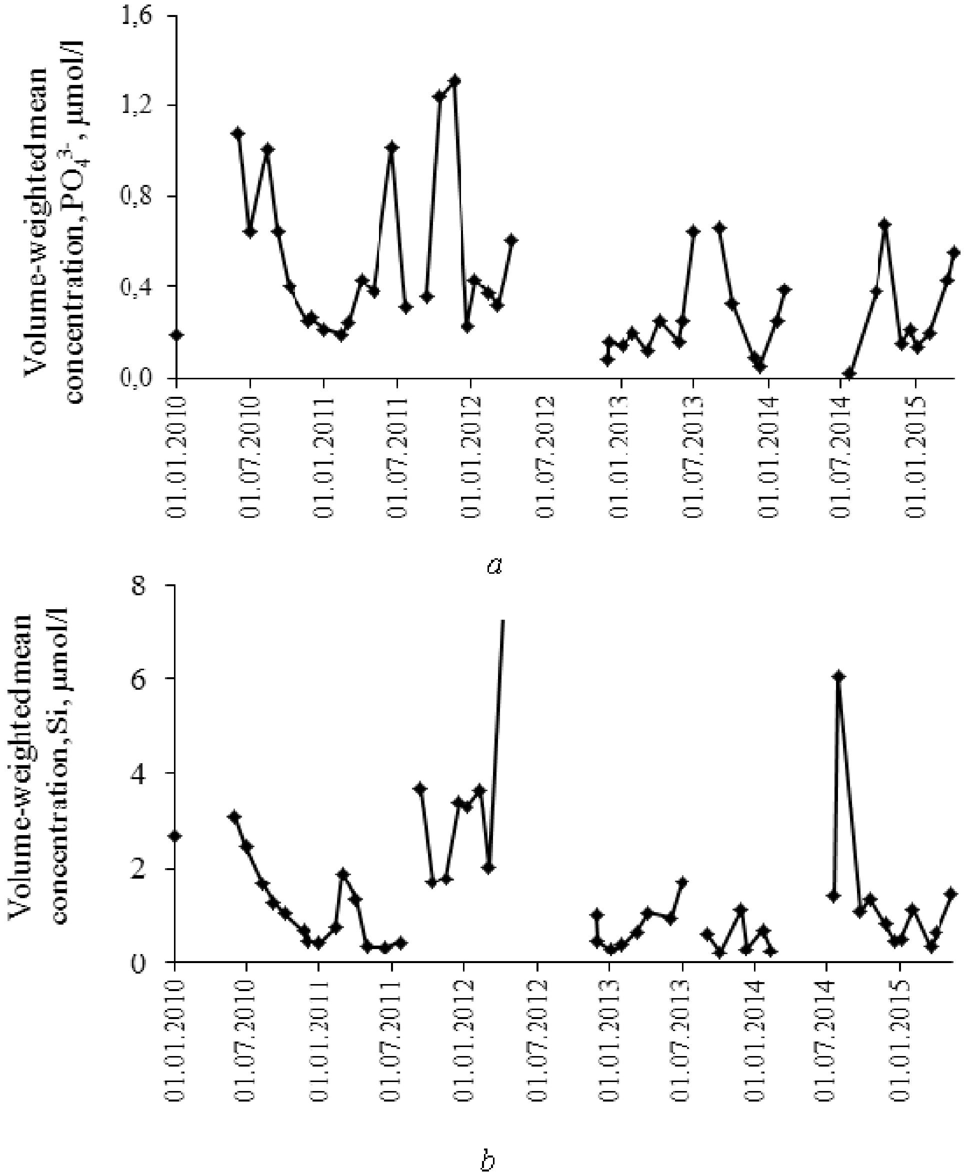

Fig. 7. Intra-annual variation of inorganic phosphorus (*a*) and silicon (*b*) weighted mean concentration in atmospheric depositions

The effect on primary production level. Inorganic nitrogen and inorganic phosphorus content ratio (N:P) in atmospheric depositions in 2010 – 2015 made up 258 which is significantly higher than Redfield ratio [9] for marine ecosystems.

Thus, atmospheric deposition input may lead to N:P ratio imbalance and, correspondingly, to the one of C:N ratio both in the Black Sea surface layer and its deep part [9].

To assess the effect of nutrients (inorganic nitrogen, phosphorus) input with atmospheric depositions on primary production level many authors [8, 10 – 12] use Redfield ratio. The paper [9] refers to primary production increase by 25 % as a result of atmospheric input of nitrogen. According to the data of [13], with 0.8 $mmolN/m^2 \cdot day$ average nitrogen input with precipitations the primary production increase is about 5.3 $mmolC/m^2 \cdot day$.

Applying the Redfield ratio C:N (106:16) in our study, we found out that average annual input of inorganic nitrogen with atmospheric precipitation, which is equal to 30.4 $mmol/m^2$, corresponded to 201.4 $mmol/m^2$ primary production value. Having considered the data of [14] about the fact that annual primary production average value made up 100 – 130 gC/m^2 in coastal regions and 120 – 170 gC/m^2 in deep regions, we determined that nitrogen flux with atmospheric depositions may result in primary production increase by 1.4 – 2.4%.

Annual inorganic phosphorus input with atmospheric depositions (118 $\mu mol/m^2$) provides primary production increase by 0.08 – 0.14% from its mean multi-annual value for the open and coastal Black Sea regions. Excluding the regeneration production (its mean value is 64 % from total primary production [15]), atmospheric inorganic phosphorus contribution to primary production formation makes up 0.5 %.

Paper [16] states that C:Si ratio for diatoms is 8:1. Consequently, it was found that additional contribution of inorganic silicon atmospheric input to primary production formation made up 0.02 % of its annual value in the Black Sea open part.

Conclusion. Nutrients (inorganic nitrogen, phosphorus, silicon) input with atmospheric depositions at the Southern coast of Crimea (Katsiveli) over 2010 – 2015 was determined. It is revealed that the main forms of nitrogen in atmospheric depositions are nitrates and ammonium. The increase of their content in warm period of the year is observed in intra-annual change for all nutrients. This can be explained both by inverse dependence of elements concentration on precipitation amount and by features of their migration and input sources. Interannual variation of phosphorus and silicon content is characterized by insignificant decrease in 2015; the one of inorganic nitrogen is characterized by fluctuations against mean value. Nutrient input with atmospheric depositions may provide primary production increase up to 2.5% in the Black Sea.

REFERENCES

1. 27-28 August 2007, The 16th Baltic Sea Parliamentary Conference, Berlin, Germany, http://www.bspc.net/page/show/26 (Access date 24.02.2016).
2. Guerzoni, S., Chester, R. & Dulac, F. [et al.], 1999, "The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea", *Progr. Oceanogr.*, vol. 44, pp. 147-190, doi: 10.1016/s0079-6611(99)00024-5.

3. Jickells, T., 1995, “Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects”, *Mar. Chem*., vol. 48, pp. 199-214.

4. Koçak, M., Kubilay, N. & Tuğrul, S. [et al.], 2010, “Atmospheric nutrient inputs to the northern Levantine basin from a long-term observation: sources and comparison with riverine inputs”, *Biogeosci.*, vol. 7, pp. 4037-4050, doi:10.5194/bg-7-4037-2010.

5. Medinets, S., Medinets, V., 2012, “Investigations of atmospheric wet and dry nutrient deposition to marine surface in western part of the Black Sea”, *Turk. J. Fish. Aquat. Sci*., vol. 12, pp. 497-505.

6. Beverland, I.J., Crowther, J.M. & Srinivas, M.S.N. [et al.], 1998, “The influence of meteorology and atmospheric transport patterns on the chemical composition of rainfall in south-east England”, *Atmos. Environ*., vol. 6, pp. 1039-1048.

7. Garban, B., Motelay-Massei, A. & Blanchoud, H. [et al.], 2004, “A single law to describe atmospheric nitrogen bulk deposition versus rainfall amount: inputs at the Seine River watershed scale”, *Water Air Soil Poll*., vol. 155, pp. 339-354.

8. Herut, B., Krom, M.D. & Pan, G. [et al.], 1999, “Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact”, *Limnol. Oceanogr*., vol. 44, pp. 1683-1692, doi:10.4319/lo.1999. 44.7.1683.

9. Burlakova, Z.P., Eremeeva, L.V. & Konovalov, S.K., 2003, “Inventory and fluxes of particulate organic carbon and nitrogen in the Black Sea oxic/anoxic water column. Oceanography of the Eastern Mediterranean and Black Sea. Proceeding of the “Second International Conference on Oceanography of the Eastern Mediterranean and Black Sea: Similarities and Differences of Two Interconnected Basins”’, 14-18 October 2002, Ankara, Turkey: TUBITAK Publishers, pp. 514-522.

10. Krishnamurthy, A., Moore, J.K. & Mahowald, N. [et al.], 2010, “Impacts of atmospheric nutrient inputs on marine biogeochemistry”, *J. Geophys. Res*., vol. 115, G01006, doi:10.1029/2009JG001115.

11. De Fommervault, O.P., Migon, C. & Dufour, A. [et al.], 2015, “Atmospheric input of inorganic nitrogen and phosphorus to the Ligurian Sea: Data from the Cap Ferrat coastal time-series station”, *Deep-Sea Res. Part I: Oceanogr. Res. Pap*.,vol. 106, pp. 116-125.

12. Tugrul, S., Murray, J.W. & Friederich, G.E. [et al.], 2014, “Spatial and temporal variability in the chemical properties of the oxic and suboxic layers of the Black Sea”, *J. Mar. Sys.*, vol. 135, pp. 29-43.

13. De Leeuw, G., Spokes, L. & Jickell, T. [et al.], 2003, “Atmospheric nitrogen inputs into the North Sea: effect on productivity”, *Cont. Shelf Res*., vol. 23, pp. 1743-1755, doi:10.1016/j.csr.2003.06.011.

14. Demidov, A.B., 2008, “Seasonal dynamics and estimation of the annual primary production of phytoplankton in the Black Sea”, *Oceanology*, vol. 48, pp. 664-678, doi: 10.1134/s0001437008050068.

15. Parkhomenko, A.V., 2005, “*Ekskretsiya fosfora zooplanktonom v Chernom more* [Phosphorus excretion by zooplankton in the Black Sea],” *Morskoy ekologicheskiy zhurnal*, no. 4, pp. 17-31 (in Russian).

16. Brzezinski, M.A., 1985, “The Si-C-N ratio of marine diatoms. Interspecific variability and the effect of some environmental variables”, *J. Phycology*., vol. 21, pp. 347-357.