ATMOSPHERIC N DEPOSITION TO THE COASTAL AREA OF THE BLACK SEA: SOURCES, INTRA-ANNUAL VARIATIONS AND IMPORTANCE FOR BIOGEOCHEMISTRY AND PRODUCTIVITY OF THE SURFACE LAYER

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Atmospheric precipitations can be an important source of nutrients to open and coastal zones of marine ecosystem. Jickells [1] has published that atmospheric depositions can support 5-25% of nitrogen required to primary production.
Bulk atmospheric precipitations have been collected in a rural location at the Black Sea Crimean coast – Katsiveli settlement, and an urban location – Sevastopol city. Samples have been analyzed for inorganic fixed nitrogen (IFN) – nitrate, nitrite, and ammonium. Depositions have been calculated at various space and time scales.
The monthly volume weighted mean concentration of IFN increases from summer to winter in both locations. A significant local source of IFN has been revealed for the urban location and this source and its spatial influence have been quantified.
IFN deposition with atmospheric precipitations is up to 5% of its background content in the upper 10 m layer of water at the north-western shelf of the Black Sea. Considering Redfield C:N ratio (106:16) and the rate of primary production (PP) in coastal areas of the Black Sea of about 100-130 g C m^{-2} $year^{-1}$ we have assessed that average atmospheric IFN depositions may intensify primary production by 4.5% for rural locations, but this value is increased many-fold in urban locations due to local IFN sources.

Key words: inorganic fixed nitrogen, atmospheric input, the Black Sea

I. INTRODUCTION

Atmospheric deposition plays a significant role in forming of the chemical composition and characteristics of surface layer of Black Sea. Indeed, many scientists [2-4] consider atmospheric deposition as one of the most important sources of nutrients and pollutants to marine ecosystems. This is specifically true for conditions of summer stratification [5], when vertical exchange is restricted.

The composition of atmospheric precipitations depends on meteorological conditions, long-range atmospheric transport, local sources to atmosphere and their spatial and temporal distribution [6].

The main disadvantage of analytical determinations of chemical composition of atmospheric deposition is that this monitoring requires great efforts to quantify temporal and spatial features of IFN deposition. Therefore, assessments based on numerical modeling are often applied [7-9]. Yet, chemical composition estimates and meteorological data are still required for these assessments. Such approach helps to quantify: a) background deposition due to long-range

atmospheric transport and b) the input of local sources to the composition of atmospheric precipitations.

Nitrogen (nitrate, ammonium) in atmospheric deposition mostly associated with anthropogenic sources: fuel burning, motor vehicle exhaust gas and farming. That is why large cities, industrial and agricultural sites are local sources of IFN, while local meteorological conditions govern their spatial pattern.

Publications on atmospheric deposition of inorganic nitrogen at the surface of the Black Sea have been highly limited until recently. We present and analyze in this work observational data for 263 precipitation events collected at Katsiveli and for 328 precipitation events collected in Sevastopol (Crimean coast of the Black Sea) from November 2003 to December 2015. Both spatial and temporal variations in background deposition and the importance of local sources of IFN have been evaluated.

II. Materials and methods

2.1. Sampling sites

Monitoring of bulk atmospheric precipitations and analysis of inorganic fixed nitrogen concentrations have been organized in Katsiveli (Southern coast of Crimea) and Sevastopol (Western coast of Crimea) (Fig. 1) from 2003 – 2008 and from 2014-2015.

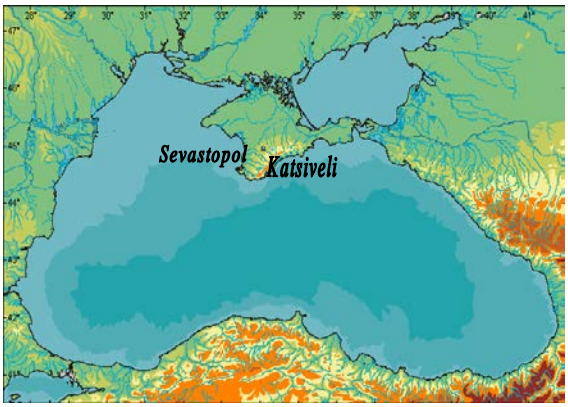


Fig. 1. Sampling sites

Katsiveli is located at the sea coast and at a distance from the nearest largest cities which could additionally support nutrients and pollutants to atmosphere and with atmospheric precipitations. Its permanent population does not exceed 550 citizens. Besides, this site is protected by 600–1100m high cliffs from northern and north-western winds, to additionally block urban air pollution. Taking these facts into account, we considered Katsiveli as a background location that characterizes large-scale processes of nutrients migration.

Sevastopol is one of the largest and industrially developed cities of Crimea. There are about 420,000 permanent residents, but this population can easily triple on summer time. Therefore it can reveal anthropogenic features.

2.2. Sampling and analysis

Of all collected samples, 61% were collected from October to March and 39% - from April to September making possible to trace intra-annual variations.

Using data on the inorganic nitrogen concentration in atmospheric depositions the annual flux of IFN was estimated [10].

Collected samples were analyzed for nitrate+nitrite and ammonium concentrations following standard analytical procedures [11]. The operational reproducibility was 12.5% and accuracy was 20% for nitrate+nitrite, and 3.1% and 9.0% for ammonium. Primary data were quality verified and statistically filtered to eliminate potentially erroneous and/or abnormal results applying the three sigma rule.

Using 2004-2008 IFN data we identified the local source of IFN: its value, seasonal and spatial effects.

Meteorological data were also recorded for the rate of precipitation, wind speed and direction, air temperature, atmospheric pressure and relative humidity making possible statistical and regression analyses.

III. Results and discussions

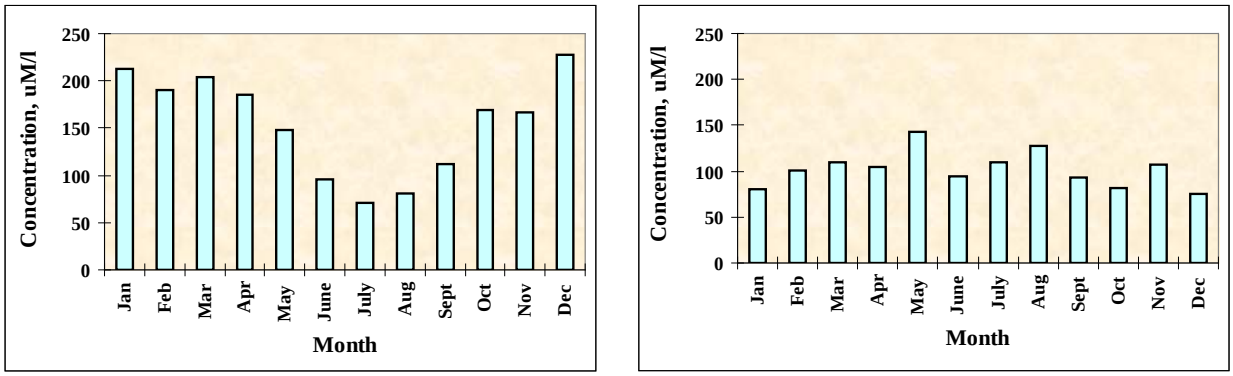
3.1 Average concentrations and their temporal variations

Atmospheric depositions of IFN in both locations were mainly presented by nitrate (53–66 %) and ammonium (33–45 %). Nitrite was in the range of 1–2% and it presented, most probably, intermediate products of oxidation of ammonium to nitrate. These results are in good agreement with published data [1, 2, 12, 13]

IFN concentrations dropped to their minimum of 22.50 µmol/l and 30.72 µmol/l in September 2014 and September 2007 in Sevastopol and Katsiveli respectively. The maximum values of 371.77 µmol/l and 395.63 µmol/l were detected in December 2006 and August 2014.

Data for permanently open and wet-only samplers showed that the flux measured for bulk deposition was only 20% higher.

The monthly volume weighted mean concentrations of IFN in atmospheric precipitations revealed the presence of seasonal oscillations in Sevastopol and Katsiveli (Fig. 2).



a) b)

Fig. 2. Intra-annual variations in monthly volume-weighted mean IFN concentrations in Sevastopol (a) and Katsiveli (b);

Significantly higher concentrations were revealed in Sevastopol from November to March, as compared to summer (Fig. 2a). It was explained by the magnitude of anthropogenic emission (Martin et al., 2008) oscillating seasonally due to variations in fuel combustion. Seasonal oscillations revealed in Katsiveli were statistically insignificant (Fig. 2b). The absence of powerful local sources of air pollution was the obvious explanation. Neither industrial, nor agricultural local sources would have been known for this rural site.

The summer volume-weighted mean concentrations were equal for Sevastopol and Katsiveli – 115.67 µmol/l and 112.63 µmol/l respectively. At the same time, the winter volume-weighted mean concentration for Sevastopol was 2-fold higher than for Katsiveli – 194.93 µmol/l and 92.76 µmol/l respectively.

The calculated average annual IFN input for urban area (Sevastopol) was about 0.49 $tkm^{-2}yr^{-1}$ and for rural area (Katsiveli) – about 0.39 $tkm^{-2}yr^{-1}$.

3.2 Spatial variability of IFN deposition

In order to analyze spatial variations in the IFN input we have followed [15] to parameterize the concentration of trace substances as a function of meteorological variables. Jenkins et al. [18] has demonstrated that nitrate concentrations in rainwater depend on local weather patterns. We have applied a multiple regression equation to bind meteorological parameters (daily data of the precipitations amount, wind direction, season and preceding dry period) with the flow of contaminants from the atmosphere.

The rate of precipitation is the most influential parameter [16] and it is assessed by the power law [7, 17]. The influence of the wind has been approximated by the third or fourth-order power law [20].

In order to reconstruct a multiple nonlinear regression equation for the IFN concentration as a function of meteorological parameters, we have followed the approach suggested by Brandon [21]. The method is based on (i) identification of regressions between the concentration of IFN and individual statistically significant meteorological variables and (ii) successive introduction of these individual regressions to the multiple regression equation.

Four meteorological variables (precipitation rate, wind speed and direction, and relative humidity) have been identified of having relevant and statistically significant influence on the concentration of IFN in samples of rainwater. They have been successively introduced to the multiple non-linear regression equation (1), and their contributions have been evaluated [22].

$$C = 1.0826 \cdot \exp^{-0.0496 \cdot Ri} \cdot (0.0012 \cdot Vx^3 - 0.008 \cdot Vx^2 + 0.0221 \cdot Vx + 1.1071) \cdot \\ \cdot (0.0004 \cdot Vy + 0.9535) \cdot (-0.0006 \cdot f + 0.96) \quad (1)$$

where R_i is the daily precipitation amount, mm; V_x and V_y are latitudinal and longitudinal wind components; f is relative humidity, %.

The influence of the rate of atmospheric precipitation reaches 68%. The contributions of other components are comparable and equal 12, 10 and 10% for the wind speed, wind direction and relative humidity, respectively.

This equation has been verified against observational data from Sevastopol, Katsiveli and Odessa, other published data [13] and unpublished data from scientific cruises. It has been found that the difference between calculated and measured values is under 14% and does not exceed analytical errors.

Applying (1) to calculate the concentration of IFN in the atmospheric precipitations for regional meteorological conditions and multiplying this concentration by the rate of precipitation, we have quantified inputs of IFN for individual rain events.

The total amount of IFN deposited at the surface of the Black Sea over the period 2004–2008 is about $1.55 \cdot 10^6$ t, which is on average about 0.75 t N km^{-2} yr^{-1}.

Spatial variations mostly depend on the distribution of precipitations over the sea. The rate of atmospheric precipitations [23] increases from the Romanian and Crimean coast to the coast of Turkey, but it reaches the highest values in the south-eastern part of the sea near Batumi. Similar spatial variations have been revealed for the magnitude of IFN deposition (Fig. 3).

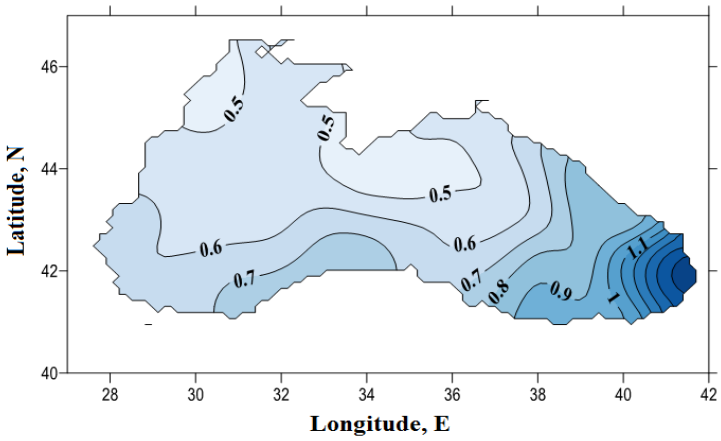


Fig. 3. The average from 2004 to 2008 annual IFN deposition (tNkm^{-2} yr^{-1}) with atmospheric depositions at the Black Sea surface

The character of seasonal distribution of IFN deposition is similar to variations of the IFN concentration in precipitations: it increases in cold period of the year, but decreases in warm period (Table 1).

Table 1. Seasonal variations in deposition of IFN at the Black Sea surface

Season	IFN deposition, t·season^{-1} (min-max)	% of the seasonal riverine input
Spring	46-68	16-24
Summer	26-38	13-19
Autumn	90-103	70-80
Winter	75-81	40-44

3.3 Local source

The difference between winter volume-weighted mean concentrations in rural and urban locations may indicate the local source of IFN to atmosphere. Taking into account that there is no difference for summer period, we conclude that this local source is most important in the cold period of the year. This local source is expected for every large city at the Black Sea coast (Istanbul, Varna, Constantsa, Odessa, Kerch, Novorossiysk, etc).

To assess the extent of its influence we have followed [14]:

$$C_j(x) = C_j \cdot \exp(\lambda_j x) \qquad (2)$$

where Cj is the maximum concentration of ingredient near the source (mg l^{-1}); λ_j is the coefficient characterizing the rate of changing concentration (km^{-1}).

The value of λ_j depends on the aerosol composition, wind speed and wind direction. For an average wind speed of about 5 m s^{-1}, values of λ_j can be calculated:

$$\lambda_j = k \cdot \exp(-0.025 \cdot \eta) \quad (3)$$

where k is the coefficient specific for the aerosol composition (for example, k=0.35 for nitrate and ammonium); η is the wind direction frequency in %.

We have found that the effect of local source associated with large cities for typical conditions of Sevastopol is limited to the coastal zone within 25 km distance.

The total amount of IFN deposited at the surface of the Black Sea in coastal 25-km area on average is about $27 \cdot 10^3$ t N yr^{-1}. The IFN deposition in this area also have a seasonal variations – it's maximum is observed in autumn and minimum – in summer. The percent of seasonal riverine input varies from 1.5-2% in summer to 3-9% in winter and 4-15% in autumn.

Considering that 25-km coastal area near Sevastopol influenced by local source of nutrients, the additional input of IFN in this area according to our estimates is about 739 t N yr^{-1}. Supposing that the 25-km area of the Black Sea may be influenced by local sources of large cities we can assess additional IFN input along the 25-km coastal area of about at least $12 \cdot 10^3$ t N yr^{-1}.

Despite the fact that local sources have no significant direct effect on off-shore areas of the sea, monitoring of IFN deposition remains important to correctly evaluate the budget of nitrogen in coastal waters near industrial sites. It is specifically true for winter, when these sources are most significant.

3.4 Influence on primary production

To asses influence of nitrogen atmospheric depositions to marine primary production (PP) many scientists [24-27] apply the Redfield C:N ratio (106:16).

We have assessed that average annual flux of IFN in coastal zone is about 53.6 mmol m^{-2} and may contribute of increasing the value of PP on by 355.1 mmol m^{-2} or 4.26 g C m^{-2}. Our data is in agreement with published values [28], where estimated atmospheric N depositions can support new production from 1.5 to 5.4 mg C m^{-2} day^{-1}. Considering data [29] that the rate of PP in coastal areas of the Black Sea of about 100-130 g C m^{-2} the average atmospheric IFN depositions may result in additional PP of 3.3-4.3% in coastal 25-km area for rural locations. Additional IFN input as result of local source influence in urban locations may increase this value many-fold. As a result the value of PP in coastal area may reach 556.5 mmol m^{-2}.

IV. Conclusions

Atmospheric deposition of IFN in two sites (urban and rural) of Crimean coast of the Black Sea has been studied.

The summer volume-weighted mean concentrations are equal in Sevastopol and Katsiveli, but the winter volume-weighted mean concentration in Sevastopol is 2-fold higher than in Katsiveli.

The calculated average annual IFN input for urban area (Sevastopol) was about 0.49 t km^{-2} yr^{-1} and for rural area (Katsiveli) – about 0.39 t km^{-2} yr^{-1}.

A significant local source of IFN has been revealed for the urban location. The effect of local source associated with large cities for typical conditions of Sevastopol is limited to coastal

zone within 25 km distance. Despite the fact that local sources have no significant direct effect on off-shore areas of the sea, monitoring of IFN deposition remains important to correctly evaluate the budget of nitrogen in coastal waters near industrial sites.

Spatial variations of IFN deposition are mostly governed by the distribution of precipitations over the sea: increases from the Romanian and Crimean coast to the coast of Turkey, but reaches maximum values in the south-eastern part of the sea near Batumi.

The average atmospheric IFN depositions may result in additional PP of 3.3-4.3% for rural locations, but this value is increased many-fold due to the influence of local sources in urban locations.

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