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OBSERVATIONAL STUDIES OF NUTRIENT LOADS ON THE BLACK SEA WITH ATMOSPHERIC PRECIPITATIONS

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There are three major sources that provide input of material to marine environments. These are coastal inputs, exchange processes at the sea surface and bottom, and atmospheric depositions. Material may come from the atmosphere in a form of wet and dry depositions. Wet depositions usually provide the major part of the atmospheric input, unless these are dry depositions of a dust-storm. There are two processes supporting atmospheric wet depositions:

incorporation of pollutants from the clouds;
dissolution of material in falling raindrops.

It has been recently realized that atmospheric depositions may become extremely important, especially for open and off-coast areas. Atmospheric wet and dry depositions may result in various effects from direct pollution to eutrophication and productivity enhancement. Thus, it is important to estimate the magnitude and a geographic pattern of atmospheric fluxes to both coastal and open areas of the sea.

This work is aimed to study the flux of nutrients onto the sea surface with atmospheric precipitations because the atmospheric input is an expectedly significant source of nutrients contributing to eutrophication of the Black Sea. This source is important as for the seashore near the urbanized and industrial regions so for the whole Black Sea. According to [1], the input of nutrients from the atmosphere onto the Black Sea surface is about 400 thousands ton/year.

The BSERP/GEF (Phase 1) monitoring program was started in 2004. Within this program, an experimental network of sampling of atmospheric precipitations was established at the seashore in Varna (Bulgaria, W part of the sea), Odessa (Ukraine, NW part of the sea), Sevastopol and Katsively (Ukraine, central part of the sea). Sampling technique and methods of chemical analyses were unified at this stage of the studies. Though the period of sampling in Varna and in Odessa was rather short, samples are currently collected in Sevastopol and Katsively. Laboratory analyses of inorganic forms of nitrogen are executed in MB UHMI, Sevastopol. Katsively serves as a background station, as there is no local source of nutrients there. Sevastopol is a typically urbanized region and samples are collected in the center of the city.

Sampling techniques and chemical analyses are in line with the manual [2] adopted and certified in Ukraine. The random error of the method does not exceed ±10%. According to this manual, the method of nitrate determination is certified for the mass concentration of 0.1 – 1.0 mg/dm3 in atmospheric depositions. The method is based on reduction of nitrate to nitrite in a copper-plated cadmium column and colorimetric determination of nitrite with Griss reagent. The method of ammonium determination is certified for the mass concentration of 0.05 – 5.0 mg/dm3 in atmospheric depositions. It based on an interaction of ammonia with Nessler`s alkaline reagent.

Published data show that the chemical composition of atmospheric depositions is rarely linked to the meteorological conditions, though meteorological conditions are of primary importance for the intensity of the atmospheric depositions and their composition. We have traced such meteorological parameters as wind velocity and direction, atmospheric pressure, air relative humidity and intensity of atmospheric precipitations. Information on the meteorological parameters is generously provided by the meteorological service in Sevastopol and Experimental Branch of Marine Hydrophysical Institute of NASU in Katsively.

The sequence of data includes information for over 100 samples collected in Sevastopol (53 samples for 2004, 50 - for 2005), and 95 samples collected in Katsively (42 samples for 2004, 53 - for 2005).

Initial data show that the atmospheric source of inorganic nitrogen depends on such meteorological parameters, as wind velocity and direction, atmospheric pressure, relative humidity and intensity of precipitations. Typical wind directions in Sevastopol and Katsively are presented in Fig. 1. The relative frequency to trace higher concentrations of inorganic forms of nitrogen in atmospheric precipitations depending on the wind direction in Katsively and Sevastopol is shown in Fig. 2.

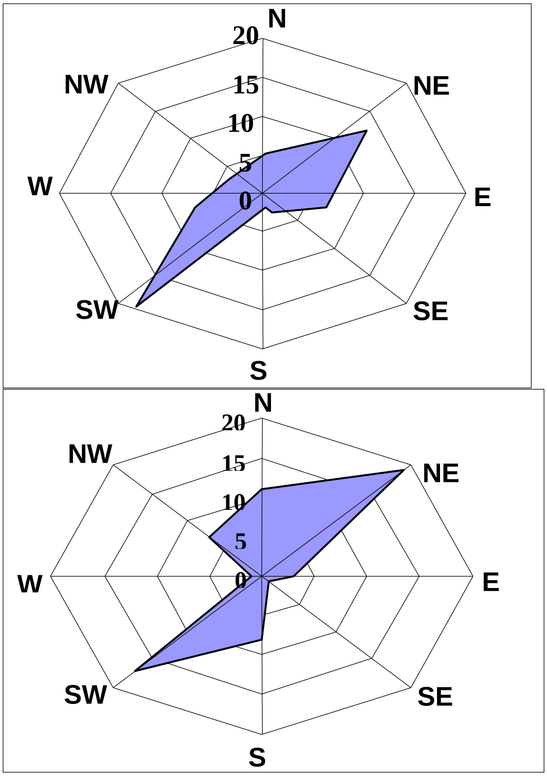
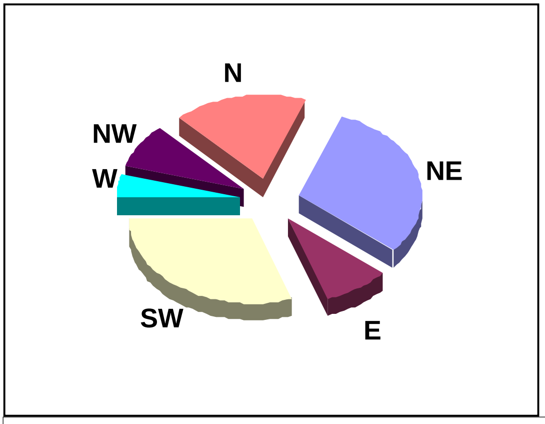


Fig. 1. Wind roses in the investigated regions (right – Sevastopol, left – Katsively)



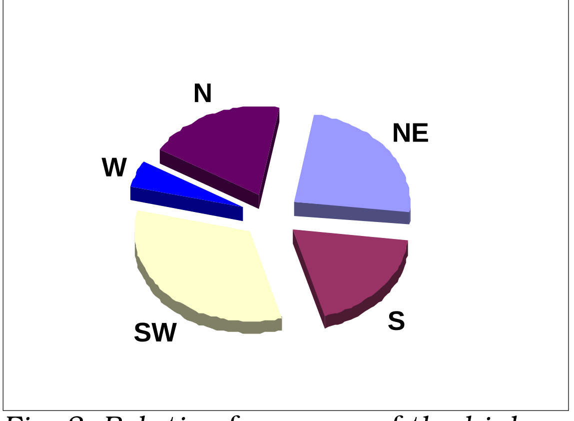


Fig. 2. Relative frequency of the higher nitrogen concentrations observed in atmospheric deposition for various wind directions in Sevastopol (right) and Katsively (left)

Results of chemical analyses show that the major forms of inorganic nitrogen in precipitations were nitrate and ammonium. The concentration of nitrogen in the samples collected in Sevastopol was always higher, as compared to the samples collected in Katsively, proving that Katsively is a background station. Data on the observed ranges of the nitrate, nitrite, and ammonium concentrations are presented in Table 1.

Table 1. Bands of concentrations for inorganic forms of nitrogen

Region	**Concentration limits mg/dm3**		
	NITRITES	**NITRATES**	**AMMONIUM**
SEVASTOPOL	**0 - 1.24**	**0.4 – 25.9**	**0.1 – 6.0**
KATSIVELY	**0 – 0.20**	**0.3 – 18.4**	**0.01 – 4.97**

Amounts Pi,j of nitrogen form depositions are estimated as products of element concentrations in the samples collected during some fall-out period and these sample volumes [3]:

$$P_{i,j} = C_{i,j} * V_i$$

,

where $C_{i,j}$ **- concentration of j-th substance in i-th collected sample of the atmospheric depositions;**

V_i **- volume of i-th collection (precipitation amount).**

The amounts of inorganic nitrogen that came with precipitations in different sampling periods are presented in Fig. 3.

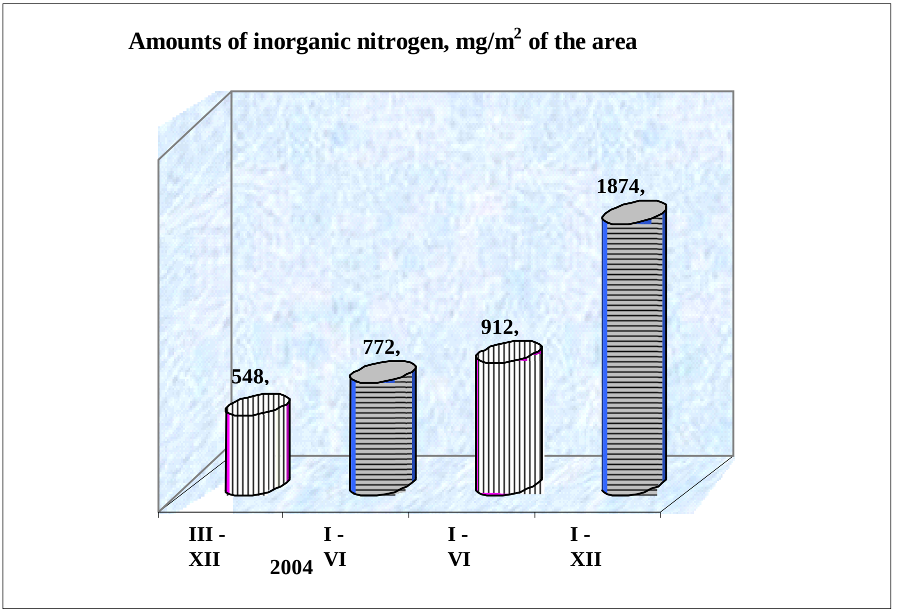


Fig. 3. Amounts of inorganic nitrogen coming with precipitations in the observed regions (▤ - Sevastopol, ▥ - Katsively)

Though the range of the inorganic nitrogen concentrations did not vary from 2004 to 2005, the frequency of nitrogen enriched atmospheric depositions increased over the same period. It resulted in 1.5-fold increase in the total inorganic nitrogen deposition both in Sevastopol and in Katsively.

In order to estimate possible correlation between nitrogen concentrations and meteorological parameters, nonlinear correlation coefficients were calculated (Table 2). Similarity of the correlation coefficient's values shows similar character of the studied parameters dependence.

Table 2. The coefficients of nonlinear correlation between inorganic nitrogen concentrations and meteorological parameters

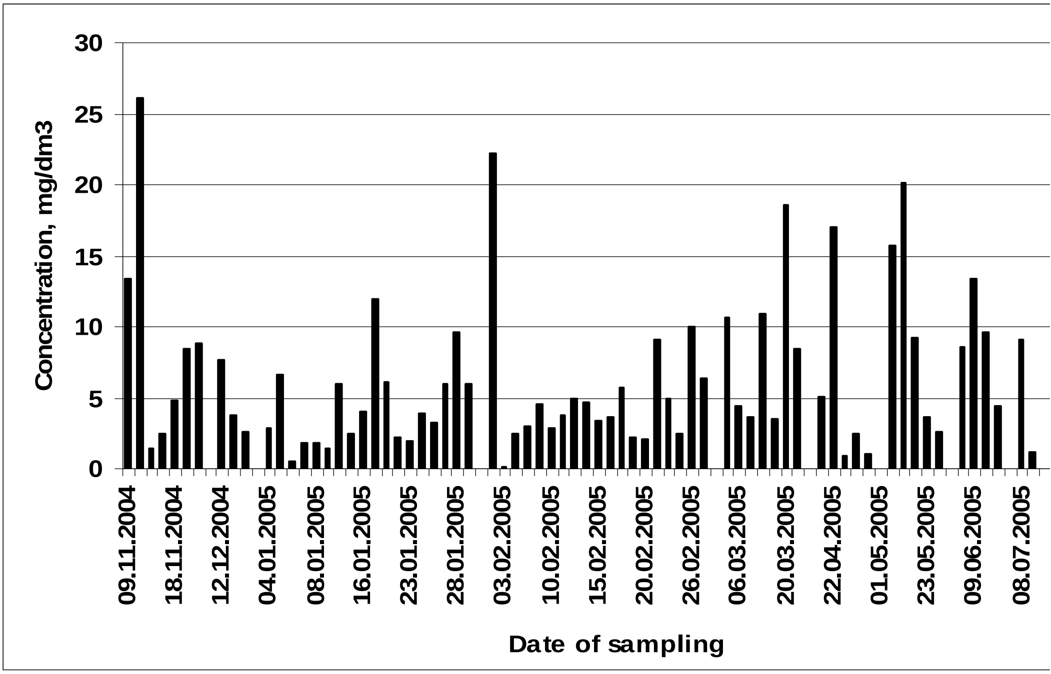
	Wind velocity	Relative humidity	Atmospheric pressure	Precipitations amount
Sevastopol	0.4	0.68	0.61	0.70
Katsively	0.4	0.68	0.62	0.74

Results of this work revealed empirical relations between the nitrogen contents and the amount of precipitations. The nitrogen concentration decreases with the increasing amount of precipitations. This was explained

by the fact of a decreasing inventory of inorganic nitrogen in the air over the precipitation periods.

Relations between the meteorological parameters and seasonal changes in the concentration of nitrogen in atmospheric depositions were also studied. Though the concentrations of inorganic nitrogen in atmospheric depositions are different in Sevastopol and Katsively, the general pattern of seasonal changes remains much the same. Higher concentrations of inorganic nitrogen have been registered from November to December and from the end of February to May (Fig. 4). The increasing nitrogen contents in the cold year period may be the result of additional fuel consumption.

The results of this work confirm rare published data on the inorganic nitrogen contents in atmospheric precipitations over the Black Sea, their seasonal variability and temporal variations in the concentration of inorganic nitrogen over the period of atmospheric deposition. At the same time, the importance of atmospheric depositions for the overall budget of nitrogen in the Black Sea remains poorly studied. Therefore, the necessity of a systematic research and monitoring of the atmospheric transport and sources of nutrients, their seasonal changes becomes extremely important and equally challenging.



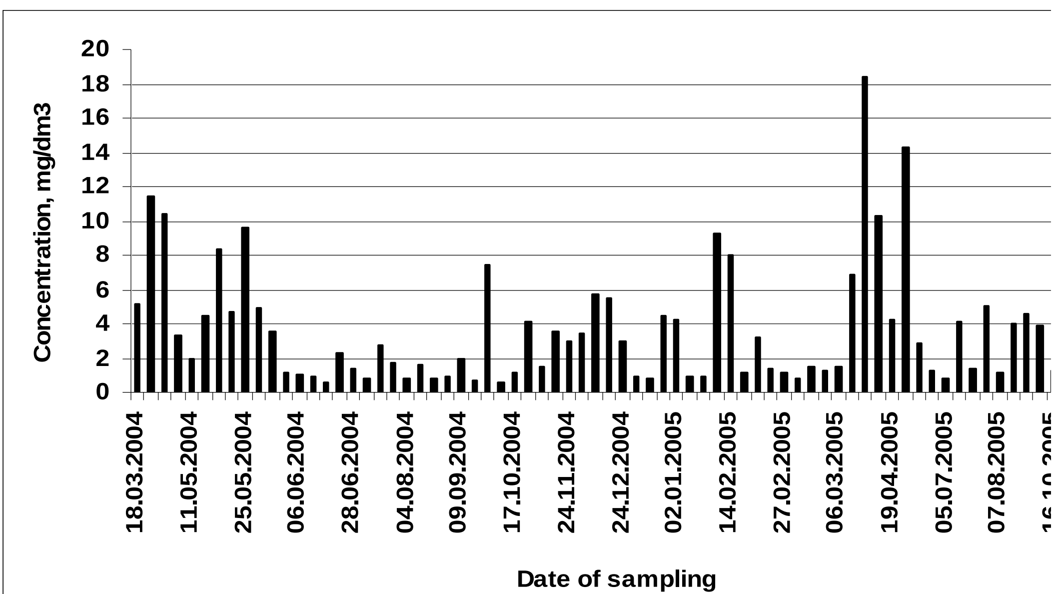


*Fig. 4. Contents of nitrogen in atmospheric depositions during different seasons of ye****ar in Sevastopol (above) and Katsively (below)***

To estimate the exact values of inorganic nitrogen deposition, the data on the concentration of nitrogen for every individual atmospheric precipitation is essential. Unfortunately, the available data are specific for a few locations of the coastal Black Sea area. Data for off-shore area are practically unavailable. To solve this problem, a computer based model was created in 2004 [4]. This system is capable to utilize the maps of the distribution of atmospheric depositions available on the Internet in order to quantify the amount and other characteristics of the depositions in various regions of the Black Sea.

The core of full data set analysis and fluxes calculation can be the computer software system developed in the framework of the BSERP/GEF Phase 1 program, which is able to solve the following problems:

To assimilate information on precipitation amounts falling onto the Black Sea shores and parts of interior.

To assimilate information on concentration of nutrients and other dissolved chemical substances in precipitations.

To calculate:

- mean values of precipitations level (in mm) for every day and every month;
- precipitation volumes of every case of rain (snow) fall on separate water areas;
- sum amounts of precipitation falling on the whole sea surface for every case and every month;
- absolute amounts of dissolved substances falling with precipitations for every substance, every case and month in whole.

To produce automatically the tables with results and maps of all calculated parameters for every case and month in whole.

To digitize automatically and assimilate in the database the most reliable graphical information on precipitation amounts from selected Internet-sites.

The results of this work showed that:

atmospheric depositions are important source of nutrients both for the seashore near the urbanized and industrial regions and for the whole Black Sea;

the major forms of inorganic nitrogen in precipitations are nitrate and ammonium;

the atmospheric source of inorganic nitrogen depends on such meteorological parameters, as wind velocity and direction, atmospheric pressure, relative humidity and intensity of precipitations;

there is a relation between the meteorological parameters and seasonal changes in the concentration of nitrogen in atmospheric depositions.

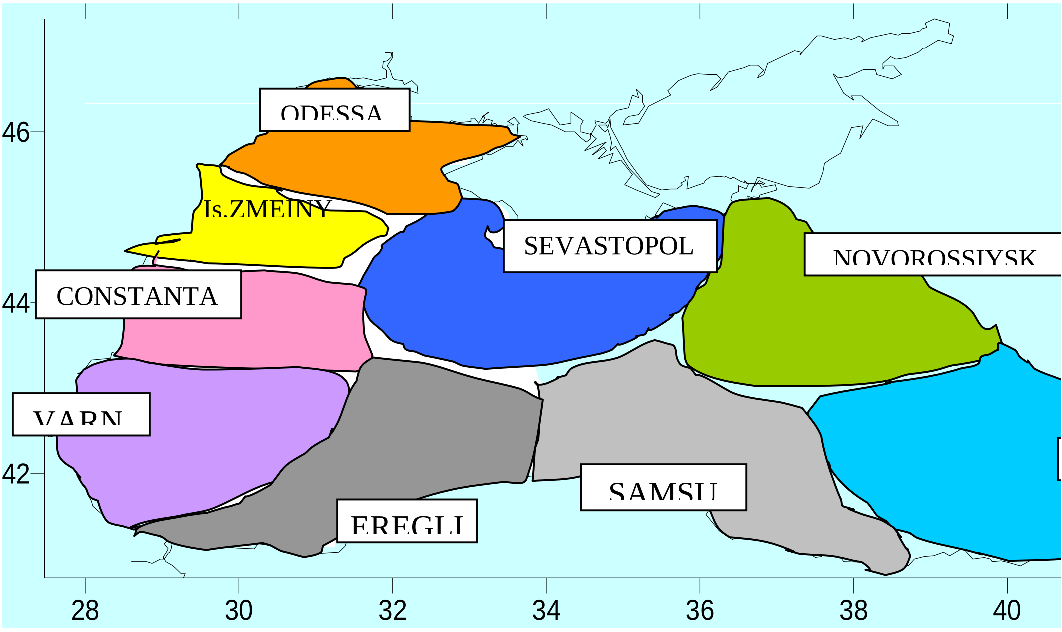


Fig. 5. The scheme of possible shore observational stations system and related regions of the sea interior

However, all data about the contents of inorganic forms of nitrogen in atmospheric depositions are received at two coastal stations only, hence, on them it is impossible to estimate the general entry of the given substances onto all water area of the Black Sea. That is why it is necessary to carry out observations at maximal number of stations in the coastal zone of the Black Sea. So we propose scheme of possible shore observational points system for precipitation measurements and chemical substances detection, and related regions for the calculations (Fig. 5.). And first of all, further international joint actions for additional nutrients data collection around the Black Sea are extremely needed to estimate the nutrient inputs onto the whole sea surface, using unified methodology of sampling and processing and necessarily considering the meteorological conditions.

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