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Modeling biogeochemical processes in the Azov Sea using statistically processed data on river flow

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Introduction. This work is aimed at solving the problem of phytoplankton dynamics in the coastal environments using the example of the Azov Sea. This takes into account the transformation of forms of phosphorus, nitrogen and silicon, as well as the aquatic medium motion, the distribution of temperatures and salinities over the sea area. River flow, varying in volume and chemical composition, affects significantly the variability of hydrophysical and biogeochemical parameters of the processes occurring in the coastal environment. This explains the need for statistical processing of the data from long-term observations over the river flow characteristics.

Materials and Methods. The mathematical model of biogeochemical cycles is based on a system of non-stationary equations of the convection–diffusion–reaction of parabolic type with nonlinear functions of sources and lower-order derivatives, to which the corresponding initial and boundary conditions are added. In the course of statistical analysis of the series of long-term observations over river flows, the values of the following indicators were found: skewness coefficient, degree of kurtosis, variance and standard deviation, coefficient of variation, autocorrelation coefficient, Neumann ratio, and Anderson criterion.

Results. The statistical analysis of the series of long-term observations over the hydrochemical indicators of the Don river suggests heterogeneity of the field data. This is due to the stochasticity of nutrient inputs and the volume of freshwater flow to the sea as a result of natural and anthropogenic factors. Field data should be correlated with seasonal changes in the aquatic environment temperature. This paper presents the results of a computational experiment to model the dynamics of phytoplankton populations in summer season, when temperatures are favorable for their reproduction and growth. The proposed mathematical model considers the spatially inhomogeneous distribution and transformation of forms of phosphorus, nitrogen, and silicon, as well as changes in salinity, temperature, and motion of the aquatic environment.

Discussion and Conclusions. The multispecies mathematical model of the dynamics of phytoplankton populations is considered with account for the transformation of forms of phosphorus, nitrogen, and silicon in the coastal environments. The analysis of data from field observations, for which its major statistical parameters are calculated, is carried out. As a result, it is concluded that data of the long-term observations are significantly variable. This is due to two reasons. Random nature of the input of nutrients and the volume of river flow as a result of anthropogenic factors is the first reason. The second reason includes the alternation of relatively high-water and low-water periods for fresh flow over the last 12-15 years. The hydrological regime is changing mainly due to the reduction of the average annual freshwater flow of the Don and partly of the Kuban. This trend is likely to increase due to climate changes, as well as with further regulation of the Don river flow after the Bagaevsky hydroelectric installation start-up. Numerical experiments based on the field data confirmed the predictive validity of the developed models and programs. They can be used to predict change in the composition and abundance (concentrations) in the Azov sea core planktonic populations, which define, on the one hand, food resources, and, on the other hand, the aquatic environment in terms of the ongoing sea salinization.

Keywords: biogeochemical cycles, phytoplankton population, biogenic substance, chemical-biological source, convection–diffusion–reaction equation, field data.

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Introduction. The sea of Azov is a large estuarine coastal system. It is the shallowest sea in the world. It warms up almost evenly in summer (with temperature differences on average no more than 4 °C). At the same time, it is characterized by a large difference in salinity — from 0% to 12-15%, since river flows provide an influx of fresh water commensurate with the total volume of sea water, and salty Black sea water comes from the Black sea near the Kerch Strait. River runoff affects significantly the biochemical composition of the water body

[1]. Mathematical modeling of biogeochemical processes, which provides performing diagnostic and prognostic calculations of the marine ecosystem dynamics, is considered important. A variable volume and hydrochemical composition of the river runoff affects significantly the parameters of hydrophysical and biological processes occurring in the coastal system. Therefore, it is advisable to conduct a statistical analysis of the data of long-term observations, in particular hydrochemical indicators of runoff of the rivers running into the sea of Azov, and to predict biogeochemical processes on the basis of statistically processed input data.

In the area of hydrodynamics and forecasting of marine systems, the works of Marchuk G. I. [2], Matishov G. G., Sukhinov A. I. [3], Berdnikov S. V., Tyutyunov Yu. V. [4], Yakushev E. V. [5], Ilyichev V. G., and others should be mentioned. The paper presents the results of complexing a mathematical model of biogeochemical cycles and a model of hydrodynamics of the sea of Azov [6–8]. This provides improving the modeling accuracy and considering such factors as hydrodynamic processes in coastal systems, heterogeneous distribution of temperatures, salinities and biogenic substances that affect the development of phytoplankton populations, the transition of biogens from one form to another [9]. It should be noted that numerical models of spatial-three-dimensional hydrophysical processes in coastal systems are the subject of a separate study of the authoring team. They provide considering the dynamically changing geometry of the bottom and coastline, wind stress on the free surface and its elevation, friction on the bottom, Coriolis force, turbulent exchange, evaporation, river runoff, deviation of pressure values in the aquatic environment from the hydrostatic approximation, etc. In this paper, the input data (distribution of the three-dimensional velocity vector, as well as salinity and temperature) are the results of numerical calculations based on the hydrophysical model [10].

Materials and Methods. To describe the model, an initial-boundary value problem is formulated for a system of parabolic equations with lower derivatives and nonlinear right-hand functions:

$$\frac{\partial q_i}{\partial t} + u\frac{\partial q_i}{\partial x} + v\frac{\partial q_i}{\partial y} + w\frac{\partial q_i}{\partial z} = div(k\,\mathrm{grad}\,q_i) + R_{q_i}, \tag{1}$$

where q_i — concentration of the i-th component [mg/l]; $i \in M$, $M = \{F_1, F_2, F_3, PO_4, POP, DOP, NO_3, NO_2, NH_4, Si\}$; $\{u, v, w\}$ — components of the water flow velocity vector [m/s]; k — turbulent exchange coefficient [m^2/s]; R_{q_i} — function — source of nutrients [mg/(l·s)].

In the equation (1), index i indicates the type of substance (Table 1).

Table 1

Biogenic substances in the model of phytoplankton dynamics

Number	Designation	Name
1	F_1	Green alga *Chlorella vulgaris*
2	F_2	Blue-green alga *Aphanizomenon flos-aquae*
3	F_3	Diatomic alga *Sceletonema costatum*
4	PO_4	Phosphates
5	POP	Weighed organic phosphorus
6	DOP	Dissolved organic phosphorus
7	NO_3	Nitrates
8	NO_2	Nitrites
9	NH_4	Ammonium
10	Si	Dissolved inorganic silicon (silicic acids)

Chemical-biological sources are described by the following equations ($i \in \{1,2,3\}$, where 1 — is ChV , 2 — $AF-A$, 3 — Sc , and $ChV, AF-A, Sc$ — symbolic designations of plankton species):

$$R_{F_i} = C_{F_i}(1-K_{F_iR})q_{F_i} - K_{F_iD}q_{F_i} - K_{F_iE}q_{F_i},\ i=\overline{1,3},$$

$$R_{POP} = \sum_{i=1}^{3} s_p K_{F_iD} q_{F_i} - K_{PD}q_{POP} - K_{PN}q_{POP},$$

$$R_{DOP} = \sum_{i=1}^{3} s_P K_{F_iE} q_{F_i} + K_{PD}q_{POP} - K_{DN}q_{DOP},$$

$$R_{PO_4} = \sum_{i=1}^{3} s_P C_{F_i}\left(K_{F_iR}-1\right)q_{Fi} + K_{PN}q_{POP} + K_{DN}q_{DOP},$$

$$R_{NH_4} = \sum_{i=1}^{3} s_N C_{F_1}\left(K_{F_iR}-1\right)\frac{f_N^{(2)}\left(q_{NH_4}\right)}{f_N\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)} q_{F_i} + \sum_{i=1}^{3} S_N\left(K_{F_iD}+K_{F_iE}\right)q_{F_i} - K_{42}q_{NH_4},$$

$$R_{NO_2} = \sum_{i=1}^{3} s_N C_{F_i}(K_{F_iR}-1)\frac{f_N^{(1)}\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)}{f_N\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)}\cdot\frac{q_{NO_2}}{q_{NO_2}+q_{NO_3}} q_{F_i} + K_{42}q_{NH_4} - K_{23}q_{NO_2},$$

$$R_{NO_3} = \sum_{i=1}^{3} s_N C_{F_i}\left(K_{F_iR}-1\right)\frac{f_N^{(1)}\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)}{f_N\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)}\cdot\frac{q_{NO_3}}{q_{NO_2}+q_{NO_3}} q_{F_i} + K_{23}q_{NO_2},$$

$$R_{Si} = s_{Si} C_{F_3}\left(K_{F_3R}-1\right)q_{F_3} + s_{Si}K_{F_3D}q_{F_3}.$$

Here, K_{F_iR} — specific respiratory rate of phytoplankton; K_{F_iD} — the specific rate of decay of phytoplankton; K_{F_iE} — specific extinction of phytoplankton; K_{PD} — specific rate of autolysis *POP*; K_{PN} — phosphatofication coefficient *POP*; K_{DN} — phosphatofication coefficient *DOP*; K_{42} — specific rate of ammonia oxidation to nitrites during nitrification; K_{23} — specific rate of oxidation of nitrites to nitrates in the process of nitrification; s_P , s_N , s_{Si} — normalization coefficients between the content of *N*, *P*, *Si* in organic matter [11–12].

The growth rate of phytoplankton is determined from the expressions

$$C_{F_{1,2}} = K_{NF_{1,2}} f_T(T) f_S(S) min\left\{f_P\left(q_{PO_4}\right), f_N\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right)\right\},$$

$$C_{F_3} = K_{NF_3} f_T(T) f_S(S) min\left\{f_P\left(q_{PO_4}\right), f_N\left(q_{NO_3}, q_{NO_2}, q_{NH_4}\right), f_{Si}\left(q_{Si}\right)\right\},$$

where K_{NF} — maximum specific growth rate of phytoplankton.
Dependences of temperature and salinity:

$$f_T(T) = \exp\left(-\alpha\left(\frac{T-T_{opt}}{T_{opt}}\right)^2\right),\ f_S(S) = \exp\left(-\beta\left(\frac{S-S_{opt}}{S_{opt}}\right)^2\right),$$

where T_{opt} , S_{opt} — temperature and salinity, optimal for this type of phytoplankton; $\alpha > 0$, $\beta > 0$ — coefficient of the interval width of tolerance of phytoplankton to temperature and salinity, respectively.

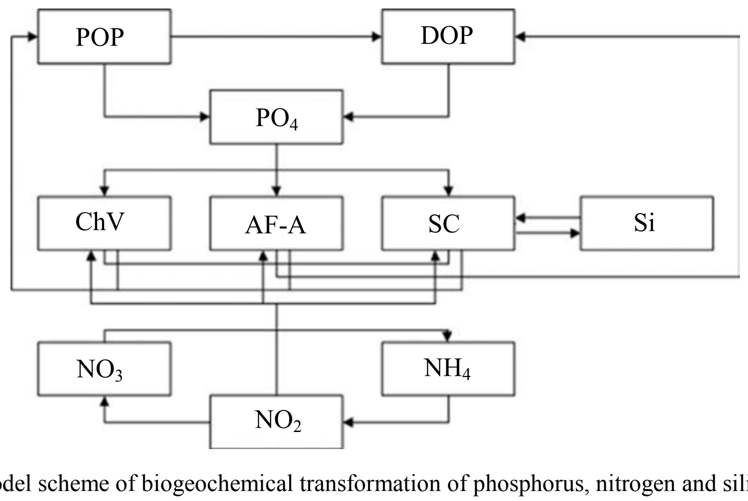

Fig. 1. Model scheme of biogeochemical transformation of phosphorus, nitrogen and silicon forms

Below are the functions that describe the content of biogens.

For phosphorus $f_P\left(q_{PO_4}\right)=\dfrac{q_{PO_4}}{q_{PO_4}+K_{PO_4}}$, where K_{PO_4} — constant of half-saturation with phosphates.

For silicon $f_{Si}\left(q_{Si}\right)=\dfrac{q_{Si}}{q_{Si}+K_{Si}}$, where K_{Si} — constant of half-saturation with silicon.

For nitrogen $f_N\left(q_{NO_3},q_{NO_2},q_{NH_4}\right)=f_N^{(1)}\left(q_{NO_3},q_{NO_2},q_{NH_4}\right)+f_N^{(2)}\left(q_{NH_4}\right)$,

$$f_N^{(1)}(q_{NO_3},q_{NO_2},q_{NH_4})=\frac{(q_{NO_3}+q_{NO_2})\exp(-K_{psi}q_{NH_4})}{K_{NO_3}+(q_{NO_3}+q_{NO_2})},\quad f_N^{(2)}(q_{NH_4})=\frac{q_{NH_4}}{K_{NH_4}+q_{NH_4}},$$

where K_{NO_3} — nitrate half-saturation constant;; K_{NH_4} — ammonium half-saturation constant; K_{psi} — inhibition coefficient of ammonia.

Assume that the coefficients included in the expressions for the source functions are positive and independent of time t.

For the system (1), an initial-boundary value problem is set in a cylindrical domain G. Let the boundary Σ of the cylindrical region G be a piecewise smooth surface and $\Sigma=\Sigma_H\cup\Sigma_o\cup\sigma$, where Σ_H — the surface of the reservoir bottom, Σ_o — the undisturbed surface of the aquatic medium, σ — lateral (cylindrical) surface.

Let u_{n} — be the normal component of the velocity vector of the water flow with respect to Σ, vector of the external normal to Σ. For example, for concentrations q_i at the lateral border:

$$q_i=0,\ \text{on } \sigma,\ \text{if } u_n<0,\ i\in M; \tag{2}$$

$$\frac{\partial q_i}{\partial n}=0,\ \text{on } \sigma,\ \text{if } u_n\ge 0,\ i\in M; \tag{3}$$

$$\frac{\partial q_i}{\partial z}=0,\ \text{on } \Sigma_o \text{ — water surface, } i\in M; \tag{4}$$

$$\frac{\partial q_i}{\partial z}=\varepsilon_{1,i}q_i,\ i\in\{F_1,F_2,F_3\},\ \frac{\partial q_i}{\partial z}=\varepsilon_{2,i}q_i;$$

$$i\in\{PO_4, POP, DOP, NO_3, NO_2, NH_4, Si\} \text{ at the bottom } \Sigma_H. \tag{5}$$

Here, $\varepsilon_{1,i}$, $\varepsilon_{2,i}$ — nonnegative constants; $\varepsilon_{1,i}$, $i\in\{F_1, F_2, F_3\}$ take into account the sinking of algae to the bottom and their flooding; $\varepsilon_{2,i}$, $i\in\{PO_4, POP, DOP, NO_3, NO_2, NH_4, Si\}$ take into account the absorption of nutrients by bottom sediments.

For a system of equations, it is required to specify at any time the velocity vector of the water flow, the salinity and temperature field, as well as the initial values of the functions q_i:

$$q_i\left(x,y,z,0\right)=q_{0i}\left(x,y,z\right),\quad \left(x,y,z\right)\in\overline{G},\ t=0,\ i\in M, \tag{6}$$

$$\mathrm{V}\left(x,y,z,0\right)=\mathrm{V}_0\left(x,y,z\right),\ T\left(x,y,z,0\right)=T_0\left(x,y,z\right),\ S\left(x,y,z,0\right)=S_0\left(x,y,z\right).$$

Statistical processing of data from long-term observations on river flows to the sea of Azov. Considerable river runoff relative to the volume of the sea affects significantly the biological and hydrophysical processes occurring in the sea of Azov [13]. A large amount of biogenic substances, including nitrogen, phosphorus and silicon, the main nutrients for phytoplankton, enter the water body from the river flows. In the twentieth century, the main part of the water inflow to the sea of Azov falls on the Don runoff — 63 % (Fig. 2–4)[1].

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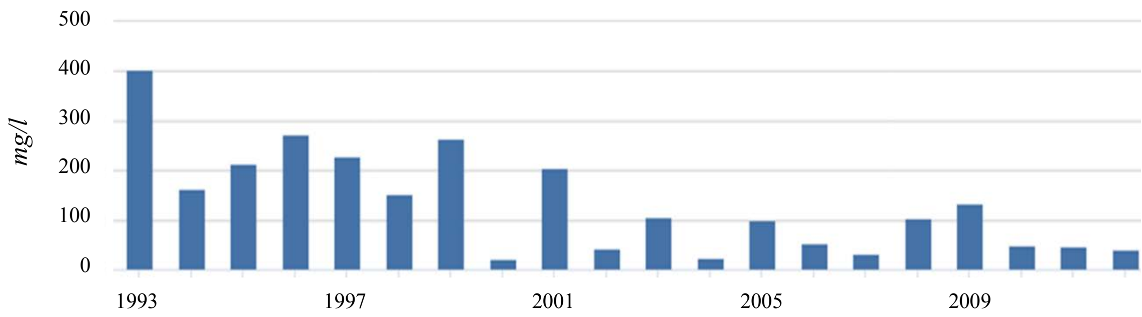

Fig. 2. Series of long-term observations of the Don river runoff (1993–2012): nitrogen concentration (N-NH_4)

[1] Ecological Atlas. Black and Azov seas. OC “Rosneft”; Arctic scientific center; NIR. Moscow, 2019. 464 p. (In Russ.)

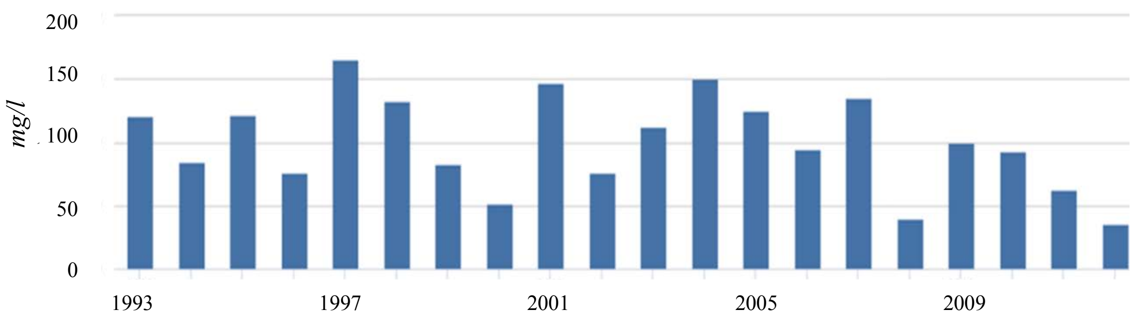

Fig. 3. Series of long-term observations of the Don river runoff (1993–2012): phosphorus concentration (PO_4)

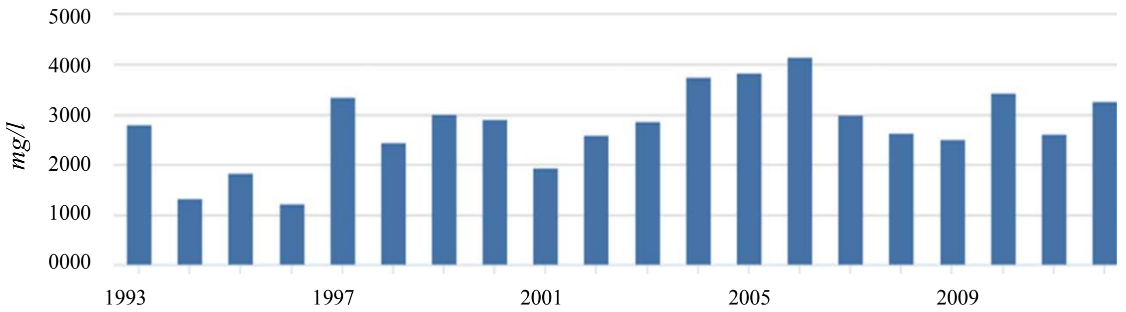

Fig. 4. Series of long-term observations of the Don river runoff (1993–2012): silicon concentration (SiO_4)

Table 2

Results of calculating the statistical parameters of field data

Indicator	***N-NH*$_4$**	***PO*$_4$**	***SiO*$_4$**
Number of values	20	20	20
Maximum value	403.9	165.0	4166.7
Minimum value	20.6	35.4	287.3
Arithmetic average value	132.3	100.1	2648.1
Variance	10362.5	1309.0	868441.9
Standard deviation	101.8	36.2	931.9
Skewness coefficient C_s	0.9	–0.1	–0.7
Kurtosis coefficient C_e	0.2	–0.9	0.2
Coefficient of variation C_v	0.8	0.4	0.4
Ratio C_s/C_v	1.2	–0.3	–2.0
Autocorrelation coefficient	0.3	–0.1	0.1
Neumann ratio	1.1	2.0	1.8

The study on the series of long-term observations of the Don runoff allows us to draw a number of conclusions.

— The nutrient concentrations considered have both positive and negative asymmetries.

— Random variables for nitrogen and silicon are shifted relative to the distribution center, as evidenced by the high value of the asymmetry coefficient.

— Large values of variances and standard deviations were obtained for all biogens.

— The autocorrelation coefficients are small; therefore, a strong nonlinear trend is characteristic of the full-scale data series.

— The variation in all rows is greater than 20 %, so the rows are highly variable.

— For nitrogen, the presence of an autocorrelation relationship according to the Anderson criterion is obvious for the number of values of 20 in the sample, since the autocorrelation coefficient exceeds 0.299 at a confidence level of 5%.

— For nitrogen, the presence of autocorrelation of residues according to the Neumann criterion is obvious at a confidence level of 5% for 20 observations, since the Neumann ratio is less than 1.2.

— Phosphorus and silicon do not show autocorrelation relationships; we reject the hypothesis of autocorrelation of residues.

As a result of statistical analysis of the field data [14], we can conclude that they are highly variable. This is due to the stochastic flow of nutrients from the Don runoff and the significantly changing volume of runoff under the impact of natural and anthropogenic factors. To use field data in the model (1) - (6), it is appropriate to take into account seasonal behavior. Hereafter, when modeling, we will consider the summer period.

Results of numerical experiments. A numerical simulation of the solution to the problem on the dynamics of phytoplankton populations in summer with account for the transformation of phosphorus, nitrogen and silicon forms, is carried out on the example of the sea of Azov. The simulated area corresponds to the physical dimensions of the sea of Azov: length — 355 km, width — 233 km, space step in horizontal directions — 1000 m. Fig. 5 shows a satellite image of the sea of Azov, confirming the compliance of the study results with full-scale data. The image shows clearly the distribution of green and blue-green algae in the Taganrog Bay area, and diatoms — in the central part of the sea.

Fig. 5. Satellite image of the sea of Azov taken with a moderate resolution spectroradiometer (MODIS) on the NASA Aqua satellite on July 31, 2004

В результате вычислительного эксперимента получены сеточные распределения концентраций основных популяций фитопланктона и питательных веществ в Азовском море (рис. 6). Период расчета — 30 суток. Этого достаточно для установления стационарных режимов в задачах динамики фитопланктона.

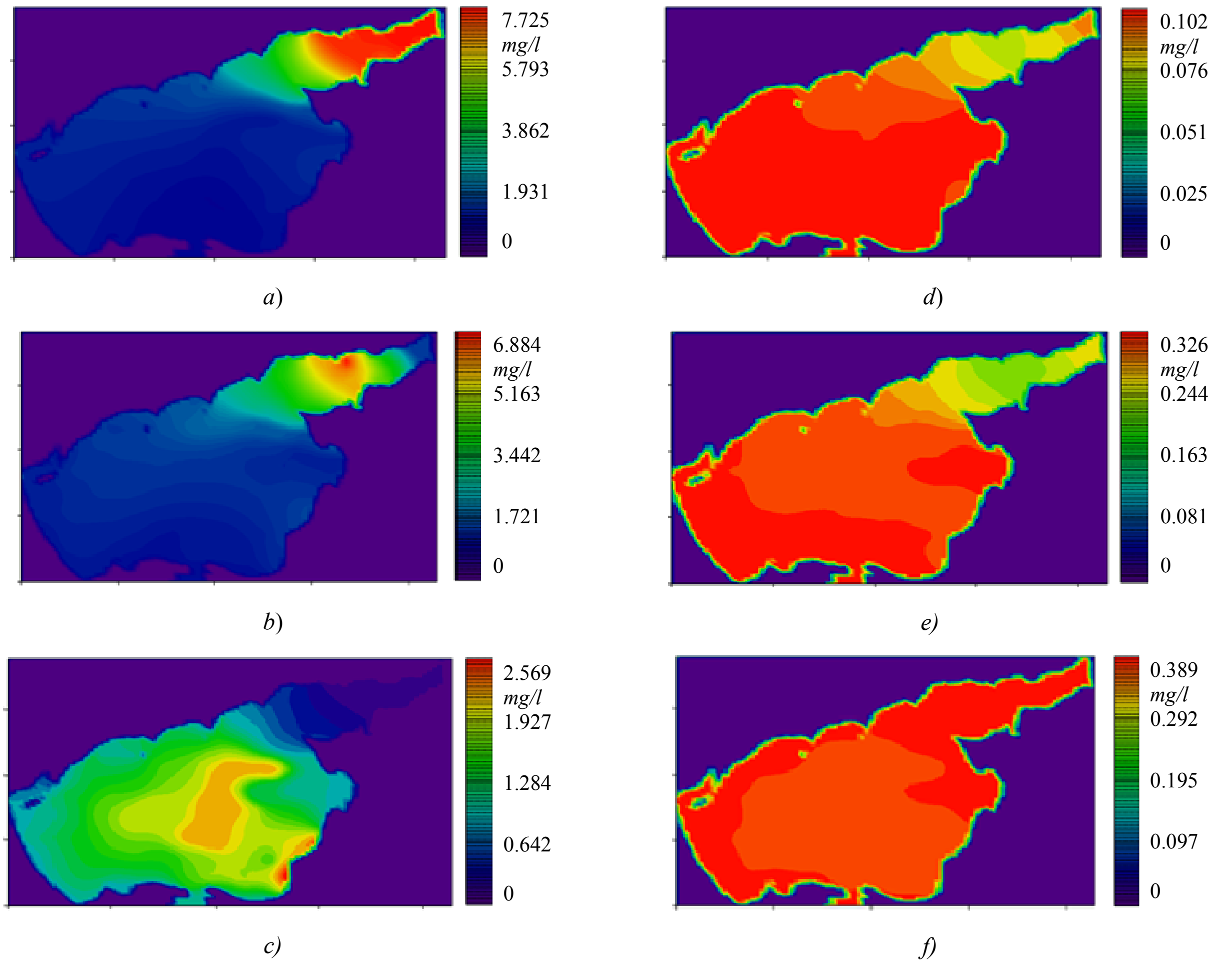

Fig. 6. Distribution of concentrations: *a*) green alga *Chlorella vulgaris*; *b*) blue-green alga *Aphanizomenon flos-aquae*; *c*) diatom *Sceletonema costatum*; *d*) phosphates; *e*) nitrates; *f*) dissolved inorganic silicon

The figures reflect the dynamics of phytoplankton populations, the cycles of phosphorus, nitrogen and silicon. In the process of extinction and decay, phytoplankton releases phosphorus in dissolved and weighed organic forms, then in the process of phosphatofication, they go inorganic — phosphates, which are consumed by phytoplankton. The nitrogen cycle is also described: in the process of vital activity, phytoplankton releases nitrogen in organic form, which decomposes to ammonia. Under the nitrification, ammonium is oxidized to nitrites, and then to nitrates. It is worth noting that phytoplankton consumes all three forms of nitrogen. The consumption and release of silicon by diatoms was stated. Comparison to the simulation results for high-water periods shows that in recent low-water years, the habitats of green and blue-green algae in the Taganrog Bay area have significantly moved (by many kilometers) eastwards, closer to the Don river, a source of fresh water.

Discussion and Conclusions. The paper presents a multi-species mathematical model of the dynamics of phytoplankton populations, form transformations of biogenic substances-phosphorus, nitrogen, and silicon compounds. The model takes into account:

— impact of salinity and temperature on the development of three main types of phytoplankton (green, blue-green and diatomic algae);

— phytoplankton uptake of phosphates and nitrogen forms;

— transition of forms of phosphorus and nitrogen from one to another;

— absorption of silicon by diatoms;

— advective and microturbulent movement of the aquatic environment;

— water flows and sources at the border.

To study the field data, a statistical analysis procedure of long-term series of observations of biogenic substances concentrations (phosphorus, nitrogen, their compounds, etc.) that enter the sea with the Don runoff has been developed and adapted. The statistical analysis of data from long-term observations, in particular hydrochemical indicators of the Don runoff, became the basis for predicting biogeochemical processes with account for the movement of the aquatic environment, the distribution of temperatures and salinity. The of numerical experiment results are consistent with the data of space sensing of the sea of Azov, which confirms the predictive value of the models used and the methods of their numerical implementation. The comparison of the distributions of green and blue-green algae populations in the Taganrog Bay for high-water and low-water periods shows that in recent low-water years, their habitats have significantly moved (by many kilometers) eastwards, closer to the Don river, a source of fresh water.

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