

## A Method for Describing Technogenic Succession of Diatom Paleocomplex

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Received June 23, 2006

DOI: 10.1134/S1028334X06090352

Diatom complexes serve as indicators of the level and character of the anthropogenic load on water ecosystems [1, 2]. Silicon shells of diatoms preserved in bottom sediments provide insights into species composition of the diatom complex, which can be used to unravel the past state of ecosystems. These data together with the chemical composition of bottom sediments allow us to link changes in the species composition of diatom algae with the level of anthropogenic load. Qualitative interpretation of this correlation is widely used for paleoreconstruction of the ecological state [3]. For the further development of this method, we suggest an approach that makes it possible to determine the quantitative correlation between the chemical composition of sediment layers and remains of the diatom flora therein and then monitor the reconstruction of the diatom complex under an environment of high technogenic pollution of waters.

Initial data were adopted from paleolimnological studies in Monche Inlet, the most polluted part of Lake Imandra, which is used for discharging sewage waters of Monchegorsk and the Severonikel copper–nickel plant, which was built in 1938 [4]. The industrial sewage waters include Cu, Ni, Zn, Cr, Cd, Pb, and other metals. Monche Inlet is a narrow 10-km-long bay. Bottom sediment cores (25 cm long) were recovered at a distance of 0.5 km from the coast at a depth of 26.4 m.

Vertical distribution of metal concentrations in bottom sediments is reported in [5]. Diatom analysis of the cores [3] revealed 267 diatom species, including 7 dominating species. Their distribution versus depth is shown in Fig. 1.

The toxicity of an aquatic environment is governed by concentration of metals in the water. However, we usually have only data on concentrations of metals in the bottom sediments for the paleoreconstruction. One can reconstruct the state of the aquatic medium by comparing concentrations of metals in the surface layer of

bottom sediments with their average concentrations in the water column. Statistically significant correlation was found only for Cu and Ni:

$$\text{Cu: } y = -0.1274c^3 + 8.230c^2 - 2.187c \quad (1)$$
$$(R^2 = 0.986),$$

$$\text{Ni: } y = 0.0698c^3 + 0.1562c^2 + 45.30c \quad (2)$$
$$(R^2 = 0.998),$$

where  $c$  is the average concentration of metal in the water column,  $\mu\text{g/l}$ ;  $y$  is the concentration of metal in the surface layer of bottom sediments (0–1 cm),  $\mu\text{g/g}$  of dry weight; and  $R^2$  is the coefficient of determination. The concentrations of other metals in water vary irregularly without any correlation with their concentration in the bottom sediments. During the period of observations in 1990–2003, the average concentrations of these metals in the water of Monche Inlet were as follows ( $\mu\text{g/l}$ ): Cd (0.335), Co (0.593), Mn (14.9), Zn (4.15), Cr (0.270), Sr (36.8), Al (29.9), Fe (40.2), and Pb (0.583).

The influence of different metals on organisms can be compared based on their equivalent concentrations responsible for equal reduction of the tested population.

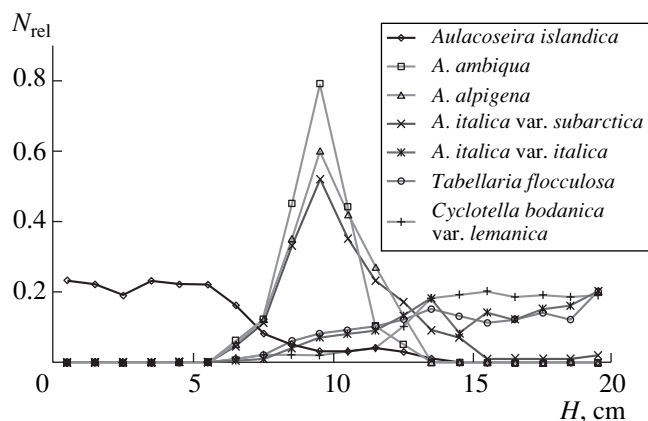
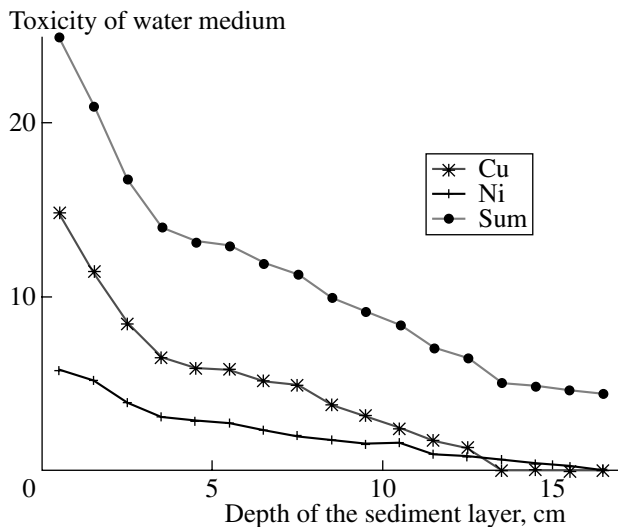


Fig. 1. Distribution of the population of dominating species of diatoms ( $N_{rel}$ ) vs. depth ( $H$ ) of sediment.

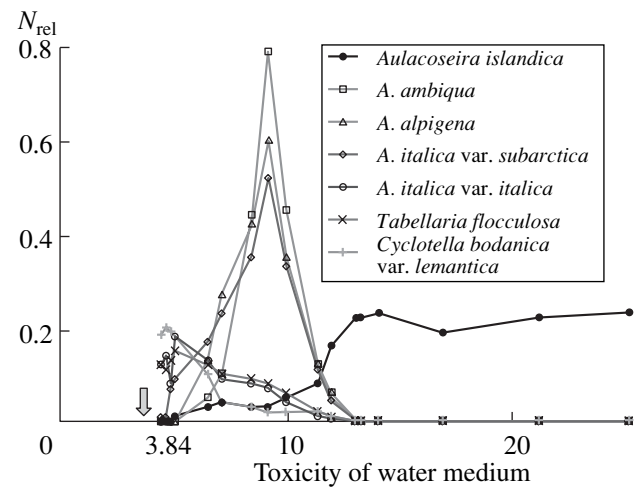


**Fig. 2.** Toxicity of Cu, Ni, and total toxicity of water medium during the deposition of bottom sediment layer vs. depth.

Such data are lacking for diatoms. Therefore, we shall use the maximum permissible concentration (MPC) applied in fishing industry as a rough estimate ( $\mu\text{g/l}$ ): Cu (1), Cd (5), Co (10), Mn (10), Ni (10), Zn (10), Cr (20), Sr (30), Al (40), Fe (100), and Pb (100). Knowing the actual concentration of metal  $i$  in aquatic medium  $c_i$  and its equivalent concentration  $c_{\text{eq},i}$  (MPC), we can determine the individual toxicity of metal  $x_i$  and total toxicity  $x$  of a group of metals using formulas [6]:

$$x_i = \frac{c_i}{c_{\text{eq},i}}, \quad x = \sum_i x_i.$$

Relations (1) and (2) make it possible to find the time-variable toxicity of Cu and Ni in water (Fig. 2). In this plot, the  $x$  axis shows the depth scale, which reflects the historical process of sediment accumulation, instead of time. The contribution of other metals (4.42 units) to toxicity of the aquatic medium can be found from the average concentrations in water and MPC values indicated above. This is the mean value for the entire period of observations. The total toxicity of all metals is also shown in Fig. 2. The maximal toxicity (25 units) is recorded in the surface layer of the sediments. It decreases sharply with increasing depth. At a depth of 10 cm, the total contribution of Cu and Ni becomes equal to the total contribution of other metals. The total toxicity of the medium reaches 4.42 units at a depth of 16–17 cm. Let us estimate, for comparison, the background toxicity using the tentative background concentrations of metals in water of Monche Inlet ( $\mu\text{g/l}$ ): Cu (1), Cd (0.03), Co (0.1), Mn (5.6), Ni (1), Zn (2), Cr (0.1), Sr (26), Al (30), Fe (34), and Pb (0.15) [5]. The calculations yield background toxicity equal to 3.84 units. This value is assumed as a new unit of toxicity, namely the background unit (B.U.).



**Fig. 3.** Population of dominating species of diatoms vs. toxicity of the water medium. Arrow indicates background toxicity.

By comparing the population of diatoms and toxicity at equal depths, we can find the dependence between these parameters (Fig. 3). Based on the variation pattern of the species population as a function of toxicity of the environment, we can distinguish three groups of diatoms: (1) *Aulacoseira alpigena*, *Cyclotella bodanica* var. *lemanica*, *Tabellaria flocculosa*; (2) *A. italica* var. *italica*, *A. italica* var. *subarctica*, *A. ambigua*; and (3) *A. islandica*. Species of one group are characterized by similar response to the changes in toxicity. The low-toxic region is dominated by North Alpine species, which are indicators of a xeno-oligosaprobe environment. The medium-toxic region mainly includes the alkaliphilic betamesosaprobe species. Finally, the high-toxic region only includes eurybiontic betamesosaprobe species [3]. For each group, we can indicate the typical interval of toxicity (in B.U.): (1)  $< 1.7$ ; (2)  $1.7-3.1$ ; (3)  $> 3.1$  (Fig. 4). Transition from one interval to another (over critical points 1.7 and 3.1) is accompanied by structural rearrangement of the diatom complex, during which the composition of dominant species changes completely.

The behavior of diatoms is regulated by two factors: toxic resistance and competitiveness of the species. Species of group 1 dominate in a low-toxic environment, gradually decreasing with increasing toxicity, and vanishing when species of group 2 appear. Thus, species of group 1 are more competitive but less resistant to toxic impact.

In contrast, species of group 2 are more stable in a medium-toxic environment, but less competitive relative to species of group 1. They become active at  $x \approx 1.7$ , when the population of group 1 decreases sufficiently. With a further increase in toxicity, the population of group 2 increases and reaches a maximum at  $x = 2.4$ .

Further increase in toxicity leads to a decrease in the population of species of group 2 and weakening of competitive impact from them, which creates favorable conditions for the growth of the unique species included in group 3. At  $x \approx 3.1$ , the population of species of group 3 becomes equal to the population of species of group 2 and remains the only dominating species in the community at greater toxicity. This group is characterized by high resistance to toxicity, which is testified by the conservation of its population even at  $x = 6.5$ .

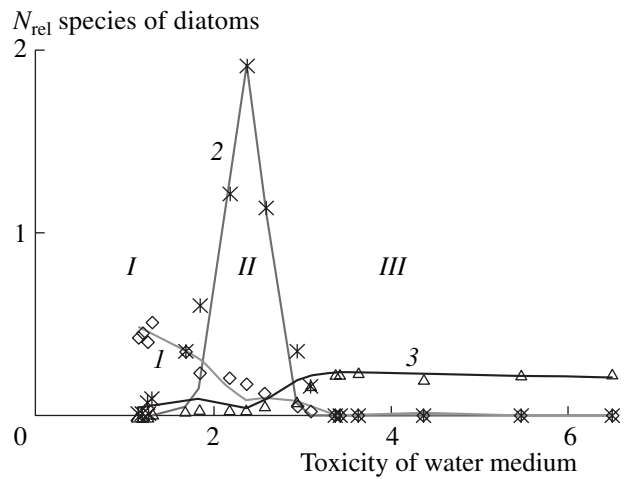
Let us consider the problem of modeling the behavior of the diatom complex described above. We shall start the analysis of the problem from the general model of competitive community and later modify it according to the peculiarities of the specific problem. The starting point is the known model of a competitive community [7]:

$$\frac{dN_i}{dt} = \frac{r_i N_i}{K_i} \left( K_i - N_i - \sum_{j \neq i} \alpha_{ij} N_j \right), \quad i = 1, 2, \dots, n, \quad (3)$$

where  $n$  is the number of species;  $N_i$  is the population of species  $i$ ;  $r_i$  is the effective rate of population growth, which takes into account its natural replenishment, on the one hand, and dying of organisms and their elimination by predators, on the other hand;  $\alpha_{ij}$  is the coefficient of competitiveness, which describes the impact (competitive pressure or inhibition) of species  $j$  on species  $i$ ;  $K_i$  is carrier volume of the environment with respect to species  $i$  in the absence of competitiveness (i.e., at  $\alpha_{ij} = 0$ ); and  $t$  is time.

Data on the population of diatoms and toxic load were averaged over a sufficiently long time interval, which can be estimated as described below. The sediment cores are divided for the analysis of chemical and diatom analysis into elementary layers 1 cm thick. In order to estimate the rate of sediment accumulation, we take into account that the entire technogenic layer of the sediment (17–20 cm) was formed during almost a 70-yr period of the existence of the Severonikel Plant. It is easy to calculate that the average rate of sediment deposition is equal to 2–3 mm/yr during this period. Thus, a layer 1 cm thick accumulated over 3–5 yr. During such a period, small-scale spatiotemporal variations in the characteristics of the environment and diatom community are averaged (including their daily, seasonal, and even interannual variations, as well as spatial inhomogeneities). Hence, model (3) should be modified not only because the necessary detailed information is usually absent, but also because it would inevitably be lost during averaging.

This statement is also valid for the coefficient of competitiveness  $\alpha_{ij}$ , which varies together with variations in the environment. Different degrees of sensitivity of species to various parameters of the environment provoke multiple changes in the dominating relations. Let us consider the influence of species  $j$  and  $k$  on spe-



**Fig. 4.** Population of dominating species of diatoms vs. toxicity of the medium relative to the background toxicity. (1–3) Group numbers; (I, II, III) domains of the corresponding groups. Markers indicate empirical data; curves, model calculations.

cies  $i$ , which is described by competitiveness coefficients  $\alpha_{ij}$  and  $\alpha_{ik}$ , respectively. In one type of environment, species  $j$  is stronger than species  $k$  and inhibits species  $i$ ; i.e.,  $\alpha_{ij} > \alpha_{ik}$ . In the other type of environment, the influence of species  $k$  dominates:  $\alpha_{ij} < \alpha_{ik}$ . Thus, as a result of averaging, we can define the influence of various competing species on species  $i$  by one phenomenological parameter  $\alpha_i$  instead of many individual interspecies coefficients of competitiveness  $\alpha_{ij}$ . The description of the community should change accordingly. Instead of sum  $\sum_{j \neq i} \alpha_{ij} N_j$  in Eq. (3), we should use

expression  $\alpha_i(N - N_i)$ , where  $N$  is the population of the community. From the physical point of view, this approach corresponds to the approximation of the average field, which implies the entire set of impacts on the given species by the community, including the consumption of nutrients, absorption of light, and excretion of metabolites inhibiting the development of competitors. Such modification of (3) yields a simpler equation

$$\frac{dN_i}{dt} = \frac{r_i N_i}{K_i} (K_i - N_i - \alpha_i(N - N_i)). \quad (4)$$

In the averaged pattern considered here, the phytoplankton community is in the quasi-equilibrium state, in which  $dN_i/dt = 0$ , and Eq. (4) is written as

$$K_i - N_i - \alpha_i(N - N_i) = 0. \quad (5)$$

The carrier volume of environment  $K_i$  (proportional to the rate of population growth  $r_i$  [8]) depends linearly on toxicity [9, 10]:

$$K_i = K_{i0} \left( 1 - \frac{x}{L_i} \right), \quad (6)$$

where  $K_{i0}$  is the volume of the environment in the absence of toxicant and  $L_i$  is lethal toxicity for isolated population  $i$ . Combining (5) and (6), we get equation system

$$K_{i0}\left(1 - \frac{x}{L_i}\right) - (1 - \alpha_i)N_i - \alpha_i N = 0,$$

$$N_i \geq 0, \quad i = 1, 2, \dots, n,$$

which describes the structure of the diatom complex at different degrees of toxicity.

We determined the parameters of this model using the least squares method on the basis of empirical data considered above. For each group of diatoms, we obtained the following values of parameters  $\alpha_i$ ,  $K_{i0}$  (rel. u.), and  $L_i$  (B.U.): (1) 0.353, 0.5, 3.76; (2) 9.15, 5.0, 5.32; (3) 0.45, 0.26, 27.2, respectively. The standard deviation of theoretical dependences from empirical data is  $\sigma = 0.48$  (rel. u.).

The calculations show satisfactory agreement of the theoretical curves with empirical data (Fig. 4). It is seen that the nontoxic environment is dominated by group 1, whose population decreases with increasing toxicity. As toxicity approaches  $x = 1.7$  (B.U.), the population of group 2 increases, dominates after this point, and suppresses the activity of the species of group 1 (this is facilitated by increasing toxicity). After reaching the peak at  $x = 2.4$ , the population of group 2 decreases sharply and completely disappears at  $x = 3.2$ , because it cannot withstand the increase in toxicity and competition with group 3. We note that if group 3 is absent, group 2 would disappear only at  $x = L_2 = 5.32$ . The population of group 3 reaches the maximum at  $x = 3.2$ . According to field data, this situation is maintained even at double toxicity.

The results described above reflect the stepwise development of the critical situation in the Monche Inlet ecosystem under conditions of strong technogenic pollution: (1)  $x = 0-1$  (background toxicity corresponding to the stage of natural ontogenesis preceding the initial period of anthropogenic impact); (2)  $x = 1-1.7$  (the stage of early distortions corresponding to the initial period of technogenic pollution); (3)  $x = 1.7$  (the first rearrangement of the structure of diatom complex: North Alpine xeno-oligosaprobe species of group 1 are substituted by alkaliphilic betamesosaprobe species of group 2); (4)  $x = 1.7-2.4$  (the stage of sharp increase in the total population of the species of group 2); (5)  $x = 2.4-3.1$  (the stage of decrease in population of group 2, i.e., the stage of progressive crisis accompanied by a sharp decrease in the total population and diversity of

species); (6)  $x = 3.1$  (the stage of the second rearrangement of the structure of the diatom complex: alkaliphilic betamesosaprobe species of group 2 are substituted by eurybiontic betamesosaprobe species of group 3); and (7)  $x > 3.1$  (the stage of crisis corresponding to a high level of pollution characterized by extremely poor species structure and conservation of the population of the dominating species even at toxicity of the environment 6.5 times greater than the background level).

Thus, our method of the description of paleolimnological data makes it possible not only to obtain the information about the toxicity of the environment and diatom composition of an aquatic ecosystem in the past, but also to establish the correlation between these two factors and divide the species into groups according to the similarity of their response to increasing toxicity. Moreover, we can indicate domains for each diatom group on the toxicity scale and determine the critical points of structural rearrangement of the diatom complex.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-05-64523.

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