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APPLIED PROBLEMS
OF ARID LANDS DEVELOPMENT

Year-to-Year Variations in the Distribution of Dissolved Forms of Biogenic Elements in Volga Delta Water and Their Correlation with Phytoplankton Biomass Variations

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Abstract—Data of field observations carried out in the Volga Delta in the period of largest biological production from 2007 to 2010 were used to establish the existence of a distinct relationship between the concentrations of dissolved forms of mineral phosphorus and silicon. The character of this relationship varies in accordance with year-to-year variations in phytoplankton biomass, which consists of more than 90% diatoms consuming both phosphorus and silicon.

Keywords: mineral phosphorus, silicon, phytoplankton, diatom algae, year-to-year variations, the Volga Delta.

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INTRODUCTION

Because of the economic importance of river mouth areas, the hydrochemical regime of biogenic elements, whose concentrations have a sizable effect on biological productivity, has attracted considerable attention. Our earlier studies in the water mixing zone between the Volga and the Caspian Sea (Savenko et al., 2006) established strong year-to-year variations in the extent of nonconservative behavior and the absolute concentrations of dissolved forms of mineral phosphorus and silicon during the summer low-water period. It can be suggested that the year-to-year variations in biogenic-element concentrations in river water are due primarily to the runoff formation conditions in the watershed, while variations in their concentrations at the marine boundary of the mixing zone are mostly governed by the rate of biological assimilation and regeneration in the nearshore zone.

However, in the mouth areas of rivers with wide deltas, of which the Volga is a typical example, the formation of water chemistry at the riverine boundary of the mixing zone is appreciably determined by the processes taking place within the water mass in delta branches and other elements of the channel network. Because of their considerable length; the abrupt drop in flow velocities; and the abundance of aquatic biota, including higher aquatic plants; the runoff of dissolved matter experiences transformation in those elements, as well as in the mixing zone of river and sea water.

To reveal the processes governing the migration of dissolved forms of biogenic elements in Volga Delta water and to determine the range of year-to-year variations in their concentrations in the period of greatest biological activity, systematic integrated studies were carried out in delta streams.

MATERIALS AND METHODS

The materials for the study were water and phytoplankton samples taken in August 2007–2010 in the channel systems of the Bakhtemir, Staraya Volga, Kamyzyak, Bolda, and Buzan branches in the Volga Delta and in the lower Akhtuba during joint expeditions of the Institute of Water Problems, Russian Academy of Sciences, and KaspNIRKh. The layout of water sampling stations in individual years is given in Fig. 1.

Water samples were taken from the surface layer by a plastic bathometer and immediately filtered through dense paper filters into polypropylene flasks, into which small amounts of chloroform (1 ml per 100 ml sample) were added to preserve biogenic elements. The concentrations of dissolved mineral phosphorus and silicon were determined by colorimetric methods with the use of ammonium molybdate with ascorbic

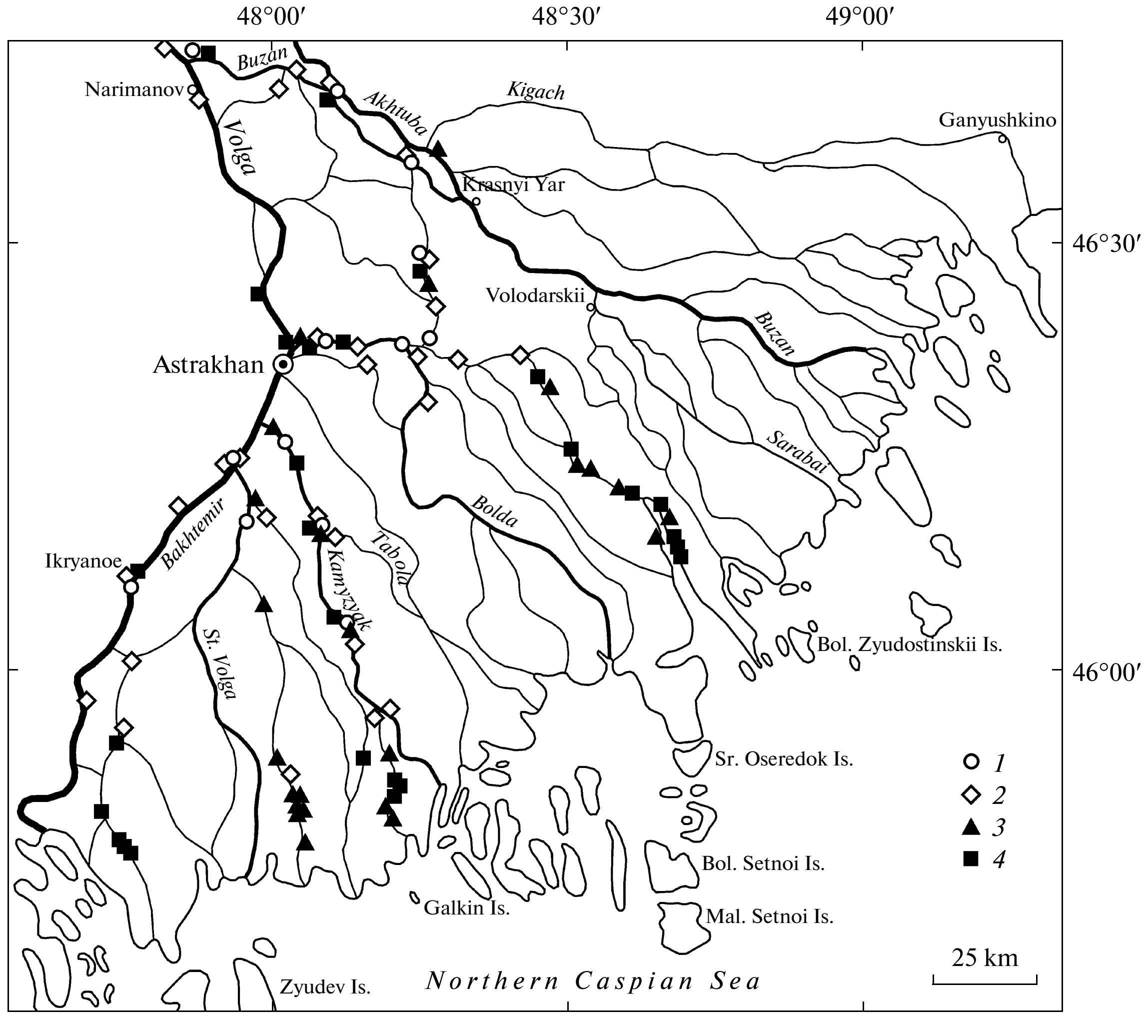

Fig. 1. Layout of water and phytoplankton sampling stations in the Volga Delta: (*1*) August 9–21, 2007; (*2*) August 6–25, 2008; (*3*) August 7–19, 2009; (*4*) August 6–22, 2010.

acid and ammonium molybdate with Mohr's salt, respectively. The concentration of total dissolved phosphorus was determined by the same procedure as that for mineral phosphorus but with the preliminary reduction of organic matter by boiling with the introduction of potassium persulfate; the concentration of chlorides was determined by volumetric mercurimetry (Lur'e, 1971). The determination error never exceeded ±3%.

Phytoplankton samples 500 ml in volume were also taken by a plastic bathometer from the surface layer and fixed by the introduction of 25 ml 40% formalin. Prior to their study, the samples were condensed by vacuum filtration through nuclear filters with a pore diameter of 1 μm. Optical microscopes with 63× and 280× magnification power were used to determine the taxa. Cells were counted on striated glasses in samples 0.1 ml in volume. Finer alga forms were counted in a Goryaev chamber. No less than 100 specimens of mass species and no less than 600 cells of all observed species were recorded in each sample (Fedorov, 1979; Fedorov, Kapkov, 2006).

RESULTS AND DISCUSSION

No mixing of river and sea water was taking place at the sampling stations, including those in the vicinity of the delta coastline: the distribution of chlorides in 2007–2010 was uniform, with concentrations of 35.7–37.0, 28.7–29.7, 25.3–27.0, and 27.9–31.4 mg/l, respectively.

A distinct relationship can be seen between dissolved mineral phosphorus (P_{min}) and silicon Si (Fig. 2). The shape of this relationship differed radically in different years, despite the fact that the surveys were carried out in the same periods. Thus, in 2007, silicon concentration abruptly increased with increasing concentration

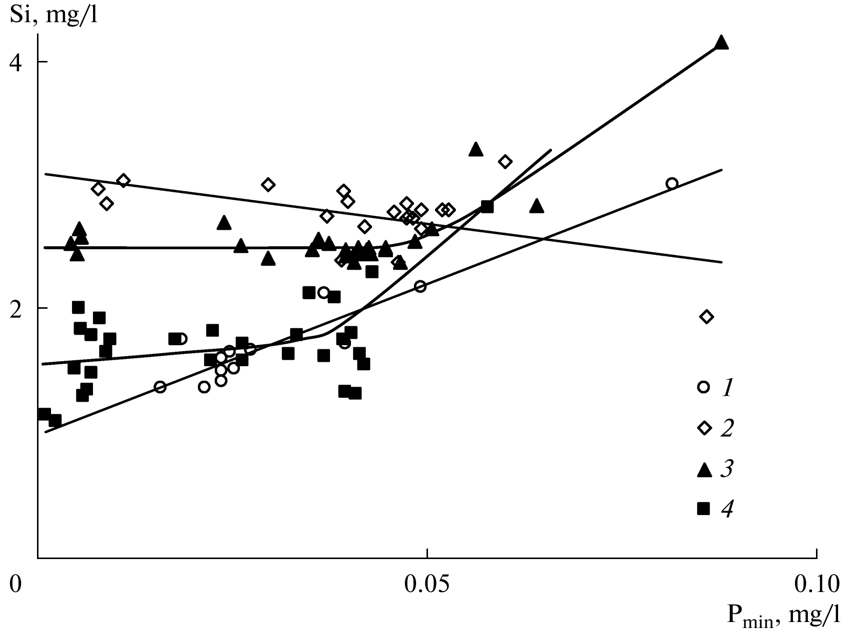

Fig. 2. Correlation between the concentrations of dissolved mineral phosphorus and silicon in Volga Delta water in August (*1*) 2007, (*2*) 2008, (*3*) 2009, and (*4*) 2010.

of dissolved mineral phosphorus, while in 2008, conversely, silicon concentration tended to decrease. The values of coefficients *a* and *b* in the relationship

$$[\text{Si, mg/l}] = a[\text{P}_{min}, \text{mg/l}] + b, \quad (1)$$

were 24.1 and 1.01 in 2007 and –8.2 and 3.12 in 2008, respectively. In 2009 and 2010, the relationship was more complex, containing two linear segments. In 2009, with phosphate concentrations between 0.04 and 0.045 mg P/l, silicon concentration remained unchanged (~2.5 mg/l), while further increase in the concentration of dissolved mineral phosphorus up to 0.088 mg P/l was accompanied by an increase in silicon concentration up to 4.2 mg/l. The values of coefficients *a* and *b* in (1) for this interval of the relationship were 37.9 and 0.78, respectively. In 2010, with phosphate concentrations between 0.001 and 0.042 mg P/l, silicon concentration gradually increased following equation (1) with coefficients *a* and *b* of 4.1 and 1.57, respectively; next, the slope abruptly increased, with the ratio Si/P_{min} reaching ~50 at a mineral phosphorus concentration of 0.058 mg P/l.

The data for 2010 also show that the share of the mineral component in the total dissolved phosphorus (P_{tot}) increases nonlinearly with an increase in the latter (Fig. 3):

$$\log(\text{P}_{min}/\text{P}_{org}) = 30.6[\text{P}_{tot}, \text{mg/l}] - 0.63, \quad r = 0.68, \quad (2)$$

where P_{org} is dissolved organic phosphorus. This suggests that the phosphate regeneration rate in destruction processes exceeds its assimilation rate in organic matter production.

Since phosphate recycling is fast enough, we can expect that changes in the shape of relationship (1) are governed by the biological consumption rate of silicon, whose remineralization rate is known to be less than that of phosphates. This assumption is confirmed by the character of year-to-year variations in the bio-

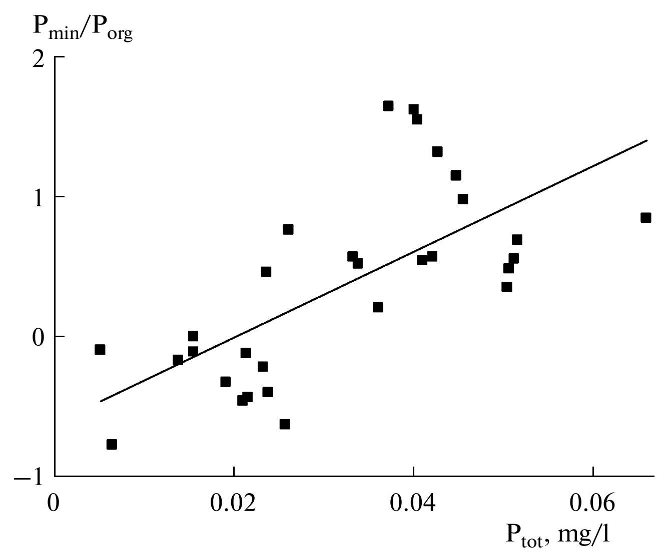

Fig. 3. Logarithm of the P_{min}/P_{org} ratio in Volga Delta water vs. the concentration of total dissolved phosphorus in August 2010.

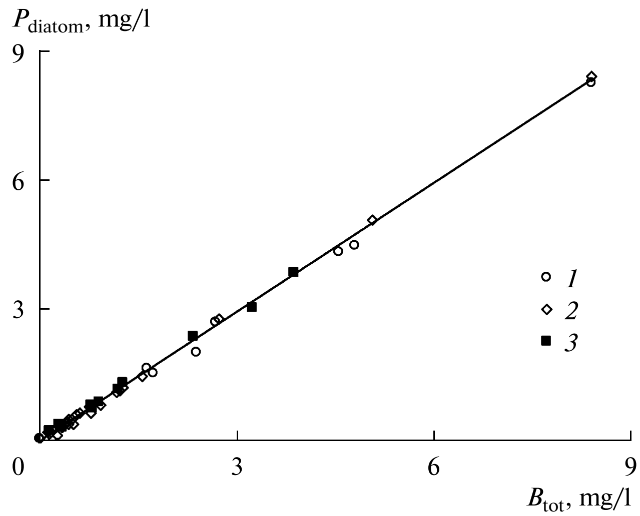

Fig. 4. Total phytoplankton biomass vs. diatom biomass in Volga Delta water in August (*1*) 2007, (*2*) 2008, and (*3*) 2010.

mass of various phytoplankton groups in Volga Delta water in August 2007–2010.

Despite the extremely uneven distribution of phytoplankton biomass in delta streams, silicon-accumulating diatom algae dominated in the biomass at all stations, as can be seen from the existence of a relationship between these variables valid throughout 2007–2010 (Fig. 4) in the form

$$B_{diatom} = 0.9855B_{tot} - 0.077, \quad r = 0.999, \qquad (3)$$

where B_{diatom} and B_{tot} are the biomasses of diatoms and phytoplankton, mg/l, respectively. This allows us to use the mean characteristics of the biomasses of phytoplankton and its individual groups for each survey (table) as representative characteristics of the productivity of delta algaflora; the mean share of diatom algae in the total biomass was constant (0.93–0.95).

According to the data given in the table, diatom vegetation was the most abundant in August 2007, which resulted in the appearance of a close positive correlation ($r = 0.94$) between the dissolved forms of mineral phosphorus and silicon throughout the range of their concentrations. In August 2008, phytoplankton was suppressed, so the diatom biomass was almost 2.5 times less than in the previous year. It appears that silicon consumption dropped in this period to values comparable to its remineralization rate, as the silicon content in solution tended to decrease. In 2010, the development of small-cell algae was also suppressed; however, diatom biomass increased somewhat compared with 2008, hence the appearance again of a direct relationship between the concentrations of dissolved phosphates and silicon. The slope of the respective curve in the main concentration interval was about 6 times less than in 2007.

Thus, the obtained data allow us to conclude that the processes of assimilation by aquatic biota and regeneration during organic matter decay play the main role in transforming the runoff of dissolved mineral phosphorus and silicon in the Volga Delta. The maximal productivity of phytoplankton, whose biomass is represented predominantly by diatoms, shows wide year-to-year variations, which determine the

Variations of the average biomass of various phytoplankton groups in Volga Delta water in August 2007–2010

Year	Average biomass, mg/l					The share of diatoms in the total biomass
	total	diatoms	blue-green	green	dinophyte	
2007	2.945	2.770	0.114	0.049	0.011	0.94
2008	1.221	1.135	0.075	0.006	0.006	0.93
2010	1.403	1.333	0.065	0.005	–	0.95

year-to-year variations in the concentrations of biogenic elements.

CONCLUSIONS

A distinct relationship was found to exist between the concentrations of dissolved forms of mineral phosphorus and silicon in Volga Delta water. The character of this relationship (simple positive relationship, linear negative relationship, or broken line) was different in different years of observations. The year-to-year variations in the parameters of the relationship between the concentrations of dissolved phosphates and silicon are governed by the variations in phytoplankton biomass, of which diatoms account for more than 90%. These algae consume not only phosphorus, but also considerable amounts of silicon.

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