

# Hypothesis on the Reasons for Strong Variability in the Concentrations of Impurities in Natural Waters

Corresponding Member of the RAS V. I. Danilov-Danilyan<sup>a,\*</sup> and O. M. Rozenthal<sup>a</sup>

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**Abstract**—A hypothesis has been put forward about the formation of increased dispersion of the concentration of substances contaminating flowing river water under the influence of internal synergistic factors. The effect is manifested in the dispersion of monitored quality factors, exceeding their average values, which in practice makes it difficult to manage water use. It is assumed that such dispersion is a consequence of the non-linearity of systems that are far from thermodynamic equilibrium. It is possible that the driving force in this case is the turbophoresis of impurity particles in a turbulent, as a rule, water flow.

**Keywords:** river flow, water flow rate, water quality, impurity concentration, thermodynamic equilibrium, kinetic energy of jets, impurity redistribution, macroeffects, turbophoresis

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## INTRODUCTION VARIABILITY OF RIVER WATER QUALITY INDICATORS

The annual state reports “On the State and Use of Water Resources” include averaged river water quality indicators with limited information about high and extremely high levels of water pollution. In real life, the composition and properties of water environments change continuously, so significant that the impurity content can change by orders of magnitude even within 24 hours. The existing monitoring systems of the ecological state of water bodies are poorly adapted to reveal such phenomena. Meanwhile, they are frequently noted in research papers. Thus, diurnal and weekly variations in the Mn content, as well as REEs, Al, and Fe, were established in the Kalix River (Sweden) ([1], pp. 225–272). Such variations are characteristic of the rivers of industrial, agricultural, and even undeveloped regions [2]. The isotope composition of river water also changes daily [3]. In [4] a pronounced periodic pattern of the electrical conductivity of water due to changes in its salinity is noted.

Underestimation of the variability of indicators of the concentration of water pollutants in natural sources leads to inadequate conclusions in monitoring the state of water resources and the anthropogenic influence on them, incorrect management solutions (the establishment of regional values of maximum

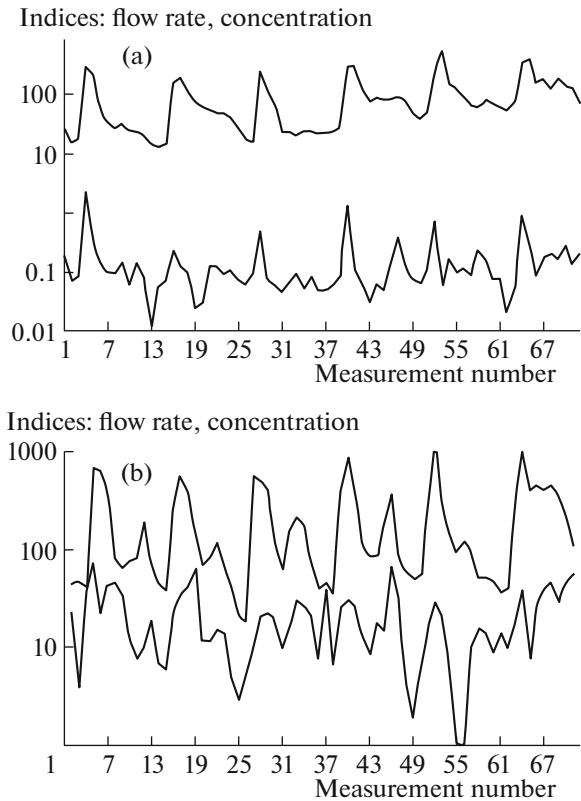
allowable concentrations (MAC) and water withdrawal), and the incorrect regulation of water treatment systems.

Attempts to explain increased dispersion of impurity concentration in river flows only by the influence of external natural and anthropogenic causes do not stand up to criticism. The water composition, of course, depends significantly on the lithological characteristics of the basin, the patterns of geochemical provinces, weathering of rocks, decomposition of plant remains, the season of the year, groundwater discharge, precipitation, and other similar factors, as well as the variability of the structure and concentration of pollutants in the industrial and municipal discharges and anthropogenic diffuse runoff. However, it is difficult to understand how redox processes in bogs can be considered the only reason for “tenfold daily variations” in the composition of water flowing out of them ([1], pp. 225–272), why the composition of thawing water from the Norwegian Jostedalsgreen glacier changes also frequently and sharply [3], and how the high sensitivity of water quality “to small changes in river depth and the flow rate in them” appears [2]. In addition, it is necessary to accept the fact that “the nature of strong quasi-periodical perturbations of mineralized water has not yet been elucidated” [4].

In industrial regions, the variability of water quality indicators is assigned to pollutants in wastewater effluents. However, sharp variations in the impurity concentration recorded here at hydrochemical stations located below the so-called section of complete mixing [5] are still incomprehensible. The distance from the local site of wastewater discharge to such stations usually does not exceed one kilometer. Even if the

<sup>a</sup>Institute of Water Problems, Russian Academy of Sciences, Moscow, 119333 Russia

\*e-mail: vidd38@yandex.ru



**Fig. 1.** River flow rate,  $\text{m}^3/\text{s}$  (upper curves), and iron content,  $\text{mg}/\text{dm}^3$  (lower curves), (a) in the Ufa River, cross section upstream from the town of Krasnoufimsk, and (b) in the Chusovaya River, cross section upstream from the confluence of the Arkhipovka River in the town of Chusovoi. Monthly data of Rosgidromet of Russia in 2013–2015. To bring to the same scale, the iron content in Fig. 1b is increased by 200 times.

mixing at stations is not absolutely complete and “wastewater is mixed with 95 or 90% of the river flow” [6], the variability in impurity concentrations cannot be so high that its standard deviation is equal to the average value or to be even greater.

In many cases, the increase/decrease in the water quality indicators is associated with seasonal changes in the river discharge. For example, it is known that the low water period at a minimum flow rate (up to  $40 \text{ m}^3/\text{s}$ ) is characterized by maximum water salinity ( $1.38\text{--}1.65 \text{ g}/\text{dm}^3$ ); with the increase in the flow rate (up to  $100\text{--}300 \text{ m}^3/\text{s}$ ) during the high water period water salinity decreases. This does not explain, of course, the reasons for the significant changes in water composition during the season (monthly, weekly, or daily), as well as cases when the river water regime phases are accompanied not by the expected trend of variation in the water quality, but the directly opposite trend. In particular, there are unresolved questions such as what “accidental” causes lead to almost complete coincidence of the increase and decrease in the river discharge, on the one hand, and the water qual-

ity, on the other. Examples of both variants are given below.

## MONITORING DATA

Figure 1 shows time series of water discharge data and pollutant contents obtained by Roshydromet services in two river basins of the Urals (the ordinate axis is scaled logarithmically). As can be seen, the reversal points of the monitored indicators in the direction of their increase or decrease often coincide or are close to each other. Although in some time intervals there are “decorrelations,” the interrelation of temporal dependences is evident here.

Because of temporal shifts, the pair correlation coefficients of dynamic and chemical characteristics for the data shown in Fig. 1 are small: 0.51 in the case of the Ufa River and 0.41 in the case of the Chusovaya River. Of course, this cannot serve as conclusive evidence of the influence of the river flow on the redistribution of pollutant contents. Moreover, the correlation coefficients were even lower for a number of other pollutants.

However, this does not mean that the data obtained can be neglected. It is not difficult, for example, to assume that, although the desired mutual influence exists, its manifestation is often leveled by the external factors listed above (systematic and random unpredictable).

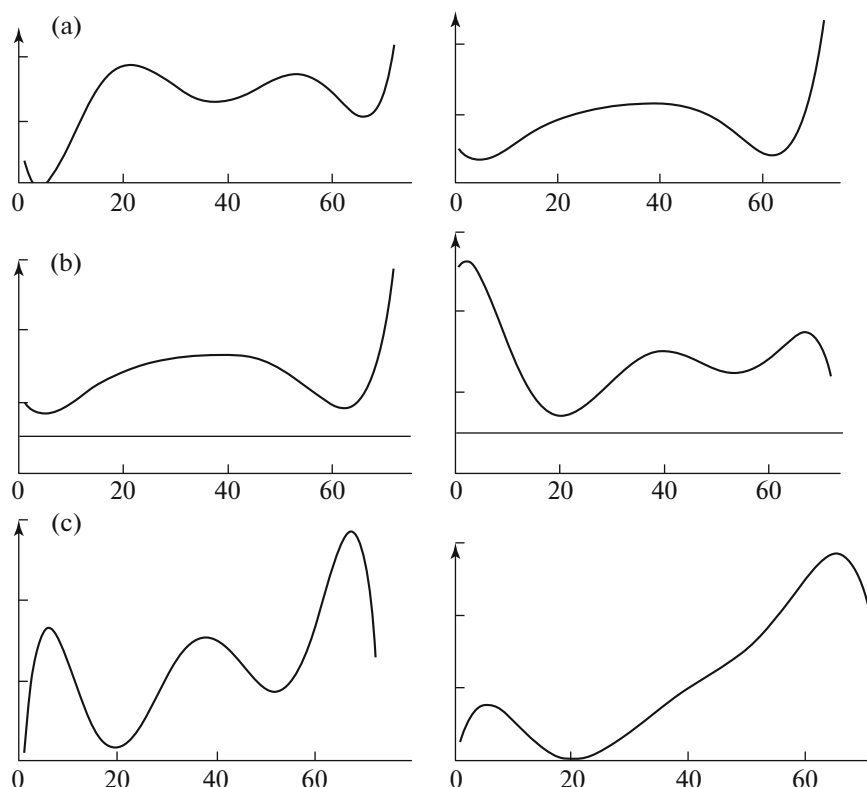
To make a stronger conclusion about the existence of the assumed relationships between the hydrodynamic characteristics of the river flow and impurity concentrations, the observed adjacent values of time series were averaged by isolating the nonrandom systematic component (time series smoothing).

The series under consideration are limited above and below, so if they were analyzed on the axis  $(-\infty, \infty)$  or any semi-axis  $(-\infty, t_0)$ ,  $(t_0, \infty)$ , it would be natural to approximate them using trigonometric polynomials  $F(t) = a_0 + \sum_{k=1}^n (a_k \cos kt + b_k \sin kt)$  at fixed constants  $a_0, a_1, a_2, \dots, a_n, b_1, \dots, b_n$ .

However, an interval bounded on both sides  $[t_1, t_70]$  is analyzed. Thus, we can try to find a suitable approximation among algebraic polynomials as well. It turned out that the algebraic polynomial of degree 6 gives an approximation better than any trigonometrical polynomial of degree 10 or higher. Since the approximation by the algebraic polynomial of degree 6 provides a very high accuracy, it was decided not to search for other approximations.

Thus, we have developed a polynomial (algebraic) model of the trend of time series based on polynomials of degree 6, which relatively fully describes the data sets that were used to plot Fig. 1 without considering their seasonality.

The desired trend lines (according to the terminology of Microsoft Excel spreadsheet software) are



**Fig. 2.** Trends in time series for the oil (a) and iron (b) content and river flow rate (c) in the Chusovaya River (left) and the Ufa River (right).

shown in Fig. 2, and the corresponding regression equations are shown in Table 1. As can be seen, the pair correlation coefficients are close to unity, which indicates the highest possible connection of the monitored indicators: the resultant (dependent) distribution of the impurity concentration and the factorial (independent) one (the river flow discharge).

The nature of the interdependence in the discharge/water quality system within the framework of the adopted “linear approach,” consistent with “common sense” [7], to the formation of random indicators is not obvious. Such a simplified approach is inadmissible when analyzing the behavior of nonlinear non-equilibrium systems, such as water flows with dispersed impurity particles. As in most natural processes considered in [7, 8], nonlinearity is manifested here in the form of energy dissipation of ordered processes and unexpected changes in the parameters monitored. In these cases, the processes are described by nonlinear equations without a single solution. Accordingly, one can neither predict the behavior of impurity particles in a river flow nor the nature of their concentrations (“self-organization”) in response to perturbation caused by the dynamic characteristics of water jets. It is possible, however, to give some general ideas of the synergetics about processes occurring in open systems far from thermodynamic equilibrium.

#### REASONS FOR THE CONNECTION OF RIVER FLOW RATE AND COMPOSITION OF RIVER WATER

One can assume that the reason for the strong variability in the impurity contents in natural waters is the impact of the water flow on the dispersion of impurity contents.

The dynamics of water jets is reduced to the flow rate with a large number of degrees of freedom due to a cascade of vortices up to the microscale level, where kinetic energy dissipation occurs. At the same time, according to A.N. Kolmogorov, the kinetic energy of water jets is dissipated. In our case, it provokes deformation of the water hydrogen bond network, which violates the hydration of impurity particles.

In such a model, small-scale high-frequency self-oscillations of the kinematic parameters of the river flow, determined by its hydraulic characteristics, act as a factor indicator affecting the redistribution of impurities (Fig. 3).

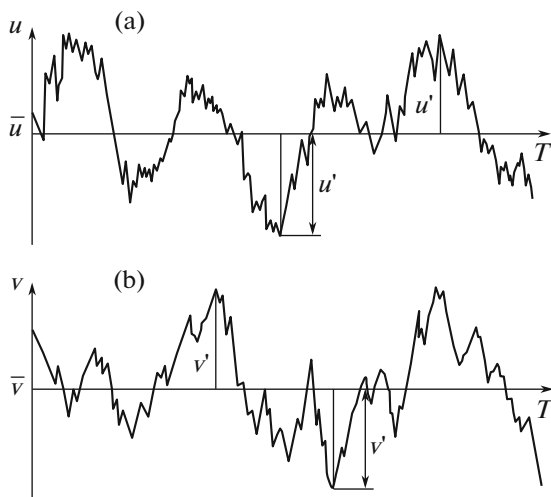
For a typical water velocity longitudinal component of 0.5 m/s of a lowland river, the magnitude of such pulsations is about  $\pm 0.1$  m/s with a change in the sign of mechanical stress almost every second in all directions of the hydrometric section. Due to the influence of such stresses, the water velocity at each point regularly changes in magnitude and direction.

**Table 1.** Averaged water flow rate, m<sup>3</sup>/s, river water quality indicators, and paired correlation coefficients *r* between them for the data from Fig. 1

River	Water flow rate	Concentration	<i>r</i>
Chusovaya	$-10^{-6}n^6 + 2 \times 10^{-4}n^5 - 0.02n^4 + 0.79n^3 - 14n^2 + 102n + 21$	iron $-4 \times 10^{-10}n^6 + 10^{-7}n^5 - 10^{-5}n^4 + 4 \times 10^{-4}n^3 - 0.0085n^2 + 0.061n + 0.19$	0.96
		oil $10^{-10}n^6 - 3 \times 10^{-8}n^5 + 2 \times 10^{-6}n^4 - 9 \times 10^{-5}n^3 + 0.0015n^2 - 0.0086n + 0.014$	0.99
Ufa	$-2 \times 10^{-7}n^6 + 3 \times 10^{-5}n^5 - 0.0029n^4 + 0.11n^3 - 2.1n^2 + 15n + 48$	iron $-9 \times 10^{-10}n^6 + 2 \times 10^{-7}n^5 - 2 \times 10^{-5}n^4 + 6 \times 10^{-4}n^3 - 0.0096n^2 + 0.034n + 0.39$	0.99
		oil $8 \times 10^{-11}n^6 - 2 \times 10^{-8}n^5 + 10^{-6}n^4 - 5 \times 10^{-5}n^3 + 0.0009n^2 - 0.0057n + 0.025$	0.98

Thus, the polluted river water flow forms an open dissipative system with quasi-periodic self-oscillations. The system continuously converts the energy of the source (water flow) into energy loss (redistribution of impurities). In particular, this is explained by the fact that impurity particles having a mass different from that of water molecules experience regular displacements (with a period of ~1 s) probably together with their nearest hydration shells and, possibly, as part of clusters consisting of hundreds and thousands of molecules. The latter are often mentioned in the literature (for example, [4]).

As a result, the impurity microseparation, regularly varying in direction and magnitude (the appearance of a set of dynamic fluctuating microsystems) occurs.



**Fig. 3.** Oscillatory pattern of change in the flow rate; (a, b) the longitudinal and vertical components of small- and large-scale oscillations, respectively [2].

Macroeffects (redistribution and “self-organization” of impurities) are manifested as a result of the interaction of microseparation pulsations with internal structural-kinetic processes in the water matrix [9].

The frequency of the latter processes can be established, for example, by analyzing the dispersion of the dielectric spectrum of water in an electromagnetic field. Molecular oscillations that create gigahertz dispersion [10] cannot affect the hydrodynamic impurity microseparation in the river flow. The times of spin–lattice and spin–spin relaxation estimated from proton magnetic resonance spectra in water are seconds [11]. The times of self-organization processes under physical, chemical, and mechanical impact are the same [9]. In particular, the elastic forces in deformations of the hydrogen-bonded network of water ensure the displacement of impurity particles to the spaces of network defects, causing by that microseparation due to internal factors ([12], pp. 151–198). It is possible that the driving force in this case is the turbophoresis [13] of noninertial (molecular) impurity particles in a turbulent, as a rule, water flow. Turbophoresis is usually considered as the migration of inertial particles in the direction of decreasing chaotic motion in the medium. This effect is opposed to diffusive equalization of the concentration.

In general, it should be recognized that, so far, instead of studying the properties and interrelations of components of natural water flows as thermodynamically nonequilibrium systems, only their response to variations in external conditions is studied by the “black box” method. This is explained, on the one hand, by a consumer attitude to hydrology to the detriment of revealing its fundamental laws and, on the other hand, by the absence of a statistical theory of polar liquids, such as water. As a result, it is difficult to judge the nature of the turbophoresis considered, the

role of ion-molecular associates of  $n \gg 1$  particles in it united due to hydration or Van der Waals interactions, conformers, and other stereoisomeric structures in mobile equilibrium and capable of interconversion [4, 9, 12].

### CONCLUSIONS

Summarizing the above, one can conclude that the admixture subsystem of the water flow, absorbing energy from the environment, forms a dissipative structure characterized by synergetic properties such as openness, complexity, instability, and fractality. This is the result of energy exchange with the environment under nonequilibrium conditions. Obviously, bifurcations [14] and breaking points are also possible. Observations over them open the possibility to predict the turbophoresis phenomenon, as well as dangerous water-ecological accidents, which seem unpredictable within the “linear approach,” and to avoid them.

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### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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### REFERENCES

1. J. Gaillardet, J. Viers, and B. Dupre, in *Treatise on Geochemistry*, Ed. by J. I. Drever (Elsevier, 2003), Vol. 5.
2. Thanh Thuy Nguyen, I. Keupers, and P. Willems, *Environ. Modell. Software* **104**, 102–117 (2018).
3. W. H. Theakstone, *J. Glaciology* **34** (118), 309–317 (1988).
4. I. M. Ageev, Yu. M. Rybin, and G. G. Shishkin, *Moscow Univ. Phys. Bull.* **71** (6), 556–562 (2016).
5. *RD (Guiding Document) no. 52.24.634-2002: The Way to Specify Point of Observation and Sampling Mode on the Base of Tracer Methods for Researching Hydrodynamic Characteristics of Water Objects* (2002). <https://meganorm.ru/Data2/1/4293848/4293848865.pdf>.
6. *RD (Guiding Document) no. 52.24.309-2016: The Way to Organize and Provide Monitoring Observations on Surface Water State and Pollution* (2016). <https://files.stroyinf.ru/Data2/1/4293748/4293748080.pdf>.
7. B. B. Mandelbrot, *The Fractal Geometry of Nature* (Times Books, 1982).
8. G. Nocolis and I. Prigogine, *Exploring Complexity: an Introduction* (Martin's Press, 1989).
9. V. I. Danilov-Danilyan and O. M. Rosenthal, *Water Resour.* **48** (2), 254–262 (2021).
10. O. M. Rozental and Yu. G. Podkin, *Dokl. Earth Sci.* **462** (2), 618–621 (2015).
11. E. M. Clop, M. A. Perillo, and A. K. Chattah, *J. Phys. Chem. B* **116** (39), 11953–11958 (2012).
12. M. N. Rodnikova, in *Structure Self-Organization in Solutions and at the Phases Boundary* (LKI, Moscow, 2008) [in Russian].
13. B. L. Sawford, *Phys. Fluids A* **3**, 1577–1586 (1991).
14. V. I. Danilov-Danilyan and O. M. Rosenthal, *J. Water Chem. Technol.* **44** (2), 132–138 (2022).

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