PROBLEMS OF INLAND WATERS

Regularities of Hydrochemical Dynamics in a Two-Dimensional Turbulent Flow of Natural Water

Corresponding Member of the RAS V. I. Danilov-Danilyan[a],* and O. M. Rosenthal[a]

Abstract—Variations in the composition and properties of natural waters, which creates numerous difficulties in water use, cannot always be explained by the influence of external forcing such as weathering or leaching of rocks, changes in the phases of the water regime, and other causes. This is especially true for sub-daily and sub-hourly variations in the water quality, which can be caused by complex, previously unknown dynamic hydrochemical processes. Such a conclusion follows from study of the turbidity and pH of natural water measured with increased frequency, the results of which are presented in this work. These results provide evidence about the existence of quasi-cyclic variations in the controlled parameters with different periods, from minute to daily. Study of the observational data allows us to assume that in this case the hydrochemical dynamics is caused by direct and reverse energy cascades in a two-dimensional turbulent flow of natural water, in which the impurity subsystem may be stratified.

INTRODUCTION

Modern hydrochemical dynamics is a branch of hydrology that studies the redistribution of substances dissolved in natural water under the influence of external forces and mass transport [1]. It currently attracts researchers due to the spread of high-frequency measurements of controlled quality indicators. Such practices include the sub-daily studies of in situ hydrochemical data, the number of which has increased in recent decades [2—8]. In these works, the authors often explain the high-frequency variability of the composition and properties of natural waters by the influence of external forcing; however, there are also assumptions about the significance of complex, previously unknown, dynamic processes of the formation of hydrochemical parameters [9—12].

Regularities of rapid changes in the composition and properties of natural waters and the nature of the time series describing this process have been studied. We used the results of measurements of the hydrogen index (pH) and turbidity of river water from the UNITOK research and development center in 2021—2022 at study sites in the cities of Angarsk (Angara River) and Khabarovsk (Amur River) at a measurement frequency of ~30 min^{-1}.

The choice of research objects made it possible to cover a relatively wide range of river water quality. Figure 1 shows that water in the Angara River (left line in Fig. 1a) is much more transparent than in the Amur (right line). In addition, Amur water differs from Angara water in a slightly increased acidity (compare Fig. 1b, left and right lines).

MODELING OF EXPERIMENTAL DATA

The results of the analysis of experimental data sets are shown in Figs. 2 and 3.

One can see a quasi-cyclical change in the water quality with different periods in both figures: the smallest ones are notable by the deviations of the markers from the trend lines, the larger ones are seen
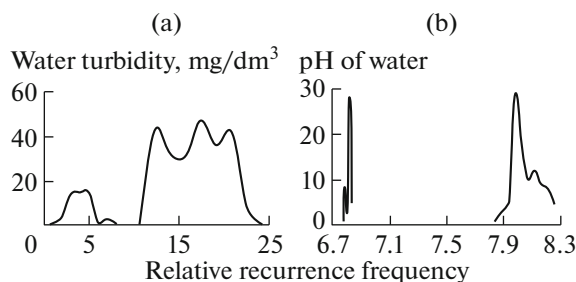
Fig. 1. Comparative recurrence of turbidity (a) and pH values (b).

^{a} *Institute of Water Problems, Russian Academy of Sciences, Moscow, 119333 Russia*
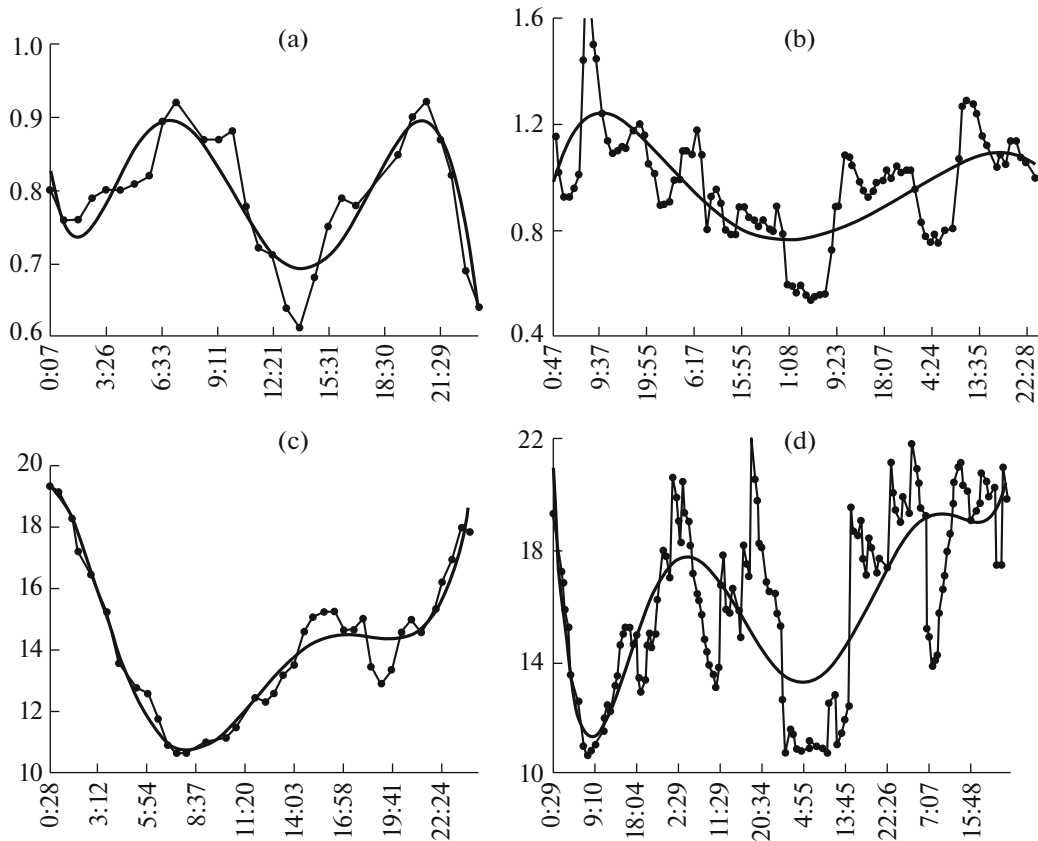**e-mail: vidd38@yandex.ru*

Fig. 2. Experimental results (markers) and the 6th order tender line for turbidity, hereinafter, mg/dm^3 in Angarsk on (a) November 25, 2021, and (b) November 15−18, 2021, and in Khabarovsk on (c) August 6, 2022 and (d) August 6−9, 2022.

in Figs. 2a, 2c, 3a, and 3c, even larger ones are in Figs. 2b, 2d, 3b, and 3d. Thus, the spectrum of oscillations described by a periodic nonharmonic function is obvious.

The quantitative indicators of the considered time series are given in Tables 1 and 2.

One can see from Tables 1 and 2 that the variation in the concentration of individual water pollutants is low compared to that usually observed [13]. This reflects the fact that, in high-frequency measurements, the changes in the controlled parameters are relatively smooth. Accordingly, there is some "spreading" of the distribution function of the considered data series compared to the normal law, which is indicated by predominantly negative values of the kurtosis coefficient. At the same time, the time series are character-

Table 1. Statistical characteristics of variations in water turbidity: ΔT is the period of oscillations isolated from the total spectrum in hours; σ is the standard deviation, CV is the coefficient of variation, As is the coefficient of asymmetry, E_X is the coefficient of kurtosis

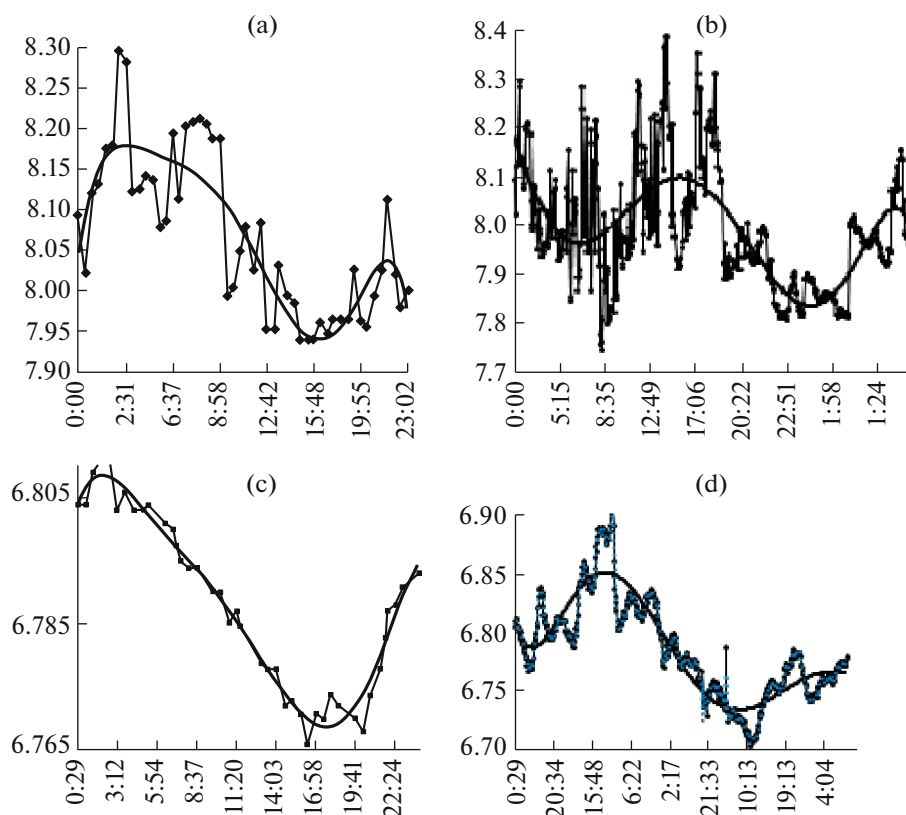| No.	ΔT	Approximating polynomial	σ	CV	As	E_X
a	14	$y = 5E{-}08x^6 - 6E{-}06x^5 + 0.0003x^4 - 0.0059x^3 + 0.0559x^2 - 0.2011x + 0.9747$	0.1	0.14	−0.3	−0.3
b	80	$y = -3E{-}11x^6 + 1E{-}08x^5 - 2E{-}06x^4 + 0.0001x^3 - 0.0048x^2 + 0.0683x + 0.9318$	0.2	0.21	0.25	1.2
c	11	$y = -7E{-}08x^6 + 1E{-}05x^5 - 0.0009x^4 + 0.0254x^3 - 0.2988x^2 + 0.5581x + 18.919$	2.4	0.17	0.4	−0.5
d	70	$y = 1E{-}10x^6 - 8E{-}08x^5 + 2E{-}05x^4 - 0.0019x^3 + 0.0903x^2 - 1.7508x + 22.73$	3.1	0.22	0.17	−0.9

Fig. 3. Experimental results (markers) and the 6th order tender line for the pH of natural water in Angarsk on (a) November 15, 2021, and (b) November 15–24, 2021, in Khabarovsk on (c) August 6, 2022, and (d) August 6–19, 2022.

ized by a right-sided asymmetry, indicating their elongated right "tail." The level of the absolute value of the asymmetry coefficient, which is inot very high and does not exceed ±0.3 in half of the cases, indicates the existence of translational symmetry, in which the properties of the time series change only slightly as a result of its shift by some vector. These are, for example, the lags of the turbidity time series at the site in Khabarovsk of six terms (in this case, the asymmetry change does not exceed 0.02), 15 terms (the asymmetry change is up to 0.05), and 22 terms (the asymmetry change is up to 0.08).

Symmetric processes are well known in hydrology. These include wave motions, eddies, ripples on the surface of the water, Benard cells, convective ridges, sands redistributed under the influence of the flow of water, etc. Natural symmetry (patterns) of water bodies [14] and hydrochemically similar monthly changes in water quality [13] were also found. All this allows us to assume that the trends of water and environmental indicators form an ordered structure, possibly under the influence of the hydrodynamic forces of the river flow, the turbulence of which is not accompanied by completely chaotic motions. Different types of sym-

Table 2. Statistical characteristics of variations in water pH (notations are the same as in Table 1)

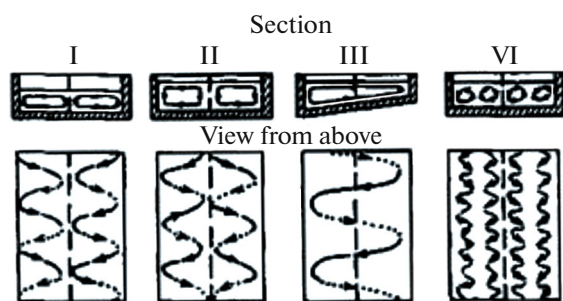| No.	ΔT	Approximating polynomial	σ	CV	As	E_X
a	21	$y = -4E{-}0.9x^6 + 5E{-}0.7x^5 - 3E{-}0.5x^4$ $+ 0.0008x^3 - 0.0108x^2 + 0.0744x + 7.9846$	0.11	0.01	0.47	−0.3
b	170	$y = 2E{-}16x^6 - 4E{-}13x^5 + 4E{-}10x^4 - 2E{-}0.7x^3$ $+ 3E{-}0.5x^2 - 0.0015x + 6.8132$	0.13	0.02	0.24	1.2
c	24	$y = 2E{-}16x^6 - 4E{-}13x^5 + 4E{-}10x^4 - 2E{-}0.7x^3$ $+ 3E{-}0.5x^2 - 0.0015x + 6.8132$	0.02	0.003	0.04	−0.5
d	310	$y = 2E{-}16x^6 - 4E{-}13x^5 + 4E{-}10x^4 - 2E{-}0.7x^3$ $+ 3E{-}0.5x^2 - 0.0015x + 6.8132$	0.04	0.005	0.57	−0.9

Fig. 4. Scheme of internal flows (according to A.I. Losievskii [16]). (I) Surface jet, (II) bottom jet, (III) macropulsations, (IV) micropulsations.

metry play a key role here [15] forming different-scale pulsations of the water flow velocity, as can be seen from Fig. 4.

Turbulent pulsations transfer the subsystem of water pollutants to a state far from thermodynamic equilibrium initiating a regime of hydrochemical oscillations of different scales, in our opinion, due not so much to the different inertia of impurity particles as to the nature of their hydration.

It is noteworthy, however, that, if the frequencies of hydrochemical oscillations were monochromatic, then it is unlikely that periodic measurements (for example, monthly, daily, or more frequent) would reveal periodicity. However, multiscale cascade processes are formed in the turbulence zone. The kinetic energy of turbulent motion initially appears on large scales and is gradually transferred to smaller and smaller turbulent eddies up to molecular ones. Along with this, an inverse cascade is also observed in the quasi-two-dimensional hydrodynamic model of a water body when energy transfers to even larger scales [17] forming large eddies.

Our hypothesis is that small-scale eddies contribute to the micro-stratification of impurity particles in water with its elastic hydrogen bonds, and the conservation of vorticity and the reverse cascade create conditions for more and more full-scale stratification of pollutants in the water flow. As a result, fluctuations in water quality indicators turn out to be incoherent polychromatic with a wide range of oscillatory modes. Therefore, there will always be harmonics the energy contribution of which to the processes responsible for the laws of hydrochemical dynamics would be notable, provided that their period is in some rational relationship with the period between measurements. Thanks to this, it is possible to observe the symmetry of the processes under consideration as a kind of consistency of individual parts, uniting them into a single whole [18].

This conclusion allows us to hope for the prospect of a reasonable forecast of the quality of natural waters. At the same time, asymmetry (Tables 1, 2), as a characteristic of the disorder of the harmonic process and disturbance of its natural course, shows the level of influence of external factors; additional grounds appear for the identification of these factors. The practical implementation of such new possibilities for assessing the quality of natural waters requires digitalization of the hydrochemical dynamics with complete information transmitted by high-frequency modulated oscillations and the main modulating signal encrypted in them.

DISCUSSION

The behavior of systems far from thermodynamic equilibrium does not obey linear laws [19]. Here the principle of superposition is violated, and the energy of interaction with the environment is no longer described by the sum of the energies of pair interactions between all possible pairs of particles. Dissipative structures exist that absorb energy from the surrounding space and demonstrate several phenomena that seem unexpected, such as fractality and auto-oscillations.

We found similar phenomena in natural water bodies that arise during an intense flow exchange of matter and energy with the environment. Thus, a single fluctuation (or a combination of them) of the concentration of water pollutants can become (as a result of positive feedback) so strong that it creates delamination, in which the previously existing structure is destroyed, and at the bifurcation point it is fundamentally impossible to predict how the further redistribution of impurities in water would develop.

A formal description of such systems is beyond the scope of this article and, moreover, is hardly accessible to the modern methods of studying nonlinear problems. It is possible, of course, to form systems of nonlinear equations of motion, but their solution turns out to be very difficult or even impossible if the acting forces cannot be determined correctly. However, it is known that, since the laws of conservation do not depend on the nature of such forces, it is sometimes possible to obtain important information about the behavior of systems even in these cases.

Let, for example, the state of the subsystem of water pollutants be described by some phase trajectory $\vec{C}(C_1, C_2, \ldots, C_n)$, and let the change in its state satisfy the sum of differential equations of the type

$$\frac{dC_i}{dt} = F_i(\vec{C}, \vec{B}), \qquad (1)$$

where, $i = 1, 2, \ldots, n$, $\vec{B} = (b_1, b_2, \ldots, b_n)$ are influencing external factors; in the case considered here, they are pulsations of the eddy-wave flow of river water.

Although there are no methods for analytically solving such differential nonlinear equations, it is still possible to get an idea of how the system they describe behaves. To do this, researchers usually linearize the equations in the vicinity of the equilibrium points. In our case, these are reference points at which the rate of

variations in the concentration of controlled indicators is zero.

It is usually assumed that a randomly chosen vector $\vec{C}^s$ is a stationary solution of the i-th equation among the system of equations. This means that $\dfrac{dC_i^s}{dt} = F_i(\vec{C}^s, \vec{B}) = 0$.

The solution of the last equation makes it possible to find the desired reference point, and the solutions of other equations of system (1) are deviations of the concentration of water pollutants by some small perturbation value $\vec{c}(t)$. Therefore, the actual deviations are equal to $\vec{C}(t) = \vec{C}^s + \vec{c}(t)$.

Expanding the characteristic $F_i(c)$ into a series with respect to c and using the chosen simplest approximation limited to linear terms, one can easily obtain $\dfrac{dc_i}{dt} = \sum_{j=1}^{n} \left.\dfrac{\partial F_i}{\partial C_j}\right|_{\vec{C}=\vec{C}^s} \cdot c_j.$

For further simplification, we denote $\sum_{j=1}^{n} \left.\dfrac{\partial F_i}{\partial C_j}\right|_{\vec{C}=\vec{C}^s}$ as α_{ij} and get a system of linear equations with constant coefficients $\alpha_{ij} = \left.\dfrac{\partial F_i}{\partial C_j}\right|_{\vec{C}=\vec{C}^s}$. Then, to search for approximate solutions, we represent c as e^{pt}, and to find the spectrum of possible values of argument p, we use the eigenvalues of matrix α_{ij}: $\det\left(\alpha_{ij} - p\delta_{ij}\right) = 0.$

This algebraic equation allows us to find the level of stability of the system; i.e., we solve the question of how often it returns to its original state after a deviation. Thus, if there is at least one solution the real part of which is $\mathrm{Re}\, p > 0$, then reference point $\vec{C}^s$ is unstable. The stability of this point appears under the condition that the real part is $\mathrm{Re}\, p < 0$ for all solutions.

Trajectories in the phase space near stable singular points represent the so-called focus, and the trajectory of the considered subsystem of impurities polluting natural water approaches it ("attracts") twisting around it in a spiral [20]. In these cases, time dependence $C(t)$ is oscillatory and decays. On the contrary, oscillations are amplified if there are unstable reference points around which the trajectory of the motion of the system performs rotational motions with an increasing radius ("scattering"). In the intermediate case, the oscillation amplitude is preserved, as shown in Fig. 5a for a model representation of the variability of the water quality index participating in one of three harmonic oscillations with periods of 6, 15, and 22, corresponding to the turbidity time series lags found earlier in the Khabarovsk site with terms of 6, 15, and 22.
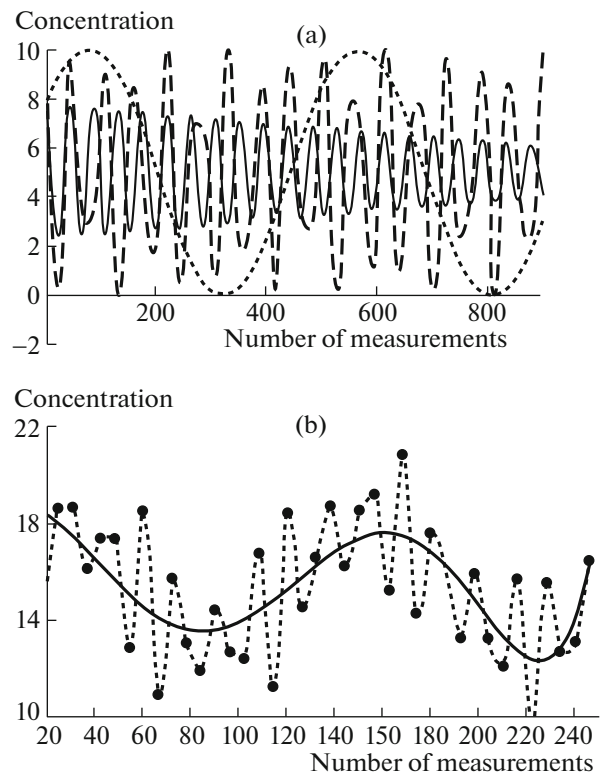

Fig. 5. Model of periodic oscillations with zero phase shift at relative frequencies: (a) 1/6, 1/11, 1/22 and (b) their superposition.

It is clear that the superposition of these oscillations cannot exactly replicate the real pattern of the observed turbidity, at least because, in the real case (Fig. 2), the amplitude of oscillations and the asymmetry coefficient are not constant.

It is not easy to form a convenient model of the motion of molecules and ions hydrated in the network of hydrogen bonds of water, obeying the laws of such a complex process as a flow. It is clear that in this case it is necessary to single out the deterministic and probabilistic components of hydrochemical dynamics. Nevertheless, it is impossible to ignore a number of elements of the similarity of the dependencies shown in Figs. 2d and 5b.

In general, it can be argued that the complex, previously unknown, dynamic processes of the formation of hydrochemical parameters assumed in several works, including [1, 9, 12], are reduced to the appearance of incoherent polychromatic oscillations with a wide range of oscillatory modes. These are the experimentally found quasi-cyclic variations in water quality with periods from minutes to days. It is possible that such hydrochemical dynamics is due to the direct and reverse energy cascades in the two-dimensional turbulent river flow, in which the admixture subsystem is subjected to delamination. As for the range of possible values of the p argument in water media, the result of

observing it will be the ability to predict bifurcations, turning points in the behavior of controlled indicators. In turn, this will open the possibility to anticipate and avoid undesirable and unexpected changes in the quality of natural water.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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