Ecological state of surface waters of rivers in industrial cities

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Abstract. The paper analyzes the chemical composition of the surface waters of a river flowing through an industrial city. Samples were taken in the Ussuri River, flowing through the city of Lesozavodsk. Four factors were derived that describe 78% of the variance of the variables. The first factor is associated with elements such as oxygen, BOD5 (Biological Oxygen Demand in 5 days), NH4, Fe, as well as phenols. Oil products and SSAS (Synthetic Surface-Active Substance) stood out in the second factor. The third factor is related to COD (Chemical Oxygen Demand), and NO3. Suspension and copper stood out as the fourth factor.

1. Introduction

The application of statistical methods to the analysis of results of studies of the chemical composition of surface waters is of particular interest. Therefore, the factor analysis method [1-2], which is widely used to identify sources of emission of tracer elements was applied as a reliable method of analysis. Since there is a correlation between the concentrations of pollutants in discharges and their content in river streams, the factor analysis method applied to the data on the chemical composition of surface waters makes it possible to distinguish groups of elements coming from different sources.

The method allows us to represent each variable (in this case, concentration) as a linear combination of independent factors. As the first step of the calculations, the matrix of pair correlation coefficients between the variables is produced. As the next step, the eigenvalues and eigenvectors are determined from the correlation matrix. Normalized vectors are factors that influence the variability of features. Factors are ranked according to the distribution of the total variance of the data. The first several factors usually describe more than 80% of the variance, which is sufficient for the interpretation of the original variables. Factors and coefficients of factor mapping (i.e. factor loads) are not uniquely determined and have several equivalent solutions. Factors Fj can be changed by orthogonal transformation (the varimax method is used in the work) with the corresponding conversion of factor loads Aij. The transformation is carried out in such a way that the resulting coordinate axes satisfy the criteria of a simple factorial structure [1]. According to the Horn rule [1], factors are selected for eigenvalues 1.

2. Materials, methods and organization of research

To properly discuss the results of the study, we should first take into account some features of the elements migration in the hydrosphere. Chemical composition of river water in cities is mainly...
influenced by the following factors: 1) the release of conditionally pure industrial waste into the waterways after treatment; 2) the influx of storm water polluted by natural dumps of waste and raw materials, soils, concentrating industrial emissions; 3) the emission of sewage by treatment facilities. Indeed, in recent years it has been established that for most of the chemical elements, the most important source is storm runoff, with which up to 85% Zn, 70% Pb, 50-70% Cd, Cu, Mn, about 40% Mo and Ni fall into the waterways [3]. The composition of storm runoff, which is the most important technogenic supplier of chemical elements to water courses, is formed by washing away soils, washing away dust from asphalt surfaces, erosion of buildings and structures, and washing out landfills. Atmospheric precipitation has a significant impact on the pollution of stormwater. According to [4], the percentage of chemical elements of aerial origin in the surface rainwater of urban areas can be from 35 to 54% for Mn, Zn, Pb and 90% for Cu. For Sn and Cr, the most significant supply is with sewage (about 50%). The input of chemical elements with conditionally pure industrial effluents into watercourses is about 5% for Cu, Cd, and Ni. Among man-made sources, the contribution to the pollution of watercourses is increasing in the following series: industrial wastewater of conditionally clean water - sewage after treatment facilities (if available) - storm surface runoff.

For research, the city of Lesozavodsk (Primorsky Territory) was chosen, in which about 30 thousand people live. The main sources of anthropogenic emissions and discharges are industrial enterprises, heat power enterprises (boiler houses), and motor vehicles. In total, the city has about 20 enterprises with significant emissions and discharges of harmful substances. The main pollutants emitted into the atmosphere: solids, sulfur dioxide, carbon monoxide, nitrogen oxides, hydrocarbons, phenols. Emissions and discharges contain a number of specific pollutants: yeast dust, furfural, methanol, organic acids, and sulfuric acid.

The research material was the data of annual observations at a network of stations of the Primorsky Administration for Hydrometeorology and Environmental Monitoring. Samples were taken in the Ussuri River, flowing through the city. The analysis involved data on the average annual concentrations of such substances as: 1) suspended solids, 2) oxygen content, 3) BOD5, 4) NH4, 5) NO3, 6) Fe, 7) Cu, 8) oil products, 9) SAS, 10) phenols; 11) COD.

### 3. Results and their consideration

The results of the correlation analysis are given in table 1, and the results of factor analysis are given in table 2.

| №  | 1    | 2    | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    |
|----|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1  | 1    | 0.03 | 0.31  | -0.06 | -0.14 | -0.13 | 0.51  | 0.04  | 0.10  | -0.25 | -0.26 |
| 2  | 1    | 0.61 | -0.35 | 0.00  | -0.49 | 0.25  | -0.11 | -0.14 | -0.37 | -0.08 |       |
| 3  | 1    | 0.40 | -0.47 | -0.43 | 0.47  | 0.36  | 0.22  | -0.50 | 0.00  |       |       |
| 4  | 1    | 0.00 | 0.35  | -0.31 | 0.34  | 0.25  | 0.47  | -0.13 |       |       |       |
| 5  | 1    | -0.05| -0.38 | -0.30 | -0.21 | 0.11  |       |       |       |       |       |
| 6  | 1    | -0.21| 0.22  | 0.12  | 0.69  | 0.12  |       |       |       |       |       |
| 7  | 1    | -0.10| -0.16 | -0.43 | -0.38 |       |       |       |       |       |       |
| 8  | 1    | 0.88 | 0.08  | -0.12 |       |       |       |       |       |       |       |
| 9  | 1    | 0.08 | -0.17 |       |       |       |       |       |       |       |       |
| 10 | 1    | 0.10 |       |       |       |       |       |       |       |       |       |
| 11 | 1    |      |       |       |       |       |       |       |       |       |       |

Hereinafter, the variable number means: 1) suspended solids, 2) oxygen content, 3) BOD5, 4) NH4, 5) NO3, 6) Fe, 7) Cu, 8) oil products, 9) SAS, 10) phenols; 11) COD.
Significant values with a confidence of 95% are values of 0.47. This is due to the fact that the significance of the correlation coefficients and factor loads is determined by the number of observations [5].

Table 2 presents the matrix of factor loads calculated for water samples taken in the city. From the data in Table 2, it can be seen that, as a result of statistical data processing, four factors were identified that describe 78% of the total variance of the variables.

| Table 2. Factor load matrix (samples taken in the city) |
| Element | A1 | A2 | A3 | A4 |
|---------|----|----|----|----|
| Suspension | 0.05 | 0.07 | -0.05 | -0.81 |
| O2 | 0.79 | -0.01 | -0.02 | 0.01 |
| BOD5 | 0.71 | 0.38 | 0.34 | -0.32 |
| NH4 | -0.62 | 0.36 | -0.18 | 0.08 |
| NO3 | -0.02 | -0.25 | -0.85 | 0.32 |
| Fe | -0.82 | 0.09 | 0.17 | 0.04 |
| Cu | 0.28 | -0.12 | 0.09 | -0.01 |
| Petroleum Products | -0.08 | 0.97 | 0.09 | -0.01 |
| SSAS | -0.07 | 0.93 | -0.01 | 0.01 |
| Phenols | -0.76 | 0.05 | 0.00 | 0.28 |
| COD | -0.04 | -0.21 | 0.80 | 0.45 |
| Total Variance, % | 31 | 52 | 66 | 78 |

The first factor, describing 31% of the variance of the variables, significantly positively loads such elements as oxygen, BOD5 and negatively: NH4, Fe, phenols. This distribution of ingredients is quite acceptable since it indicates the effect of pollution by these components on the oxygen content in water. The first factor can be interpreted as an anthropogenic component of discharges of industrial enterprises. The second factor, which describes 21% of the variance of the variables, was oil products and surfactants. Surfactants can mainly enter watercourses with sewage and the release of petroleum products into this factor indicates one source of these pollutants entering the city's watercourses. Falling into the third factor, which describes 14% of the variance of variables, COD with a significant load and NO3 with a negative load is completely logical since the content of NO3 in water should be inversely related to the COD content. In the fourth factor, which describes 12% of the dispersion, two elements stand out: suspension and copper. Suspended matter should mainly flow into streams with storm runoff. Thus, copper can enter watercourses most likely as a flush from the underlying surface of the city.

4. Conclusion
Thus, the first factor can be interpreted as an anthropogenic component of discharges of industrial enterprises. The second factor can be defined as domestic sewage. The third factor characterizes the concentration of oxygen in water. The fourth factor can be defined as flushing from the underlying surface.

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