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# Deconvolution of water chemistry concentrations into components: background, anthropogenic, and resulting from changes in meteorological parameters

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**SUMMARY**

Following most EU countries, Ukraine implements the ecological principle of water resources management, the main purpose of which is to achieve a "good" ecological status for all water bodies.

The High ecological status corresponds to the natural conditions of aquatic ecosystems, when indicators of the water chemistry are within their natural concentrations. Considering the current anthropogenic pressure, the ranges of natural variability of concentrations are important, being a natural background.

The main goal of this work was to develop a new stochastic approach to estimating background concentrations. Using the convolution theory and random processes theory, at the first stage, we developed an algorithm for separating the actual concentrations of water chemistry parameters into natural and anthropogenic components. At the second stage, the task was to take into account changes in meteorological parameters during the deconvolution of actual concentrations. The result of this work is a methodology that would allow separating the actual concentrations of water chemistry not only into the background and anthropogenic components but also assess the component resulting from changes in meteorological parameters.

Practical application of the developed technique has been demonstrated on the example of sulfate ions in the water of the Bilenka river.

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**Introduction**

Following most EU countries, Ukraine implements the ecological principle of water resources management. The main purpose is to achieve a "good" ecological status for all water bodies. As a general rule, the excellent ecological state corresponds to the natural conditions of aquatic ecosystems, when indicators of the water chemistry are within their natural concentrations. Considering the current anthropogenic pressure, the ranges of natural variability of concentrations are important, being a natural background. Several methods are used to determine a natural background, but they are not sufficiently reliable. The results of stochastic analysis of natural processes (*Bendat et al., 1989; Prigogine, 1991; Nicolis et al., 1990*) inspired us to develop a new approach to estimating background concentrations. Using the convolution theory (*Yanoshi, 1968*) and random processes theory (*Gikhman et al., 1971; Stepanov, 2009*), at the first stage, we developed an algorithm for separating the actual concentrations of water chemistry parameters into natural and anthropogenic components. We verified deconvolution results by blind testing in 10 series of 365 values of ammonium nitrogen concentrations in each. The test showed a 90% efficiency of the algorithm (*Osadchiy et al., 2013*). At the second stage, the task was to take into account changes in meteorological parameters during the deconvolution of actual concentrations. The purpose of this work is to develop a methodology that would allow separating the actual concentrations of water chemistry not only into the background and anthropogenic components but also assess the component resulting from changes in meteorological parameters.

**Materials**

We used a long-term data set on the surface water chemistry obtained by the State Emergency Service of Ukraine on the hydrometric monitoring networks. A set of observations must cover economic activities of different intensities. Human activity over time was classified according to its impact on water quality: (1) until 1960 - slight impact; (2) 1961-1991 - intensive impact; (3) after 1992 - reduced impact. This paper presents the results of the analysis of sulfate ion changes in the Bilenka river (the Siverskyi Donets basin). The river has sulfate type of water and highly suffers from human pressure. Since 2000, sulfate ions content in the river waters began to increase. Consequently, we came up with a hypothesis that the increase in sulfate ions caused changes in meteorological parameters.

**Theory & Method**

The Kolmogorov axioms (*Kolmogorov, 1974*), which have proved their validity for both random events (**A**) and random variables (A), become a theoretical basis of our methodology. This allowed considering instantaneous values of the concentrations of the components of the standard monitoring as random variables. First, we formulated hypotheses on the ways individual components enter the river network. These hypotheses were transformed later into statistical ones, which were tested using established mathematical procedures (*Kazakevich, 1977; Lvovskiy, 1988; Novitsky et al., 1985*).

The starting point is that each actual value of the chemical component concentration ($Y$) is the sum of three elements: concentration of anthropogenic origin ($X_2$); concentration resulting from changes in meteorological parameters ($X_3$); concentration typical for natural conditions ($X_4$). Obviously, the sum of ($X_3 + X_4$) amidst the change of meteorological parameters is a characteristic of the general background concentration. Hence, we formulated two statistical hypotheses. (1) The law of statistical distribution of actual concentrations of a component ($Y$) is a convolution of two laws: the law of statistical distribution of natural concentrations ($X_1$) and the law of statistical distribution of man-made concentrations ($X_2$). (2) In its turn, the law of statistical distribution of natural background concentrations ($X_1$) is a convolution of the law of statistical distribution of concentrations resulting from changes in meteorological parameters ($X_3$) and the law of statistical distribution of background concentrations ($X_4$). In addition, we involved two more hypotheses: (1) the statistical distribution of concentrations ($X_4$) inherent in the climate norm is subject to

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Gauss's law that is identified with 0.95 reliability; (2) the statistical distribution of concentrations ($X_3$) resulting from climate change is subject to Gauss's law that is identified with 0.99 reliability.

The reason for involving the convolution hypothesis is as follows. Deconvolution is the opposite operation to convolution, which allows calculating the parameters of the laws of statistical distributions: human-caused concentrations ($X_2$), concentrations resulting from changes in meteorological parameters ($X_3$), and background concentrations ($X_4$). Parameters of laws such as mathematical expectation, standard deviation, kurtosis, and eccentricity, are used mainly for solving practical problems. However, the instantaneous values concentrations ($X_2$), ($X_3$), ($X_4$) are of particular importance. These values allow verifying results of the separation of the actual concentrations of various chemical components by blind testing. To calculate the instantaneous values of concentrations, we used the third (**III**) and fourth (**IV**) Kolmogorov axioms. According to the fourth (**IV**) axiom, if events $X_1$ and $X_2$ do not intersect, namely are independent, then:

$$P \ (Y) = P(X_1 + X_2) = P(X_1) + P(X_2). \tag{1}$$

By the Kolmogorov third (**III**) axiom *[P(Ω) = 1]*, a critical practical consequence is that the instantaneous values of the actual concentrations of the chemical component (***Y***) correspond to the instantaneous values of concentrations of natural origin ($X_1$) and instantaneous values of concentrations of anthropogenic origin ($X_2$) in the same way how their instantaneous probabilities correspond. In other words, having the probabilities of *P(Y), P(X₁),* and *P(X₂)*, it becomes possible to calculate ($X_1$) and ($X_2$). To do this, we made the proportions and obtained the corresponding equations:

$$X_1 = [Y * P(X_1)] \ / \ [P(X_1) + P(X_2)], \tag{2}$$
$$X_2 = [Y * P(X_2)] \ / \ [P(X_1) + P(X_2)]. \tag{3}$$

Similarly:

$$X_3 = [X_1 * P(X_3)] \ / \ [P(X_1) + P(X_3)], \tag{4}$$
$$X_4 = [X_1 * P(X_4)] \ / \ [P(X_1) + P(X_4)]. \tag{5}$$

The following question is how to calculate the probabilities of *P(Y), P(X₁), P(X₂), P(X₃)*, and *P(X₄)* if they are related to events. By Kolmogorov, we studied time sequences of concentrations *(Y), (X₁), (X₂), (X₃),* and *(X₄)* as random functions {Y, $X_1, X_2, X_3, X_4$}. It's critical to emphasize that the obtained instantaneous values of concentrations are necessary to verify the reliability of the results. However, these values have limitations for assessing the future state of water bodies, as such assessment is possible only based on analysis of change dynamics of chemical components. In this case, the formulated statistical hypotheses were formally presented for calculation by two convolution equations (*Yanoshi, 1968*):

$$p_Y(y) = \int_{-\infty}^{+\infty} p_{X2}(y - x1) \, p_{X1}(x1) dx, \tag{6}$$

$$p_{X1}(x1) = \int_{-\infty}^{+\infty} p_{X3}(x1 - x4) \, p_{X4}(x4) dx, \tag{7}$$

where $p_Y(y)$ - probability density of the actual concentrations of the component; $p_{X1}(x1)$ - probability density of natural background concentrations (reference state + climate change); $p_{X2}(y-x1)$ - probability density of concentrations of anthropogenic origin; $p_{X3}(x1-x4)$ - probability density of concentrations resulting from climate change; $p_{X4}(x4)$ - probability density of the concentrations of the reference state (climate norm).

It is worth noting that the reconstruction of the process of component concentrations based on the results of observations is a significant probabilistic problem. In our case, the reconstruction was performed by the method of intersections of a set of observations at certain time intervals (*Kazakevich, 1977*).

The law of statistical distribution of actual concentrations of components $p_Y(y)$ was identified using the **Gaussian 1 model** (*Novitsky et al., 1985*). The parameters of this model, including $\mu_Y$ - mathematical expectation, $\sigma_Y$ - standard deviation, and $\varepsilon_Y$ - kurtosis, were obtained based on a long-term set of observed concentrations (***Y***).

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The law of statistical distribution of natural concentrations (background + climate change) $p_{X1}(x1)$ was identified thanks to the **Gaussian 1** model. The parameters of this model, $\mu_{X1}$, $\sigma_{X1}$, when $\varepsilon_{X1} = 0$, were calculated for that part of the sorted set of actual concentrations, which has a normal distribution with a reliability of **0.99**. The law of statistical distribution of concentrations inherent in climate norm $p_{X4}(x)$ was identified thanks to the Gaussian model 1. The parameters of this model $\mu_{X4}$, $\sigma_{X4}$, at $\varepsilon_{X4} = 0$ were calculated for the part of the sorted set of actual concentrations, which has a normal distribution with a reliability of **0.95**. The limit values, which are sorted in ascending order of concentrations and subject to Gauss's law, with the reliability of 0.99 or 0.95, were determined by the following algorithm (Figure 1). (1) We calculated the unbiased values of kurtosis ($\varepsilon$) and eccentricity ($s$) of the sorted set. (2) We calculated unbiased estimates of $G_1$ and $G_2$ of kurtosis and eccentricity sample values. (3) We calculated standard deviations $S_{G1}$ and $S_{G2}$ of excess and eccentricity unbiased sample values. (4) We applied the hypothesis of a normal distribution of concentrations with the reliability of 0.99 to the part of the sorted set where the following conditions were met (*Lvovskiy, 1988*):

$$|G_1| \leq 3 S_{G1} \tag{8}$$

$$|G_2| \leq 3 S_{G2} \tag{9}$$

If the following conditions were met

$$|G_1| \leq 2 S_{G1} \tag{10}$$

$$|G_2| \leq 2 S_{G2} \tag{11}$$

then this part of the sorted set of actual concentrations was subject to Gauss's law with the reliability of 0.95 (*Lvovskiy, 1988*).

The law of statistical distribution of human-caused concentrations of $p_{X2}(y\text{-}x)$ was identified by the **Gaussian 1** model. The model parameters $\mu_{X2}$, $\sigma_{X2}$, and $\varepsilon_{X2}$ were calculated, according to the properties of the convolution:

$$\mu_{X2} = \mu_Y - \mu_{X1}, \tag{12}$$
$$\sigma_{X2} = (\sigma_Y^2 - \sigma_{X1}^2)^{0.5}, \tag{13}$$
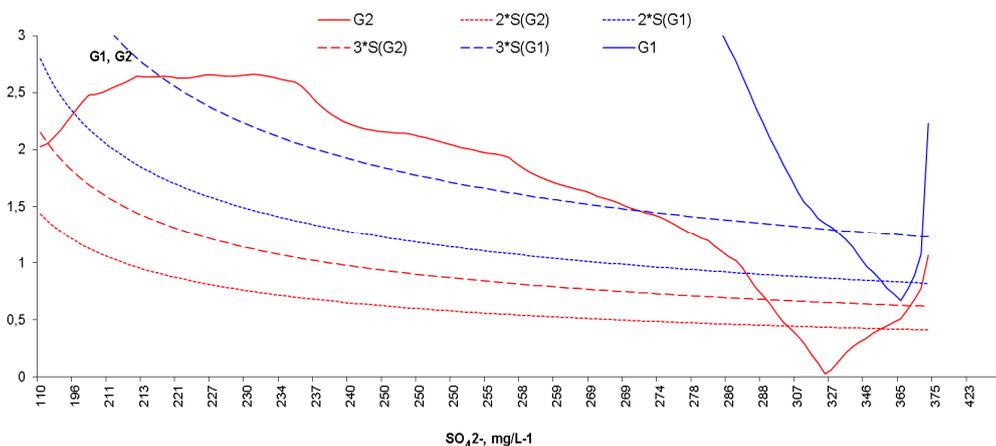$$\varepsilon_{X2} = (\varepsilon_Y^4 - \varepsilon_{X1}^4)^{0.25}. \tag{14}$$



***Figure 1*** *Determining the limit values of sorted concentrations of sulfate ions that are subject to Gauss's law with the reliability of 0.99, or 0.95. Observations from 1992 to 1996 0.5 km above the mouth of the Bilenka river.*

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Similarly, we identified the law of statistical distribution of concentrations due to climate changes $p_{X3}(x1-x4)$. The parameters of the statistical distribution of concentrations $X_3$ were calculated from the relations:

$$\mu_{X3} = \mu_{X1} - \mu_{X4}, \tag{15}$$
$$\sigma_{X3} = (\sigma_{X1}^2 - \sigma_{X4}^2)^{0.5}, \tag{16}$$

**Results**

The results obtained are presented in Table 1.

We found out: a) there was no significant influence of human activity and climatic factors on the sulfate ions ($SO_4^{2-}$, mg/dm$^3$) concentrations in the Bilenka river during 1992-2001; b) there was an increase in anthropogenic impact, and the maximum was observed from 2002 to 2006 during 2002-2016; c) the impact of climate change was increasing since 2002, and during 2007-2016, the concentrations of sulfate ions reached values commensurate with the natural background (Table 1).

**Table 1** *Separation of the sulfate ions in the Bilenka river into components at 95% confidence intervals of the average*

| Period | Actual natural (background + climate change) | Natural (background, climate norm) | Human-caused | Climate change |
|---|---|---|---|---|
| 1992-1996 | 266,49 ±8,70 | 261,56 ± 7,73 | 2,96 ± 2,00 | 4,94 ± 4,01 |
| 1997-2001 | 253,65 ±6,30 | 252,63 ± 5,99 | 0,00 ± 0,00 | 1,02 ± 1,00 |
| 2002-2006 | 337,00 ±8,64 | 252,63 ± 5,99 | 138,51 ± 6,33 | 84,37 ± 6,12 |
| 2007-2011 | 469,13 ±3,10 | 252,63 ± 5,99 | 63,96 ± 7,81 | 216,50 ± 5,54 |
| 2012-2016 | 459,32 ±3,64 | 252,63 ± 5,99 | 46,79 ± 5,95 | 206,69 ± 5,58 |

**Conclusions**

The proposed methodology allows separating the actual concentrations of the water chemistry parameters into the background concentrations, anthropogenic components, and the components resulting from climate change.

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