Investigation of Selected Physicochemical Indicators of Surface Water Quality in the Unregulated Varínka Stream, Slovakia

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https://doi.org/10.29227/IM-2025-02-02-084

Submission date: *2025-04-03* | Review date: *2025-04-26*

Abstract

Physicochemical indicators of surface water quality play a crucial role in influencing biological processes in surface waters. In the context of climate change, changes in river hydrological regimes also affect surface water quality. This study aims to evaluate long-term data on dissolved oxygen (DO), surface water temperature (Tw), acidity (pH) and conductivity (EC) in the undisturbed Varínka stream in the northern part of Slovakia, covering the period from 1972 to 2017. The study focuses on identifying significant changes in physicochemical indicators of surface water quality and analyzing monthly and annual trends. The results reveal significant increasing trends in acidity and conductivity values in the Varínka stream. The next section examines regression relationships between selected indicators and models them. Cross-correlation between individual indicators showed that most do not follow a linear pattern, but some correlation coefficients (between surface water temperature and dissolved oxygen) were significantly different from zero. An autoregressive model was tested to model the selected surface water quality indicators, enabling the identification of risks associated with changing values. This model's predictive ability allows for early identification of potential threats and supports the implementation of cost-effective measures to protect surface water resources. The study concludes that the SARIMA model can effectively simulate changes in surface water temperature, dissolved oxygen, and conductivity, providing valuable information for surface water management and conservation strategies.

Keywords: *physicochemical indicators of surface water quality, climate change, long-term trends, autoregressive models*

1. Introduction

Water is a renewable but limited natural source, an important component of natural ecosystems. As a result of human activity and climate change, growing of the extreme hydrological and meteorological phenomena in their frequency of occurrence, duration and severity are expected ([1]; [2]; [3] or [4]). That may directly or indirectly influence the quality in surface waters. Due to the multifunctional and multiple uses of water, as well as the inconsistency between the temporal and spatial distribution of water sources and requirements, and the reuse of water along the rivers, it is necessary to coordinate water management and the use of water resources [5]. Water Resources Concept [6] states „it is important to recognize that water quality and quantity are closely linked in terms of good condition". On 12th May 2021, the European Commission adopted the EU Action Plan: „Towards zero air, water and soil pollution "([7]).

Regular water sampling from rivers in Slovakia began in 1963 in response to the deteriorating water quality caused by the growth of industry and agricultural production. From 1963 to 1967, surface water quality results were published within Czechoslovakia, with reports issued in Prague. Since 1981, the Slovak Hydrometeorological Institute (SHMÚ) in Bratislava has published yearbooks, where all data from this period are archived [8]. By 2001, surface water quality in Slovakia was monitored at 178 primary and three special sampling sites. The method for evaluating surface water quality was based on the classification system defined in the Slovak Technical Standard STN 75 7221 [9], which came into effect in January 1999. This system classified surface water quality into five categories, ranging from Class I (very clean water) to Class V (very heavily polluted water), using threshold values calculated from 24 measurements taken over two years. Currently, the assessment of surface water quality in Slovakia follows the principles of the EU Water Framework Directive (EPC, 2000) and considers a range of biological, chemical, and physicochemical indicators. The indicators are evaluated in accordance with Slovak Government Regulation NV No. 269/2010 Coll., as amended by Regulation No. 398/2012 Coll. By determining the physicochemical properties of surface water and the concentration of selected substances, its quality can be assessed. Slovak Hydrometeorological Institute (SHMI) provides the assessment of hydrological characteristics and surface water quality in Slovakia according to mentioned regulations of the Slovak Republic. A method for identifying long-term trends of individual physicochemical indicators of surface water quality in surface rivers was processed in [10]. The methodology was based on the requirements of Directive 2000/60/EC and existing data from the database of the SHMI. In recent years, the evaluation of quality elements on selected profiles of Slovak rivers or the transport of pollution in surface waters was investigated by [11]; [12]; [13]. Velísková et al. [14] addressed pollution source localization in open sewers, proposing an operational method successfully tested on real data, highlighting the influence of parameter sensitivity on localization accuracy. These works concluded that the state of surface water quality after 1989 has generally improved. However, it is still necessary to monitor trends in surface water temperature, surface pollution, and in the case of small rivers, the trend of pollution by organic or inorganic substances. The type and concentration of chemical elements in the surface waters of rivers are changed due to different types of natural processes, which depends on environmental factors influenced by still changing natural and anthropogenic activities. Monitoring of the trends in surface water quantity and quality deserves special attention in the research to quantify the possible threat to its balanced regime.

As mentioned above, climate change and anthropogenic activities affect water quantity and quality, with a negative impact on the hydrological and qualitative regime of rivers. Therefore, it is necessary to understand and analyse their changes, as well as the mutual relationship between quantitative characteristics and physicochemical indicators of surface water quality. Such knowledge enables the

prevention and response to crisis phenomena and is one of the prerequisites for a quick and correct solution to eliminate their consequences. While the potential impacts of climate change on surface water availability have been widely studied in recent decades, their impact on surface water quality is still less researched. The main objectives of this paper are to assess the potential threat to its balanced regime:

• To detect and analyse long-term trends in the oxygen (DO) and temperature regime (Tw) of surface water in five selected unregulated rivers of Slovakia, as well as changes in acidity (pH) and conductivity (EC) in these rivers.

• To perform a cross-correlation analysis of selected physicochemical indicators of surface water quality.

• To model the selected physicochemical indicators of surface water quality using a selected autoregressive model to capture and account for patterns and trends within the time series data, including seasonality and periodicity.

2. Data and methods

2.1 Data

The Varínka stream basin is located in the Malá Fatra National Park (in Slovak: Národný park Malá Fatra), in the northwest part of the Malá Fatra mountains called Krivánska Malá Fatra. The mountain is covered mainly by mixed beech forests, and with fir and spruce at higher elevations. Dwarf pine and meadows occur at the highest altitudes. The Varínka stream (stream ID 4-21-05-6465) is created from several brooks in the Vrátna Valley, near to the Terchová village (Figure 1). The Varínka stream is the area of European importance especially for travertine springs and hydrophilic tall herb fringe communities. The basin has an area of 167.307 km^2 and stream length is 24.46 km. The Varínka originates from Krivánska Fatra, the Malá Fatra subunit. Source of the Varínka is located on the northern slope of the mountain section of the ridge between the peaks Chleb (1647 m a. s. l.) and Hromove (1636 m a. s. l.). The Varínka stream flows on bottom of the Vrátna Valley and flows into the Váh River in Varin village.

Monthly concentrations and values of four physicochemical indicators of surface water quality (DO, Tw, as well as changes in pH and EC) in these five unregulated rivers in Slovakia were used for long-term trend detection and interdependence analysis. Figure 1 illustrates the scheme of the geographical location of the selected river and location of sample point. The data comes from the database "Summary Records of Waters" managed by the Slovak Hydrometeorological Institute of the Slovak Republic. Table 1 lists the basic geographical characteristics of the selected unregulated rivers at the sample points.

Tab. 1. Basic geographical characteristics of the selected unregulated Varínka stream

River	Sample site	Period	Area [km^2]	River km	Elevation [m a. s. l]	Forest [%]
Varínka	Varín	1972–2017	190	0.5	350	60

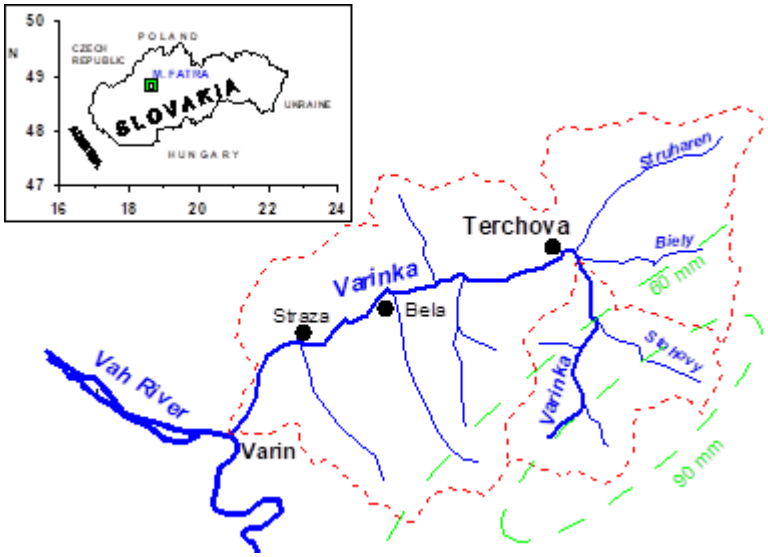


Fig. 1. Scheme of the Varínka basin.

2.2 Methods

The Mann-Kendall nonparametric test (M-K test) was used for determining the significant trends detection of monthly and annual confrontations of selected indicators of oxygen river regime. The nonparametric tests are more suitable for the detection of trends in hydrological time series, which are usually irregular, with many extremes [15]; [16]. MAKESENS 2-tailed test is used for four different α significance levels. The significance level of the test α- is a chosen number from the interval from 0 to 1, or 100% (the smaller the better, but α = 0.05 or 5%) is most often used. A significance level of 0.05 means that there is a 5% probability that the values of xi are from a random distribution, and with that probability we make an error in rejecting H0 (the null hypothesis) of no trend. A significance level of 0.001 means that the existence of a monotonic trend is very likely.

We evaluated the significance of the trend in our study at selected significant levels or levels of trend significance).

*** if the trend is at α = 0.001 – the validity of H0 is improbable

** if the trend is at α = 0.01 - 1% error in rejecting H0

* if the trend is at α = 0.05 - 5% error in rejecting H0

+ if the trend is at α = 0.1 - 10% error in rejecting H0

Empty - the level of significance is greater than 0.1, we cannot rule out that H0 is true.

The most important trend is assigned three stars (***), with the gradual decrease in importance, the number of stars also decreases. Statistically, we evaluate the significance of a trend using the Z value. A positive Z value indicates an upward (growing) trend, while a negative value indicates a decreasing trend. If the absolute value of Z is less than the significance level, there is no trend.

Cross-correlation and modelling of selected physicochemical indicators of surface water quality on unregulated Slovak rivers
To assess the strength of interdependence between individual selected components of the hydrosphere, the equation (1) was used [17]:

$$\sigma_R = \frac{1-R^2}{\sqrt{n}} \quad (1)$$

Where: σ_R – correlation coefficient error R; n – number of variables included in the analysis.
For a significantly different correlation coefficient from zero, criterion (2) must be valid

$$|R| \geq 3.\sigma R \quad (2)$$

Individual physicochemical indicators of surface water quality exhibit mutual relationships and dependencies, which can be observed using regression analysis. Correlation analysis examines the relationship between two random variables xi and yi. The correlation coefficient r(x, y) is used to quantify the dependence between quantities, if it exists.

$$r_{(x,y)} = \frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2 \sum_{i=1}^{n}(y_i-\overline{xy})^2}} \quad (3)$$

By standardizing the random variables, we obtained a new dimensionless measure of dependence, which takes on values from the interval (−1; 1). The sign of the correlation coefficient depends on the covariance, according to which we interpret the value of the coefficient:

- r(x,y) > 0 ⇔ direct dependence,
- r(x,y) < 0 ⇔ indirect dependence,
- r(x,y) = 0 ⇔ independence (correlation).

Regression analysis models the relationship between a dependent variable and one or more independent variables. It is used to predict or explain the dependent variable based on the values of the independent variable(s). In hydrology, regression equations are often used to estimate relationships between various hydrological quantities when modelling and analysing various processes. Sime basic types of regression equations commonly used in hydrology are: linear, nonlinear, multiple, polynomial, exponential, and logarithmic.

One type of model that models and forecasts future behaviour based on past data, and where there is a correlation between the time series values and their preceding and succeeding values, is the autoregressive model ([18]; [19]; [20]). For the modelling of physicochemical indicators of surface water quality an autoregressive integrated moving average (ARIMA) and seasonal ARIMA (SARIMA) models without/with the selected regressor were tested. The models are designed to capture and account for patterns and trends within time series data. The seasonal component is particularly important in the ARIMA model because it allows modelling data with seasonal fluctuations or cycles. The model involves fitting a regression equation to the data, where the dependent variable is the time series data and the independent variables are the series lags and lagged errors. The model is usually estimated using the maximum likelihood estimation, and the accuracy of the model can be evaluated using various statistical criteria. To identify this model, it is necessary to analyse the individual components of the time series in the following order: trend identification; choosing the type of model and determining the order of the model; estimation of model parameters; model validation. The general form of the ARIMA (p, d, q)x(P, D, Q)$_L$ model takes the following form:

$$\varphi(B)\boldsymbol{\varphi}(B^L)\,\nabla^D\,\nabla_L^D Y_t = \boldsymbol{\Theta}(B)\Theta(B^L)E_t, \quad (4)$$

where:

E_t - independent and normally distributed random variable with zero mean value μ=0 and variance σE2; p - trend autoregressive order; d - trend difference order; q - trend moving average order; P - seasonal autoregressive order; D - seasonal difference order; Q - seasonal moving average order; L - the number of time steps for a single seasonal period (an L of 12 for monthly data suggests a yearly seasonal cycle; B - reversion shift operator defined as $BY_t = Y_{t-1}$; ∇^d - the backwards difference operator; φ - the regular AR (auto-regressive) operator of the order p; Θ - is the regular SMA (moving average) operator of the order q; $\nabla^D{}_L$ - the seasonal backwards difference operator; $\boldsymbol{\varphi}$ - is the regular SAR (seasonal auto-regressive) operator of the order P; $\boldsymbol{\Theta}$ - is the regular SMA (seasonal moving average) operator of the order Q.

3. Results

This part of the paper aims to evaluate the selected physicochemical indicators of surface water quality (DO, Tw, pH and EC) to assess the development of changes in Varínka stream: Varín. Monthly data from the analyzed period was evaluated. Figure 2 illustrates the measured concentration values of selected surface water quality indicators. The input data was validated by graphically plotting the measured values. Data points that noticeably disrupted the smooth progression of measurements and were likely errors were excluded from the series, though their number was minimal. For the series of monthly values for selected surface water quality parameters over the analysed periods, the 10th, 50th, and 90th percentiles (the percentiles estimate the P10, P50, and P90 values) were calculated. According the P90 values (or P10 values in the case of oxygen) we classify the categories of the quality surface water in Slovakia defined in Decree No. 418/2010, OG of the Ministries of Agriculture, Environment, and Regional Development of the Slovak Republic on the Implementation of Certain Provisions of the Water Act. Figure 3 (a)-(d) illustrates P10, P50 and P90 concentration and values of selected quality indicators at sample site in selected unregulated rivers of Slovakia during analyzed period. The surface water quality indicators according mentioned standards were not be exceeded in selected site points of the streams during the analyzed period (Figure 3(a)), except pH values where the limit 8.5 was exceeded.

The Mann-Kendal nonparametric test was used to detect the significance changes in trends of analyzed surface physicochemical indicators of surface water quality. Results of the M-K test for long-term trend of monthly and annual concentration of DO, Tw, pH and EC for Varínka River: Varín are listed in Table 2. The significant (***) increasing monthly and annual long-term trends were identified in values of acidity (pH) and the conductivity (EC) and annual values show significant increasing long-term trends Figure 4 illustrates example of long-term trend of annual values of the pH and EC. The significant (**) trends of the surface water temperature Tw and dissolved oxygen were identified in month of May and June. River alkalinization, caused by factors like temperature, acid deposition, and land use, increases pH [21]. Moniewski (2015) links this to higher photosynthetic activity in algae [22]. This is also related to the increase in the DO in the surface water [23], which we did not observe in our case, the DO values in the study streams were relatively stable.

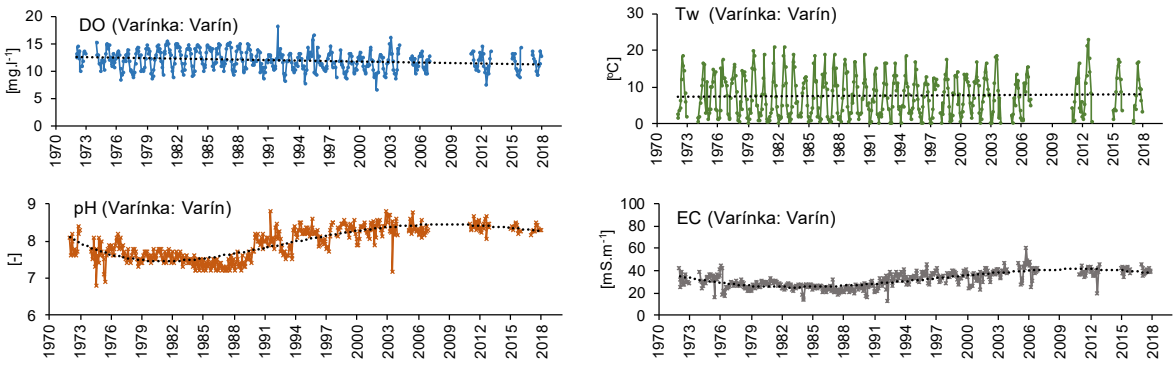


Fig. 2. Concentration (values) and long-term trends of monthly physicochemical indicators of surface water quality forVarínka stream: Varín.

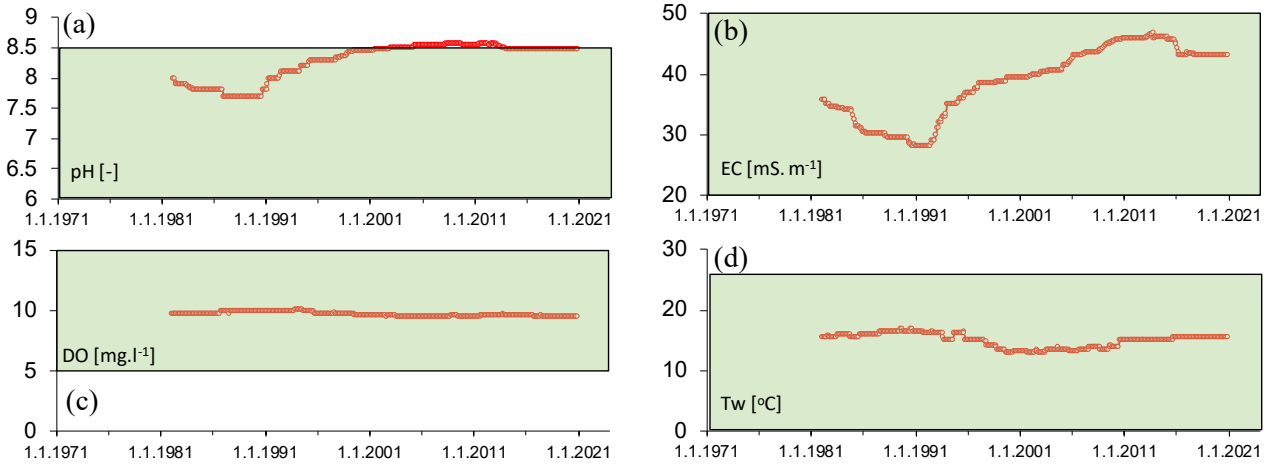
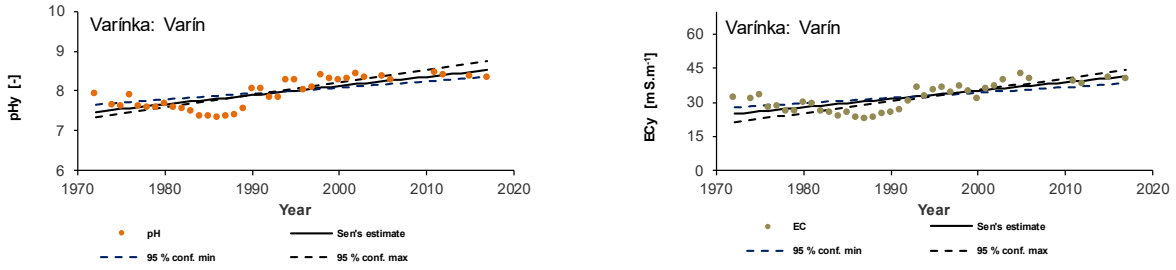


Fig. 3. Ten-year moving averages of P90/P10 values for concentration and values of selected quality indicators for Varínka stream: Varín during the analyzed period 1972–2019 and standards limits (green place) (For example, the value for 1980 represents the 90th percentile calculated from data spanning 1971 to 1980).

Tab. 2 Results of the M-K test for long-term trend of monthly and annual concentration of DO, Tw, pH and EC for Varínka River: Varín

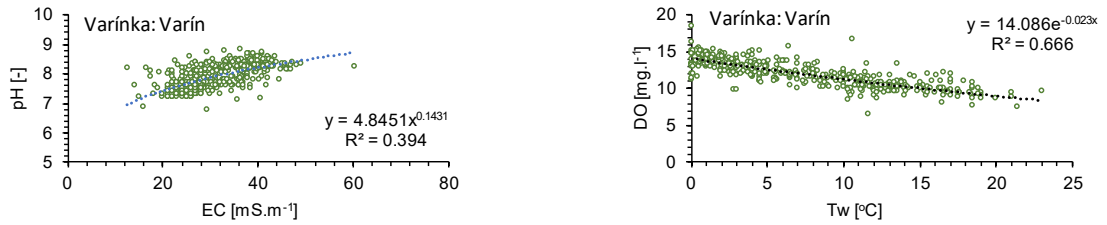
Varínka: Varín																
	DO [mg. l^{-1}]				Tw [°C]				pH [-]				EC [mS.m^{-1}]			
month	n	Sign	skew	R corr.	n	Sign	skew	R corr.	n	Sign	skew	R corr.	n	Sign	skew	R corr.
I	37	**	-0.06	0.54	37				37	***	0.02	0.63	37	**	0.37	0.48
II	37	+	-0.03	0.26	37				37	***	0.02	0.69	37	***	0.42	0.59
III	37	*	-0.03	0.39	37				37	***	0.03	0.63	37	*	0.29	0.47
IV	37	**	-0.05	0.49	37	*	0.06	0.33	37	***	0.02	0.7	37	*	0.22	0.47
V	37	**	-0.05	0.39	37	*	0.08	0.23	37	***	0.02	0.75	37	***	0.27	0.57
VI	37				37	+	0.05	0.27	37	***	0.04	0.82	37	***	0.41	0.74
VII	37	*	-0.02	0.36	37				37	***	0.03	0.69	37	***	0.37	0.7
VIII	37				37				37	***	0.03	0.74	37	***	0.38	0.71
IX	37	*	-0.04	0.42	37				37	***	0.02	0.65	37	***	0.45	0.59
X	37				37				37	***	0.03	0.7	37	***	0.46	0.7
XI	37				37				37	***	0.03	0.66	37	***	0.40	0.74
XII	37				37				37	***	0.02	0.67	37	***	0.47	0.72
Ann	37	**	-0.03	0.52	37				37	***	0.02	0.78	37	***	0.37	0.74



(a) (b)

Fig. 4. Examples of long-term annual values of the pH and EC, linear trend (black line) with confidence interval (dash line) in the Varínka: Varín a) acidity pH and b) conductivity EC.

The Cross-correlation between individual indicators showed, that more of them does cannot follow a linear pattern and did not meet the criterion (2), but some correlation coefficients were significantly different from zero. The correlation coefficient R between the dissolved oxygen DO and the surface water temperature Tw indicators reached of R=-0.816. Based on trend analysis, we also examined the dependence between acidity pH and conductivity (EC). The relationship between pH and EC in surface river waters can be complex and depends on various factors and is not strictly linear, but there may be some correlation between these two parameters depending on the specific conditions in the river. Factors such as the concentration of various ions, chemical reactions, and salt dissolution may be responsible for a nonlinear relationship in the case of acidity pH and conductivity (EC) of surface water. The correlation coefficient R between the acidity pH and conductivity EC indicators reached value of R=0.629. Figure 5 (a)-(b) illustrates example of the scatter plots of the dependencies between EC and pH indicators and the dependencies of DO and Tw indicators for Varínka: Varín of the whole measured periods.



(a) (b)

Fig. 5. a) correlation between conductivity EC and acidity pH and b) correlation between the dissolved oxygen DO and the surface water temperature Tw at Varínka: Varín for the whole measured period.

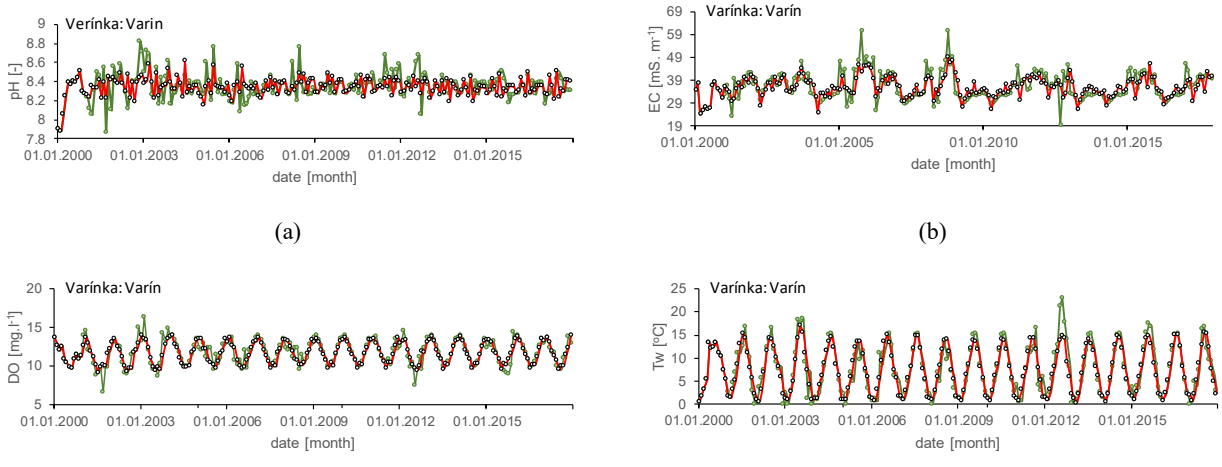
At the sampling site, surface water quality data typically had a low sampling frequency (ranging from monthly to quarterly). Due to the large time gaps in the data and the inconsistent duration of measurements, we found it difficult to conduct a more detailed correlation or dependency analysis. Additionally, this inconsistency posed challenges for later modelling of monthly concentrations using the selected model. As a result, we aimed to choose a period that was free from significant data inconsistencies. Although much surface water quality data has been available since the 1970s, we used data up from year 2000 for the modelling the monthly values of physicochemical indicators of surface water quality (pH, EC, DO and Tw) at the selected sampling site of selected Slovak stream Varínka The last 24 months of the analyzed period were used to validate the model. Several auto regression models were tested to identify a suitable model that would model the monthly concentration of the selected physicochemical indicators of the surface water quality. For selected models the marginal significance levels of each model parameter (P-value) were less than 0.05, so any parameter of the model has not to be excluded (standard errors were less than 0.08 and Mean Average Percentage Errors were less than 10 %). The autoregression models type of ARIMA achieved the least satisfactory results in pH modeling. The math adjustment of the root square was used for values of surface water temperature. The best fit selected SARIMA (p, d, q)x(P, D, Q)$_L$ models for individual physicochemical indicators of surface water quality are listed in Table 3.

Figure 6 (a)-(d) illustrates the results of the modeling of selected indicators on the Varínka stream: Varín, and Figure 7 (a)-(d) illustrates the validation of the selected autoregressive models and the prediction of the modeled concentrations of four physicochemical indicators of surface water quality for 48 months.

Tab 3. The best fit selected SARIMA (p, d, q)x(P, D, Q)$_L$ models

River	pH [-]	EC [mS.m^{-1}]	DO [mg. l^{-1}]	Tw [°C]
Varínka: Varín	(0,0,0)x(2,1,2)$_{12}$	(2,0,0)x(2,1,2)12	(1,0,0)x(0,1,1)$_{12}$	(2,0,2)x(0,1,1)$_{12}$
MAPE [%]	1.01	8.95	5.62	-
R$_{measured/modelled}$*	0.59	0.73	0.86	0.92

* R$_{measured/modelled}$ is for period 2000–2017



(a) (b)

(c) (d)

Fig. 6. Simulation of monthly concentration of analyzed physicochemical indicators of surface water quality at Varínka: Varín 2000–2019 by using the selected models ARIMA

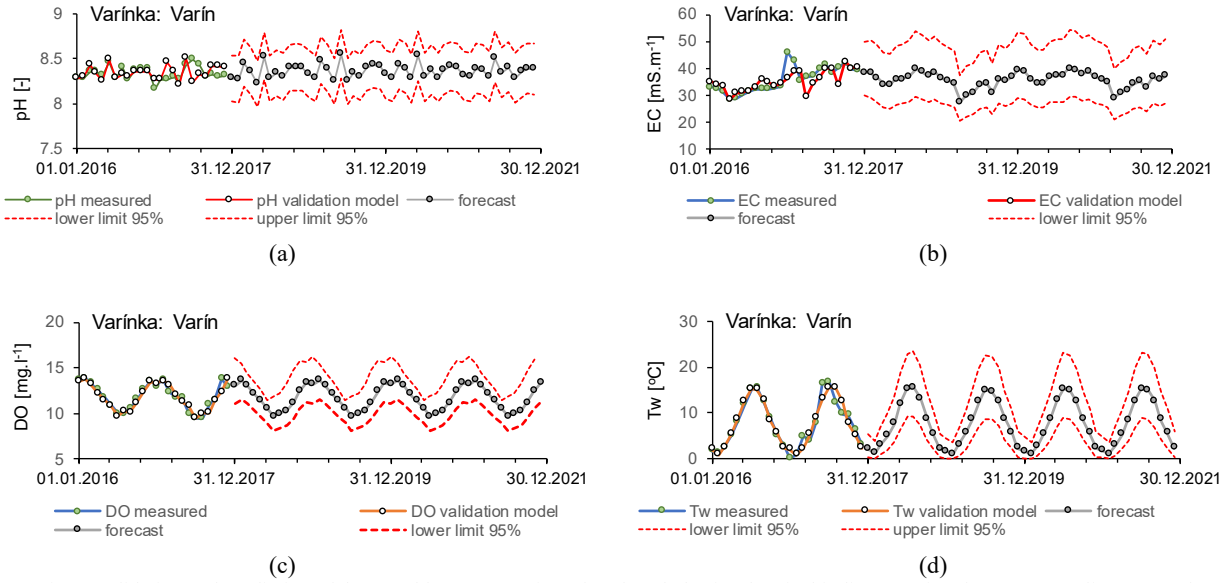


Fig 7. Validation and prediction of the monthly concentration of analyzed physicochemical indicators of surface water quality at Varínka: Varín by using the selected models ARIMA.

4. Conclusion

The first part of the present study was aimed to evaluate the long-term trend development of physicochemical indicators of surface water quality (pH, EC, DO and Tw) in the Varínka stream at Varín sample site. A trend analysis was made for the period of 1972–2019. The results of the trend analysis showed a significant increasing of long-term trends (*** and R up to 0.5) in mean monthly acidity and conductivity, in all months of the years. An increase in long-term trend of monthly and annual concentrations of the analysed pH indicator can indicate that the surface water is becoming more alkaline. The observed increase in pH of the surface waters of unregulated streams can be caused by alkaline substances in rocks, plant photosynthesis, the reduction of organic acids, runoff of agrochemicals, the absence of acidic sources, industrial pollution, and climatic conditions. The rising conductivity in Varínka suggests higher concentrations of dissolved ions, possibly resulting from pollution sources such as fertilizers, industrial chemicals, wastewater, or natural geochemical processes. Elevated conductivity is often linked to increased levels of mineral salts or pollutants, which can harm aquatic ecosystems.

The changes can significantly affect the chemical, biological, and physical properties of surface water, potentially leading to negative impacts on aquatic organisms and the overall health of the ecosystem. The lack of significant trends in surface water temperature and dissolved oxygen (DO) suggests that these parameters have remained relatively stable over the study period. However, their potential responses to other environmental factors, such as land use changes or hydrological modifications, should be monitored in future studies. Further studies could focus on identifying the specific causes of changes in acidity pH and conductivity EC, such as more detailed assessments of pollution sources or agricultural practices. Future research will also focus on the analysis of regulated rivers, which could increase the generalizability of the findings and provide more robust insights into surface water quality trends across Slovakia.

Monthly concentrations and values of physicochemical indicators of surface water quality (pH, EC, DO and Tw) were modelled using autoregressive models of ARIMA (p, d, q)x(P, D, Q)$_L$. The best fitting ARIMA models, with significant parameters (p-value < 0.05) were selected. The ARIMA models demonstrated a good fit for most of the physicochemical indicators of the surface water quality, with high correlation coefficients between modelled and measured values and acceptable MAPE values, indicating their potential utility in predicting changes in surface water quality. The autoregression models type of ARIMA achieved the least satisfactory results in pH modelling bud the statistical criterion MAPE reach very good value. The ARIMA model was then used to predict the 48 (4 years) of monthly concentrations and values of physicochemical indicators of surface water quality (pH, EC, DO and Tw) of the Varínka stream. Our results showed that the ARIMA model can be used to effectively simulate changes in the monthly concentrations and values of physicochemical indicators of surface water quality (EC, DO and Tw) of the Varínka stream. The findings of the study provide valuable information for surface water quality management and conservation strategies.

Acknowledgments

This work was supported by the project VEGA No. 2/0015/23 “Comprehensive analysis of the quantity and quality of water regime development in streams and their mutual dependence in selected Slovak basins.

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