Spatial relationship between hydrodynamic and physico-chemical parameters of surface water for a basin with shale rock series as an indicator of intensity and direction of chemical denudation in the Western Carpathians

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Abstract

Hydrochemical evaluation of stream quality in the Western Carpathians requires a system approach, gradually excluding factors less or more responsible for washing, mixing contaminants and their farther transportation in the stream channel. In this work, the spatial autoregression model was used to estimate the relationship between hydrodynamic and physico-chemical parameters of surface water in various groups and variants of basin use. The highest mean shear stress was 0.178 N·m⁻² in forest surface water. The highest mean Reynolds number (23654) was recorded in the stream channel at permanent grassland, and the lowest number (0.426) at arable lands. Analysis of spatial autoregression to a high degree showed space-time relations in various measurement points. The turbulent diffusion coefficient should be regarded in the space-physical model, constructed based on the influence of hydrodynamic indicators on the shaping of physico-chemical parameters in the flysch basin. The autoregression confirmed that the turbulent diffusion coefficient played a high role for ions K⁺ and P-PO₄³⁻ in surface water at arable lands.
and for cation K⁺, as well as total iron for grassland (p<0.05). A relation for physico-chemical
was not found for surface water in forests. The results, to a high degree, will be used to create an
erosion model concerning the alimentation of alluvial deposits from weathered Carpathian flysch
or surface wash depending on the material delivery in a basin.

1. Introduction

The factors influencing the physico-chemical state of surface water to the highest degree
are soil, relief (Shi et al., 2016), and soil plant cover occurring in the river-bank zone (Andersson
et al., 2015; Teixeira and Marques, 2016). In flysch basins, surface runoff is selective because
transported material often undergoes local accumulation on a slope during delivery to a stream
(Gil and Kotarba, 1977). Reliability of results is ensured when the picture of surface erosion is
being captured in mountain valleys, and proper frequency of measurement series is carried out,
with specification of measurement error (Halecki et al., 2018a).

Investigations of water erosion can be carried out from a theoretical point of view and the
use of mathematical models (Panagos et al., 2015), for example, in the aspect of modelling the
scope of nitrates in surface runoff (Wang et al., 2014). Further, empirical equations and
theoretical methods are used for the settlement of river material quantity in various measurement-
control points (Mazur and Palys, 1992) and intensity degree of suspended sediment transportation
in the shape of mechanical weathered rock mantle (Izmailow et al. 2008; Starkel 2011, Bryndalet
al. 2014; Comino et al., 2016). It is important to remember that technical solutions simulating
digital sediment transportation are only approximate and do not reflect real data. The cause of
unreliable results is the short or irregular frequency of field measurements (Haleckiet al., 2018 b).

Material transported in the Beskidy region basins is connected with land use and the
occurrence of shale rock series (Haleckiet al., 2018 c). Material delivered from slopes determines
the concentration of particular ions transferred in the stream channel. Ions can originate from the
dissolution of mineral fertilisers from adjacent areas of agricultural use (Hall et al. 2014; Gernezet
et al., 2015). The fundamental biogenic indicators in the hydro-chemical evaluation of surface water
are phosphates and nitrates. Nitrogen most often appears as an ammonium ion
(N-NH₄⁺), testifying point contamination of surface water. Nitrate (N-NO₃⁻) and nitrite nitrogen
(N-NO₂⁻) are indicators of the long-term influence of pollutants, particularly in the proximity of
crops. In summer and early autumn, N-NO₃⁻ decreases, which is connected with the plant’s

https://doi.org/10.5194/hess-2023-97
Preprint. Discussion started: 2 May 2023
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demand for nutrients (Ulênet al., 2012). The concentration of calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), sodium (Na\(^+\)), potassium (K\(^+\)), total iron (Fe\(_{\text{tot}}\)), and nitrite nitrogen (N-NO\(_2\)) is differentiated in spring. This shows that plants accumulate more nutrients during the warmer season (Padmalalet al., 2012). For estimation of the physico-chemical quality of surface water, the good indicators regarding transformation and accumulation are various forms of phosphorus. They pose a high threat to the purity of surface water as factors that favour eutrophication and excessive rise of biomass of particular algae (Smoroń, 2012). Changes in biogen concentration in surface streams are influenced by the spatial distribution of arable land (Arienzoet al., 2012; Tasdighiet al., 2017).

Sedimentary rock undergoes an intensive leaching process. In surface water, sodium cations can originate from industrial waste and potassium from agricultural cultivations, where potassium fertilisers are used (Oster et al., 2016). Hydrolytic decay of minerals containing sodium salts (aluminosilicates) and weathering of sedimentary rocks contribute to the creation of alimentation (source) for sodium and potassium cations in surface water (Zhang et al., 2017). Magnesium salts occur in all natural waters, both surface and underground. Leached Ca\(^{2+}\) and Mg\(^{2+}\) cations penetrate the basin by infiltrating rainfall from fertilised cultivated areas and supplying surface water (Grochowska, 2016). Increased concentration of Ca\(^{2+}\) and Mg\(^{2+}\) cations in surface water testify to the occurrence of calcareous rocks, marls, and dolomites and depends on the degree of basin management (Halecki, 2015). In addition, the concentration of Ca\(^{2+}\) cations and SO\(_4^{2-}\) anions in small stream channels is attributed to geology, mainly the calcium carbonate and sulphate concentration in the clastic rockmantle. Moreover, certain water quality factors require specialist investigation and hydrochemical evaluation according to the World Health Organisation (WHO) standards. These include Ca\(^{2+}\) and Mg\(^{2+}\) cations, N-NO\(_2\), N-NO\(_3\), SO\(_4^{2-}\), and phosphate phosphorus (P-PO\(_4^{3-}\)) anions, and salinity indicators - specifically the electric conductivity of water and the concentration of dissolved substances (sum of determined mineral substances in a shape of fine clastic material) with total suspension (Shigutet al., 2017).

Dissolved oxygen is essential for the evaluation of water conditions. The activity of microorganisms responsible for oxidation of organic compounds is examined using two indicators, namely biochemical oxygen demand (BOD) and chemical oxygen demand (COD). In evaluating surface water quality, higher oxygen use indicates contamination (Bo et al., 2017; Effendi et al., 2018). On the other hand, a lower dissolved oxygen concentration can show biochemical decay of accumulated organic substances, respiration of water organisms, or...
oxidation of inorganic substances (Matta et al., 2017). Furthermore, water temperature controls the solubility of solid substances and the concentration of suspension (Saito et al., 2005a). So, low temperature weakens the chemical and biological activity of water and increases viscosity, enabling the transportation of material (Jarocki, 1957). Higher values of dissolved oxygen and BOD are connected with their high sensitivity to changes in water caused by the activity of water engineering (Parmar and Keshari, 2012). Essential differences between BOD and COD of anthropogenic origin have been recorded in a seasonal hydro-chemical evaluation period (Bellver-Domingo and Hernández-Sancho, 2018). Seasonal evaluation of temperature, pH, COD, BOD and heavy metals: Fe, Mn, Ni, Cd, Cr, Co, Cu, Pb and Zn, is needed either for determination of the recommended level and permissible concentration of pollutants for drinking water (Vincent-Akpundin, 2015). The anthropogenic activity contributes to delivering heavy metals to surface water, mainly by using industrial objects (Juahire et al., 2010; Weber et al., 2014; Assouline et al., 2015; Hu et al., 2015; Vadde et al., 2018).

Contamination of surface water is proven by the decay of living organisms, which mineral composition is related to the increase of sulphates. Chlorine is also present in the form of chloride anions (Cl\(^-\)). In surface water, it is transported as a result of weathering of rock-forming minerals. Dissolution of evaporates (sedimentary rock) enriched in anhydrite constitutes a natural source of SO\(_4^{2-}\) anions. Further, sulphate ions do not undergo sorption in an underground environment, and similar to Cl\(^-\), it is the indicator of pollutant penetration to underground water (Sapek, 2008; Geurtset al., 2009).

The first detailed aim of this study was to arrange useful values of the basin and, secondly, to conduct a hydro-chemical evaluation of the surface water in various land configurations of the basin lithology. The third aim was to determine hydraulic conditions in the flysch stream channel. A final goal was to determine the main factors intensifying short-term relations between hydrodynamic parameters of mountain streams and chemical compounds leached from the slope to the water of the flysch stream as a result of interrill erosion. For such detailed aims, hypotheses were formulated, methods and schemes of frequency measurement series were set, and specifications of measurement errors were elaborated.

2. Methods
2.1. Investigated site and uptake and examination of surface water samples

The measurements were carried out in the Smugawka stream in the Beskid Wyspowy, the Western Carpathians (Poland). The localisation of sampling points and land use is presented in Figure 1. Slopes and exposition are shown in Figures 2. Water samples were taken in 1 dm³ volume containers once a month to determine the physico-chemical parameters of surface water. The sampling period occurred in the spring-summer season (from March) and fall-winter (to November) from 2014 to 2018. Sampling was carried out punctually, in cross-section levels, in source and outlet places for the dimension of samples to be multiplied. After filling, each container was emptied and then filled with flowing water for 120 seconds.

Figure 1. Localisation of sampling points and land use
One water sample was enough to determine the mean concentration of dissolved material (Brański, 1968; Dalbianco et al., 2017) because it represents all hydrometric sections of the channel in which strong longitudinal and transversal dispersion occurs. Moreover, the relationship between the concentration of dissolved material is directly proportional to water flow and in accordance with the hydrological system of a stream (Wojtasik and Szatten, 2014). Six samples were taken during each field visit. Measurement of convection intensity was carried out with flow intensity. At <0.3 m, water was taken directly to the container. After determining the relationship between the mean concentration of total suspension in the section and the concentration of punctual sediment in a cross-section, the number of samples was limited to 2-4. The database contained 24 variables (physico-chemical features) in 25 replications. In summary, 600 samples were taken for laboratory analysis. To assure comparability of results, investigations into physico-chemical surface water quality during field visits (additionally there were carried out 250 measurements) were conducted, recording actual results at low water levels and during freshets.

### 2.2. Hydro-chemical indicators

Geodetic measurements were made using the tachymeter TOPCON GTS-226. Five cross-sections of the bed channel slopes, from 0.79 to 2.18%, were localised along all stream lengths (from sources to outlet). The average distance between them was 875 m. Granular measurements of bottom sediment were carried out using the Wolman method (Wolman, 1954). In every...
measurement point, 15 cobbles were taken, and their mean axis “b” was measured. The grain size
distribution curves were drafted, and their characteristic diameters: d_{min}, d_{30}, d_{50}, d_{70}, and d_{max} and
competent diameter: d_m were determined. Measuring points were located crosswise channel in a
distance of 0.5 m.

Hydrodynamic measurements were carried out at the same points as the granular ones.
Measurements were made using a hydrometric current meter VALEPORT Model 801 Flat EM
flow meter. This device allows the measurement of mean flow velocity in assigned time intervals.
It also measures instantaneous velocity and filling in the stream channel. The measurement scope
of the device is 5.0 m∙s^{-1}, and exactness ± 0.001 m∙s^{-1}. Through this device, mean velocity V_{mean} on
the height 0.4 m above the bottom, maximum velocity V_{max}, and instantaneous velocity V
measured just above the bottom, allowed calculation of dynamic velocity based on charts of
velocity distribution above the bottom in a semi-logarithmic system (Gordon et al., 2007):

\[ V_* = \frac{a}{5.75}[m \cdot s^{-1}] \]

where:

a = coefficient of straight line slope

V = f(h), taking an equation form of y = ax + b (x = height above bottom, the measurement of
velocity was carried out, b = free term of the equation).

Knowing dynamic velocity, shear stress was calculated as follows:

\[ \tau = \rho \cdot (V_*)^2[N \cdot m^{-2}] \]

where:

\( \rho \) = water density (kg ∙ m^{-3})

The Reynolds number (mean, maximum, and grain) was used to determine the type of
flow pattern as laminar or turbulent. Further, the Freud number (mean and maximum) is a
measurement of bulk flow characteristics. These were respectfully calculated using the following
equations:
Re_{sr} = \frac{V_{sr} \cdot h}{u}

Re_{max} = \frac{V_{max} \cdot h}{u}

Re_{dm} = \frac{V \cdot d_{m}}{u}

Fr_{sr} = \frac{V_{sr}}{\sqrt{gh}}

Fr_{max} = \frac{V_{max}}{\sqrt{gh}}

where:

h = filling (m),
g = acceleration of gravity (m\cdot s^{-2}),
υ = kinematic coefficient of water viscosity, calculated from the equation:

υ = \frac{0.00178}{\rho(1 + 0.0337t + 0.000221t^2)} \text{[m}^2\cdot\text{s}^{-1}]}

where:

t = water temperature(0°C)

In this study, hydrodynamic indicators allowed the calculation of the distance of full mix in surface water, used in the analysis of spatial autoregression. Dynamic velocity (u) in the stream was calculated using the following equation (Loga, 2016):

u = \sqrt{h \cdot g \cdot S} \text{[m} \cdot \text{s}^{-1}],

where:

h = mean height of water (m),
g = acceleration of gravity (m\cdot s^{-2}),
S = slope of channel bottom (%).

There is a risk connected to the negative influence of the frequency of measurements. In short periods of freshets, some part of the yearly sediment load cannot be observed. Therefore,
the following equation was used to present a moment in which the mix of material in water occurs (a load of total suspended sediment and physico-chemical composition). That is some quantitative representativeness of transported material. In addition, the turbulent diffusion coefficient \(D_{tv}\) was calculated for transverse mix in the particular years in a so-called natural channel (Loga 2016):

\[D_{tv} = 0.6 \cdot h \cdot u \ [m^2 \cdot s^{-1}],\]

where:

- \(h\) = mean height (m),
- \(u\) = dynamic velocity (m·s\(^{-1}\)).

\[\text{2.3. Determination of physico-chemical properties of surface water}\]

In the experimental area, the physico-chemical properties of surface water were measured. The reaction pH of water was examined using the potentiometric method with a CP-104 ELMETRON equipped with a combined electrode. Specific electrical conductivity, expressed in dS·m\(^{-1}\), was measured with a conductometer Elmetron CC-101. The concentration of dissolved oxygen in (mg·dm\(^{-3}\)) and the degree of water saturation by oxygen were determined using the electrochemical method using an oxygen-meter Elmetron CO-411. Further, the water temperature (°C) was measured by a digital thermometer built in waterproof oxygen-meter CO-411. The total content of dissolved substances in ppm was calculated by means of a digital TDS device. In the laboratory, the following physico-chemical properties of water were determined using the UNICAM SOLAAR 969 atomic absorption spectrophotometer: Ca\(^{2+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Fe\(_{tot}\), and manganese Mn\(^{2+}\). Moreover, N-NH\(_4\)+, N-NO\(_3\)-, N-NO\(_2\)-, P-PO\(_4\)\(^{3-}\), and Cl\(^{-}\) were determined by the colorimetric flow-injection method on the computer-controlled FIA Star 5000 apparatus of the FOSS firm. Sulphates (SO\(_4\)\(^{2-}\)) were determined gravimetrically. Biological Oxygen Demand (BOD\(_5\)) was analysed by the Winkler method: water samples were treated with manganese sulfate MnSO\(_4\), alkaline potassium iodide KI, and sulfuric acid H\(_2\)SO\(_4\), followed by titration with sodium thiosulfate Na\(_2\)S\(_2\)O\(_3\). The chemical oxygen demand (ChZT-Mn) was calculated by the
permanganate method by heating the water sample with potassium permanganate in an acidic environment, and the amount of consumed oxygen was determined by titration.

During subsequent readings of water levels, samples were taken from the stream by the bathometric method (containers with a volume of 1 dm$^3$). The concentration of total suspended solids was determined by the gravimetric method after drying using tared filters with an accuracy of ± 0.0005 g. The dry residue (sum of mineral particles from the transported samples) from the collected material was filtered to determine the different composite concentrations. The ionic forms of zinc (Zn$^{2+}$), lead (Pb$^{2+}$), cadmium (Cd$^{2+}$) and copper (Cu$^{2+}$) were determined once per quarter with the coulometric method using an electrochemical analyser for the determination of trace amounts of heavy metals (EcaFlow 150 GLP by PolEko). The nephelometric-laser method was also used to assess the degree of water turbidity using a Hach Lange 2100QS nephelometer (turbidimeter) in the range of 0–2000 FNU, per the international standard (Nephelometric Turbidity Unit; NTU).

2.4. Data reduction to a spatial model and statistical analysis

Before the analyses were performed, the asymptotic distribution for the $\chi^2$ Jarque-Ber (JB) test statistic was studied, which takes kurtosis and skewness into account (Jarque and Bera, 1987). The data was grouped in ascending order by the Anderson-Darling concordance test, determined by the empirical distribution, and the normalisation for the mean and standard deviation was calculated (Stephens, 1986). The test determines a weighted Cramér-von Mises distance between the empirical ($F_n$) and theoretical ($F$) cumulative distribution factors, with weights corresponding to the reciprocal of the empirical cumulative distribution (Anderson and Darling, 1954). The Shapiro-Wilk test, based on positional statistics, was also used. The keynote of this analysis is collinearity between the empirical quantile (i.e., the ordinal statistic) and the theoretical quantile (i.e., the expected value of the ordinal statistic) along the $y = x$ straight line (Shapiro and Wilk, 1965).

The homogeneity of variance was analysed by Levene’s test (Levene, 1960). To reduce the number of variables, the Principal Component Analysis (PCA) was used, presenting the relationships between significant physico-chemical properties in the surface water of the stream running near arable land, grasslands, and forests. Statistical significance for the matrix of correlation coefficients and the strength of the relationship between the variables were assessed
with the Barlett sphericity test (Bartlett, 1950; Williams et al., 2010). Partial correlations with bivariate correlation coefficients were performed using the Keiser-Mayer-Olkin coefficient (KMO), determining the accuracy of selecting variables for the tested model. Adequate variables have a KMO coefficient> 0.5 (MacCallum, 1983; Hair et al., 1995; Tabachnick and Fidell, 2007; Szüle 2016).

In order to show the relationship between the tested physico-chemical properties of surface water, values for eigenvectors were given, approximating the influence of primary variables on the main component. The most significant variables were interpreted through factor loadings, which also reflect the influence of individual variables on a given principal component. The study used a correlation matrix, and the factor loadings were interpreted as correlation coefficients between the original variables and the next analysed main component. Following the PCA method, the variance size for each computed component and the so-called primary variables were indicated. The most important variables were selected for further data processing based on the value of factor loadings. The analysis was performed in PQ Stat Software, version 1.6.6.

Spatial autoregression is a tool for predicting features in a linear system. The analysis aimed to determine the factors that influence the temporal changes in the physico-chemical composition of surface water. Therefore, the study used a spatial autoregression model with a lagged response, facilitating the study of the relationship between the distance of complete mixing and physico-chemical features randomly distributed in the water column. The general form of spatial autoregression is given by the formula (Rangel et al., 2010):

\[ Y = \rho \cdot W_y + X \beta + \epsilon \]

where:
- \( Y \) = vector (N \cdot 1) of the explained spatial process through a responsive (explained) variable,
- \( W_y \) = weight matrix of the vicinity of the examined variables in different locations (N \cdot N matrix of spatial weights),
- \( \rho \) = spatial autoregression parameter reflecting the strength of the relationship between the variables (spatial interaction parameter),
- \( X \) = matrix (N \cdot K) of explanatory processes,
- \( \beta \) = vector (K \cdot 1) of structural indices,
The spatial autoregression model was used to show the relationship between the variables distributed in space over the course of a measurement series for homogeneous areas and to facilitate the analysis of the variables, especially with water flows greater than average. The transverse turbulence diffusion coefficient was assumed as the dependent variable, and surface water’s physico-chemical features were considered independent variables. The simultaneous autoregressive model (SAR), with a system of lagged predictors (Rangel et al., 2010), was used to calculate the spatial dependencies:

\[ C = \sigma^2 [(1 - \rho \cdot W)^T]^{-1} [(1 - \rho \cdot W)]^{-1} \]

where:
- \( C \) = vector of the explained spatial process through a responsive (dependent) variable,
- \( W \) = weight matrix of the vicinity of the examined variables in different locations matrix (N • N) of spatial weights,
- \( \sigma^2 \) = residual variance between observations,
- \( \rho \) = spatial autoregression parameter reflecting the strength of the relationship between the variables (spatial interaction parameter),
- \( I \) = linear transformation (matrix of N • N-type) of the dependent variable.

The autoregression analysis documented the overarching variables for each type of land use, combining the physico-chemical characteristics of the surface water. The calculations were made in the SAM 1.6.6 software.
3. Results

3.1. Physico-chemical and hydrodynamic features of the stream bed

The range of concentrations of the salinity indicators is presented in Table 1, and the range of concentrations of metals, including heavy metals, for the Smugawka stream throughout the study period is provided in Table 2. In surface water flowing out of arable land, a strong positive correlation was found for Ca$^{2+}$ and P-PO$_4^{3-}$ for the first two factors of principal component analysis (Table 3). In grassland, the water temperature played an important role, distinguishing strong factor loadings. In contrast, the concentration of Fe$_{org}$ showed a positive correlation with the first and a high negative correlation with the second factor of the PCA (Table 4). Water temperature and concentration of ChZT-Mn were also characterised by the highest variance for the factor axes in all tested surface water samples and the highest factor loadings (Table 5 and Figure 3). The transport intensity increased with the following gradient: forests > grassland > arable land (Table 6).

Table 1. The range of concentrations of salinity indicators for the Smugawka stream during the study period

<table>
<thead>
<tr>
<th>Salinity indicators</th>
<th>Unit</th>
<th>Measuring point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface warrrunoff from arable land</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface water runoff from grassland</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface water runoff from forests</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>[mg·dm$^{-3}$]</td>
<td>4,80–88,31</td>
</tr>
<tr>
<td>K$^+$</td>
<td></td>
<td>1,78–5,20</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td></td>
<td>6,64–10,92</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td></td>
<td>39,53–133,08</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td></td>
<td>43,87–204,24</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td></td>
<td>23,94–134,45</td>
</tr>
<tr>
<td>*CZSR</td>
<td></td>
<td>101–147</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>[µS·cm$^{-1}$]</td>
<td>156–240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>247–350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>148–256</td>
</tr>
</tbody>
</table>

*CZSR – Total content of dissolved substances

Table 2. The range of concentrations of metals, including heavy metals, for the Smugawka stream during the study period

<table>
<thead>
<tr>
<th>Indicators of metal concentrations</th>
<th>Unit</th>
<th>Measuring point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface warrrunoff from arable land</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface water runoff from grassland</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface water runoff from forests</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>[µg·dm$^{-3}$]</td>
<td>12,53–50,10</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td></td>
<td>1,61–6,80</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td></td>
<td>0,01–1,10</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td></td>
<td>1,51–3,04</td>
</tr>
</tbody>
</table>
Table 3. Factor loadings obtained from principal component analysis (PCA) for the studied physicochemical characteristics from surface water samples taken at arable land

<table>
<thead>
<tr>
<th>Variable</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Factor 5</th>
<th>Factor 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>-0.72</td>
<td>0.60</td>
<td>-0.10</td>
<td>0.05</td>
<td>-0.06</td>
<td>0.46</td>
</tr>
<tr>
<td>pH</td>
<td>-0.13</td>
<td>0.35</td>
<td>-0.78</td>
<td>-0.06</td>
<td>0.49</td>
<td>-0.11</td>
</tr>
<tr>
<td>N-NO₂</td>
<td>0.31</td>
<td>0.17</td>
<td>0.19</td>
<td>0.90</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.88</td>
<td>0.92</td>
<td>-0.03</td>
<td>-0.07</td>
<td>-0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.84</td>
<td>-0.86</td>
<td>0.02</td>
<td>-0.16</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>P-PO₃³⁻</td>
<td>0.93</td>
<td>0.87</td>
<td>-0.01</td>
<td>-0.15</td>
<td>0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.87</td>
<td>-0.78</td>
<td>-0.51</td>
<td>0.13</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>-0.15</td>
<td>0.24</td>
<td>0.78</td>
<td>-0.21</td>
<td>0.52</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4. Factor loadings obtained from principal component analysis (PCA) for the studied characteristics from surface water samples taken in grasslands

<table>
<thead>
<tr>
<th>Variable</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Factor 5</th>
<th>Factor 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of water</td>
<td>0.82</td>
<td>0.76</td>
<td>-0.60</td>
<td>0.10</td>
<td>-0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>K⁺</td>
<td>-0.59</td>
<td>0.51</td>
<td>-0.19</td>
<td>-0.53</td>
<td>-0.20</td>
<td>-0.13</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-0.61</td>
<td>0.54</td>
<td>0.17</td>
<td>-0.26</td>
<td>0.43</td>
<td>0.001</td>
</tr>
<tr>
<td>Na⁺</td>
<td>-0.85</td>
<td>-0.73</td>
<td>0.04</td>
<td>-0.03</td>
<td>-0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>Temperature of water</td>
<td>0.84</td>
<td>0.86</td>
<td>-0.28</td>
<td>0.41</td>
<td>-0.03</td>
<td>0.32</td>
</tr>
<tr>
<td>ChZT-Mn</td>
<td>0.92</td>
<td>0.87</td>
<td>-0.51</td>
<td>0.21</td>
<td>0.33</td>
<td>0.08</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.97</td>
<td>-0.78</td>
<td>-0.48</td>
<td>-0.44</td>
<td>0.12</td>
<td>0.23</td>
</tr>
<tr>
<td>Conductance</td>
<td>0.23</td>
<td>-0.35</td>
<td>-0.30</td>
<td>0.21</td>
<td>0.53</td>
<td>-0.59</td>
</tr>
<tr>
<td>BZT₁</td>
<td>-0.16</td>
<td>-0.53</td>
<td>0.08</td>
<td>-0.64</td>
<td>0.46</td>
<td>0.22</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-0.38</td>
<td>0.13</td>
<td>0.55</td>
<td>0.13</td>
<td>0.50</td>
<td>-0.07</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>-0.56</td>
<td>-0.81</td>
<td>0.15</td>
<td>0.35</td>
<td>0.33</td>
<td>0.65</td>
</tr>
<tr>
<td>Feog</td>
<td>-0.51</td>
<td>0.84</td>
<td>-0.13</td>
<td>-0.01</td>
<td>-0.17</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 5. Factor loadings obtained from principal component analysis (PCA) for the studied physicochemical characteristics from surface water samples taken in forests

<table>
<thead>
<tr>
<th>Variable</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Factor 5</th>
<th>Factor 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of water</td>
<td>0.85</td>
<td>0.86</td>
<td>-0.28</td>
<td>0.41</td>
<td>-0.03</td>
<td>0.32</td>
</tr>
<tr>
<td>ChZT-Mn</td>
<td>0.92</td>
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<td>0.21</td>
<td>0.33</td>
<td>0.08</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.97</td>
<td>-0.78</td>
<td>-0.48</td>
<td>-0.44</td>
<td>0.12</td>
<td>0.23</td>
</tr>
<tr>
<td>Conductance</td>
<td>0.23</td>
<td>-0.35</td>
<td>-0.30</td>
<td>0.21</td>
<td>0.53</td>
<td>-0.59</td>
</tr>
<tr>
<td>BZT₁</td>
<td>-0.16</td>
<td>-0.53</td>
<td>0.08</td>
<td>-0.64</td>
<td>0.46</td>
<td>0.22</td>
</tr>
<tr>
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<td>0.13</td>
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</tr>
<tr>
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<td>0.15</td>
<td>0.35</td>
<td>0.33</td>
<td>0.65</td>
</tr>
<tr>
<td>Feog</td>
<td>-0.51</td>
<td>0.84</td>
<td>-0.13</td>
<td>-0.01</td>
<td>-0.17</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Feog [mg·dm⁻³] 0.53–0.91 0.03–1.04 0.1–0.81
Mn²⁺ 0.12–0.18 0.06–0.09 0.09–0.10
Figure 3. PCA analysis and scree plots for physicochemical characteristics for samples taken in surface water: arable land (a, b), grassland (c, d), forest (e, f)
Table 6. Range of average values of soil material loss in the form of total suspended solids throughout the study period depending on the land use of the Smugawka catchment area

<table>
<thead>
<tr>
<th>Index of eroded soil material</th>
<th>Unit</th>
<th>Arable land</th>
<th>Grasslands</th>
<th>Forests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circadian concentration of total suspended solids [mg dm⁻³]</td>
<td>4.94–18.34</td>
<td>0.93–9.92</td>
<td>0.71–5.92</td>
<td></td>
</tr>
<tr>
<td>Total suspended solids load [Mg]</td>
<td>0.05–0.52</td>
<td>0.05–0.34</td>
<td>0.02–0.23</td>
<td></td>
</tr>
<tr>
<td>Annual total suspended solids load [Mg·rok⁻¹]</td>
<td>18.69–190.27</td>
<td>19.65–126.95</td>
<td>7.38–53.78</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Data reduction and spatial model

Spatial autoregression was used to reveal the relationships between the studied variables. Relationships with some physico-chemical features of surface water were detected in the model. The SAR equation for the entire catchment area showed that P-PO₄³⁻, N-NO₂⁻, TDS, and the concentrations Na⁺, Mg²⁺, Ca²⁺ and Mn²⁺ (Table 7) are appropriate predictors for judging the distance of complete mixing. In general, the autoregressive modelling can be summed up by the fact that the few relationships for the physico-chemical characteristics of the surface water with the transverse turbulence diffusion coefficient of the flysch stream were significant (p < 0.05). In the spatial autoregression model divided into variants of use, statistically significant relationships were found for K⁺ and P-PO₄³⁻ in surface water of arable land and for Fe log in surface water at grassland. No significant relationships were found at the measurement points in surface water near forests (Table 8). In the spatial autoregression model for the whole with the explanatory variable (the distance of complete mixing) detected the spatial dependencies for P-PO₄³⁻, N-NO₂⁻, Mn²⁺, TDS, Na⁺, Mg²⁺, Ca²⁺, and Mn²⁺ (Table 9).

Table 7. The results of the spatial autoregression model of the SAR type for the entire catchment.

<table>
<thead>
<tr>
<th>Physicochemical characteristics</th>
<th>OLS ratio</th>
<th>SAR ratio</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>-1.22</td>
<td>0.36</td>
<td>0.67</td>
</tr>
<tr>
<td>Temperature</td>
<td>10.41</td>
<td>16.28</td>
<td>5.90</td>
</tr>
<tr>
<td>Oxygen indicators</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen concentration</td>
<td>-0.46</td>
<td>-0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>Degree of oxygen saturation</td>
<td>-0.03</td>
<td>-0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>BZT₅</td>
<td>-1.19</td>
<td>-1.77</td>
<td>0.37</td>
</tr>
<tr>
<td>ChZT-Mn</td>
<td>6.46</td>
<td>4.55</td>
<td>1.09</td>
</tr>
<tr>
<td>Biogenic indicators</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-PO₄³⁻</td>
<td>12.95</td>
<td>11.72</td>
<td>1.47</td>
</tr>
</tbody>
</table>
### Table 8. Results of the spatial autoregression model of the SAR type (The transverse turbulence diffusion coefficient was used as the dependent variable, and the most important physicochemical characteristics of surface water selected on the basis of principal component analysis for each use variant were used as predictors)

<table>
<thead>
<tr>
<th>Variable</th>
<th>SAR ratio</th>
<th>Standard factor</th>
<th>Standard error</th>
<th>t</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Survey points in the watercourse next to arable land</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-(\text{NH}_4^+)</td>
<td>(11,40)</td>
<td>(16,2)</td>
<td>(1,78)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-(\text{NO}_3^-)</td>
<td>-0.03</td>
<td>(4,88)</td>
<td>(0,36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-(\text{NO}_2^-)</td>
<td>(0,64)</td>
<td>(14,83)</td>
<td>(2,71)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity indicators</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>CZSR</em></td>
<td>5,70</td>
<td>(8,53)</td>
<td>(0,27)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>-0.31</td>
<td>(0,18)</td>
<td>(0,14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>(0,06)</td>
<td>(0,71)</td>
<td>(0,02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+)</td>
<td>(0,49)</td>
<td>(-0,61)</td>
<td>(0,17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(^+)</td>
<td>(2,92)</td>
<td>(10,95)</td>
<td>(1,06)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>-0.46</td>
<td>(6,32)</td>
<td>(0,82)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>-2.93</td>
<td>(-4,41)</td>
<td>(1,41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>-1.19</td>
<td>(4,83)</td>
<td>(-1,72)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals, including heavy metals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>-0.14</td>
<td>(0,14)</td>
<td>(0,02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>-0.62</td>
<td>(3,12)</td>
<td>(0,09)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(^+)</td>
<td>-0.03</td>
<td>(4,89)</td>
<td>(0,83)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(^+)</td>
<td>(0,98)</td>
<td>(3,12)</td>
<td>(0,56)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>(6,46)</td>
<td>(12,81)</td>
<td>(1,37)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>(17,46)</td>
<td>(11,27)</td>
<td>(1,45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Measurement points in the watercourse next to grasslands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-(\text{NH}_4^+)</td>
<td>(11,40)</td>
<td>(16,2)</td>
<td>(1,78)</td>
<td></td>
<td></td>
</tr>
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<td>-0.03</td>
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<td></td>
<td></td>
</tr>
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<td>(0,64)</td>
<td>(14,83)</td>
<td>(2,71)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* *CZSR* – Total content of dissolved substances

https://doi.org/10.5194/hess-2023-97

Preprint. Discussion started: 2 May 2023
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4. Discussion

An innovative solution proposed in this dissertation is the combination of multidimensional statistics methods and a spatial model. During the preparation of the results, a close relationship was determined between selected physico-chemical characteristics of surface water quality using the spatial autoregression equation.

4.1. Influence of hydrodynamic parameters on the ionic composition of surface water

Determining the level of micro-pollutants, especially heavy metals, is essential for monitoring areas exposed to contamination in long-term studies. The ionic composition of surface water determines the intensity and direction of the chemical denudation process conditioned by lithology (Kim et al., 2012; Ziadat et al., 2015). It also determines the quality of the surface watercourses inventory and the hydrographic network’s operation (Trivedi, 2010). Through PCA, the parent variables for each type of land use were documented. For further spatial analysis, the physico-chemical features of surface water with the highest factor loadings were selected. A high negative correlation was only calculated in the first PCA factor for the concentration of K\(^+\) and in the second PCA factor for concentrations of Mg\(^{2+}\) and Na\(^+\). This may be because these ions runoff from the catchment area.

Water self-purification processes are essential in the assessment and protection process (Moore and Langner, 2012; Halecki, 2015). Identifying the sources of nitrate pollution is one of the priority actions (Bu et al., 2017) because anthropogenic pollutants are different in surface water and may change seasonally (Xu et al., 2014; Hu et al., 2015). As for arable land, K\(^+\)
showed a negative relationship with the first factor of the PCA. A negative relationship was also found for Na\(^+\). This may mean that their concentration has been systematically decreasing. In water samples collected near forested areas, a high factor load was calculated for the water temperature and concentration of ChZT-Mn. They were also characterised by the highest variance for the factor axes in all tested surface water samples and the highest factor loadings. The water temperature could play a significant role in the concentration of ions dissolved in the water of the flysch stream.

The state when the material was mixed in the water was considered in processing the results. For this purpose, the transverse turbulence diffusion index was calculated to determine transport intensity. The highest value of transport intensity, 1.02, was recorded in the riverbed of the stream adjacent to arable land. According to PCA, the most important chemical parameter associated with this land use types is Ca\(^{2+}\) and P-PO\(_4^{3-}\). This is an interesting result because, when assessing the impact of arable lands on the physico-chemical quality of surface water, particular attention should be paid to the supply of phosphates and nitrates (Halecki et al., 2017). The quantitative share of ions depends on the type of rocks and the physical properties of the substrate, especially the infiltration coefficient, and for clastic weathering, on their mechanical composition (Szostakiewicz-Hołownia, 2012). This aspect is of particular concern for flysch catchments built of the Magura and Sub-Magura layers (Starkel, 2006; Starkelet. al., 2007).

The diversified rock bottom relief impacts high water turbulence and, thus, the transport of weathered loads (Priess et al., 2015; Szatten, 2016). Stationary tests with a high measurement frequency are then performed to determine the relationship between flooding and suspension concentration in particular years (Huan, 2011). On the other hand, in the Beskidy catchments, which include the variability of the transported clastic weathered water, quantitative relationships between hydrological parameters and their supply against the background of water erosion have been shown (Brański, 1975; Brański, 1990). The most significant distance of full mixing was calculated for points in surface water near arable land at 52.26 m.

4.2. Relationships between hydrological parameters and their supply against the background of water erosion

The intensity of transport of chemical compounds depends on turbulence and dispersion due to spatial differentiation of the flow velocity. Turbulent vortices create a locally
inhomogeneous and non-stationary velocity field, accelerating mixing (Loga, 2016). This hydrodynamic parameter was calculated for each cross-section on each section of the stream to approximate the transport mechanism of the investigated ion forms and other materials dissolved in water. The Reynolds number reached the highest values in the stream bed adjacent to the permanent grassland, similar to the tangential stress. The bottom sediment ranged from 32 to 41 mm in the entire catchment area. It was observed that material with more significant fractions is collected at the flysch bed surrounded by permanent grasslands.

### 4.3. Model of developed techniques of spatial autoregression

Ions in water may be related to land use, and the detection of heavy metals in surface water determines its economic value (Fu et al., 2014; Liao et al., 2016) and the health of the inhabitants of the surrounding areas, especially in terms of therapeutic properties of Carpathian rivers (Operacz et al., 2018). The spatial pattern and correlations between the variables in the entire catchment area have been shown based on the spatial autoregression model, empirical equations, and multivariate analysis. Furthermore, the research confirms that in a small flysch catchment, it is possible to balance the material leached from the soil because the chemical denudation process shows a relationship with the concentration of dissolved electrolytes in the flysch stream (Halecki et al., 2019).

The model of developed techniques of spatial autoregression also enabled the inclusion of spatial analysis in the extrapolation of hydrochemical data and the intensity of erosion processes during multiple measurement series. The technique of spatial autoregression was chosen for its more effective presentation of these relationships and was used to verify the analysed data in a spatial system. The applied analysis helped to check whether the variables are affected by different land use modifications. The independent variables were the physico-chemical features of surface water at different land use variants. Spatial SAR model resultsshowed that P-PO$_4^{3-}$ and K$^+$ ions are leached mainly from soil in arable lands. Moreover, a statistically significant relationship between K$^+$ and Fe$_{org}$ cations was observed in surface water flowing from grasslands. However, the SAR model of spatial autoregression did not detect statistically significant differences in the ionic composition of surface water flowing out of the forests. The land use could have contributed to the differences generated by the model. Therefore, the methods used to
evaluate the surface washout and soil erosion studies on used slopes, especially for agricultural purposes, should be improved (Bakker et al., 2008; Smolska et al., 2010).

The spatial autoregression model for the whole with the explanatory variable (the distance of full mixing) detected the spatial dependencies for P-PO$_4^{3-}$, Mn$^{2+}$, N-NO$_2^-$, TDS, Na$^+$, Mg$^{2+}$, Ca$^{2+}$ and Mn$^{2+}$. Since different hydraulic conditions were detected for each variant of land use, it should be passed that the direction of the catchment development impacts the physico-chemical quality of surface water.

4.4. Recommendations for hydraulic tests and physico-chemical assessment of surface water

Forecasting the physico-chemical quality of surface water and determining the relationships between the concentration of metals, including heavy metals, requires the determination of decisive indicators. Spatial autoregression is currently one of the most effective methods of water quality forecasting for various sources of pollution (Yang et al., 2017). The analysis of spatial autoregression primarily showed the spatio-temporal relationships at various measuring points. Furthermore, including spatial analysis to determine many pollutants flowing into the waters allows for solving technical problems related to surface washout and proper use of arable land in the catchment area.

For spatial studies, the appropriate number of samples plays a crucial role in building a spatial model (Vallejos and Osorio 2014), especially in work related to the physico-chemical quality of surface water (Mahjouri and Kerachian, 2011). This means that the assessment of surface water quality features depends on the spatial scale. Therefore, the evaluation of surface water quality should be combined with a spatial analysis (Dash et al., 2015). The amount of leached total suspended solids delivered during water erosion is a value recorded during short-term flooding rainfalls. So, based on the hydrochemical properties, it is possible to determine surface water quality (Misaghi et al., 2017). Only relevant parameters should be considered in assessing the physico-chemical quality of surface water in agricultural areas and grasslands. It is vital to choose a method consistent with the sample size (Griffith, 2005) in order to formulate a dynamic model (Finley et al., 2012) or to calculate water quality indices (Yadav et al., 2015; Naubi et al., 2016). Thus, the optimisation of spatial sampling is crucial (Hu and Wang, 2011) in monitoring surface water pollution (Wu et al., 2005). The conclusions from this dissertation will find practical application in isolating the primary factors favouring water erosion in streams with...
larger catchment areas. In addition, recognising the effects of water erosion will be necessary for evaluating the surface delivery of the material in further scientific research. The continuation of scientific work in this field should focus on investigating the relationship between individual washings and the concentration of material in the valleys of streams and rivers.

5. Conclusions

The effect of this work is important for determining the sources of diffuse pollution flowing to the stream from agricultural areas in the periodic assessment of the physico-chemical quality of surface water. The research thread undertaken in the dissertation will help determine the intensity of water erosion and assess the sources of surface water supply. The assessment of this phenomenon should aim at explaining the size of the load calculated into the delivery zones of the transported material to the flysch stream and erosive factors, including susceptibility to leaching. Some results will undoubtedly be used to create models of erosive feeding of alluvial deposits from weathered flysch or surface wash, depending on the material delivery in the catchment area. The results related to land use and its impact on the transport of chemical compounds may be helpful in environmental management in mountain areas and chemical monitoring in determining the course of erosion processes. Over the years, assessment of land use changes may be of value for local residents involved in agriculture. Moreover, the assessment of the short-term change in the concentration of the physico-chemical composition in the flysch riverbed will be valuable for scientific purposes to develop a plan for the management and elimination of pollutants resulting from anthropogenic pressure.

Highlights:

1. The physico-chemical composition of the flysch stream depends on the hydraulic conditions.
2. The catchment use determines the intensity and direction of the chemical denudation process.
3. The turbulent diffusion coefficient may influence the dissolved electrolytes in the stream.
4. The spatial autoregression model detected relationships for nutrients leached from arable land.
5. The assessment of the physico-chemical properties of surface water depends on the spatial scale.

**Financial Support**

The publication was co-financed from the subsidy granted to the Krakow University of Economics, Project nr 28/GGR/2021/POT.

**References**


