






Changes in hydraulic and physico-water parameters of surface waters under the influence of anthropogenic activities in the Western Carpathians

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Abstract: To evaluate the quality of watercourses in the Western part of Carpathians from a hydro-chemical perspective, a systematic approach is required. This involves gradually excluding factors that contribute to the washing, mixing, and transportation of contaminants in the watercourse pathway. The model that considers spatial dependencies by autoregression was implemented in this study to determine the correlation between hydrodynamic and physico-chemical characteristics of waters at surface in different groups and forms of catchment use. The surface water at forested areas had the maximum average shear stress of $0.178 \text{ N}\cdot\text{m}^{-2}$. The watercourse at sustained grassland had the maximum average Reynolds number (Re) of 23,654 and the minimum number of 0.426 at arable lands. Spatial autoregression analysis revealed space-time relations in various measurement points. When constructing the space-physical model, it is important to consider the influence of hydraulic characteristic parameters on the generation of physicochemical indicators in the flysch basin. Specifically, it may be beneficial to take into account the turbulent diffusion coefficient. The autoregression analysis demonstrated that for the ions P-PO_4^{3-} and K^+ in surface water on cropland and for total iron and the cation K^+ on grassland ($p < 0.05$), the turbulent diffusion coefficient proved to be of great importance. The study did not identify any physicochemical dependency for woodland surface waters. The findings can be utilised to create an erosion model that considers the contribution of material supply in a catchment area, specifically from weathered Carpathian flysch or surface runoff, to the alimentation of alluvial deposits.

Keywords: chemical denudation, hydraulic characteristics parameters, intensity index, physicochemical characteristics of water

INTRODUCTION

Altitudinal distribution (Shi, Xia and Zhang, 2016), the soils, and the vegetation ground cover in the riparian zone (Andersson *et al.*, 2015; Teixeira and Marques, 2016) are the primary factors

affecting the surface water physicochemical state. Surface runoff is selective in flysch basins, due to the fact that transported material frequently accumulates locally on an incline during its transport to a watercourse (Gil and Kotarba, 1977). Collecting the surface erosion image in mountainous valleys, making the

appropriate series of measurements, and defining the imprecision of the measurements ensures the credibility of the results (Halecki, Kruk and Ryczek, 2018a).

Research on erosion caused by water can be conducted using a theory and mathematical simulation. For instance, it is possible to create a model for the nitrate form in the surface water (Wang *et al.*, 2014) as demonstrated by Panagos *et al.* (2015). In addition, the sedimentation of river material at various gauging stations (Mazur and Palys, 1992) and the transport intensity of suspended bed material in the form of mechanically altered rock covering are determined using mathematical equations and theoretic models (Izmailow, Kamykowska and Krzemien, 2008; Starkel, 2011; Bryndal, 2014; Comino *et al.*, 2016). Regarding the accuracy of computational models used for digital numerical simulations of sediment movement, it is suggested that these models may only provide approximations and not fully account for the actual data (Halecki, Kruk and Ryczek, 2018b). Additionally, inconclusive results may arise due to infrequent or short frequency of field measurements, as noted by Halecki, Kruk and Ryczek (2018b).

The transportation of matter in the basins of the Beskidy area is related to the occurrence of a series of shale rocks and land management (Halecki, Kruk and Ryczek, 2018c). The level of certain ions transported in the watercourse bed is determined by the material delivered from the slopes. Ions can be the result of mineral fertiliser leaching from adjacent agricultural land (Hall *et al.*, 2014; Gernez *et al.*, 2015). Phosphates and nitrates are commonly used as biogenic markers in the hydrochemical characterisation of the aquatic environment. Nitrogen most commonly occurs as ammonium ions (N-NH_4^+), which may suggest the possibility of contamination of water at surface. The potential impact of contaminants, specifically near the farm fields, is demonstrated by nitrite nitrogen (N-NO_2^-) and nitrate (N-NO_3^-). According to Ulén *et al.* (2012), it can be observed that the concentration of NO_3^- tends to drop between June and September, depending on the nutrient demand of the vegetation. Between March and June, the concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), total iron (Fe_{tot}), potassium (K^+), and nitrite nitrogen (N-NO_2^-) fluctuates. Padmalal *et al.* (2012) suggest that plants have a tendency to uptake more nutrient-rich material during periods of higher temperatures. Phosphorus forms are useful indicators for evaluating the physico-chemical quality of surface waters, as they can reveal transformation and accumulation. They also pose a significant threat to surface water purity by promoting eutrophication and excessive growth of certain algae (Smoroń, 2012). The spatial distribution of cropland is a crucial factor in surface water biogenesis (Arienzo *et al.*, 2012; Tasdighi, Arabi and Osmond, 2017).

According to Oster, Sposito and Smith (2016), it is possible for sedimentary rocks to experience considerable leaching as a result of the presence of sodium cations in surface water, which may have been generated by waste from industry, and K^+ cations from agricultural fields where fertilisers containing K^+ are applied. Zhang *et al.* (2017) claim that the presence of Na^+ and K^+ in surface waters is mainly due to the hydrolytic breakdown minerals that contain aluminosilicates and the erosion of sedimentary rocks. Magnesium salts are present in all surface and subsurface natural waters. According to Grochowska (2016), the basin receives cations of Mg^{2+} and Ca^{2+} that have been leached through rainfall infiltration from fertilised cropland and

surface water supply. The high levels of Mg^{2+} and Ca^{2+} cations in surface water provide evidence for the presence of limestone, dolomites and marls, and are related to the extent of watershed use (Halecki, 2015). In small stream channels, the levels of Ca^{2+} and SO_4^{2-} are primarily influenced by the underlying geology, specifically the presence of calcium carbonate and sulphate accumulation in the mantle of clastic rocks. Additionally, particular factors in aquatic quality require special examination and hydrochemical assessment in accordance with the standards of the World Health Organisation (WHO). The substances analysed in this study include cations such as Ca^{2+} and Mg^{2+} , anions such as N-NO_2^- , N-NO_3^- , SO_4^{2-} and phosphate phosphorus (P-PO_4^{3-}), as well as indicators of salinity, specifically water's electrical conductivity and the dissolved matter concentration (the sum of identified mineral matter in the form of finely divided plastic material) with total suspension (Shigut *et al.*, 2017). Assessing water conditions requires measuring dissolved oxygen (*DO*) levels. Chemical oxygen demand (*COD*) and biochemical oxygen demand (*BOD*) are two indicators used to evaluate the activity of microorganisms responsible for oxidising organic compounds. According to Bo *et al.* (2017) and Effendi, Muslimah and Permatasari (2018), higher oxygen consumption can be an indicator of pollution in surface water quality assessment. In contrast, a lower concentration of *DO* may indicate various processes, such as the biochemical decomposition of organic matter that has accumulated, the oxygen respiration of aquatic species, or the oxidation of certain inorganic matter (Matta *et al.*, 2017). Moreover, the temperature of the water has an effect on the suspension concentration and on solids solubility (Saito, Hayamizu and Okada, 2005). According to Jarocki (1957), it can be observed that the biological and chemical water activity decreases at low temperatures, the viscosity rises and the matter can be transported. Water engineering activity can induce alterations in water that affect the levels of *DO* and *BOD*, as noted by Parmar and Keshari (2012). During the seasonal hydro-chemical evaluation period, according to the research by Bellver-Domingo and Hernández-Sancho in 2018, significant differences were recorded between *BOD* and *COD* of anthropogenic origin. The assessment involved monitoring of various parameters including pH, temperature, heavy metals, *COD* and *BOD*. To determine recommended levels and permissible concentrations of pollutants for drinking water, analysis of several heavy metals, including Mn, Cd, Cr, Ni, Co, Cu, Pb, Zn and Fe, is necessary (Vincent-Akpu, 2015). Contamination with heavy metals in surface water is primarily caused by anthropogenic activities related to industrial processes (Juhair *et al.*, 2010; Weber *et al.*, 2014; Assouline *et al.*, 2015; Hu *et al.*, 2015; Vadde *et al.*, 2018).

The presence of organic decomposition may suggest the possibility of surface water contamination, as it is often linked to an increase in sulphate mineral composition. Also, chlorine appears as chloride anions (Cl^-) and is transported in the water as a result of the erosion of bedrock minerals. The leaching of evaporates enriched in anhydrite, a type of sedimentary rock, provides a naturally occurring source of SO_4^{2-} anions. Furthermore, in a subsurface setting, sulphate ions are not sorbed and together with Cl^- , they serve as indicators of contaminant intrusion into groundwater (Sapek, 2008; Geurts *et al.*, 2009).

The authors of the article set a number of aims. In the first place they wanted to determine the practical benefits of the

catchment area. They also sought to carry out a hydrochemical surface water assessment across a range of land-use settings in the catchment lithology. What is more, they aimed at establishing the hydraulic parameters in the flysch stream bed. Finally, they wanted to establish principal determinants that intensify the transient relationships between the mountain stream hydrodynamic parameters and the chemical compounds leached by erosion from the slope into the flysch stream water. In order to attain the aforementioned objectives, a set of assumptions were formulated, schemes and methods of frequency measurement trend were defined, and measurement errors were specified.

METHODS

THE INVESTIGATED SITE, UPTAKE AND ASSESSMENT OF SURFACE WATER SAMPLES

The Beskid Wyspowy region of the Western Carpathians in Poland is home to the Smugawka stream, where the samples were collected. The outlet of the Smugawka stream has geographical coordinates: 49°41'33.6" N; 19°56'45.24" E. The catchment area amounts 7.52 km², main watercourse length is 4.42 km and its mean slope is 0.062, watercourses network density amounts 2.43 km·km⁻² and catchment 0.191. Geologically it is mainly created by Carpathian flysch, particularly vulnerable to erosion processes. Figure 1 displays the sampling points and land use, while Figures 2 illustrates the slopes and exposition. Water samples, collected once a month in 1 dm³ volume containers, were used to investigate the surface

water physico-chemical characteristics of. Samples were collected between March and November during both the spring–summer and autumn–winter seasons during the period 2014–2018. Sample collection was undertaken at specific cross-section levels, both at the source and outlet locations, to increase the sample size. Each container was subjected to a continuous flow of water for duration of 120 s, during which it was filled, then emptied, and then again filled with water.

A single sample of water was sufficient to calculate the average level of dissolved material (Brański, 1968; Dalbianco *et al.*, 2017) due to the fact that the sample represented all channel hydrometric sections where significant lengthwise and crosswise dispersion occurred. Moreover, it is worth noting that the quantity of dissolved material was found to be in a direct proportion to the flow of water, which is consistent with the hydrological structure of the stream according to Wojtasik and Szatten (2014). During each field visit, six samples were collected. Convection intensity was measured using flow intensity. Water samples were collected directly from depths less than 0.3 m. The study chose to limit the number of samples to two to four after establishing the correlation between the concentration of punctual sediment in the cross-section and the total suspension average concentration in the section. The database consisted of 24 physico-chemical variables replicated 25 times. In total, 600 samples were collected for laboratory analysis. For comparability of results, physical and chemical quality studies of the surface water were undertaken during the field visits (an additional 250 samples were taken), and actual results at low flows and during periods of freshwater inflow were noted.

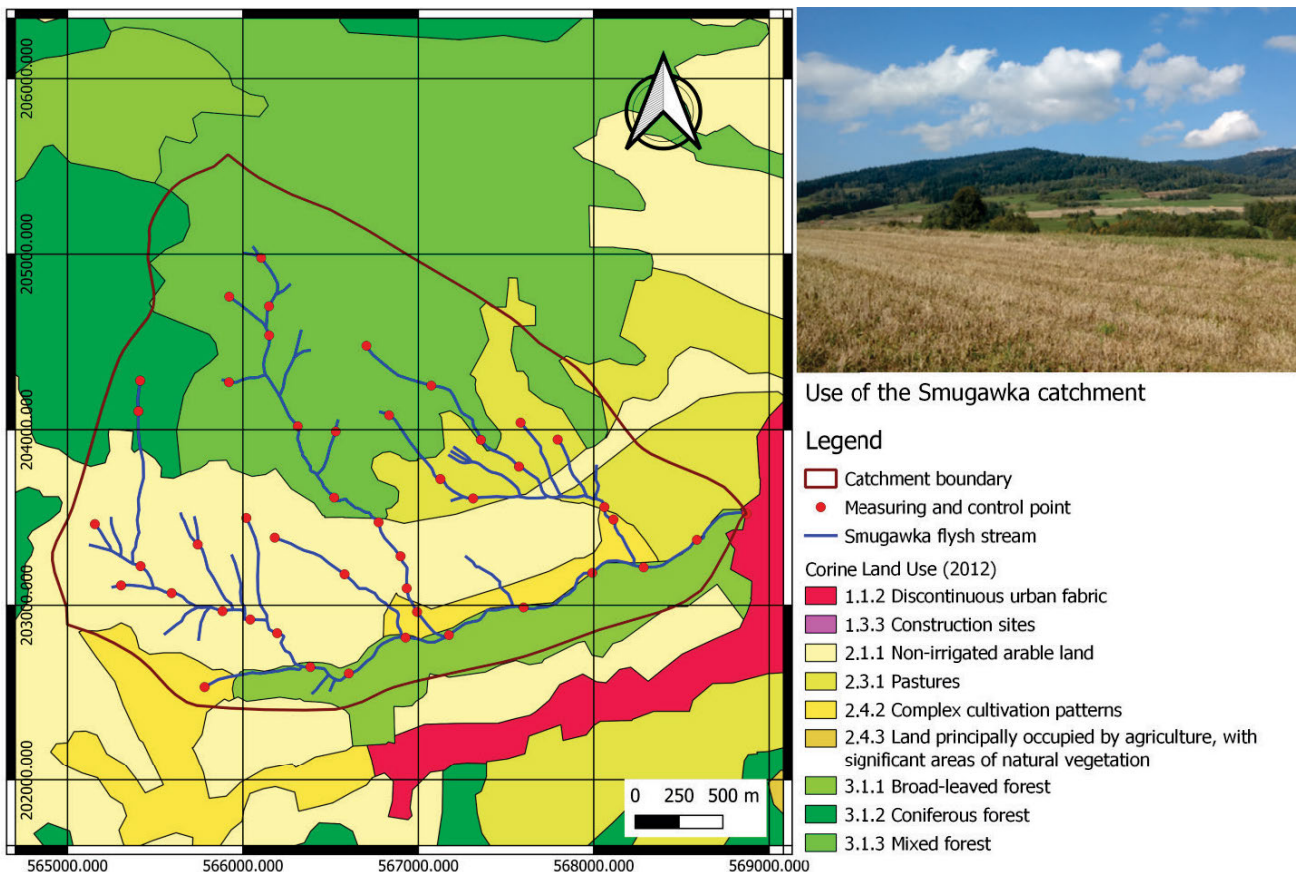


Fig. 1. Map of land development with locations of scientific sampling points; source: own elaboration

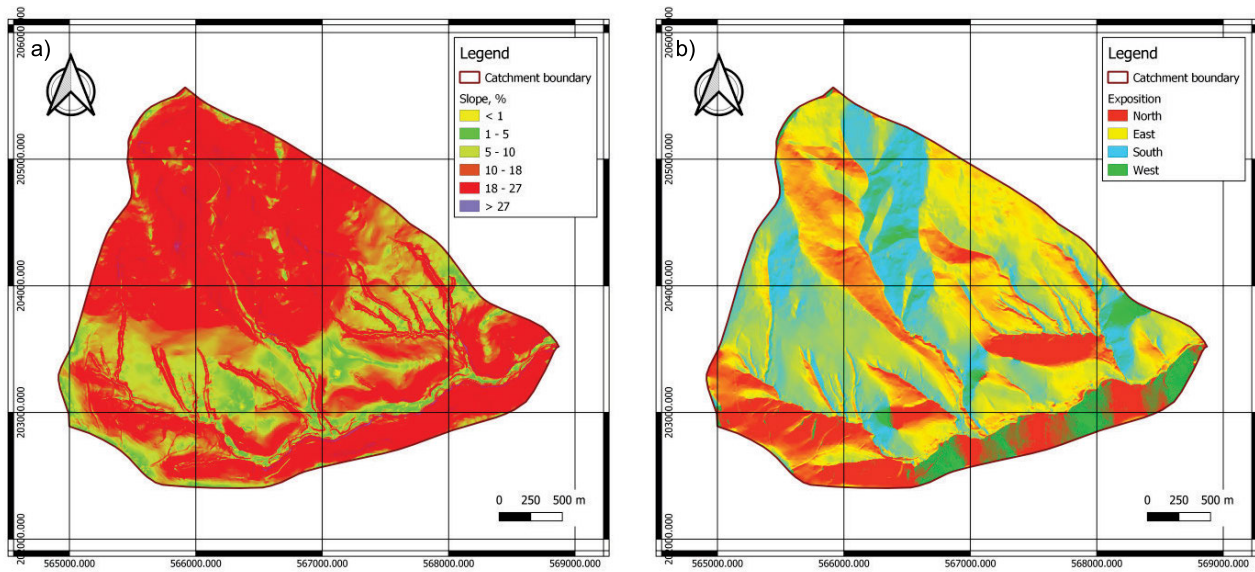


Fig. 2. Map of the Smugawka stream catchment: a) slope, b) exposition; source: own elaboration

HYDRO-CHEMICAL INDICATORS

A TOPCON GTS-226 tachymeter was deployed for geodetic measurements. Along the entire length of the streams, from the source to the outlet, five cross-sections of the streambed slopes were located, with a range of 0.79 to 2.18%. Their distance from each other averaged 875 m. The Wolman method (Wolman, 1954) was used to measure the grain size of the bed sediment. At each sampling location, the authors collected 15 cobbles and measured their average axis 'b'. The particle size of grains distribution curves were drawn and their representative diameters d_{min} , d_{30} , d_{50} , d_{70} , and d_{max} and effective diameter (d_m) were calculated. Sampling locations were placed throughout the channel at 0.5 m intervals.

A VALEPORT Model 801 Flat EM hydrometric current meter was deployed at the locations of the granular measurements for hydrodynamic measurements. This instrument enables the measurement of average flow velocity (v) at designated time intermissions, as well as instantaneous velocity and stream channel filling and has a measurement range of $5.0 \text{ m}\cdot\text{s}^{-1}$ with an accuracy of $\pm 0.001 \text{ m}\cdot\text{s}^{-1}$. It provided measurements for the mean velocity (v_{mean}) at the height of 0.4 m above the stream bottom, the maximum velocity (v_{max}), and the instantaneous velocity (v) measured directly over the stream bottom. The dynamic velocity was calculated using velocity distribution charts over the bed in a semi-logarithmic system (Eq. 1) (Gordon *et al.*, 2007):

$$v_* = \frac{a}{5.75} \quad (1)$$

where: v_* = dynamic velocity ($\text{m}\cdot\text{s}^{-1}$), a = constant determined empirically ($\text{m}\cdot\text{s}^{-1}$).

Taking into account the dynamic velocity (v_*), the determination of shear stress (τ) was performed in the following manner (Eq. 2):

$$\tau = \rho(v_*)^2 \quad (2)$$

where: τ = shear stress ($\text{N}\cdot\text{m}^{-2}$), ρ = density of water ($\text{kg}\cdot\text{m}^{-3}$).

The pattern of the flow, whether turbulent or laminar, was determined using the Reynolds number (Re) (maximum, mean and grain). Additionally, the Freud number (Fr) (mean and maximum) was used to measure mass flow characteristics. These values were computed utilising the Equations (3)–(7):

$$\text{Re}_{mean} = \frac{v_{mean}h}{\nu} \quad (3)$$

$$\text{Re}_{max} = \frac{v_{max}h}{\nu} \quad (4)$$

$$\text{Re}_{dm} = \frac{v_*d_m}{\nu} \quad (5)$$

$$\text{Fr}_{mean} = \frac{v_{mean}}{\sqrt{gh}} \quad (6)$$

$$\text{Fr}_{max} = \frac{v_{max}}{\sqrt{gh}} \quad (7)$$

where: h = filling (m), d_m = effective diameter, g = acceleration of gravity ($\text{m}\cdot\text{s}^{-2}$), ν = kinematic coefficient of water viscosity ($\text{m}^2\cdot\text{s}^{-1}$), derived from the Equation (8):

$$\nu = \frac{0.00178}{\rho(1 + 0.0337T + 0.000221T^2)} \quad (8)$$

where: T = water temperature ($^{\circ}\text{C}$).

In this investigation, hydrodynamic indices were utilised to assess the degree of total mixing in surface waters. The findings were subsequently employed in a spatial autoregression study. The dynamic velocity (u) within the stream was calculated using the subsequent equation (Loga, 2016):

$$u = \sqrt{hgS} \quad (9)$$

where: h = mean height of water (m), S = slope of channel bottom (%).

There is a potential risk connected with the frequency of measurements negatively influencing the results. It is possible that during short periods of high water flow, some of the annual sediment transport may not be immediately apparent. To solve this issue, the following equation was applied to identify the point in time when the mixture of substances in the water became evident. This includes the total suspended sediment load and the physico-chemical composition, offering a quantitative depiction of the transported materials. Furthermore, Loga (2016) calculated the turbulent diffusion coefficient ($D_{t,y}$) for transverse mixing in a natural channel during specific years.

$$D_{t,y} = 0.6hu \quad (10)$$

where: $D_{t,y}$ = turbulent diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), h = average height of water (m), u = dynamic velocity ($\text{m} \cdot \text{s}^{-1}$).

ANALYSING THE PHYSICO-CHEMICAL CHARACTERISTICS OF SURFACE WATER

The experimental site underwent an examination of the physico-chemical attributes of surface water. The pH level of the water was assessed through the potentiometric technique, employing an ELMETRON CP-104 equipped with a composite electrode. The precise electrical conductivity ($\text{dS} \cdot \text{m}^{-1}$), was ascertained by using an Elmetron CC-101 conductometer. The DO concentration ($\text{mg} \cdot \text{dm}^{-3}$) and the degree of oxygen saturation of the water were calculated by means of the electrochemical method using an Elmetron CO-411 oxygen meter. Additionally, the water temperature (T , in $^{\circ}\text{C}$) was determined utilising the built-in digital thermometer of the waterproof CO-411 oxygenmeter. A digital TDS instrument was used to measure the total concentration of dissolved substances in parts per million (ppm). The UNICAMSOLAAR 969 atomic absorption spectrophotometer was employed to determine physico-chemical water properties of in the laboratory. These included Na^+ , K^+ , Mg^{2+} , Fe_{tot} , and manganese Mn^{2+} .

In addition, the FOSS FIAStar 5000 computer-controlled instrument was used to measure the concentrations of Cl^- , N-NH_4^+ , N-NO_3^- , N-NO_2^- , and P-PO_4^{3-} , by means of the flow-injection colourimetric method. Gravimetric analysis was utilised to determine the concentration of sulphates (SO_4^{2-}). The Winkler method was employed to analyse the biological oxygen demand (BOD_5) of the water samples. This involved treating the samples with alkaline potassium iodide KI, manganese sulphate MnSO_4 and sulphuric acid H_2SO_4 , followed by titrating with sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3$.

The chemical oxygen demand (COD-Mn) was assessed using the permanganate method. In this process, the water sample underwent heating with potassium permanganate (KMnO_4) under acidic conditions, and the consumed oxygen amount was subsequently calculated through titration. After measuring the water level, samples were obtained from the stream utilising the bathometric method (1 dm^3 vessels). The concentration of total suspended solids (TSS) was determined gravimetrically by drying and weighing on pre-weighed filters with precision of $\pm 0.0005 \text{ g}$. The gathered material underwent filtration to assess the concentrations of various components by measuring the dry residue, encompassing the total mineral particles from the transported samples. The colourimetric method was used in

order to identify the ionic forms of cadmium (Cd^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}) and lead (Pb^{2+}) once per quarter. An electrochemical analyser (EcaFlow 150 GLP by PolEko) was utilised to identify minute quantities of heavy metals. Water turbidity levels were evaluated using the nephelometric-laser method within the range of 0-2000 FNU, in accordance with the international standard (Nephelometric Turbidity Unit; NTU), with a Hach Lange 2100QS nephelometer (turbidimeter).

TRANSFORMATION OF DATA INTO A SPATIAL MODEL AND SUBSEQUENT STATISTICAL ANALYSIS

Before conducting the analyses, an exploration of the asymptotic distribution was undertaken. χ^2 Jarque-Ber (JB) test statistic considers both kurtosis and skewness (Jarque and Bera, 1987). After arranging the data in ascending order, based on the concordance test by Anderson-Darling, for the empirical distribution, normalisation for average and standard deviation was performed (Stephens, 1986). The statistical test computes a weighted Cramér-von Mises distance between the theoretical (F) and empirical (Fn) cumulative distribution functions, with weights equivalent to the inverse of the empirical cumulative distribution (Anderson and Darling, 1954). Moreover, the Shapiro-Wilk test, utilising positional statistics, was employed. As noted by Shapiro and Wilk (1965), the main concern in the investigation is the relationship between the experiential quantile (the ordinal statistic) and the theoretic quantile (the expected value of the ordinal statistic) along the straight line $y = x$. Levene's test (Levene, 1960) was applied to analyse the homogeneity of variance. In order to minimise the number of variables, principal component analysis (PCA) was utilised to illustrate the interrelationships among key physico-chemical parameters in the stream surface water adjacent to cropland, grassland, and woodland. Then, the Bartlett sphericity test (Bartlett, 1950; Williams, Brown and Onsmann, 2010) was used to evaluate the statistical significance of the matrix of the strength of the relationship between the variables and the correlation coefficients (r). The KMO (Keiser-Mayer-Olkin) coefficient was utilised to partial correlations with bivariate correlation coefficients to determine the accuracy of the selection of variables for the tested model. Variable adequacy is defined as a KMO coefficient > 0.5 (MacCallum, 1983; Hair *et al.*, 1995; Tabachnick and Fidell, 2007; Szüle, 2016).

Eigenvector values that approximate the impact of the raw variables on the principal component, were presented to illustrate the connection between the tested physico-chemical properties of the studied surface water. Factor loadings, reflecting the influence of each variable on a specific principal component, were used to interpret the most significant variables. In this study, a correlation matrix was employed in which the coefficients of correlation between the original variables and the subsequent primary component under investigation were taken as the factor loadings. The PCA method was employed to denote the variance size for the individual computed components and the designated primary variables. By considering the factor loadings, the most pertinent variables were chosen for subsequent data processing. PQ Stat software version 1.6.6 was used for the analysis.

A technique that can be employed to successfully estimate characteristics in systems that are linear is spatial autoregression. The purpose of the investigation concerned the determinants of

seasonal fluctuations in the surface water physico-chemical composition. To achieve this, the research adopted a spatial autoregression model with a lagged response, which facilitated the study of the correlation between the length of full mixing and the physico-chemical characteristics dispersed freely in the hydro-column. From the equation (11) (Rangel, Diniz-Fiho and Bini, 2010), the general form of the spatial autoregression was derived:

$$Y = \rho W_y + X\beta + \varepsilon \quad (11)$$

where: Y = vector ($N \cdot 1$) representing the explained spatial process through a responsive (explained) variable, ρ = spatial autoregression parameter indicating the strength of the relationship between the variables (spatial interaction parameter), W_y = weight matrix of the vicinity of the examined variables in different locations ($N \cdot N$ matrix of spatial weights), β = vector ($K \cdot 1$) of indices related to the structure, X = matrix ($N \cdot K$) of explanatory processes, ε = vector ($N \cdot 1$) of the random term (the discrepancy between estimated values and spatial variability not accounted for by the model; stochastic element). The application of spatial autoregressive models has made it possible to show the relation between the spatially distributed variables for uniform areas during a measurement sequence and to allow the variables to be investigated more easily, in particular in the case of exceptionally high runoff. The dependent variable was the transverse turbulence diffusion coefficient and the independent variables were the physico-chemical properties of the surface water. In order to calculate the spatial dependencies, a system of lagged predictors (Rangel *et al.*, 2010) which is part of the SAR (spatial autoregression) was employed:

$$C = \sigma^2[(I - \rho \cdot W)^T]^{-1}[I - \rho \cdot W]^{-1} \quad (12)$$

where: W = a matrix ($N \cdot N$) of spatial weights, indicating the proximity of the variables at different locations, C = vector of the explained spatial process through a responsive (dependent) variable, ρ = parameter of spatial autoregression that reflects the strength of the relationship between the variables (spatial interaction parameter), σ^2 = residual variance between observations, I = linear transformation (matrix of $N \cdot N$ -type) of the dependent variable.

The main variables for the various kinds of land use incorporating the physico-chemical features of the surface water were documented in the autoregression analysis. SAM 1.6.6 software was used for the calculations.

RESULTS

ATTRIBUTES OF THE STREAM BED RELATED TO BOTH PHYSICO-CHEMICAL AND HYDRODYNAMIC CHARACTERISTICS

Table 1 illustrates the concentration levels of the indicators of salinity, whereas Table 2 shows the metal concentration levels, particularly heavy metals, in the Smugawka stream over the entire time span of the investigation. There was a significant positive correlation for Ca^{2+} and $P-PO_4^{3-}$ for the first two factors of the principal component analysis (Tab. 3) – in surface waters flowing out of cropland. Water temperature, distinguished by strong factor

Table 1. Concentration ranges of water salinity indicators in the Smuwigaka stream

Salinity indicator	Unit	Surface water runoff from		
		arable land	grassland	forests
EC	$\mu S \cdot cm^{-1}$	156–240	247–350	148–256
SO_4^{2-}	$mg \cdot dm^{-3}$	43.87–204.24	23.56–193.36	45.05–120.93
Cl^-		23.94–134.45	35.05–195.36	24.59–145.48
Na^+		4.80–88.31	3.91–68.72	8.92–37.54
K^+		1.78–5.20	0.68–10.40	3.20–5.40
Mg^{2+}		6.64–10.92	3.74–19.35	10.34–22.59
Ca^{2+}		39.53–133.08	31.22–147.23	58.63–80.82
TDS		101–147	78–199	148–178

Explanations: EC = electrical conductivity, TDS = total content of dissolved substances.

Source: own study.

Table 2. Concentration range of metal in the Smugawka stream involving heavy metals

Indicators of metal concentrations	Unit	Surface water runoff from		
		arable land	grassland	forests
Zn^{2+}	$\mu g \cdot dm^{-3}$	12.53–50.10	2.93–41.90	19.94–47.80
Pb^{2+}		1.61–6.80	0.01–7.60	0.01–1.34
Cd^{2+}		0.01–1.10	0.10–1.90	0.01–1.50
Cu^{2+}		1.51–3.04	0.91–1.50	0.01–0.70
Fe_{tot}	$mg \cdot dm^{-3}$	0.53–0.91	0.03–1.04	0.10–0.81
Mn^{2+}		0.12–0.18	0.06–0.09	0.09–0.10

Source: own study.

Table 3. Factor loadings derived from principal component analysis (PCA) for the studied physico-chemical characteristics from surface water samples taken in grasslands, arable land from forests

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Arable lands						
TSS	-0.15	0.24	0.78	-0.21	0.52	0.04
K^+	-0.72	0.60	-0.10	0.05	-0.06	0.46
N- NO_2	0.31	0.17	0.19	0.90	0.15	0.01
Ca^{2+}	0.88	0.92	-0.03	-0.07	-0.01	0.14
Mg^{2+}	0.84	-0.86	0.02	-0.16	0.07	0.13
P- PO_4^{3-}	0.93	0.87	-0.01	-0.15	0.04	0.18
Na^+	0.87	-0.78	-0.31	0.13	0.19	0.23
Grasslands						
T	0.82	0.76	-0.60	0.10	-0.10	0.12
TSS	-0.63	0.58	-0.62	-0.17	0.08	-0.14
Fe_{tot}	0.75	-0.63	-0.15	-0.22	0.22	0.19
K^+	-0.59	0.51	-0.19	-0.53	-0.20	-0.13
Ca^{2+}	-0.61	0.54	0.17	-0.26	0.43	0.001
Na^+	-0.85	-0.73	0.04	-0.03	-0.13	0.11

cont. Tab. 3

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Forests						
<i>T</i>	0.84	0.86	-0.28	0.41	-0.03	0.32
Na^+	0.97	-0.78	-0.48	-0.44	0.12	0.23
BOD_5	-0.16	-0.53	0.08	-0.64	0.46	0.22
Mg^{2+}	-0.38	0.13	0.55	0.13	0.50	-0.07
Fe_{tot}	-0.51	0.84	-0.13	-0.01	-0.17	0.10
<i>COD-Mn</i>	0.92	0.87	-0.51	0.21	0.33	0.08
<i>EC</i>	0.23	-0.35	-0.30	0.21	0.53	-0.59
<i>DO</i>	-0.56	-0.81	0.15	0.35	0.33	0.65

Explanations: *TSS* = total suspended solids, *T* = temperature of water, *BOD*₅ = biochemical oxygen demand, *COD-Mn* = chemical oxygen demand, *DO* = dissolved oxygen, *EC* = electrical conductivity.
Source: own study.

loadings, had a significant role in the grasslands. Meanwhile, the Fe_{tot} levels were positively correlated with the first and highly negatively correlated with the second factor of the principal component analysis as shown in Table 3. Also, the temperature of water (*T*) and chemical oxygen demand (*COD-Mn*) concentration presented the highest variance for the factor axes and the highest factor loadings in all surface water samples tested (Tab. 3, Fig. 3). The intensity of transport increased according to the sequence: forest > grassland > cropland as shown in Table 1.

THE REDUCTION OF DATA AND THE FORMULATION OF A SPATIAL MODEL

In order to demonstrate correlations between the studied values, the paper applied the spatial autoregression technique. The model unveiled associations among specific physico-chemical attributes of surface water. The SAR autoregression formula for the whole catchment area indicated that P-PO_4^{3-} , N-NO_2^- , total dissolved

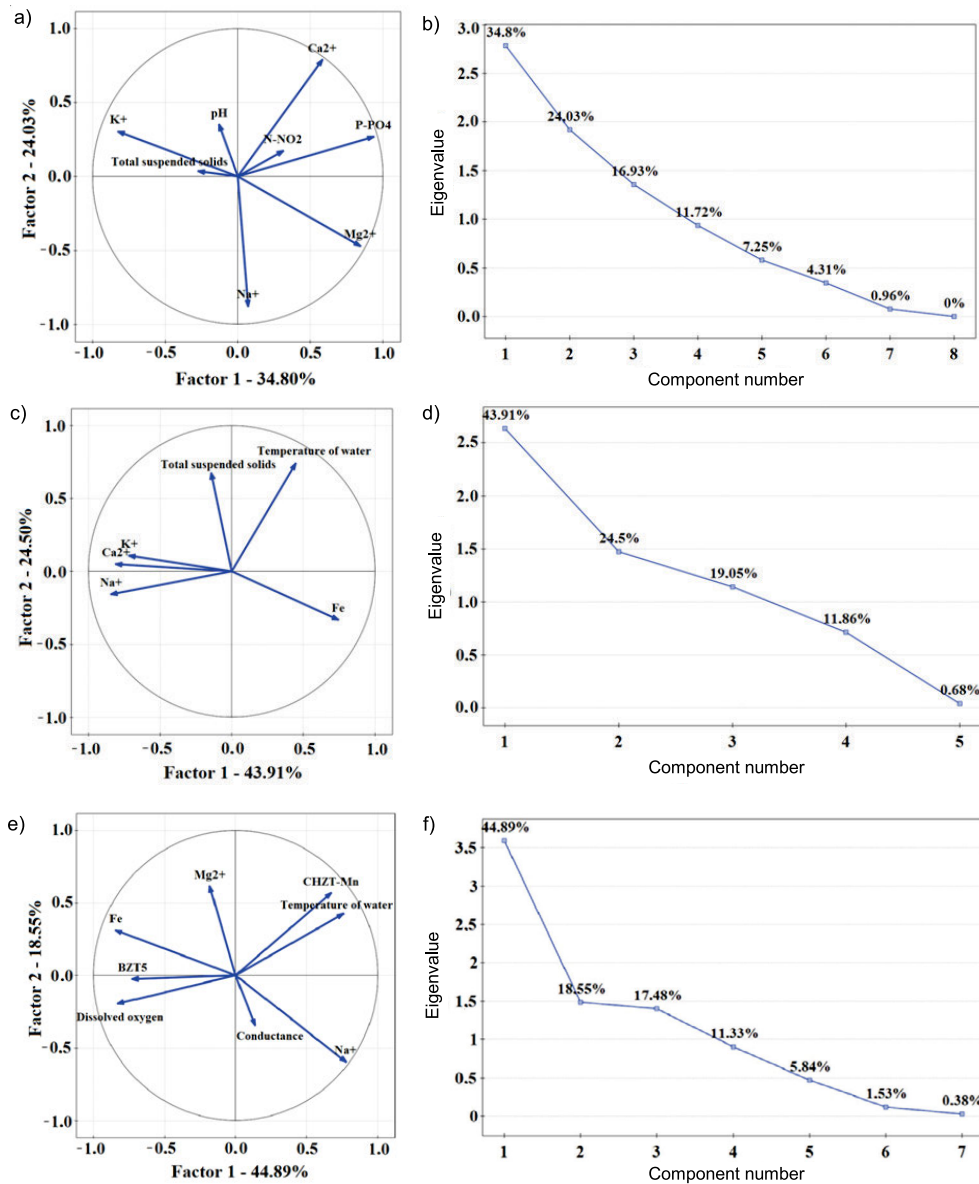


Fig. 3. Principal component analysis (PCA) and score plots illustrating physico-chemical characteristics for samples taken in surface water: a), b) arable land, c), d) grassland, e), f) forest; source: own study

Table 4. Soil material loss in the form of total suspended solids (TSS) over the study period (2014–2018) in the Smugawka catchment as a function of land use

Index of eroded soil material	Unit	Arable land	Grasslands	Forests
Circadian concentration of TSS	mg·dm ⁻³	4.94–18.34	0.93–9.92	0.71–5.92
Annual TSS load	Mg·y ⁻¹	18.69–190.27	19.65–126.95	7.38–53.78

Source: own study.

solids (TDS) as well as the concentrations of Mg²⁺, Ca²⁺, Na⁺ and Mn²⁺ (Tab. 5) are reliable predictors for determining the full mixing distance. Overall, the autoregressive model combines the correlations between the physico-chemical properties of the surface water and the coefficient of transverse turbulence diffusion in the flysch stream. Only a small number of these relationships were statistically significant ($p < 0.05$). Statistically significant

Table 5. The results of the SAR-type spatial autoregression model for the entire catchment

Physico-chemical characteristics	SAR ratio	OLS ratio	Standard error
TSS	0.36	-1.22	0.67
T	16.28	10.41	5.90
Oxygen concentration	-0.23	-0.46	0.19
Degree of oxygen saturation	-0.04	-0.03	0.01
BOD ₅	-1.77	-1.19	0.37
COD-Mn	4.55	6.46	1.09
P-PO ₄ ³⁻	11.72	12.95	1.47
N-NH ₄ ⁺	16.2	11.40	1.78
N-NO ₃ ⁻	4.88	-0.03	0.36
N-NO ₂ ⁻	14.83	0.64	2.71
TDS	8.53	5.70	0.27
SO ₄ ²⁻	0.18	-0.31	0.14
Cl ⁻	0.71	0.06	0.02
Na ⁺	-0.61	0.49	0.17
K ⁺	10.95	2.92	1.06
Mg ²⁺	6.32	-0.46	0.82
Ca ²⁺	-4.41	-2.93	1.41
EC	4.83	-1.19	-1.72
Zn ²⁺	0.14	-0.14	0.02
Pb ²⁺	3.12	-0.62	0.09
Cd ²⁺	4.89	-0.03	0.83
Cu ²⁺	3.12	0.98	0.56
Fe _{tot}	12.81	6.46	1.37
Mn ²⁺	11.27	17.46	1.45

Note: For this study, the distance of full mixing was chosen as the explanatory variable, while the physico-chemical features of the surface water were used as predictors in the model.

Explanations: SAR = spatial autoregression, OLS = ordinary least squares regression, other symbols as in Tabs. 1–3.

Source: own study.

relationships were found for K⁺ and P-PO₄³⁻ in surface waters near cropland and additionally for Fe_{tot} in surface waters near grassland in the spatial autoregression model with a breakdown by use variant. No significant relationships were found at surface water monitoring sites in the close proximity of forests (Tab. 8). In the spatial autoregression model encompassing the entire catchment, incorporating the explanatory variable (the distance of full mixing) the spatial relationships were identified for N-NO₂⁻, Mn²⁺, P-PO₄³⁻, Na⁺, TDS, Mg²⁺, Mn²⁺, and Ca²⁺ (Tab. 5).

Table 6. The type spatial autoregression (SAR) model results using the main physico-chemical features of surface water chosen and the transverse turbulence diffusion coefficient as the dependent variable and based on principal component analysis for each use variant as predictors

Variable	SAR ratio	Standard factor	Standard error	t	p
Measurement points in the watercourse next to arable land					
The constant of the equation	9.46	–	5.35	0.23	3.50
K ⁺	-0.85	0.82	0.83	-4.06	0.004
pH	-2.50	-0.39	5.34	-2.25	0.32
N-NO ₂	0.009	0.05	0.02	0.36	0.78
Ca ²⁺	-0.83	8.14	1.67	3.97	0.15
Mg ²⁺	-0.37	0.04	0.01	0.01	0.04
P-PO ₄ ³⁻	-2.96	0.02	0.02	-2.05	0.006
Na ⁺	25.75	4.77	1.34	-4.06	4.95
TSS	2.56	0.32	0.34	3.72	10.03
Measurement points in the watercourse next to grasslands					
The constant of the equation	1.19	–	1.79	0.66	1.45
T	0.04	0.01	0.42	0.10	0.51
The constant of the equation	0.12	0.02	1.27	0.09	0.92
Fe _{tot}	-0.02	-0.45	0.006	-4.00	0.01
K ⁺	0.35	0.003	12.10	3.97	0.004
Ca ²⁺	-7.82	-0.09	0.30	0.01	0.99
Na ⁺	-1.95	-0.11	0.17	-2.05	0.07
T	-2.96	-0.81	0.93	-1.58	0.15
Measurement points in the watercourse near the forests					
The constant of the equation	–	-0.90	0.24	-3.49	0.01
T	-0.03	-0.03	0.07	-0.45	0.66
COD-Mn	-0.11	0.10	0.15	-0.72	0.49
Na ⁺	-0.04	-0.04	0.29	-0.51	0.88
Conductance	-0.03	0.09	0.27	0.53	0.56
BOD ₅	0.008	0.009	0.22	0.03	0.97
Mg ²⁺	-0.20	-0.13	0.09	-2.12	0.07
DO	-0.46	0.003	0.004	0.21	0.99
Fe _{tot}	-0.03	0.19	0.06	0.15	0.24

Explanations: t = test for linear regression, p = probability of observing a sample statistics, other explanations as in Tabs. 1–5.

Source: own study.

DISCUSSION

GENERAL INFORMATION

The combination of multi-dimensional statistical methods and a spatial model was proposed as an innovative solution in this study. The spatial autoregression equation identified a noteworthy correlation among specific physico-chemical attributes of the quality of surface water during the analysis of the outcomes.

RELATIONSHIP BETWEEN HYDRODYNAMIC PARAMETERS AND SURFACE WATER IONIC COMPOSITION

Monitoring areas at risk of contamination in long-term studies requires measuring micro-pollutant levels, particularly heavy metals. Lithology-dependent direction and intensity of chemical denudation process are influenced by surface water ionic composition (Kim *et al.*, 2012; Ziadat *et al.*, 2015). Additionally, the quality is affected by the inventory of surface watercourses and the operation of the hydrographic network (Trivedi, 2010). The principal component analysis (PCA) was utilised to identify the primary variables for each type of use. To conduct further spatial analysis, only the surface water physicochemical features with the highest factor loadings were chosen. The first PCA factor showed a high negative correlation for K^+ concentration. A strong negative correlation was also determined for the second PCA factor for Mg^{2+} and Na^+ concentrations. This indicates that these ions may have been draining from the catchment.

Processes of water self-purification are an important aspect of water evaluation and protection (Moore and Langner, 2012; Halecki, 2015). The identification of sources of nitrate pollution is a key action (Bu *et al.*, 2017), given that anthropogenic pollution varies in surface waters and can fluctuate periodically (Xu *et al.*, 2014; Hu *et al.*, 2015). Similarly, for cropland, K^+ cations exhibited a negative correlation with the first principal component analysis factor. The results indicate a negative correlation for Na^+ cations, which may suggest a systematic decline in their concentration. The temperature of water and $COD-Mn$ concentration had a high factor loading in the water samples taken near forested areas. These variables also exhibited the greatest variance along the factor axes in all surface water samples and had the highest factor loadings. The presence of dissolved ions in the water of the flysch stream might have been influenced by the water temperature.

The study considered the state at which the material mixed with water by calculating the transverse turbulence diffusion index and transport intensity. The stream bed adjacent to the arable land recorded the highest transport intensity value of 1.02. The PCA identified Ca^{2+} and $P-PO_4^{3-}$ as the most significant chemical parameters connected with this type of land use. When evaluating the impact of cropland on the physico-chemical surface water quality, it is crucial to consider the levels of phosphate and nitrate (Halecki *et al.*, 2017). The proportion of ions present quantitatively is influenced by the rock type and physical features of the substrate, in particular by its coefficient of infiltration and, in the case of clastic rock erosion, by its mechanical structure (Szostakiewicz-Hołownia, 2012). This is a key issue for the flysch catchments, which consist of Magurian and sub-Magurian layers as pointed out by Starkel (2006) and Starkel, Pietrzak and Łajczak (2007).

The transportation of eroded materials can be influenced by the topography of the rock bed, as noted by Priess *et al.* (2015) and Szatten (2016). Therefore, on an annual basis, stationary surveys with a high frequency of measurements are conducted to establish the correlation between flooding and suspended solids concentration (Huan, 2011). In the Beskidy basins, in contrast, quantitative correlations between hydrological characteristics and their input with respect to aquatic erosion were demonstrated, taking into account the fluctuations of the clastic weathered water transported (Brański, 1975; Brański, 1990). The study found that the longest full mixing distance was 52.26 m for locations in surface water close to cropland.

CORRELATIONS AMONG HYDROLOGICAL PARAMETERS AND THEIR AVAILABILITY IN EROSION OF WATER

Chemical compounds transport intensity is influenced by dispersion and turbulence resulting from variations in flow velocity. According to Loga (2016), turbulent eddies produce a locally non-stationary and inhomogeneous velocity field, which accelerates mixing. Therefore the parameters of hydrodynamics were determined for each stream section so as to describe the transport mechanism of the studied types of ions and other matter dissolved in the water. The highest values of Reynolds number (Re) and tangential stress were found in the riverbed neighbouring the perennial grassland. The range of bedload was 32–41 mm across the catchment, with larger fractions observed to accumulate near the bed of the flysch stream.

AN ADVANCED MODEL APPLYING TECHNIQUES OF SPATIAL AUTOREGRESSION

Fu *et al.* (2014) and Liao *et al.* (2016) posit that it is likely that ions in water are linked to the utilisation of land and the heavy metals detection in surface water is vital due to its economic value. Operacz *et al.* (2018) suggest that these findings have potential implications for residents' health, particularly with regard to the curative nature of Carpathian streams. The spatial patterns and relationships among the parameters in the catchment were demonstrated on the basis of a spatial autoregression model, the multivariate analysis and empirical equations. The study confirms that material leached from the soil can be balanced in a small flysch catchment due to the fact that the process of chemical denudation is correlated with solubilised ions concentration in the flysch watercourse (Halecki *et al.*, 2019).

The advanced model of the spatial autoregression procedure allowed for the extrapolation of hydrochemical records and the erosion intensity over a number of measurement series. The spatial autoregression procedure was adopted to more effectively represent these correlations, in order to verify the analysed data in a spatial system. The investigation aided in confirming the impact of various alterations in land use on the variables. The study analysed the surface water physico-chemical characteristics in in multiple land utilisation scenarios. The SAR-type spatial autoregression model results indicated that K^+ and $P-PO_4^{3-}$ ions were primarily leached from arable land. Additionally, a significant correlation was found between K^+ and Fe_{tot} cations in surface water from grassland. According to the results of the SAR spatial autoregression model, there were no statistically relevant varia-

tions in the ionic composition of the surface water flowing out of the woodland. It is possible that the nature of the land utilisation was responsible for the variations obtained by the model. Hence, Smolska (2010) and Bakker *et al.* (2008) maintain that methods for assessing soil erosion and surface washout should be refined in research conducted on slopes, particularly those employed for use in agriculture.

The study utilised this model of spatial autoregression to identify relationships between various physico-chemical variables and the full mixing distance. The study found significant relationships for Mn^{2+} , $P-PO_4^{3-}$, Na^+ , $N-NO_2^-$, TDS , Ca^{2+} , Mg^{2+} and Mn^{2+} . The hydraulic conditions for each use variant were found to be different, suggesting that catchment development may influence surface water physico-chemical quality.

RECOMMENDATIONS FOR CONDUCTING HYDRAULIC TESTS AND EVALUATING PHYSICO-CHEMICAL CHARACTERISTICS OF SURFACE WATER

To predict the physico-chemical surface water quality as well as to determine correlations between metal concentrations, including heavy metals, decisive indicators need to be identified. At present, the method of spatial autoregression is one of the most efficient methods for predicting the quality of water coming from different pollution sources (Yang *et al.*, 2017). The spatial autoregression analysis generally revealed spatio-temporal correlations at different monitoring sites. Integrating spatial analysis into the identification of various influent pollutants facilitates the resolution of technical challenges associated with surface washout as well as the proper utilisation of cropland within the catchment.

The importance of an adequate sample size in spatial model building cannot be overstated for spatial studies (Vallejos and Osorio, 2014), particularly in relation to surface water physico-chemical quality (Mahjouri and Kerachian, 2011). This highlights the need for the spatial analysis to be combined with the evaluation of surface water quality attributes (Dash *et al.*, 2015). The total suspended solids (TSS) leached during water erosion is a measure obtained during transient heavy rainfall flows. Therefore, the quality of surface water can be estimated with reference to its hydrochemical characteristics (Misaghi *et al.*, 2017). The physico-chemical characteristics of surface water in farm as well as grassland regions can be evaluated by focusing solely on pertinent parameters. When developing a dynamic model as Wu, Zheng and Chien (2005) suggest or computing indicators of water quality following Yadav *et al.* (2015) or Naubi *et al.* (2016) recommendations, the selection of an appropriate method for the sample size is of paramount importance (Griffith, 2005). Hence, in monitoring pollution of surface waters (Wu, Zheng and Chien, 2005), the spatial sampling optimisation is crucial (Hu *et al.*, 2015). It is expected that the outcomes of this research could be applied in a practical way to identify the main factors that promote water erosion in streams with bigger catchments. Additionally, the identification of water erosion effects will aid in evaluating the surface transport of materials in future investigations. It is suggested that future research in the area needs to be directed at determining correlations between unit washes and material concentrations in stream and river channels.

CONCLUSIONS

The research conducted showed the seasonal variation of the physico-chemical surface water quality what enables significantly identification of sources of diffuse pollution from agricultural areas into the stream. The study facilitates the determination of water erosion intensity and the evaluation of surface water supply sources. It explained the load size determined in the zones of delivery of the material transferred to the flysch stream and the factors of erosion, including leaching vulnerability. The findings may aid in the development of schemes for the erosive supply of alluvial deposits from surface washes or eroded flysch as a function of material supply in the catchment. The outcomes regarding the use of land and its impact on chemical compounds transport could help to manage the environment in mountainous regions and to monitor chemicals to determine progression of the processes of erosion. Assessing changes in land use over time could also benefit local residents engaged in agriculture. Additionally, evaluating the concentration change of the physico-chemical composition of the flysch streambed in the short time period will be valuable for the research purposes of drawing up a concept for managing and eliminating the pollutants resulting from man's activities. The next investigation should concern variation of physico-water parameters for various rainfall periods in the context of climate change.

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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