1 **Spatial relationship between hydrodynamic and physico-chemical parameters of surface**

2 **water for a basin with shale rock series as an indicator of intensity and direction of**

3 **chemical denudation in the Western Carpathians**

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20 **Keywords:**

21 hydrodynamic parameters, physico-chemical parameters of water, indicator of intensity, chemical

22 denudation

23 **Abstract**

24 Hydrochemical evaluation of stream quality in the Western Carpathians requires a system

25 approach, gradually excluding factors less or more responsible for washing, mixing contaminants

26 and their farther transportation in the stream channel. In this work, the spatial autoregression

27 model was used to estimate the relationship between hydrodynamic and physico-chemical

28 parameters of surface water in various groups and variants of basin use. The highest mean shear

29 stress was 0.178 N·m^2 in forest surface water. The highest mean Reynolds number (23654) was

30 recorded in the stream channel at permanent grassland, and the lowest number (0.426) at arable

31 lands.Analysis of spatial autoregression to a high degree showed space-time relations in various

32 measurement points. The turbulent diffusion coefficient should be regarded in the space-physical

33 model, constructed based on the influence of hydrodynamic indicators on the shaping of physico-

34 chemical parameters in the flysch basin. The autoregression confirmed that the turbulent

35 diffusion coefficient played a high role for ions K$^+$ and P-PO$_4$$^{3-}$ in surface water at arable lands

36 and for cation K^+, as well as total iron for grassland ($p<0.05$). A relation for physico-chemical

37 was not found for surface water in forests. The results, to a high degree, will be used to createan

38 erosion model concerning the alimentation of alluvial deposits from weathered Carpathian flysch

39 or surface wash depending on the material delivery in a basin.

40 **1.   Introduction**

41   The factors influencing the physico-chemical state of surface water to the highest degree

42 are soil, relief (Shi et al., 2016),and soil plant cover occurring in the river-bank zone (Andersson

43 et al., 2015; Teixeira and Marques, 2016). In flysch basins, surface runoff is selective because

44 transported material often undergoes local accumulation on a slope during delivery to a stream

45 (Gil and Kotarba, 1977).Reliability of results is ensured when the picture of surface erosion is

46 being captured in mountain valleys, and proper frequency of measurement series is carried out,

47 together with specification of measurement error (Halecki et al., 2018a).

48   Investigations of water erosion can be carried out from a theoretical point of view and the

49 use of mathematical models (Panagoset al., 2015), for example,in the aspect of modelling the

50 scape of nitrates in surface runoff (Wang et al., 2014). Further, empirical equations and

51 theoretical methods are used for the settlement of river material quantity in various measurement-

52 control points (Mazur and Pałys, 1992) and intensity degree of suspended sediment transportation

53 in the shape of mechanical weathered rock mantle (Izmaiłowet al. 2008; Starkel 2011, Bryndalet

54 al. 2014; Comino et al., 2016). It is important to remember that technical solutions simulating

55 digital sediment transportation are only approximate and do not reflect real data. The cause of

56 unreliable results is the short or irregular frequency of field measurements (Haleckiet al., 2018 b).

57   Material transported in the Beskidy region basins is connected with land use and the

58 occurrence of shale rock series (Haleckiet al., 2018 c). Material delivered from slopes determines

59 the concentration of particular ions transferred in the stream channel. Ions can originate from the

60 dissolution of mineral fertilisersfrom adjacent areas of agricultural use (Hall et al.,2014; Gernezet

61 al., 2015). The fundamental biogenic indicators in the hydro-chemical evaluation of surface water

62 are phosphates and nitrates. Nitrogen most often appears as an ammonium ion

63 ($N-NH_4^+$), testifying point contamination of surface water. Nitrate ($N-NO_3^-$) and nitrite nitrogen

64 ($N-NO_2^-$) are indicators of the long-term influence of pollutants, particularly in the proximity of

65 crops. In summer and early autumn, $N-NO_3^-$ decreases, which is connected with the plant's

66   demand for nutrients (Ulénet al., 2012). The concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}),

67   sodium (Na^+), potassium (K^+), total iron (Fe_{tot}), and nitrite nitrogen ($N-NO_2$) is differentiated in

68   spring.Thisshows thatplants accumulate more nutrients during the warmer season(Padmalalet al.,

69   2012). For estimation of the physico-chemicalquality of surface water, the good indicators

70   regarding transformation and accumulation are various forms of phosphorus. They pose a high

71   threat to the purity of surface water as factors that favour eutrophication and excessive rise of

72   biomass of particular algae (Smoroń, 2012). Changes in biogen concentration in surface streams

73   are influenced by the spatial distribution of arable land (Arienzoet al., 2012; Tasdighiet al., 2017).

74   Sedimentary rock undergoes an intensive leaching process. In surface water, sodium

75   cations can originate from industrial waste and potassium from agricultural cultivations, where

76   potassium fertilisersare used (Oster et al., 2016). Hydrolytic decay of minerals containing sodium

77   salts (aluminosilicates) and weathering of sedimentary rocks contribute to the creation of

78   alimentation (source) for sodium and potassium cations in surface water (Zhang et al., 2017).

79   Magnesium salts occur in all natural waters, both surface and underground. Leached $Ca^{2+}$and

80   Mg^{2+} cationspenetrate the basin by infiltrating rainfall from fertilisedcultivated areas and

81   supplying surface water (Grochowska, 2016). Increased concentration of $Ca^{2+}$and Mg^{2+}cations in

82   surface water testify to the occurrence of calcareous rocks, marls, and dolomites and depends on

83   the degree of basin management (Halecki, 2015). In addition, the concentration of Ca^{2+}cations

84   and SO_4^{2-}anions in small stream channels is attributed to geology, mainly the calcium carbonate

85   and sulphate concentration in the clastic rockmantle. Moreover, certain water quality factors

86   require specialistic investigation and hydrochemical evaluation according to the World Health

87   Organisation (WHO) standards. These include Ca^{2+} and Mg^{2+}cations,$N-NO_2^-$, $N-NO_3^-$, SO_4^{2-}, and

88   phosphate phosphorus ($P-PO_4^{3-}$) anions, and salinity indicators - specificallythe electric

89   conductivity of water and the concentration of dissolved substances (sum of determined mineral

90   substances in a shape of fine clastic material) with total suspension (Shigutet al., 2017).

91   Dissolved oxygen is essential for the evaluation of water conditions. The activity of

92   microorganisms responsible for oxidation of organic compounds is examined using two

93   indicators, namely biochemical oxygen demand (BOD) and chemical oxygen demand (COD). In

94   evaluating surface water quality, higher oxygen use indicates contamination (Bo et al., 2017;

95   Effendi et al., 2018). On the other hand, a lower dissolved oxygen concentration can show

96   biochemical decay of accumulated organic substances, respiration of water organisms, or

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97   oxidation of inorganic substances (Matta et al., 2017).Furthermore, water temperature controls

98   the solubility of solid substances and the concentration of suspension (Saito et al., 2005a). So,

99   low temperature weakens the chemical and biological activity of water and increases viscosity,

100 enabling the transportation of material (Jarocki, 1957). Higher values of dissolved oxygen and

101 BOD are connected with their high sensibility to changes in water caused by the activity of water

102 engineering (Parmar and Keshari, 2012). Essential differences between BOD and COD of

103 anthropogenic origin have been recorded in a seasonal hydro-chemical evaluation period

104 (Bellver-Domingo and Hernández-Sancho, 2018). Seasonal evaluation of temperature, pH, COD,

105 BOD and heavy metals: Fe, Mn, Ni, Cd, Cr, Co, Cu, Pb and Zn, is needed either for

106 determination of the recommended level and permissible concentration of pollutants for drinking

107 water (Vincent-Akpuandin, 2015). The anthropogenic activity contributes to delivering heavy

108 metals to surface water, mainly by using industrial objects (Juahiret al., 2010; Weber et al., 2014;

109 Assoulineet al., 2015; Hu et al., 2015; Vaddeet al., 2018).

110 Contamination of surface water is proven by the decay of living organisms, which mineral

111 composition is related tothe increase of sulphates. Chlorine is also present in the form of chloride

112 anions (Cl⁻). In surface water, it is transported as a result of weathering of rock-forming minerals.

113 Dissolution of evaporates (sedimentary rock) enriched in anhydrite constitutes a natural source of

114 SO_4^{2-} anions. Further, sulphate ions do not undergo sorption in an underground environment, and

115 similar to Cl⁻, it is the indicator of pollutant penetration to underground water (Sapek, 2008;

116 Geurtset al., 2009).

117 The first detailed aim of this study was to arrange useful values of the basin and,

118 secondly,to conduct a hydro-chemical evaluation of the surface water in various land

119 configurations of the basin lithology. The third aim was to determinehydraulic conditions in the

120 flysch stream channel. A final goal was to determine the main factors intensifying short-term

121 relations between hydrodynamic parameters of mountain streams and chemical compounds

122 leached from the slope to the water of the flysch stream as a result of interrill erosion. For such

123 detailed aims, hypotheses were formulated, methods and schemes of frequency measurement

124 series were set, and specifications of measurement errors were elaborated.
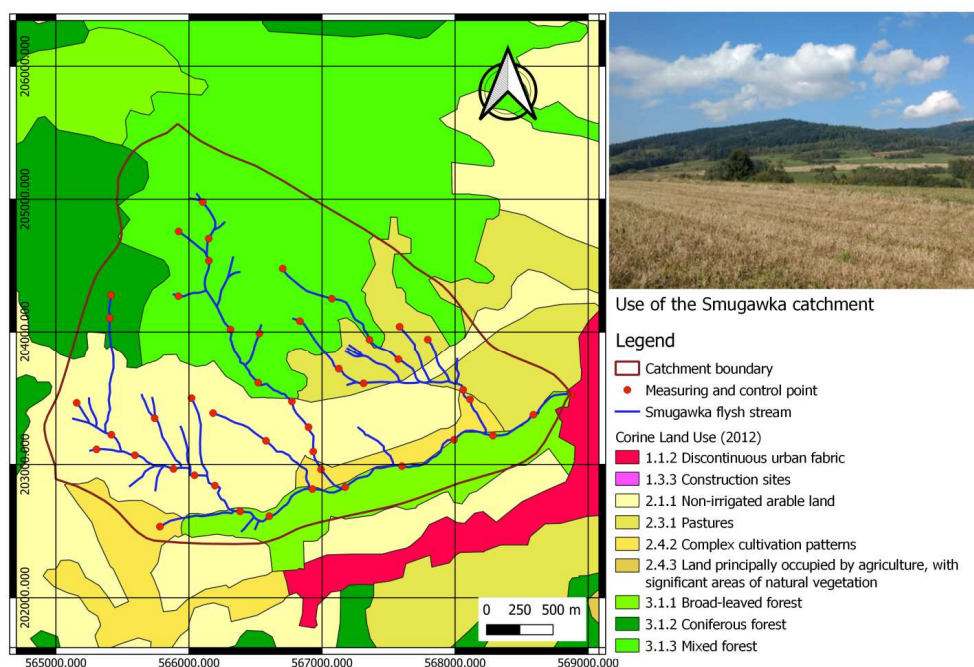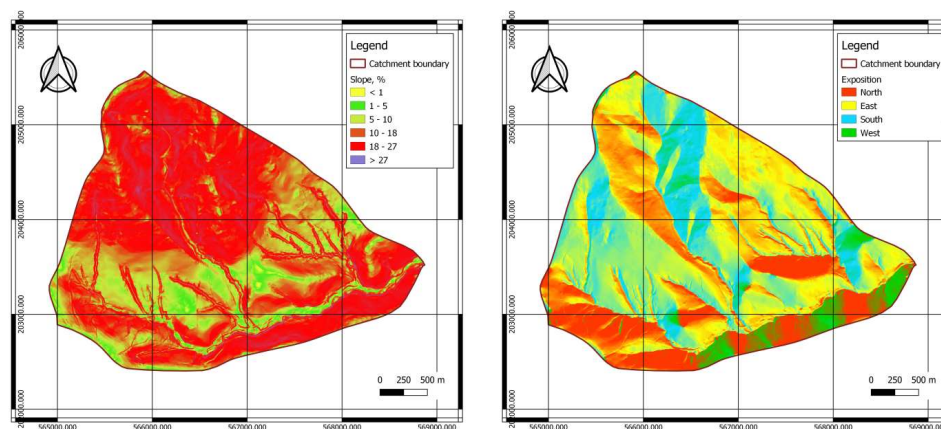
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126 **2. Methods**

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 localisationof sampling points and land use is presented in Figure 1. Slopes and exposition are shown in Figures 2. Water samples were taken in 1 dm^3 volume containers once a month to determinethe 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

Figure 2. Slope and exposition of the Smugawka stream catchment

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 takenfor 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 madeusingthe tachymeter TOPCON GTS-226. Five cross-sections of the bed channel slopes, from 0.79 to 2.18%, were localisedalong 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

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158   measurement point, 15 cobbles were taken, and their mean axis „b" was measured. The grain size

159   distribution curves were drafted, and their characteristic diameters: d_{min}, d_{30}, d_{50}, d_{70}, and d_{max} and

160   competent diameter: d_m were determined. Measuring points were located crosswise channel in a

161   distance of 0.5 m.

162   Hydrodynamic measurements were carried out at the same points as the granular ones.

163   Measurements were made using a hydrometric current meter VALEPORT Model 801 Flat EM

164   flow meter. This device allows the measurement of mean flow velocity in assigned time intervals.

165   It also measures instantaneous velocity and filling in the stream channel. The measurement scope

166   of the device is 5.0 m·s⁻¹, and exactness ± 0.001 m·s⁻¹. Through this device, mean velocity V_{mean} on

167   the height 0.4 m above the bottom, maximum velocity V_{max}, and instantaneous velocity V

168   measured just above the bottom, allowed calculation of dynamic velocity based on charts of

169   velocity distribution above the bottom in a semi-logarithmic system (Gordon et al., 2007):

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

170   where:

171   a = coefficient of straight line slope

172   V = f(h), taking an equation form of y = ax + b (x = height above bottom, the measurement of

173   velocity was carried out, b = free term of the equation).

174   Knowing dynamic velocity, shear stress was calculated as follows:

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

175   where:

176   ρ = water density (kg · m⁻³)

177

178   The Reynolds number (mean, maximum, and grain) was used to determine the type of

179   flow pattern as laminar or turbulent. Further, the Freud number (mean and maximum) is a

180   measurement of bulk flow characteristics. These were respectfully calculated using the following

181   equations:

$$Re_{śr} = \frac{V_{śr} \cdot h}{\upsilon}$$

$$Re_{max} = \frac{V_{max} \cdot h}{\upsilon}$$

$$Re_{dm} = \frac{V_* \cdot d_m}{\upsilon}$$

$$Fr_{śr} = \frac{V_{śr}}{\sqrt{gh}}$$

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

182   where:

183   h = filling (m),

184   g = acceleration of gravity (m·s^{-2}),

185   υ= kinematic coefficient of water viscosity, calculated from the equation:

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

186   where:

187   t = water temperature(0°C)

188

189   In this study, hydrodynamic indicators allowed the calculation of the distance of full mix

190   in surface water, used in the analysis of spatial autoregression. Dynamic velocity (u) in the stream

191   was calculated using the following equation (Loga, 2016) :

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

192   where:

193   h = mean height of water (m),

194   g = acceleration of gravity (m·s^{-2}),

195   S = slope of channel bottom (%).

196

197   There is a risk connected to the negative influence of the frequency of measurements.

198   In short periods of freshets, some part of the yearly sediment load cannot be observed. Therefore,

199   the following equation was used to present a moment in which the mix of material in water

200   occurs (a load of total suspended sediment and physico-chemical composition). That is some

201   quantitative representativeness of transported material. In addition, the turbulent diffusion

202   coefficient ($D_{t,y}$) was calculated for transverse mix in the particular years in a so-called natural

203   channel (Loga 2016):

$$D_{t,y} = 0{,}6\,h \cdot u \quad [m^2 \cdot s^{-1}],$$

204   where:

205   h = mean height (m),

206   u = dynamic velocity ($m \cdot s^{-1}$).

207

2.3. Determination of physico-chemical properties of surface water

209   In the experimental area, the physico-chemical properties of surface water were measured.

210   The reaction pH of water was examined using the potentiometric method with a CP-104

211   ELMETRON equipped with a combined electrode. Specific electrical conductivity, expressed in

212    $dS \cdot m^{-1}$, was measured with a conductometer Elmetron CC-101. The concentration of dissolved

213   oxygen in ($mg \cdot dm^{-3}$) and the degree of water saturation by oxygen were determined using the

214   electrochemical method using an oxygen-meter Elmetron CO-411. Further, the water temperature

215   (°C) was measured by a digital thermometer built in waterproof oxygen-meter CO-411. The total

216   content of dissolved substances in ppm was calculated by means of a digital TDS device. In the

217   laboratory, the following physico-chemical properties of water were determined using the

218   UNICAM SOLAAR 969 atomic absorption spectrophotometer: Ca^{2+}, Na^+, K^+, Mg^{2+}, Fe_{tot}, and

219   manganese Mn^{2+}.

220   Moreover, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, $P\text{-}PO_4^{3-}$, and Cl^- were determined by the colorimetric

221   flow-injection method on the computer-controlled FIA Star 5000 apparatus of the FOSS

222   firm. Sulphates (SO_4^{2-}) were determined gravimetrically. Biological Oxygen Demand (BOD_5) was

223   analysed by the Winkler method: water samples were treated with manganese sulfate $MnSO_4$,

224   alkaline potassium iodide KI, and sulfuric acid H_2SO_4, followed by titration with sodium

225   thiosulfate $Na_2S_2O_3$. The chemical oxygen demand (ChZT-Mn) was calculated by the

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226 permanganate method by heating the water sample with $KMnO_4$ potassium permanganate in an

227 acidic environment, and the amount of consumed oxygen was determined by titration.

228   During subsequent readings of water levels, samples were taken from the stream by the

229 bathometric method (containers with a volume of 1 dm^3). The concentration of total suspended

230 solidswas determined by the gravimetric method after drying using tared filters with an accuracy

231 of ± 0.0005 g. The dry residue (sum of mineral particles from the transported samples) from the

232 collected material was filtered to determine the different composite concentrations. The ionic

233 forms of zinc (Zn^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}) and copper (Cu^{2+}) were determined once per

234 quarter with the coulometric method using an electrochemical analyser for the determination of

235 trace amounts of heavy metals (EcaFlow 150 GLP by PolEko). The nephelometric-laser method

236 was also used to assess the degree of water turbidity using a Hach Lange 2100QS nephelometer

237 (turbidimeter) in the range of 0–2000 FNU, per the international standard (Nephelometric

238 Turbidity Unit; NTU).

239 **2.4.Data reduction to a spatial model and statistical analysis**

240   Before the analyses were performed, the asymptotic distribution for the χ^2 Jarque-Ber (JB)

241 test statistic was studied, which takes kurtosis and skewness into account (Jarque and Bera,

242 1987). The data was grouped in ascending order by the Anderson-Darling concordance test,

243 determined by the empirical distribution, and the normalisation for the mean and standard

244 deviation was calculated (Stephens, 1986). The test determines a weighted Cramér-von Mises

245 distance between the empirical (Fn) and theoretical (F) cumulative distribution factors, with

246 weights corresponding to the reciprocal of the empirical cumulative distribution (Anderson and

247 Darling, 1954). The Shapiro-Wilk test, based on positional statistics, was also used. The keynote

248 of this analysis is collinearity between the empirical quantile (i.e., the ordinal statistic) and the

249 theoretical quantile (i.e., the expected value of the ordinal statistic) along the y = x straight line

250 (Shapiro and Wilk, 1965).

251   The homogeneity of variance was analysed by Levene'stest (Levene, 1960). To reduce the

252 number of variables, the Principal Component Analysis (PCA) was used, presenting the

253 relationships between significant physico-chemical properties in the surface water of the stream

254 running near arable land, grasslands, and forests. Statistical significance for the matrix of

255 correlation coefficients and the strength of the relationship between the variables were assessed

256 with the Barlett sphericity test (Bartlett, 1950; Williams et al., 2010). Partial correlations with

257 bivariate correlation coefficients were performed using the Keiser-Mayer-Olkin coefficient

258 (KMO), determining the accuracy of selecting variables for the tested model. Adequate variables

259 have a KMO coefficient> 0.5 (MacCallum, 1983; Hair et al., 1995; Tabachnick and Fidell, 2007;

260 Szüle 2016).

261   In order to show the relationship between the tested physico-chemical properties of

262 surface water, values for eigenvectors were given, approximating the influence of primary

263 variables on the main component. The most significant variables were interpreted through factor

264 loadings, which also reflect the influence of individual variables on a given principal

265 component.The study useda correlation matrix, and the factor loadings were interpreted as

266 correlation coefficients between the original variables and the next analysed main component.

267 Following the PCA method, the variance size for each computed component and the so-called

268 primary variableswere indicated. The most important variables were selected for further data

269 processing based on the value of factor loadings. The analysis was performed in PQ Stat

270 Software, version 1.6.6.

271   Spatial autoregression is a tool for predicting features in a linear system. The analysis

272 aimed to determine the factors that influence the temporal changes in the physico-

273 chemicalcomposition ofsurface water. Therefore, the study used a spatial autoregression model

274 with a lagged response, facilitating the study of the relationship between the distance of complete

275 mixing and physico-chemical features randomly distributed in the water column. The general

276 form of spatial autoregression is given by the formula (Rangel et al., 2010):

$$Y = \rho \cdot Wy + X\beta + \varepsilon$$

277 where:

278 Y = vector ($N \cdot 1$) of the explained spatial process through a responsive (explained) variable,

279 W_y = weight matrix of the vicinity of the examined variables in different locations ($N \cdot N$ matrix

280 of spatial weights),

281 ρ = spatial autoregression parameter reflecting the strength of the relationship between the

282 variables (spatial interaction parameter),

283 X = matrix ($N \cdot K$) of explanatory processes,

284 β = vector ($K \cdot 1$) of structural indices,

285 ε = vector (N · 1) of the random term (estimation error and spatial noise not described by the

286 model; random effect).

287

288   The spatial autoregression model was usedto show the relationship between the variables

289 distributed in space over the courseof a measurement series for homogeneous areas and to

290 facilitate the analysis of the variables, especially with water flows greater than average. The

291 transverse turbulence diffusion coefficient was assumed as the dependent variable, and surface

292 water's physico-chemical features were considered independent variables. The simultaneous

293 autoregressive model (SAR), with a system of lagged predictors (Rangel et al., 2010), was used

294 to calculate the spatial dependencies:

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

295 where:

296 C = vector of the explained spatial process through a responsive (dependent) variable,

297 W = weight matrix of the vicinity of the examined variables in different locations matrix (N • N)

298 of spatial weights,

299 σ^2 = residual variance between observations,

300 ρ = spatial autoregression parameter reflecting the strength of the relationship between the

301 variables (spatial interaction parameter),

302 I = linear transformation (matrix of N ·N-type) of the dependent variable.

303   The autoregression analysis documented the overarching variables for each type of land

304 use, combining the physico-chemical characteristics of the surface water. The calculations were

305 made in the SAM 1.6.6 software.

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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_{og} 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

Salinity indicators	Unit	Measuring point		
		Surface waterrunoff from arable land	Surface water runoff from grassland	Surface waterrunoff from forests
Na^+	[mg·dm^{-3}]	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
SO_4^{2-}		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
*CZSR		101–147	78–199	148–178
Electricalconductivity	[µS·cm^{-1}]	156–240	247–350	148–256

*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

Indicators of metal concentrations	Unit	Measuring point		
		Surface waterrunoff from arable land	Surface water runoff from grassland	Surface waterrunoff from forests
Zn^{2+}	[µg·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	0,01–1,90	0,01–1,50
Cu^{2+}		1,51–3,04	0,91–1,50	0,01–0,70

Fe_{og}	$[mg \cdot dm^{-3}]$	0,53–0,91	0,03–1,04	0,1–0,81
Mn^{2+}		0,12–0,18	0,06–0,09	0,09–0,10

332

333 Table 3. Factor loadings obtained from principal component analysis (PCA) for the studied
334 physicochemical characteristics from surface water samples taken at arable land

335

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
K^+	-0,72	0,60	-0,10	0,05	-0,06	0,46
pH	-0,13	0,35	-0,78	-0,06	0,49	-0,11
$N-NO_2$	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
Total suspendedsolids	-0,15	0,24	0,78	-0,21	0,52	0,04

336

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

339

| Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Temperature of water	0,82	0,76	-0,60	0,10	-0,10	0,12
Total suspendedsolids	-0,63	0,58	-0,62	-0,17	0,08	-0,14
$Fe_{og.}$	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

340

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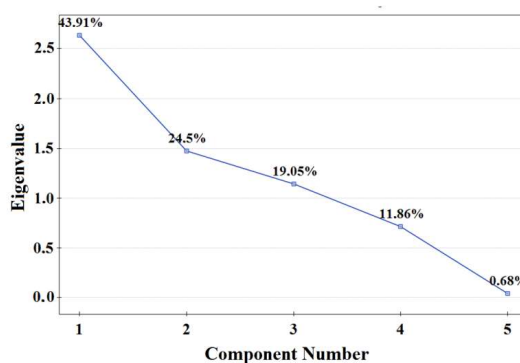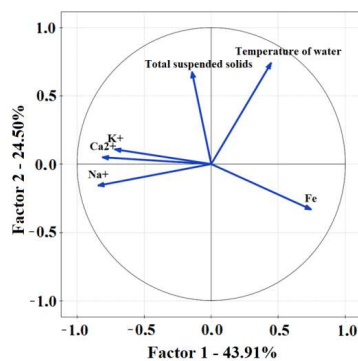342 physicochemical characteristics from surface water samples taken in forests

343

| Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Temperature of water	0,84	0,86	-0,28	0,41	-0,03	0,32
ChZT-Mn	0,92	0,87	-0,51	0,21	0,33	0,08
Na^+	0,97	-0,78	-0,48	-0,44	0,12	0,23
Conductance	0,23	-0,35	-0,30	0,21	0,53	-0,59
BZT_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
Dissolvedoxygen	-0,56	-0,81	0,15	0,35	0,33	0,65
$Fe_{og.}$	-0,51	0,84	-0,13	-0,01	-0,17	0,10

344
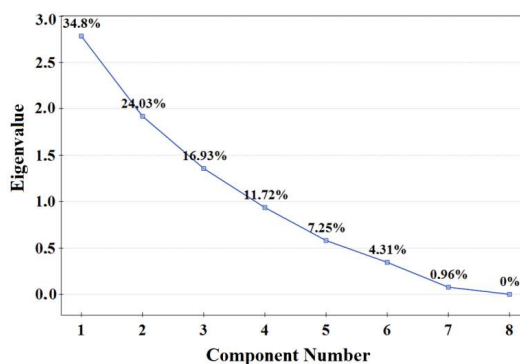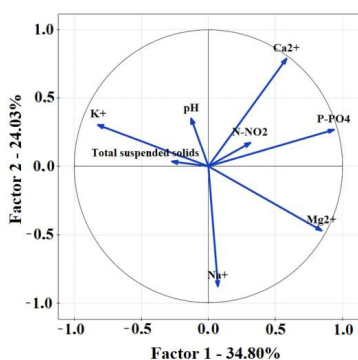
a) PCA analysis for physicochemical characteristics for samples collected in surface water near arable land

b) Scree plot for samples taken in surface water near arable land

c) PCA analysis for physicochemical characteristics for samples collected in surface water from grasslands

d) Scree plot for sample taken in surface water from grasslands
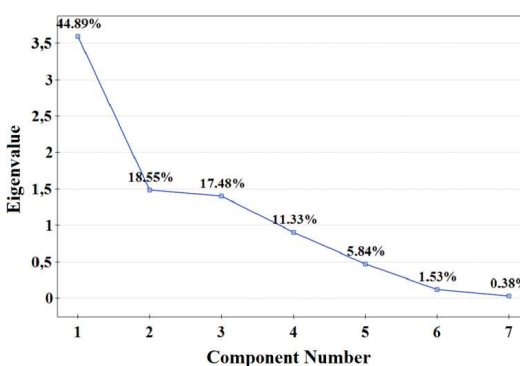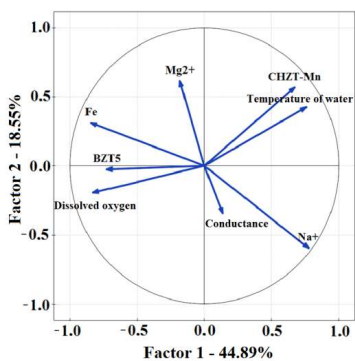
e) PCA analysis for physicochemical characteristics for samples collected in surface water near forests

f) Scree plot for samples taken in surface water near forests

345
346 Figure 3. PCA analysis and scree plots for physicochemical characteristics for samples taken in surface water: arable
347 land (a, b), grassland (c, d), forest (e, f)

348 Table 6. Range of average values of soil material loss in the form of total suspended solids
349   throughout the study period depending on the land use of the Smugawka catchment area
350

Index of erodedsoilmaterial	Unit	Arable land	Grasslands	Forests
Circadianconcentration of totalsuspendedsolids	[mg·dm^{-3}]	4,94–18,34	0,93–9,92	0,71–5,92
Total suspendedsolidsload	[Mg]	0,05–0,52	0,05–0,34	0,02–0,23
Annualtotalsuspendedsolidsload	[Mg·rok^{-1}]	18,69–190,27	19,65–126,95	7,38–53,78

351
352

3.2. Data reduction and spatial model

354   Spatial autoregression was used to reveal the relationships between the studied variables.
355 Relationships with some physico-chemical features of surface water were detected in the model.
356 The SAR equation for the entire catchment area showed that $P-PO_4^{3-}$, $N-NO_2^-$, TDS, and the
357 concentrations Na^+, Mg^{2+}, Ca^{2+} and Mn^{2+} (Table7) are appropriate predictors for judging the
358 distance of complete mixing. In general, the autoregressive modelling can be summed up by the
359 fact that the few relationships for the physico-chemicalcharacteristics of the surface water with
360 the transverse turbulence diffusion coefficient of the flysch stream were significant ($p < 0.05$). In
361 the spatial autoregression model divided into variants of use, statistically significant relationships
362 were found for K^+ andP-PO_4^3 in surface water ofarable land and forFe_{og} in surface water at
363 grassland. No significant relationships were found at the measurement points in surface water
364 near forests (Table 8). In the spatial autoregression model for the whole with the explanatory
365 variable (the distance of complete mixing)detected the spatial dependencies for $P-PO_4^{3-}$, $N-NO_2^-$,
366 Mn^{2+}, TDS, Na^+, Mg^{2+}, Ca^{2+}, and Mn^{2+} (Table 9).

367 Table 7. The results of the spatialautoregression model of the SAR type for the entirecatchment.
368 The - distance of fullmixing was chosen as the explanatoryvariable,
369 and physicochemicalcharacteristics of surfacewaterweretaken as predictors of the model
370

Physicochemicalcharacteristics	OLS ratio	SAR ratio	Standard error
Physicalcharacteristics			
Total suspendedsolids	-1,22	0,36	0,67
Temperature	10,41	16,28	5,90
Oxygenindicators			
Oxygenconcentration	-0,46	-0,23	0,19
Degree of oxygensaturation	-0,03	-0,04	0,01
BZT$_5$	-1,19	-1,77	0,37
ChZT-Mn	6,46	4,55	1,09
Biogenicindicators			
$P-PO_4^{3-}$	12,95	11,72	1,47

$N-NH_4^+$	11,40	16,2	1,78
$N-NO_3^-$	-0,03	4,88	0,36
$N-NO_2^-$	0,64	14,83	2,71
Salinityindicators			
*CZSR	5,70	8,53	0,27
SO_4^{2-}	-0,31	0,18	0,14
Cl^-	0,06	0, 71	0,02
Na^+	0,49	-0,61	0,17
K^+	2,92	10,95	1,06
Mg^{2+}	-0,46	6,32	0,82
Ca^{2+}	-2,93	-4,41	1,41
Electricalconductivity	-1,19	4,83	-1,72
Metals, including heavy metals			
Zn^{2+}	-0,14	0,14	0,02
Pb^{2+}	-0,62	3,12	0,09
Cd^{2+}	-0,03	4,89	0,83
Cu^{2+}	0,98	3,12	0,56
Fe_{og}	6,46	12,81	1, 37
Mn^{2+}	17,46	11,27	1,45

371   *CZSR – Total content of dissolvedsubstances

372

373   Table 8. Results of the spatial autoregression model of the SAR type (The transverse turbulencje
374   diffusion coefficient was used as the dependent variable, and the most import ant
375   physicochemical characteristics of surface water selected on the basis of principal component
376   analysis for each use variant wereused as predictors)

377

Variable	SAR ratio	Standard factor	Standard error	t	p
Surveypoints in the watercoursenext 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
Total suspended solids	2,56	0,32	0,34	3,72	10,03
Measurementpoints in the watercoursenext to grasslands					
The constant of the equation	1,19	-	1,79	0,66	1,45
Temperature of water	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
$Fe_{og.}$	-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
Temperature of	-2,96	-0,81	0,93	-1,58	0,15

water					
Measurementpoints in the watercoursenear the forests					
The constant of the equation	-	-0,90	0,24	-3,49	0,01
Temperature of water	-0,03	-0,03	0,07	-0,45	0,66
ChZT-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
BZT_5	0,008	0,009	0,22	0,03	0,97
Mg^{2+}	-0,20	-0,13	0,09	-2,12	0,07
Dissolved oxygen	-0,46	0,003	0,004	0,21	0,99
$Fe_{og.}$	-0,03	0,19	0,06	0,15	0,24

378

379 **4. Discussion**

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

384

385 **4.1.Influence of hydrodynamic parameters on the ionic composition of surface water**

386   Determining the level of micro-pollutants, especially heavy metals, is essential for
387 monitoring areas exposed to contamination in long-term studies. The ionic composition of
388 surface water determines the intensity and direction of the chemical denudation process
389 conditioned by lithology (Kim et al., 2012; Ziadat et al., 2015). It also determines the quality
390 ofthe surface watercourses inventory and the hydrographic network's operation (Trivedi, 2010).
391 Through PCA, the parent variables for each type of land usewere documented. For further spatial
392 analysis, the physico-chemical features of surface water with the highest factor loadings were
393 selected. A high negative correlation was only calculated in the first PCA factor for the
394 concentration of K^+ and in the second PCA factor for concentrations of Mg^{2+} and Na^+. This may
395 be because these ions runoff from the catchment area.
396   Water self-purification processes are essential in the assessment and protection process
397 (Moore and Langner, 2012; Halecki, 2015). Identifying the sources of nitrate pollution is one of
398 the priority actions (Bu et al., 2017) because anthropogenic pollutants are different in surface
399 water and may change seasonally (Xu et al., 2014; Hu et al., 2015). As for arable land, K^+

400   showed a negative relationship with the first factor of the PCA. A negative relationship was also

401   found for Na^+. This may mean that their concentration has been systematically decreasing. In

402   water samples collected near forested areas, a high factor load was calculated for the water

403   temperature and concentration of ChZT-Mn. They were also characterised by the highest

404   variance for the factor axes in all tested surface water samples and the highest factor loadings.

405   The water temperature could play a significant role in the concentration of ions dissolved in the

406   water of the flysch stream.

407   The state when the material was mixed in the water was considered in processing the

408   results. For this purpose, the transverse turbulence diffusion index was calculated to determine

409   transport intensity. The highest value of transport intensity, 1.02, was recorded in the riverbed of

410   the stream adjacent to arable land. According to PCA, the most important chemical parameter

411   associated with this land use typeis Ca^{2+} and $P-PO_4^{3-}$. This is an interesting result because, when

412   assessing the impact of arable lands on the physico-chemical quality of surface water, particular

413   attention should be paid to the supply of phosphates and nitrates (Halecki et al., 2017). The

414   quantitative share of ions depends on the type of rocks and the physical properties of the

415   substrate, especially the infiltration coefficient, and for clastic weathering, on their mechanical

416   composition (Szostakiewicz-Hołownia, 2012). This aspect is of particular concernfor flysch

417   catchments built of the Magura and Sub-Magura layers (Starkel, 2006; Starkelet. al., 2007).

418   The diversified rock bottom relief impacts high water turbulence and,thus, the transport of

419   weathered loads (Priess et al., 2015; Szatten, 2016). Stationary tests with a high measurement

420   frequency are then performed to determine the relationship between flooding and suspension

421   concentration in particular years (Huan, 2011). On the other hand, in the Beskidy catchments,

422   which include the variability of the transported clastic weathered water, quantitative relationships

423   between hydrological parameters and their supply against the background of water erosion have

424   been shown (Brański, 1975; Brański, 1990). The most significant distance of full mixing was

425   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

428   The intensity of transport of chemical compounds depends on turbulence and dispersion

429   due to spatial differentiation of the flow velocity. Turbulent vortices create a locally

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430   inhomogeneous and non-stationary velocity field, accelerating mixing (Loga, 2016). This

431   hydrodynamic parameter was calculated for each cross-section on each section of the stream to

432   approximate the transport mechanism of the investigated ion forms and other materials dissolved

433   in water. The Reynolds number reached the highest values in the stream bed adjacent to the

434   permanent grassland, similar to the tangential stress. The bottom sediment ranged from 32 to 41

435   mm in the entire catchment area. It was observed that material with more significant fractions is

436   collected at the flysch bed surrounded by permanent grasslands.

4.3. Model of developed techniques of spatial autoregression

438   Ions in water may be related to land use, and the detection of heavy metals in surface

439   water determines its economic value (Fu et al., 2014; Liao et al., 2016) and the health of the

440   inhabitants of the surrounding areas, especially in terms of therapeutic properties of Carpathian

441   rivers (Operacz et al., 2018). The spatial pattern and correlations between the variables in the

442   entire catchment area have been shown based on the spatial autoregression model, empirical

443   equations, and multivariate analysis. Furthermore, the research confirms that in a small flysch

444   catchment, it is possible to balance the material leached from the soil because the chemical

445   denudation process shows a relationship with the concentration of dissolved electrolytes in the

446   flysch stream (Halecki et al., 2019).

447   The model of developed techniques of spatial autoregression also enabled the inclusion of

448   spatial analysis in the extrapolation of hydrochemical data and the intensity of erosion processes

449   during multiple measurement series. The technique of spatial autoregression was chosen for

450   itsmore effective presentation of these relationships and was used to verify the analysed data in a

451   spatial system. The applied analysis helped to check whether the variables are affected by

452   different land use modifications. The independent variables were the physico-chemicalfeatures of

453   surface water at different land use variants. Spatial SAR model resultsshowed that $P-PO_4^{3-}$ and

454   K^+ ionsare leached mainlyfrom soil in arable lands.Moreover, a statistically significant

455   relationship between K^+ and Fe_{og} cations was observed in surface water flowing from grasslands.

456   However, the SAR model of spatial autoregression did not detect statistically significant

457   differences inthe ionic composition of surface water flowing out of the forests. The land use

458   could have contributed to the differences generated by the model. Therefore, the methods used to

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459 evaluate the surface washout and soil erosion studies on used slopes, especially for agricultural

460 purposes, should be improved (Bakker et al., 2008; Smolska et al., 2010).

461   The spatial autoregression model for the whole with the explanatory variable (the distance

462 of full mixing) detected the spatial dependencies for $P-PO_4^{3-}$, Mn^{2+}, $N-NO_2^-$, TDS, Na^+, Mg^{2+},

463 Ca^{2+} and Mn^{2+}. Since different hydraulic conditions were detected for each variant of land use, it

464 should be passed that the direction of the catchment development impacts the physico-chemical

465 quality of surface water.

466 **4.4. Recommendations for hydraulic tests and physico-chemical assessment of surface water**

467   Forecasting the physico-chemical quality of surface water and determining the

468 relationships between the concentration of metals, including heavy metals, requires the

469 determination of decisive indicators. Spatial autoregression is currently one of the most effective

470 methods of water quality forecasting for various sources of pollution (Yang et al., 2017). The

471 analysis of spatial autoregression primarily showed the spatio-temporal relationships at various

472 measuring points. Furthermore, including spatial analysis to determine many pollutants flowing

473 into the waters allows for solving technical problems related to surface washout and proper use of

474 arable land in the catchment area.

475   For spatial studies, the appropriate number of samples plays a crucialrole in building a

476 spatial model (Vallejos and Osorio 2014), especially in work related to the physico-chemical

477 quality of surface water (Mahjouri and Kerachian, 2011). This means that the assessment of

478 surface water quality features depends on the spatial scale. Therefore, the evaluation of surface

479 water quality should be combined with a spatial analysis (Dash et al., 2015). The amount of

480 leached total suspended solids delivered during water erosion is a value recorded during short-

481 term flooding rainfalls. So, based on the hydrochemical properties, it is possible to determine

482 surface water quality (Misaghi et al., 2017). Only relevant parameters should be considered in

483 assessing the physico-chemical quality of surface water in agricultural areas and grasslands. It is

484 vitalto choose a method consistent with the sample size (Griffith, 2005) in order to formulate a

485 dynamic model (Finley et al., 2012) or to calculate water quality indices (Yadav et al., 2015;

486 Naubi et al., 2016). Thus, the optimisation of spatial sampling is crucial (Hu and Wang, 2011) in

487 monitoring surface water pollution (Wu et al., 2005). The conclusions from this dissertation will

488 find practical application in isolating the primaryfactors favouring water erosion in streams with

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489   larger catchment areas. In addition, recognising the effects of water erosion will be necessaryfor

490   evaluating the surface delivery of the material in further scientific research. The continuation of

491   scientific work in this field should focus on investigating the relationship between individual

492   washings and the concentration of material in the valleys of streams and rivers.

493   **5. Conclusions**

494   The effect of thiswork is important for determining the sources of diffuse pollution

495   flowing to the stream from agricultural areas in the periodic assessment of the physico-chemical

496   quality of surface water. The research thread undertaken in the dissertation will help determine

497   the intensity of water erosion and assess the sources of surface water supply. The assessment of

498   this phenomenon should aim at explaining the size of the load calculated into the delivery zones

499   of the transported material to the flysch stream and erosive factors, including susceptibility to

500   leaching. Some results will undoubtedly be used to create models of erosive feeding of alluvial

501   deposits from weathered flysch or surface wash, depending on the material delivery in the

502   catchment area. The results related to land use and its impact on the transport of chemical

503   compounds may be helpful in environmental management in mountain areas and chemical

504   monitoring in determining the course of erosion processes. Over the years, assessment of land use

505   changes may be of valuefor local residents involved in agriculture. Moreover, the assessment of

506   the short-term change in the concentration of the physico-chemical composition in the flysch

507   riverbed will be valuable for scientific purposes to develop a plan for the management and

508   elimination of pollutants resulting from anthropogenic pressure.

509   **Highlights:**

510   1. The physico-chemical composition of the flysch stream depends on the hydraulic
511   conditions.

512   2. The catchment use determines the intensity and direction of the chemical denudation
513   process.

514   3. The turbulent diffusion coefficient may influence the dissolved electrolytes in the
515   stream.

516   4. The spatial autoregression model detected relationships for nutrients leached from
517   arable land.

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5. The assessment of the physico-chemical properties of surface water depends on the spatial scale.

Financial Support

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