Original Research

Determinants of Seasonal Changes in Streamwater Chemistry in Small Catchments with Different Land Use: Case Study from Poland's Carpathian Foothills

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Abstract

Our paper aims at identifying factors that determine seasonal changes in streamwater chemistry in three catchments with different land use (woodland, agricultural, mixed-use) in the Carpathian Foothills in southern Poland. The study involved weekly and biweekly water sampling in the 2003 and 2004 hydrological years and the analysis of specific conductivity (SC), pH, main ions, and nutrients. R-mode factor analysis was used to identify four factors: (i) streamflow, (ii) climate seasonality, (iii) water circulation, and (iv) nitrification processes.

Despite the fact that the same environmental factors were identified in all three catchments, some factors produce a different type of ion response in different types of catchments. The streamflow factor produces the same changes in geologically controlled parameters (SC, main ions) in all catchments but different changes in nutrient concentrations in the woodland and agricultural catchments. In the woodland catchment, nutrients come primarily from diffuse sources (soil flushing), while in the agricultural catchment, nutrients come primarily from point sources (sewage) as result of unregulated wastewater management. The climate factor primarily controls the concentrations of nutrients. High temperatures during the vegetation season usually correlate with increases in nutrient concentrations, especially that of PO_4^{3-}. This atypical phenomenon is seldom reported in the literature, especially in relation to woodland catchments. The third factor is associated with water circulation in the catchment under different hydrological conditions – during flood events and during low-flow periods. The fourth factor is most likely associated with nitrification processes.

Keywords: Carpathian Foothills, human impact, land use, nutrients, seasonal dynamics

Introduction

In a fluvial environment, fluctuations in stream discharge are an important factor driving seasonal changes in water chemistry, which may be related to seasonal changes in the hydrological flow paths of the chemical compounds that contribute to streamflow [1-4]. Cameron [2] measured seasonal changes in the Cl^- and Na^+ concentration in the Fraser River in British Columbia, Canada, which were related to seasonal variations in the dilution of the year-round stable supply of ions from pulp mills. Muscutt and Withers [5], in their study of 98 polluted rivers across

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England and Wales, (including the River Thames), found higher PO_4^{3-} concentrations during summer, which corresponded to smaller discharges, and lower PO_4^{3-} concentrations during winter when discharges were larger. The pattern observed was consistent with the dilution of PO_4^{3-} derived from point sources. Similar conclusions about possible causes of seasonal concentration of PO_4^{3-} in rivers were derived by Edwards [6] and Rinella and Janet [7]. Contrastingly, research by Pionke et al. [8] located in a hilly farmed catchment in Pennsylvania, observed increasing PO_4^{3-} concentrations in accordance with increasing discharges, which peaked during summer peak flows. The source of PO_4^{3-} was surface runoff (diffuse source), which originated primarily from relatively small areas (variable source areas) located near the stream.

Seasonal changes in the concentration of nutrients may strongly depend on the biological activity of a catchment. Numerous researchers have documented seasonal variations of NO_3^- concentrations with lower concentrations observed during the vegetation growth season than outside of this period [3, 9-19]. However, in comparison, other researchers, including Taylor et al. [20] and Feller and Kimmins [21], found no relationship between vegetation growth and NO_3^- concentrations.

Another process determining the seasonal variations in the streamwater chemistry is a change in groundwater chemistry arising from the seasonal variations in temperature and soil pCO_2 that affect weathering rates [22]. Sullivan and Drever [19] observed heightened ion concentrations in the small catchment of Peru Creek in the Rocky Mountains during the springtime thaws. These changes were attributed to the flushing of accumulated weathering products from the upper levels of the operational Pennsylvania mines.

In addition to fluctuations in discharge, changes in catchment vegetation amounts and the influence of groundwater, atmospheric composition can also affect fluvial chemistry. Lynch and Corbett [23] demonstrated that atmospheric deposition of sulphate affects streamwater chemistry, even if changes are not always synchronized. The catchments investigated showed that sulphate deposition occurred during dry summer seasons and flushing during subsequent wet spring seasons. Such episodic behavior of SO_4^{2-} strongly influenced by antecedent conditions was found by Evans et al. [24].

This research on small catchments was aimed at identifying the drivers of seasonal chemistry changes in streams situated within the Carpathian Foothills of Poland.

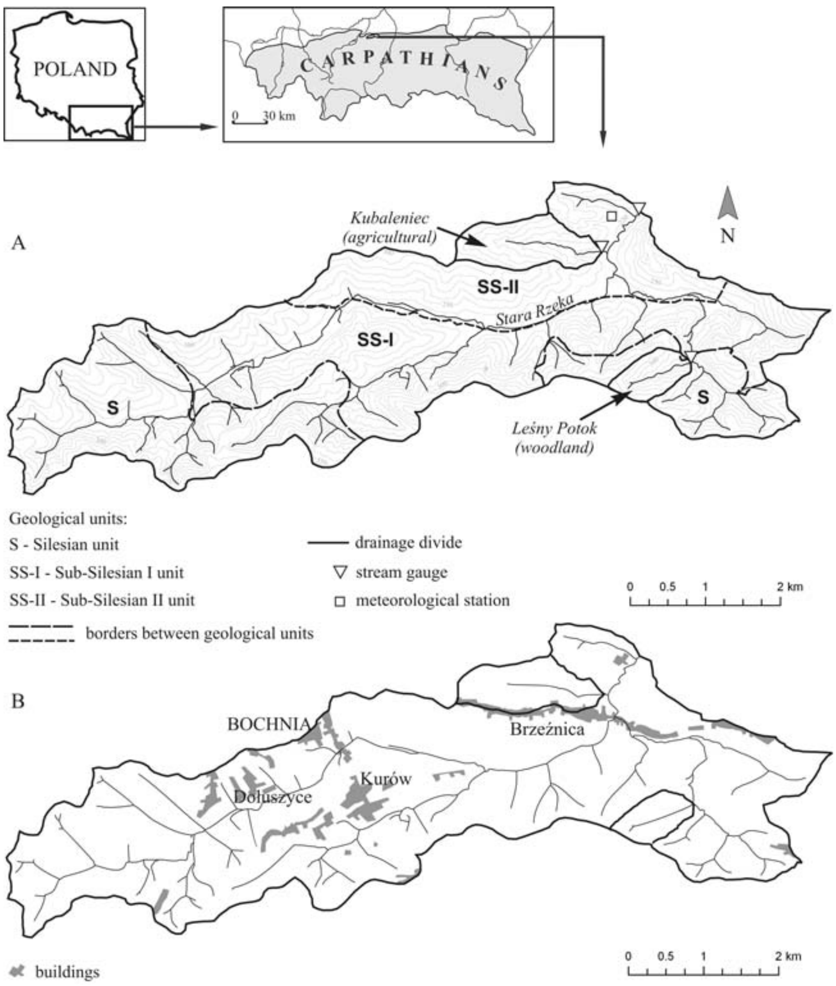

Fig. 1. Study area: A – hypsometry and geology, B – villages and built-up areas.

Table 1. Research area description.

Characteristic		Unit	Stara Rzeka (mixed)	Kubaleniec (agricultural)	Leśny Potok (woodland)
	Area	km^2	22.22	1.03	0.48
	Mean elevation	m a s l	278.6	260.9	304.6
	Mean slope	º	7.65	6.22	9.99
Tectonic units	Silesian	%	36.87	0.00	98.51
	Sub-Silesian I		41.34	0.00	1.49
	Sub-Silesian II		21.79	100.00	0.00
Land use	Forests		41.86	0.54	99.37
	Arable land		36.25	69.29	0.16
	Orchards		2.45	5.07	0.00
	Meadows and pastures		14.92	20.35	0.13
	Rural built-up areas		4.52	4.75	0.34

This region, as is the case of other parts of Central and Eastern Europe, is experiencing significant economic transformation that manifests itself in terms of land use and land management, especially in agricultural areas. Among the many changes that have affected rural areas, one important change, from an environmental point of view, has been the installation of water supply systems with no sewage networks and wastewater treatment plants. This has led to an increase in water use and a consequent rise in the quantity of wastewater produced. With no sewage system in place, rural wastewater ends up in rivers and other natural bodies of water.

One purpose of this paper is to compare the factors that affect water chemistry changes in agricultural catchments altered additionally by people who do not yet have a system of wastewater management in place as well as in a natural woodland catchment. While a number of papers describe the effect of land use and land management on ion concentrations [e.g. 25], it is interesting to learn how anthropogenic factors shape changes in streamwater chemistry during the course of a year. The documentation of such man-made changes – before a treatment plant is built – will have a practical dimension as it will help to assess the effectiveness of water treatment efforts once a wastewater treatment plant and a sewage system are constructed in the catchment of interest. The purpose of this paper is to answer the following questions:

1. Which factors play the most important role in determining streamwater chemistry?
2. What is the significance of anthropogenic factors in determining the streamwater chemistry?

The paper is based on data collected in three small Carpathian catchments, but we expect similar environmental and anthropogenic processes (e.g. hydrological regime, raw sewage discharge) to affect changes in streamwater chemical composition in other regions of Central and Eastern Europe.

Study Area

The research was conducted in the northern, marginal portion of the Carpathian Foothills in southeastern Poland. The Stara Rzeka catchment, located within these foothills, constitutes mixed land use from which the two sub-catchments are defined: Leśny Potok (woodland) and Kubaleniec (agricultural) (Fig. 1). The study area spans two mantle units, the Silesian and Sub-Silesian (I and II), consisting of Cretaceous and Tertiary (Miocene) *flysch* formations. The Silesian unit consists primarily of sandstones and shales. The Sub-Silesian I unit comprises sandstones, claystones, shales, clays, and conglomerates, while Sub-Silesian II comprises claystones, marly clays, gypsum, sandstones, and a salt series [26]. The entire area of the catchment is lined with a thick layer of dusty loess-like formations, up to more than ten metres thick with their *Haplic Luvisols*, *Stagnic Luvisols*, *Cambic Luvisols*, and *Eutric Gleysols* [27].

Land use in the Stara Rzeka catchment (22.22 km^2) is categorized as 42% woodland, 36% arable land, and 15% meadows and pastures (Table 1). A number of villages in the catchment exert a significant influence on the quality of surface and ground water (Fig. 1). The local communities benefit from water mains or individual water abstraction sources, such as wells and springs. However, there is no central sewage system, which results in only a small proportion (less than 10%) of waste water being adequately treated. Most household and farm wastewater is released into roadside ditches and channels, which then drain into streams. According to Pietrzak [28], the amount of untreated wastewater released annually by households in the Stara Rzeka catchment could form a layer of 6-7 mm. Agricultural land is routinely fertilized with solid manure, and meadows located in flat-bottomed valleys are fertilized using liquid manure.

Table 2. Hydrological (mean values) and hydrochemical (median values) characteristics of streamwater in the studied catchments. Data from 2003 and 2004 hydrological years.

	Hydrological parameters		Hydrochemical parameters													
	Discharge	Specific runoff	SC	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	NH_4^+	NO_2^-	NO_3^-	PO_4^{3-}
	[$dm^3 \cdot s^{-1}$]	[$dm^3 \cdot s^{-1} \cdot km^{-2}$]	[$\mu S \cdot cm^{-1}$]		[$mg \cdot dm^{-3}$]										
Stara Rzeka	97.01	4.37	472	7.70	60.0	15.9	18.0	4.1	214.1	55.7	20.4	0.324	0.076	4.80	0.20
Kubaleniec	3.38	3.25	543	7.71	74.7	16.1	29.8	4.0	237.9	73.5	35.4	0.087	0.046	7.15	0.15
Leśny Potok	1.39	2.90	431	7.90	45.0	17.7	10.0	1.7	181.8	62.0	7.7	0.077	0.021	2.80	0.07

The Kubaleniec sub-catchment (1.03 km^2) is a typical foothill agricultural catchment located within the Sub-Silesian II unit. Arable land accounts for 69%, meadows and pastures 20%, and woodland 0.5% (Table 1). Farms with long, narrow plots dominate land use within the catchment [29]. The village of Brzeźnica is located on the catchment boundary and effluent sourced from here contributes significantly to streamwater pollution, as household and farming wastewater is discharged into the flat-bottomed Kubaleniec valley.

The Leśny Potok sub-catchment (0.48 km^2) lies within the Silesian unit and more than 99% of the catchment is woodland. Woodland is approximately 40-80 years old and is composed mainly of beech trees, firs, and complexes closely linked genetically to mixed *Pino-Quercetum* forests. The basin features a wet flat-bottomed valley, often populated with young alder trees, and many steep-sided V-shaped valleys forming deep-cutting badlands. Due to its hostile environment the catchment has not been subjected to settlement pressures (Table 1).

Meteorological, Hydrological, and Hydrochemical Background Information

The meteorological data comes from a meteorological station located in the downstream part of the Stara Rzeka catchment (Fig. 1). The 2003 and 2004 hydrological years were marked by a slightly lower average annual air temperature (8.5ºC) than a multi-year average (1993-2002), which was 8.8ºC. The distribution of average monthly temperatures in 2003-04 resembled that of the analyzed multi-year period. Only during the winter months were there cases of air temperatures lower than those from the multi-year period (Fig. 2). The warmest month was August, with an average temperature of 19.1ºC. The coolest month was January with an average temperature of -3.0ºC.

The 2003 and 2004 hydrological years were characterized by a low annual precipitation average (522.5 mm) relative to a multi-year average (1993-2002), which was 735.0 mm for the Stara Rzeka catchment. The distribution of monthly precipitation averages in 2003-04 resembled that of the multi-year average; the highest precipitation was recorded during the warm months (May-July) and the lowest precipitation during the cool months (November-March) (Fig. 2).

2003-04 was characterized by low average annual specific runoff in the Stara Rzeka catchment (4.4 $dm^3 \cdot s^{-1} \cdot km^{-2}$) relative to the multi-year average from 1993-2002 (7.1 $dm^3 \cdot s^{-1} \cdot km^{-2}$). This large difference in runoff was caused by the region's poor ability to retain water due to the presence of virtually impermeable loam in the parent material [30]. The distribution of average monthly specific runoff values was characterized by two peaks:

i) a mid-winter and spring melt peak (January-March)
ii) a summer flood season peak (July) (Fig. 2).

In agricultural catchments (Stara Rzeka and Kubaleniec), runoff rates were the highest during the snowmelt season and in the woodland catchment (Leśny Potok) during the summer season. Snowmelt in the woodland catchment took place later and was not as abrupt as in the two agricultural catchments.

The three streams analyzed were clearly different in terms of chemical composition. The highest SC and main ion concentrations were recorded in the agricultural Kubaleniec catchment, while the lowest in the woodland Leśny Potok catchment (Table 2). Geological structure was a key factor. The Kubaleniec catchment sits on top of Miocene formations with inserts made of highly soluble salts. The Leśny Potok catchment, on the other hand, sits atop more resistant Silesian unit sandstone [31].

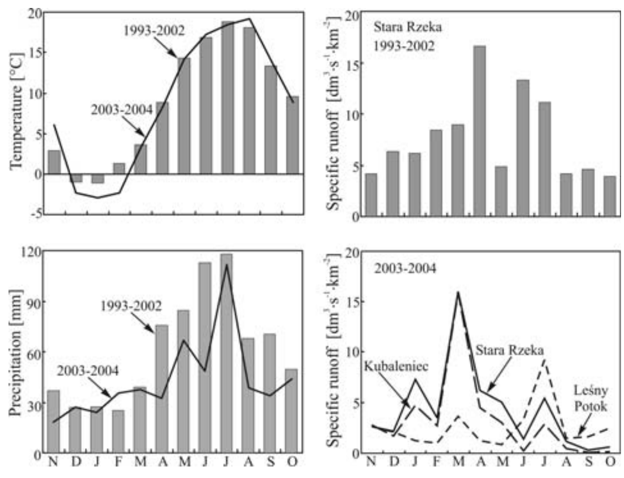

Fig. 2. Average monthly air temperatures, precipitation and specific runoff values during the study period (2003-04) and multi-year period (1993-2002).

The streams that drain agricultural catchments were characterized by nutrient concentrations several times greater than the woodland stream. A very high NH_4^+ concentration was detected in the Stara Rzeka catchment, while in the Kubaleniec catchment, the concentration of NO_3^- was very high. Steadily rising concentrations of nutrients have been detected in recent years in streams draining agricultural catchments with the cause being unregulated sewage system management [32].

Materials and Methods

Fieldwork

Research was conducted throughout 2003 and 2004 hydrological years (November 2002 to October 2004). Specific conductivity (SC), pH, and water temperature were measured every day at about 8 a.m. in the Stara Rzeka and Kubaleniec catchments. In the Leśny Potok catchment, such measurements were made on a weekly basis. Every Monday between 8 a.m. and 10 a.m. water samples were collected from all streams of interest in order to determine the concentrations of main ions. Concentrations of nutrient ions were determined every two weeks. Water samples were collected in 0.5 dm^3 disposable polyethylene bottles for SC, pH, and main ion analysis, while 0.2 dm^3 bottles were used for nutrient collection.

Streamwater levels were gauged on a continuous basis using float-type flow loggers until May 2003, which were then replaced with pressure-type water level sensors (Aplisens SG-25 and Peltron PLH 27) measuring at ten-minute intervals. Discharges were calculated based on rating curves experimentally developed for individual profiles. Rating curves were created based on the procedure by Dingman [33] and Wanielista et al. [34].

Laboratory Analysis

Chemical analyses of water samples were performed at the field laboratory of Jagiellonian University located in the Stara Rzeka catchment. Samples were processed at room temperature (19-20ºC) for SC and pH. Samples were then passed through SARTORIUS filters (0.45 µm) pending further analysis. Due to the low stability of nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}), chemical analysis was performed immediately after sampling with these compounds measured first, followed by analysis of the main ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-). The following analytical methods were used for individual ion types: acidimetric (HCO_3^-), argentometric (Cl^-), and spectrophotometric, using a Merck SQ 118 spectrophotometer (Mg^{2+}, SO_4^{2-}, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}); and flame photometric using a JENWAY PFP 7 device (Ca^{2+}, Na^+, K^+).

Statistical Analysis

R-mode factor analysis (extraction method: principal components) was used. This method reduces a large number of variables to a smaller number of factors that are not correlated with each other [35]. Each individual factor can be interpretable. This means that each factor can be associated with some specific source or process [36]. A matrix of factor loadings, one of the most important parts of factor analysis output, was used. Factor loadings provide a measure of the correlation between the factors and variables being analyzed [37].

All of the variables measured from bi-weekly water samples were used, as were average air temperature during the two weeks prior to sampling (T_{air}), and water temperature (T_{water}) and discharge (Q) recorded at the time of sampling. The Kolmogorov-Smirnov Test and Liliefors Test were used to check for the normality of variable distributions. All of the data exhibited log-normal distributions. The Keiser criterion was used to separate out the factors and a significance of $p<0.05$ was used across all calculations. The following categories were applied to factor loadings: high – over 0.75, and moderate – 0.40-0.75. The higher the factor loading, the stronger the relationship between the given variable and the selected factor. The same classification was used in papers on similar topics by Evans et al. [24] and Bernal et al. [38].

Chemical changes occurring over time were analyzed using all available data (see Section 4.1). Variance in variables due to the influence of river discharge was removed using the LOWESS smoothing method (LOcally WEighted Scatterplot Smooth), a robust curve-fitting procedure described by Cleveland [39, 40]. A smoothness coefficient of f=0.65 was used. The LOWESS technique describes the relationship between concentration and discharge. Seasonal analysis was then conducted on the residuals using the concentration-discharge relationship. Positive values of residuals indicated values greater than those on the LOWESS curve, while negative values of residuals indicated values below that on the LOWESS curve. The LOWESS procedure does not require variables to be normally distributed, which is beneficial when analyzing hydrochemical data [41, 42].

Results

Monthly Variation of Streamwater Chemistry

Streamwater chemistry displayed consistent monthly variation throughout the year in all of the study catchments. The highest specific conductivity (SC) values were recorded during low streamflow periods in late summer and autumn (Fig. 3). The lowest values were found in late winter and during springtime thaws in all watercourses. Monthly variation of the Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, and Cl^- concentrations (data not shown) followed the SC pattern. A slightly different pattern emerged with K^+ and SO_4^{2-} concentrations (Fig. 3). Concentrations of K^+ increased in summer and autumn months in agricultural and mixed catchments. K^+ concentrations in the woodland Leśny Potok catchment peaked during thaw periods. The lowest SO_4^{2-} concentrations in the agricultural catchment were recorded during

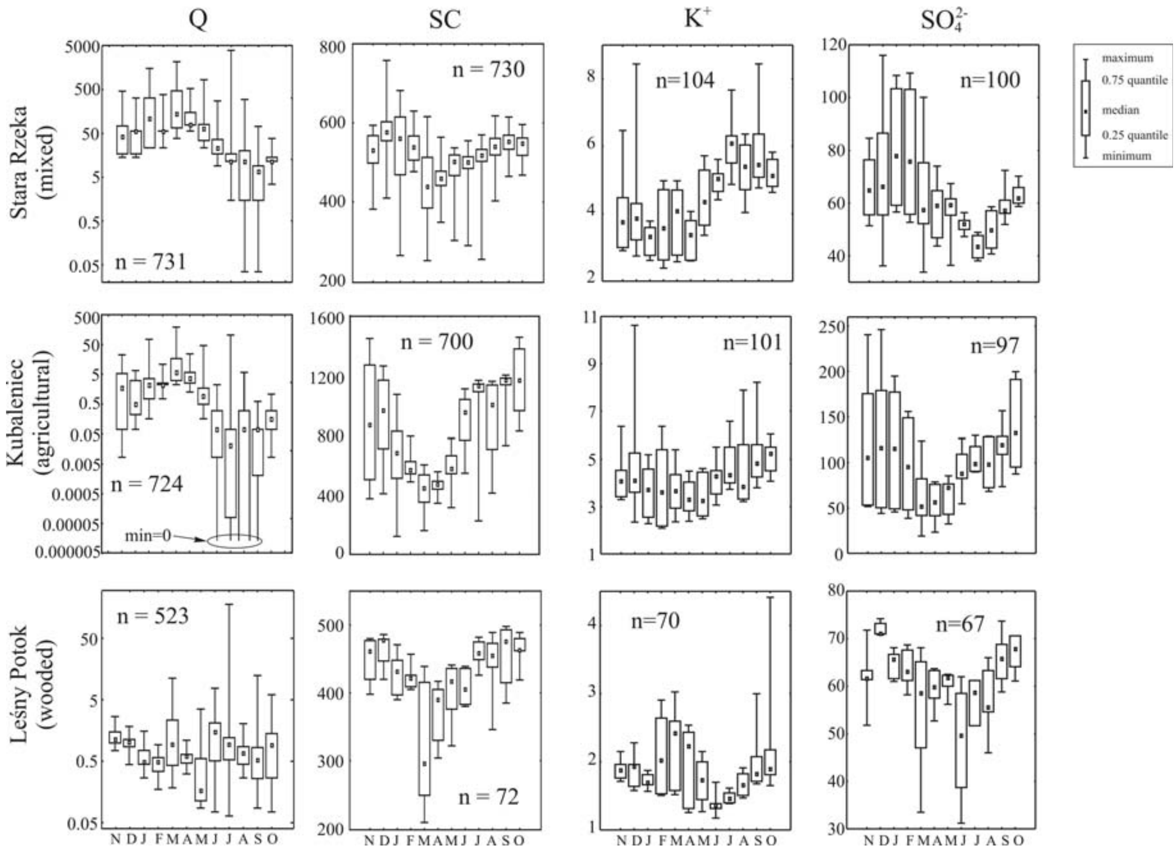

Fig. 3. Monthly changes of discharge Q [$dm^3 \cdot s^{-1}$], SC [$\mu S \cdot cm^{-1}$], K^+, and SO_4^{2-} concentrations [$mg \cdot dm^{-3}$] – statistical characteristics during hydrological years 2003 and 2004 (n – number of samples).

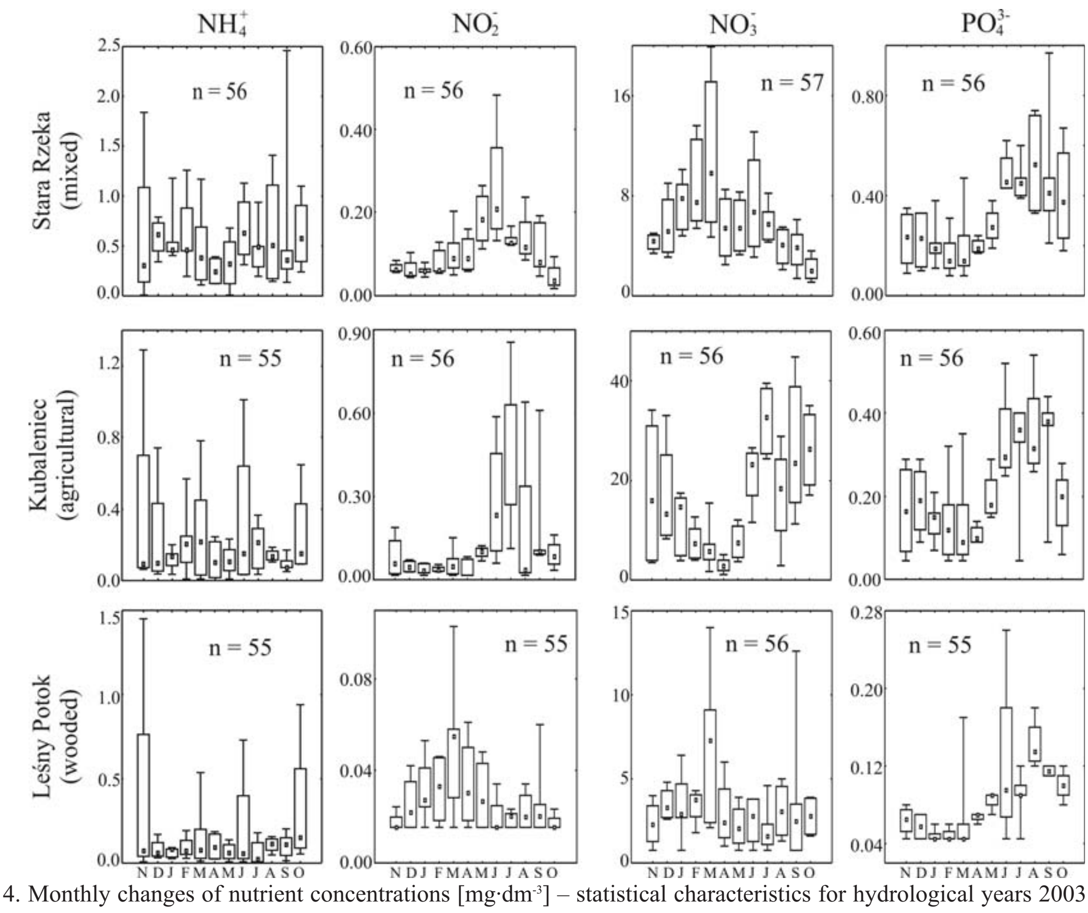

Fig. 4. Monthly changes of nutrient concentrations [$mg \cdot dm^{-3}$] – statistical characteristics for hydrological years 2003 and 2004 (symbols as in Fig. 3).

spring and summer months in the woodland and mixed catchments.

The most distinct monthly pattern among the nutrient compounds was displayed by PO_4^{3-} concentrations (Fig. 4). All watercourses displayed similar patterns with lower concentrations during winter and spring, and higher concentrations during summer and autumn. NO_3^- concentration curves were similar for woodland and mixed catchments, with the highest values in winter and spring and the lowest values in summer and autumn. This pattern was reversed in the agricultural catchment, with the highest NO_3^- values in summer and the lowest in spring. The NO_2^- ion displayed similarities between the agricultural and mixed catchments, peaking in late spring and summer, whereas high values in the woodland catchment were recorded in winter and early spring. The least pronounced chemical change was variations in NH_4^+ concentrations.

Factors Determining Streamwater Chemistry Changes

Factor analysis produced four factors for each of the streams that explained over 80% of the variation in each catchment. The streamflow factor (F1) explained 53% of the variation in the agricultural catchment, 48% in the woodland catchment, and 36% in the mixed catchment. The factor expressed a causal relationship; the larger the discharge, the lower the concentration of most main ions (except K^+ and in some cases – SO_4^{2-}) and the lower the SC (Tables 3, 4, and 5). The factor loadings of virtually all the variables were very high (≥0.90). The lowest factor loadings were found in the mixed-use catchment, as shown by the lowest eigenvalue found for the mixed-use catchment, calculated as a sum of squares of factor loadings (Tables 3, 4, and 5). Nutrients were also controlled by the factor, albeit to a lesser extent and with positive or negative factor loadings, dependent on the type of catchment. Larger discharges raised NO_2^- and NO_3^- concentrations in the woodland and mixed catchments, while in the agricultural catchment they markedly decreased them.

The second factor (F2) involved seasonal air and water temperature change. The seasonal factor explained 24% of the variation in the mixed catchment, 19% in the woodland catchment, and 16% in the agricultural catchment. The factor loadings of the aforesaid variables were not as high as those associated with factor 1 – most ranged from 0.40 to 0.75 (Tables 3, 4 and 5). The factor primarily controlled changes in PO_4^{3-} (mixed and woodland catchments), NH_4^+

Table 3. Factor loadings – Stara Rzeka. Loadings in range 0.40-0.75 are given in parentheses, loadings less than 0.40 are excluded.

Parameter	F1	F2	F3	F4
T_{air}		-0.93		
T_{water}		-0.89		
Q	(0.74)	(0.54)		
pH		(-0.50)		(-0.59)
SC	-0.93			
Ca^{2+}	-0.88			
Mg^{2+}	-0.89			
Na^+	-0.94			
K^+		(-0.67)	(-0.52)	
HCO_3^-	(-0.72)		(0.44)	
SO_4^{2-}	(-0.45)		(-0.48)	
Cl^-	(-0.68)	(0.47)		
NH_4^+			(-0.64)	
NO_2^-		(-0.40)	(-0.53)	
NO_3^-	(0.49)		(-0.43)	(-0.45)
PO_4^{3-}		(-0.63)	(-0.67)	
Eigen value	5.73	3.81	2.33	1.06
Explained variation	0.36	0.24	0.15	0.07
Cumulation	0.36	0.60	0.75	0.82

Table 4. Factor loadings – Kubaleniec. Loadings in range 0.40-0.75 are given in parentheses, loadings less than 0.40 are excluded.

Parameter	F1	F2	F3	F4
T_{air}	(-0.40)	-0.83		
T_{water}		-0.83		
Q	0.93			
pH	(-0.42)	(-0.67)		
SC	-0.97			
Ca^{2+}	-0.93			
Mg^{2+}	-0.94			
Na^+	-0.96			
K^+			(-0.74)	
HCO_3^-	(-0.61)		(0.62)	
SO_4^{2-}	-0.75	(0.42)		
Cl^-	-0.97			
NH_4^+		(0.58)		(0.67)
NO_2^-	(-0.62)			(0.57)
NO_3^-	-0.87			
PO_4^{3-}	(-0.60)		(-0.55)	
Eigen value	8.41	2.60	1.77	0.99
Explained variation	0.53	0.16	0.11	0.06
Cumulation	0.53	0.69	0.80	0.86

Table 5. Factor loadings – Leśny Potok. Loadings in range 0.40-0.75 are given in parentheses, loadings less than 0.40 are excluded.

Parameter	F1	F2	F3	F4
T_{air}		-0.84		
T_{water}		-0.81		
Q	(0.76)			
pH	-0.89			
SC	-0.96			
Ca^{2+}	-0.96			
Mg^{2+}	-0.95			
Na^+	-0.93			
K^+		(0.45)	(-0.70)	(-0.41)
HCO_3^-	-0.98			
SO_4^{2-}		(0.56)		
Cl^-	(-0.47)	(0.60)	(-0.50)	
NH_4^+			(-0.45)	(0.68)
NO_2^-	0.79			
NO_3^-	(0.64)		(-0.41)	
PO_4^{3-}	(-0.44)	(-0.68)		
Eigen value	7.64	3.02	1.66	1.01
Explained variation	0.48	0.19	0.10	0.06
Cumulation	0.48	0.67	0.77	0.83

(agricultural), NO_2^- (mixed), pH (agricultural and mixed), K^+ (mixed and woodland), SO_4^{2-} (agricultural and woodland), and Cl^- (mixed and woodland). Generally, the greater the observed air and water temperature the greater the observed concentrations of PO_4^{3-} and pH, and the lower the concentrations of NH_4^+. Concentrations of K^+ followed different patterns in different watercourses. For example, in the woodland catchment higher temperatures resulted in lower K^+ concentrations, while in the mixed catchment higher temperatures resulted in higher K^+ concentrations. In the case of SO_4^{2-} and Cl^- the relationship with air temperature and water temperature was inverse.

The circulation factor (F3) explained 15% of the variation in Stara Rzeka, 11% in Kubaleniec, and 10% in Leśny Potok. The F3 factor shaped the nutrient concentrations of controlled ions (PO_4^{3-}, NH_4^+, NO_2^-, NO_3^-) and K^+ (Tables 3-5). The ion concentrations were inversely related to HCO_3^- – and in some cases positively correlated with SO_4^{2-} and Cl^-. The factor loadings of the aforesaid ions ranged from 0.40 to 0.75. The highest loadings were those of K^+ (0.74 in agricultural catchment, 0.70 in woodland catchment).

Finally, the fourth factor (F4) explained 7% of the variation in the mixed catchment and 6% in both the woodland and agricultural catchments. Ions with a high factor load showed various forms of mineral nitrogen: NH_4^+, NO_2^-, and NO_3^- (Tables 3, 4 and 5). The factor loadings of these ions ranged from 0.40 to 0.75. The largest factor loading was that of NH_4^+ (over 0.65 in agricultural and woodland catchments).

Flow-Adjusted Monthly Streamwater Chemistry Changes

Factor analysis revealed that stream discharge was the main factor driving changes in water chemistry. Therefore, changes in chemical concentrations were subsequently investigated while controlling for changes in stream discharge. The question is: What would changes in water chemistry look like over the course of the year without the effect of discharge – the principal determinant of water chemistry. Flow-adjusted data showed that in the woodland catchment, SC (Fig. 5) and the majority of main ions (data not shown) recorded higher concentrations in summer and autumn months (residuals from LOWESS>0) than in winter and spring months (residuals from LOWESS<0). The agricultural catchment and the mixed catchment showed higher SC values and the majority of main ion concentrations in autumn and winter than in spring and summer. Flow-adjusted seasonal effects are well expressed by seasonal hysteretic loops. For example, the agricultural catchment demonstrated higher SC values in autumn and winter than in spring and summer at given streamflow rates (Fig. 6). Following the removal of discharge effects, K^+ and SO_4^{2-} behaved differently than other ions in all the streams studied (Fig. 5). During the summer, K^+ concentrations were the lowest in the woodland catchment and highest in the mixed-use catchment. The flow-adjusted SO_4^{2-} concentrations were higher in the winter months than in the summer months in all three catchments.

Flow-adjusted nutrient concentrations were generally highest in vegetative periods and lowest in the dormant ones (Fig. 7). This pattern was most evident in PO_4^{3-} concentrations throughout all watercourses, with higher levels in spring and summer than in autumn and winter. Only NO_2^- and NO_3^- in the woodland catchment recorded slightly lower flow-adjusted concentrations in the growing season.

Discussion

Streamflow change was the main factor driving seasonal chemistry change in small catchments of the Carpathian Foothills. Similar results have been obtained by Cameron [2], Bhangu and Whitfield [11], Feller and Kimmins [21] on Canadian rivers, Muscutt and Withers [5] and Edwards [6] in the UK, Rinella and Janet [7] in the USA, Piñol et al. [22] in Spain, and Pekárová et al. [43] in Slovakia. Increased flows in the Stara Rzeka catchment, recorded during winter and spring snowmelts, caused a reduction in SC and in the concentration of most of the main ions due to the dilution effect. This process affects parameters associat-

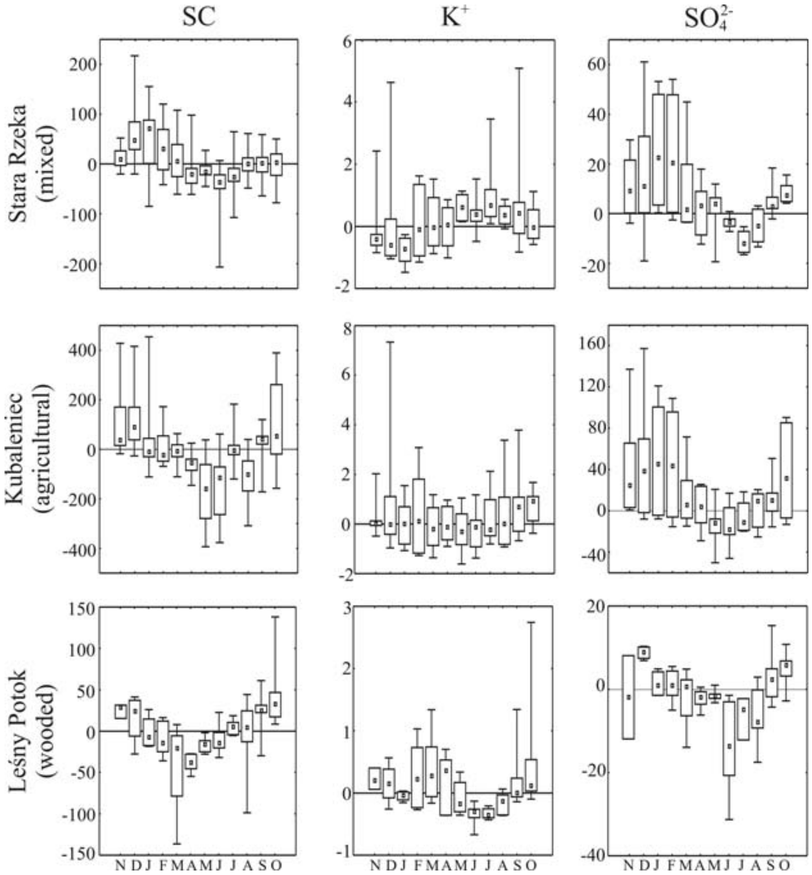

Fig. 5. Monthly changes of SC [$\mu S \cdot cm^{-1}$], K^+, and SO_4^{2-} concentrations [$mg \cdot dm^{-3}$] after removing discharge effects – statistical characteristics of residuals from the LOWESS smoothing in hydrological years 2003 and 2004 (symbols as in Fig. 3).

ed with parent material weathering called geologically controlled ions [44]. The factor loadings for the Cl^- and Na^+ ions in the Kubaleniec catchment are very high (-0.97 and -0.96, respectively). This is due to the presence of halite inclusions of the Bochnia series in the parent material of this catchment [26]. In fact, the site is only 30 km away from the historic Wieliczka salt mine, designated a UNESCO World Heritage Site in 1978. In the Leśny Potok catchment, the HCO_3^- and Ca^{2+} ions possess high factor loadings (-0.98 and -0.96, respectively). The catchment's parent material consists primarily of sandstone with carbonate joints. The weakest relationship between the main ions and discharge was identified in the mixed-use catchment. This is due to the heterogeneous nature of this catchment. Unlike the two nested catchments, the mixed-use catchment is not geologically homogeneous. Earlier research in this catchment performed during floods of different origin has shown this to be true [45]. The relationship between the main ions and discharge had become weakened by the mixing of waters from different parts of the Stara Rzeka catchment.

Streamflow also appeared to be the main driver of seasonal changes in nutrient concentrations (except for NH_4^+). During snowmelt, high flows raised the concentrations of compounds derived from diffuse sources, e.g. NO_3^- and NO_2^- in the woodland and the mixed catchments. Concurrently, concentrations of ions mainly derived from point sources, e.g. NO_2^-, NO_3^-, and PO_4^{3-}, were reduced due to dilution effects in the agricultural catchment. This type of relationship between biogenic compound concentration and discharge is characteristic of highly polluted streams. This is first and foremost the result of unregulated sewage system management. Villages located in the Stara Rzeka catchment were hooked up to water supply systems after 1989, but no sewage system or wastewater treatment plant was built. Water use increased rapidly as the water supply

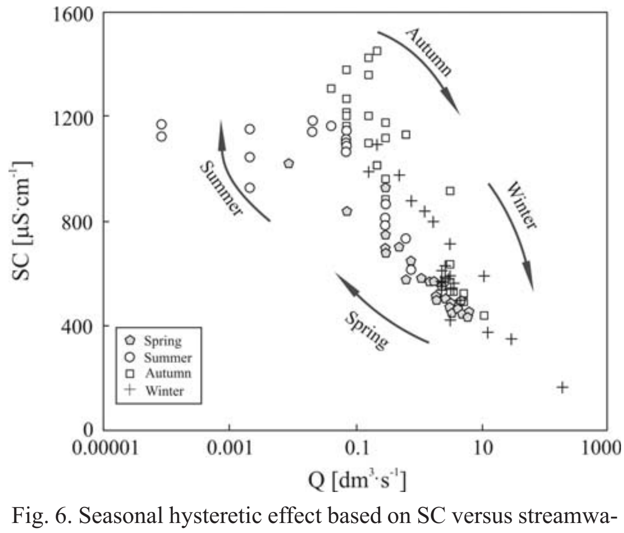

Fig. 6. Seasonal hysteretic effect based on SC versus streamwater discharge (Q) in the agricultural catchment of Kubaleniec.

system came online and sewage generation increased correspondingly. Prior to the political and economic transformation era in Poland, most villages obtained water from small local sources such as wells and springs. This forced people to conserve water. Today, most untreated rural sewage flows into rivers and Kubaleniec is one of them. This situation represents a sort of transition state characteristic of all of Central and Eastern Europe. A wastewater treatment plant is being built in the Stara Rzeka catchment and in other rural areas as well. A sewage system is also being constructed. In 1995 only 5.9% of the rural population in Poland had access to wastewater systems. The rate of access increased steadily during the years that followed: in 2000 – 11.5%, in 2005 – 19.0%, in 2009 – 23.5% [46]. European Union clean water requirements [47] and funds slated for environmental protection offer hope that the quality of the water in this region will improve in the next few years.

Air and water temperature, variables that influence vegetation growth, were additional indirect drivers of streamwater chemistry (climatic factor). Certain nutrients showed unexpected increases during summer months when vegetation growth was high; PO_4^{3-} levels increased in all streams. This was particularly unexpected in the Leśny Potok (woodland) catchment as phosphates are generally regarded to be among the most undersupplied of compounds in natural ecosystems, limiting the primary production of nutrient compounds [48, 49]. PO_4^{3-} increases in the woodland catchment of Leśny Potok during the vegetation growth period, suggesting that the compound was not in deficit. Higher concentrations in summer than in winter most likely were a result of intensive decay of organic matter, one of the main sources of phosphorus in natural catchments. Research conducted by Drewnik [50] has shown this to be true in the Stara Rzeka catchment. According to Drewnik [50], between 71% and 98% of organic matter (understood to be cellulose) decays during a ten week period in the summer (June-August). The percentages vary depending on sampling site. Research in other regions of the world confirms that increased air temperature and microorganism activity intensify the pace of organic decay during the summer [51-53]. The wet flat-bottomed valley of the Leśny Potok catchment and the channel itself are thickly lined with decaying grass and tree remains. The higher summer temperatures of air and water favour a mobility of phosphorus absorbed in colloidal clay and the transition of PO_4^{3-} into a solution [49]. This process is aided by the presence of loess-type formations in the cover of the Stara Rzeka catchment, which includes substantial colloidal clay content (10-20%) [27]. The combination of these effects may have caused summer supplies of PO_4^{3-} to exceed the demand of local vegetation for the compound in the woodland catchment. A similar increase in PO_4^{3-} levels during summer and autumn was noted by Pekárová et al. [43] in several small woodland catchments in the Slovakian Carpathians, but no explanation was provided.

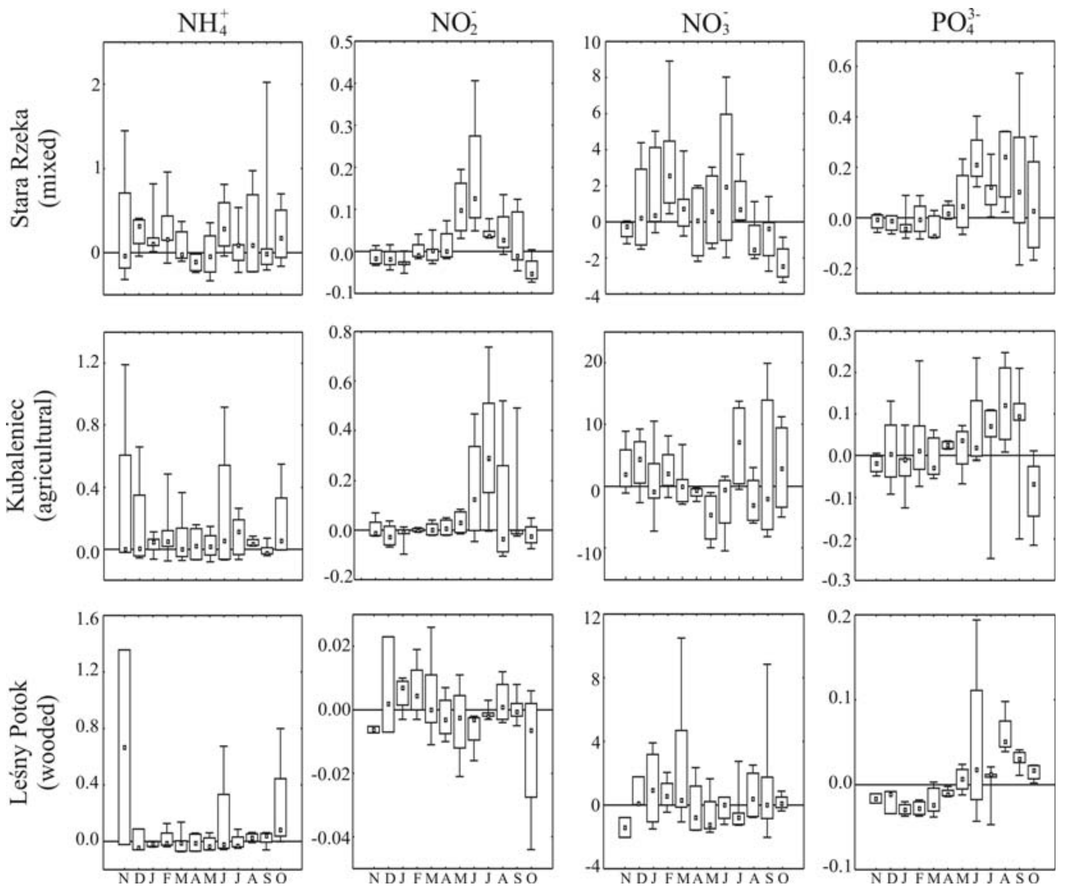

Fig. 7. Monthly changes of nutrient concentrations [mg·dm⁻³] after removing discharge effects – statistical characteristics of residuals from LOWESS smoothing in hydrological years 2003 and 2004 (symbols as in Fig. 3).

During summertime, PO_4^{3-} concentrations in the agricultural and mixed catchments increased as a result of the concentrating effects of reduced streamflows and the increase in household and farming wastewater discharges. Additionally, wastewater that normally reaches the watercourse channels via roadside ditches is less impeded in the summer than in winter, when the ditches are blocked by snow. Intense decay and a high rate of mineralization of organic matter, both natural and anthropogenic (wastewater), also may favor higher PO_4^{3-} concentrations in the summer, as is evident given increased chemical oxygen demand levels ($ChOD_{Cr}$) in the mixed land use catchment of Stara Rzeka (Fig. 8).

The impact of vegetation growth on the levels of NH_4^+, NO_2^-, and NO_3^- was negligible, as indicated by the original and flow-adjusted data. The woodland catchment showed a slight reduction in the NO_2^- and NO_3^- concentrations, while in the agricultural catchment these concentrations increased. This pattern is not typical and is largely unaccounted for in the literature. NO_3^- concentrations are typically observed to increase in winter and diminish in the summer as a result of increased absorption by plant life [9-12, 14-16, 43]. The lack of significant reduction of nutrients during the summer in the semi-natural Leśny Potok catchment is likely to be attributed to low absorption rates of nutrients by aging trees. Low absorption rates of nutrients by aging trees was documented by Murdoch and Stoddard [17] and Vitousek and Reiners [54]. During the vegetation growth periods, the woodland catchment received elevated concentrations of nutrients likely sourced from intensely decaying organic matter. Unclear reductions in nitrogen compound concentrations in the Leśny Potok catchment may be an effect of the young alder trees in the valley. The alder is known for its capability to bind atmospheric nitrogen in a process that enriches the soil with this compound [55-57]. The substantial impact of anthropogenic activity on streamwater quality in the agricultural catchment undoubtedly distorts natural nutrient concentrations.

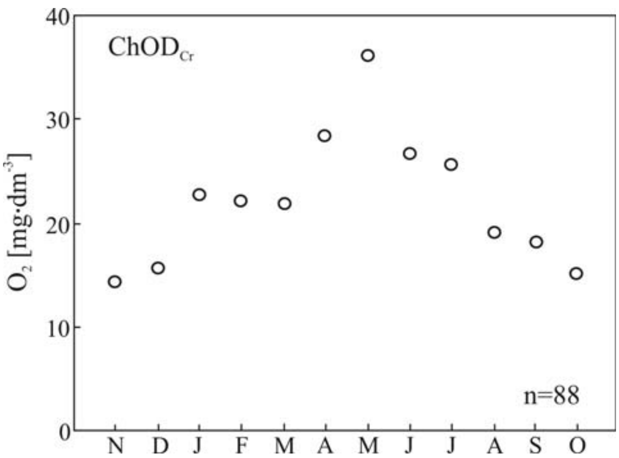

Fig. 8. Seasonal changes of chemical oxygen demand ($ChOD_{Cr}$) in Stara Rzeka streamwater: mean values from 1988-2004, n – number of samples (based on data from the State Inspectorate of Environmental Protection in Kraków).

The relationship between the concentration of K^+ and air temperature and water temperature is different in the woodland catchment and anthropogenically altered catchments. In the woodland catchment, the higher the air and water temperature, the lower the concentration of K^+. On the other hand, in the mixed-use catchment, the higher the air and water temperature, the higher the concentration of K^+. This relationship is very weak in the agricultural catchment (factor loading <0.40). In the woodland catchment, an increase in the K^+ concentration is readily apparent during snowmelt season, when the products of autumn and winter weathering and decomposition are washed away. The same tendency holds true in catchments experiencing human pressure. But K^+ concentration is the greatest in the summer season. It appears to be due to higher K^+ content in soils in the summer and a greater possibility of ion flushing from farmland (absence of frost). Higher K^+ content in soils in the summer season results from:

(i) more organic matter decomposition derived from natural and anthropogenic sources (manure, wastewater)
(ii) the application of mineral fertilizers directly prior to the growing season.

The flushing out of K^+, nitrogen, and phosphorus takes place rather intensively during summer rainstorms. The intense flushing out of K^+ *via* surface runoff is aided by extensive downslope plowing in the Carpathian Foothills. The mean concentration of K^+ in surface runoff from agricultural areas is higher during summer floods than during winter snowmelt floods (4.6 and 2.5 mg·dm^{-3}, respectively).

While circulation and nitrification factors also affected water chemistry in the foothill watercourses, their impact was decidedly smaller than that of the first two factors. The analysis of relationships identified by the factors is difficult and requires a detailed analysis of changes in water chemistry during a given year. The circulation factor affected the nutrient concentrations (PO_4^{3-}, NH_4^+, NO_2^-, NO_3^-) and K^+ where an inverse relationship to the change in HCO_3^- concentration occurred. The three nutrients and K^+ are usually associated with event water: surface or sub-surface water circulation [6, 58, 59], while the remaining compound is related to pre-event water: deeper ground circulation [44]. This type of response, regardless of changes in discharge (factor 1), can be observed in late spring and early summer (June and July – Fig. 5). This is the period of the largest fluctuations in discharge (Fig. 3) and correspondingly the largest changes in the paths of delivery of water to stream channels. When flood-driven discharge increases, biogenic compounds and K^+ that have accumulated as a result of the decomposition of organic matter in the autumn and winter are flushed out. At low discharge, streams are recharged largely by deeper circulation waters, which explains why the concentration of HCO_3^- increases and the concentration of biogenic compounds and K^+ decreases.

Flow-adjusted analysis indicates that regardless of changes in discharge, the concentrations of most ions are higher during the summer than during the winter. In the case of biogenic compounds and K^+, as shown by the analysis of the second factor and third factor, this is most likely due to the more intense decomposition of organic matter during the summer when the quantity of these ions is greater than during the winter. The degree of flushing of the soil cover in the catchment and the resulting availability of chemicals for transport seem to play a significant role in SC values and concentrations of most of the main ions. This was responsible for the so-called seasonal hysteresis effect, whereby SC and main ion concentrations were lower in the spring and early summer than in the autumn and winter, despite similar streamflow rates. Low ion concentrations were attributed to melt-water depleting soil chemicals available for transport. High ion concentrations were attributed to chemical replenishment in the catchment during intense chemical weathering of the regolith during the warm season; a process responsible for the transfer of soluble substances into soils and subsequently into groundwater and surface water [60]). Other researchers have also shown that chemical weathering rates accelerate with an increase in temperature, precipitation, and soil moisture [60-64]. Moreover, vegetation and soil microbes promote weathering by modifying pH and generating organic acids and CO_2 [65].

Finally, the fourth factor controls mainly the change in the concentration of mineral forms of nitrogen. Yet, it is very difficult to link this factor to any specific natural process, as the combination of key ions in each of the three catchments studied is different. For example, in the Stara Rzeka catchment, the only inorganic form of nitrogen identified was NO_3^-, while in the Leśny Potok catchment it was NH_4^+, and in the Kubaleniec catchment it was NH_4^+ and NO_2^-. Moreover, the factor loadings of these ions were not high (Tables 3-5). Nevertheless, it may be presumed that the fourth factor is associated with nitrification in the water.

Conclusions

Seasonal changes of streamwater chemical composition are mainly related to changes in river discharge during a year (the streamflow factor). The streamflow factor affects changes in characteristics connected with geology (SC, most main ions) in the same way in all catchments. This means that the higher the discharge, the lower the values of these characteristics. Changes of this type are controlled by the process of dilution. In the case of some nutrients, the discharge factor causes different changes in catchments of different land use. This type of difference is most clearly evident when comparing a woodland catchment and an agricultural catchment for NO_2^- and NO_3^- ions (high factor loadings). In a woodland catchment, a growing rate of discharge increases the concentration of these ions, while in an agricultural catchment the opposite is true. This type of relationship indicates that in a woodland catchment, these ions primarily come from diffuse sources (soil flushing), while in an agricultural catchment they come mainly from point sources (wastewater). As part of the political and economic transformation process in Poland in the 1990s, it was quite common to see a water supply network being extended to rural areas with no accompanying sewage system or wastewater treatment plant. This practice led to an increase in water usage and a corresponding increase in wastewater generation. It is very often the case that this type of sewage ends up in local rivers with no prior treatment.

The air and water temperature change (climatic factor) mainly controls nutrient concentrations. However, patterns of these changes are atypical and poorly documented. During the summer, at the time of maximum vegetation growth, nearly all nutrients increase their concentrations, especially PO_4^{3-}. Only in the woodland catchment is there a slight reduction in NO_2^- and NO_3^- concentrations. This is most likely attributed to high decay rates of organic matter originating from either natural (woodland catchment) or anthropogenic (agricultural and mixed catchments) sources. Nitrogen reductions in the natural woodland catchment may also be attributed to young alder trees absorbing atmospheric nitrogen and transferring nitrogen complexes into the valley soils. The impact of anthropogenic factors in the agricultural and mixed catchments is so great that it completely distorts the subtle play of concentrations of nutrients from natural absorption by plants.

The third factor is associated with the circulation of water in a catchment featuring a variety of hydrological conditions. The circulation factor affects nutrient concentrations (PO_4^{3-}, NH_4^+, NO_2^-, NO_3^-) and K^+ with an inverse relationship with HCO_3^- concentration being observed. The first group of variables is associated with shallow water circulation (throughflow and overland flow) during flood events. On the other hand, HCO_3^- is associated with deeper groundwater circulation, which becomes significant at baseflow conditions. Chemical composition appeared to be significantly affected by the degree to which the soil is flushed and the subsequent availability of chemicals for transport. The effect of seasonal hysteresis is observed, whereby the majority of ion concentrations are lower in the spring and early summer when chemicals are flushed from the soil during the preceding thaw periods. Supplies of available compounds are replenished by intense chemical weathering of the soil cover during the summer season, which increases concentrations during the autumn and winter.

The fourth factor exerts a minimal influence on the overall chemical composition of streamwater systems; it explains only a small fraction of variability in the water chemical characteristics of interest and controls primarily the change in the concentration of inorganic forms of nitrogen. Finally, it is most likely associated with nitrification in the water.

The impact of human pressure is reflected in changes in the natural annual ion circulation cycle. This is especially true of biogenic compounds and K^+. Despite the fact that the same environmental factors were identified in all three studied catchments, some factors prompt a different type of ion response in different types of catchments: woodland, agricultural and mixed-use. This is due to differences in:

(i) catchment ion supplies
(ii) the sources of the ions in each type of catchment
(iii) ion transport pathways in each of the three catchments.

In the natural catchment, diffuse sources are prevalent, while in anthropogenic catchments point sources such as raw sewage outflows also play an important role. This problem affects not only rural areas in Poland but also rural areas in other post-communist countries in Europe. Poland's membership in the European Union offers the opportunity to take advantage of environmental protection funds that may help Poland catch up in the area of environmental protection.

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