Annual Changes in the Chemical Composition of Stream Water in Small Catchments with Different Land-use (Carpathian Foothills, Poland)

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Abstract: The aim of the study was to identify the factors that influence annual changes in the chemical composition of stream waters. The research area was located in the marginal zone of the Carpathian Foothills (Poland) in the Stara Rzeka catchment (mixed land-use) and its two sub-catchments: Leśny Potok (wooded) and Kubaleniec (farmed). Hydrochemical studies were carried out during the 1998–2004 water years and with separate recording frequencies for individual parameters. Measures used included specific conductance (SC), pH and the concentration of the main ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-) and nutrient compounds (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}). Tendencies towards changes in chemical parameters were estimated using the Seasonal Kendall Test. Elimination of flow rate impact on the chemical composition of stream waters was achieved using the residuals from the LOWESS analysis. During the analysed period, a statistically significant increase in SC and the concentration of the majority of main ions occurred. Additionally, there was an increase in the concentration of nutrient compounds in watercourses undergoing the anthropogenic impact (Kubaleniec, Stara Rzeka), as opposed to the Leśny Potok stream draining the wooded catchment. The SC changes were determined by a decrease in the annual river run-off and simultaneous ion concentration (natural factor). In the Stara Rzeka catchment, the increase in NH_4^+ concentration was caused by the increase in sewage discharge into the river (anthropogenic factor). Another factor that contributed to the annual changes of water chemistry was gradually deeper and deeper water-circulation (circulation factor), responsible for an increase in the concentration of Na^+ and Cl^- and a decrease of HCO_3^- and Ca^{2+}.

Keywords: river water chemistry; water pollution; nutrient compounds; flow tendency

One of the major factors responsible for annual changes in the chemical composition of stream waters is that related to the fluctuations of river flow. Muscutt and Whithers (1996) based on their own studies on sewage pollution of rivers in England and came to the conclusion that, due to the dilution of sewage, the PO_4^{3-} concentration in rivers during wet years was lower than in dry years. Some authors even more strongly emphasized and demonstrated that river flow fluctuations were the only factor responsible for annual changes in the chemical composition of stream waters (Tonderski 1997; Laznik *et al.* 1999).

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Catchment saturation with chemical compounds and diminishing water retention capabilities for the new supply of those compounds may cause an increase in their concentration in rivers. According to Ryan *et al.* (1989), an increase in sulphate concentrations in rivers draining two small catchments in the USA was caused by catchment saturation with sulphur (S saturation concept). Similarly, catchment saturation with nitrogen, deposited from the atmosphere, may cause a constant increase in nitrate concentration in rivers (N saturation concept) (Aber *et al.* 1989; Lepisto 1995; Peterjohn *et al.* 1996).

Anthropogenic activity is frequently a cause of annual changes in the chemical composition of stream waters. Man affects river quality by changing the amount and quality of household sewage delivered to the river. A reduction of sewage and an improvement of its quality have an effect on the water chemical compounds and instantly lead to a decrease in NH_4^+ concentration and, to a lower extent, to a decrease in PO_4^{3-} (Muscutt & Whithers 1996; Lehmann & Rode 2001; Trench 2004).

Economic changes in eastern European countries after the political transformation processes of 1989 have led to significant agricultural reforms, including: radical drop in fertilizer use and a decrease in agricultural production, which has eventually led to a quality improvement of the superficial waters in several countries, e.g. Slovakia (Pekarova & Pekarov 1996) and Estonia (Loigu & Iital 2003). Stålnacke *et al.* (2003) did not observe such phenomenon in Latvian rivers, what they explained as being due to the lag time between the use of fertilizers and their delivery to the stream waters.

The aim of our study carried out in small catchments located in the Carpathian Foothills was to recognise annual changes in the chemical composition of stream waters and identify natural and anthropogenic factors affecting stream-water quality. In order to define the importance of anthropogenic impact in the Stara Rzeka catchment two homogeneous sub-catchments were selected for the study: the semi-natural wooded sub-catchment of Leśny Potok and the farmed one – Kubaleniec.

Study area

The research area is situated in the northern, marginal portion of the Carpathian Foothills (S. Poland) (Figure 1). The Stara Rzeka catchment (22 km^2) spans two tectonic units, Śląska and Podśląska, consisting of Cretaceous and Tertiary (Miocene) flysch formations. These are topped with a thick layer of loess-like formations. The Śląska unit consists primarily of sandstones, shales and claystones, while the Podśląska unit comprises claystones and marly clays, as well as some of the Bocheńska salt series (Olewicz 1973). The local salt and gypsum inclusions are the reason for locally high chloride, sodium or sulphur concentrations in ground-water. As a consequence this may result in relatively high concentration of the ions during low flow events when the share of ground-water component in the stream-water rises.

The Stara Rzeka catchment is characterised by a complex land use structure, with forests accounting for 42%; arable land for 36% and meadows and pastures for 15% of the area (Święchowicz & Michno 2005). While forests dominate in the southern part of the drainage basin, the arable land, meadows and pastures dominate in the northern part. There are a number of villages in the basin that have much influence on the quality of superficial and ground-waters. The local communities have the benefit of water mains or individual water abstraction sources, such as wells and springs, but no central sewer, with the result that only a small proportion (less than 10%) of the water is treated. Most of the household and farm wastewater is discharged into roadside ditches and canals and drained into the rivers. Local farmers commonly fertilise their fields with solid manure and their meadows, located in flat-bedded river valleys, with liquid manure.

The Kubaleniec sub-catchment (1.03 km^2) is located within the Podśląska unit. It is a typical foothill farming catchment: arable land accounts for 69%, meadows and pastures for 20% and forests for just 0.5% (Święchowicz & Michno 2005). It is dominated by small farms with long and narrow plots. The high degree of plot fragmentation has produced a dense network of field roads (3.6 km/km^2) (Święchowicz 2002). The village of Brzeźnica is located on the watershed and constitutes a major source of stream-water pollution. A portion of the Brzeźnica community discharge their household and farming waste water into the flat-bedded Kubaleniec valley.

The Leśny Potok sub-catchment (0.48 km^2) lies within the Śląska unit. More than 99% of its area is wooded. The forest is mostly composed of beech trees, firs and complexes closely linked to mixed Pino-Quercetum forests. The basin specifically features a wet flat-bedded valley and many side valleys in the form of deep-cutting badlands and V-shaped valleys. So far the basin has not been subject to settlement pressure, due to an unfavourable environment and especially its steep slopes (10–15°).

MATERIALS AND METHODS

Fieldwork

Streamwater samples were taken at water gauge sections closing the catchment of Stara Rzeka and sub-catchments of Kubaleniec and Leśny Potok (Figure 1). Field measurements included specific conductance (SC), pH and water temperature. The study was carried out during the 1998–2004 water years and with separate recording frequencies for individual parameters (Table 1).

Stream water levels were gauged on a continuous basis, with a float-type recorder until May 2003 and afterwards with pressure-type water level sensors (Aplisens SG-25 and Peltron PLH 27) at ten-minute intervals. The discharge was calculated based on rating curves developed experimentally for each profile.

Laboratory analysis

Chemical water analysis was performed at the Hydrochemistry Laboratory of the Institute of Geography and Spatial Management of the Jagiellonian University located in the Stara Rzeka catchment. Samples delivered from the field were kept until the water reached room temperature (19–20°C) and measured again for SC and pH. The reference temperature for SC was 25°C. The samples were then filtered through SARTORIUS (0.45 μm) filters for further analysis.

Due to the low stability of nutrient compounds (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}), chemical analysis needs to be performed soon after sampling (House & Warwick 1998), and so these compounds were marked first. In wintertime this was done after the samples reached room temperature. This was followed by main ions analysis (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^-), spectrophotometric – using a Merck SQ 118 spectrophotometer (Mg^{2+}, SO_4^{2-}, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}), and flame photometric – with a JENWAY PFP 7 photometer (Ca^{2+}, Na^+, K^+).

Statistical analysis

Tendencies towards annual changes in the chemical composition were estimated using the Seasonal Kendall Test (Hirsch *et al.* 1991; Helsel & Hirsch 2002). The test is designed for the analysis of annual parameter changes that are also subject to seasonal changes (Ryan *et al.* 1989; Murdoch & Stoddard 1992; Zipper *et al.* 2002; Neitzert 2003; Palmer *et al.* 2004). Slope of the trend line was determined by the Kendall Slope Estimator.

Moreover, the Seasonal Kendall Test was also used for the evaluation of tendencies in changes in chemical composition, without reference to

Table 1. Streamwater sampling

Stream	Sampling time (hydrological year)	Sampling frequency	Chemical analysis
Kubaleniec	1998–2001	weekly	SC, pH
	2002–2004	daily	SC, pH
	2002–2004	weekly	main ions, SC, pH
	2002–2004	biweekly	biogenes, main ions SC, pH
Leśny Potok	2003–2004	biweekly	biogenes, main ions, SC, pH
Stara Rzeka	1998–2001	weekly	SC, pH
	2002–2004	daily	SC, pH
	2002–2004	weekly	main ions, SC, pH
	2002–2004	biweekly	biogenes, main ions SC, pH

SC – specific conductance

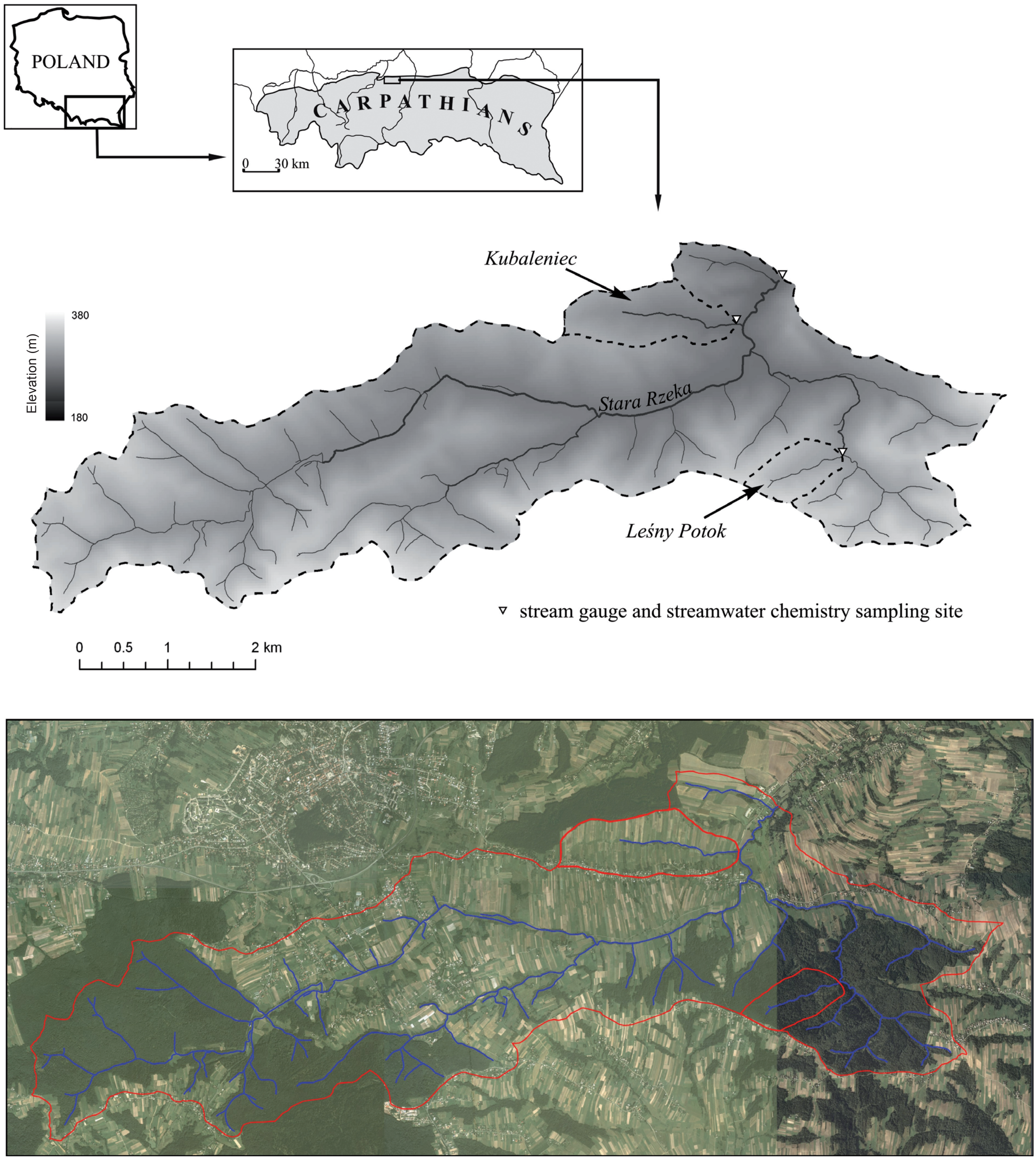

Figure 1. Location of the study area

flow changes. Elimination of the flow rate impact on the chemical composition was achieved by matching the LOWESS curve (LOcally WEighted Scatterplot Smooth) with the casual nexus: flow rate and chemical composition, using the residuals from LOWESS (Helsel & Hirsch 2002). Seasonal Kendall Test and LOWESS analysis were based on raw data. A similar technique to eliminate flow rate impact on changes in the chemical properties was applied by: Hirsch *et al.* (1991), Smith *et al.* (1996), and MacCoy (2004).

Used measures included: monthly median of chemical properties obtained from a weekly analysis of specific conductance (SC), pH and the main ions. An analysis of nutrients was carried out once every two weeks. Tendencies in flow changes were calculated from mean monthly flow rates based on data from daily measurements. In order to determine the relation between chemical properties and flow, the Pearson linear correlation was used following normalization and standardization of the raw data. A significance limit of < 0.05 was applied in all statistical calculations.

RESULTS

Annual trends in chemical parameters

During the analyzed years, a significant increase in SC was observed in all rivers studied (Tables 2 and 3). Among the main ions, a significant increase was observed in the concentration of Na^+ in Stara Rzeka and Leśny Potok, K^+ and SO_4^{2-} in Stara Rzeka and Kubaleniec, Cl^- in Stara Rzeka and HCO_3^- in Leśny Potok.

As far as nutrient compounds are concerned there was a significant increase in the concentration of PO_4^{3-} in Stara Rzeka and Kubaleniec, NH_4^+ in Stara Rzeka and NO_3^- in Kubaleniec. No significant changes were observed for any other parameter.

Table 2. River flow and water chemistry trend analysis for Stara Rzeka and Kubaleniec according to Seasonal Kendall Test (*Q*, SC, pH: 1998–2004; main ions, nutrient compounds: 2002–2004)

Parameter	Kubaleniec	Stara Rzeka
Q	−0.702	−12.710
SC	+20.750	+13.950
pH	–	–
Ca^{2+}	–	–
Mg^{2+}	–	–
Na^+	–	+1.716
K^+	+0.431	+0.644
HCO_3^-	–	–
SO_4^{2-}	+23.590	+5.337
Cl^-	–	+1.225
NH_4^+	–	+0.099
NO_2^-	–	–
NO_3^-	+5.050	–
PO_4^{3-}	+0.053	+0.070

– statistically insignificant; *Q* – river flow; SC – specific conductance

Table 3. Water chemistry trend analysis for Leśny Potok according to Seasonal Kendall Test (2003–2004)

Parameter	Leśny Potok
SC	+27.250
pH	+0.070
Ca^{2+}	+7.087
Mg^{2+}	+1.765
Na^+	+0.893
K^+	–
HCO_3^-	+27.150
SO_4^{2-}	–
Cl^-	–
NH_4^+	–
NO_2^-	–
NO_3^-	–
PO_4^{3-}	–

– statistically insignificant; SC – specific conductance

An increase in SC and the concentration of some ions followed a significant decrease in the flow rate of the streams. The highest value of SC was recorded in the 2003 hydrological year, in parallel with extremely low flow rates (Figure 2). This was caused by a very low precipitation; in 2003 the total precipitation amounted to 440.9 mm, whereas the mean precipitation for the years 1986–2004 was 656 mm.

Flow-adjusted annual trends in chemical parameters

Changes in the majority of the chemical properties in the foothill stream waters depended on the fluctuation in the flow rates, as demonstrated by the high and significant correlation coefficients between the chemical composition and the flow rate (Table 4). In the majority of cases the relationship was negative and resulted from a dilution process during high flow periods and a process of concentration of ions during low flows. A positive relationship was observed with nitrates: NO_2^- and NO_3^- in Leśny Potok and NO_3^- in Stara Rzeka. These leads to the question of whether the river flow was the only factor having a significant influence on changes in the chemical composition of stream waters.

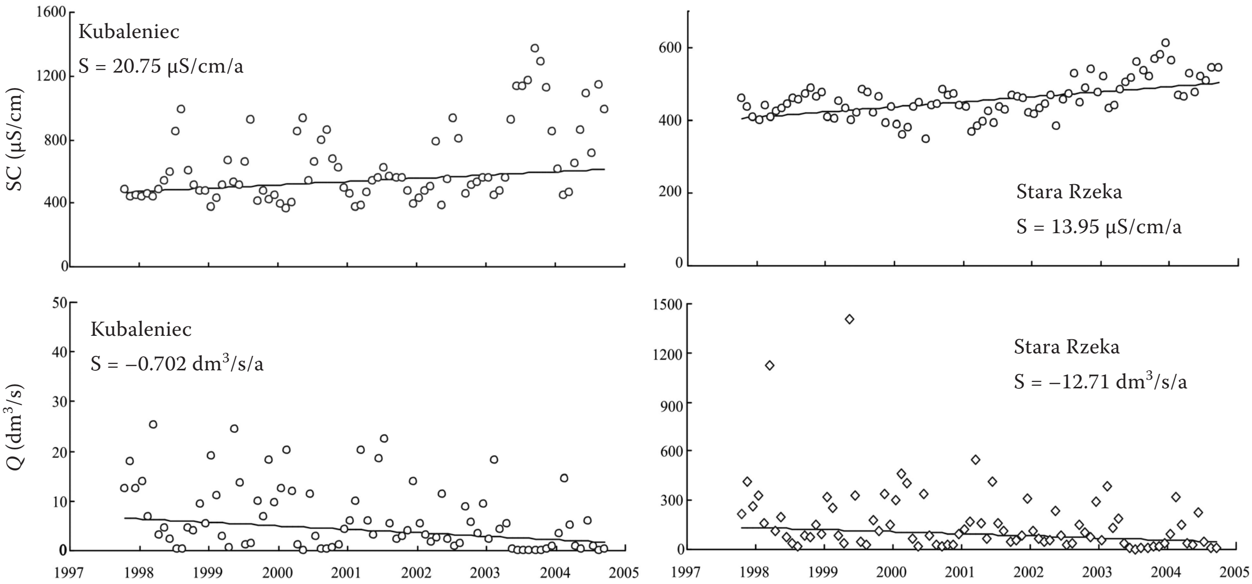

Figure 2. River flow (Q) and water specific conductance (SC) trend analysis for the Stara Rzeka and Kubaleniec according to Seasonal Kendall Test (S – Kendall Slope Estimator)

After elimination of the impact of flow rate, an increasing trend in SC and NH_4^+ concentration was observed in Stara Rzeka (6.9 µS/cm/a and 0.1 mg $NH_4^+/dm^3/a$ respectively) (Table 5). Among the main ions, both in Stara Rzeka and Kubaleniec, there was an increase in Na^+ and SO_4^{2-} concentration, as well as Cl^- concentration only in Stara Rzeka along with a parallel decrease in Ca^{2+} and HCO_3^- concentration. In the majority of cases these changes were much higher in the farmed catchment of Kubaleniec than in the catchment of Stara Rzeka with its mixed land use. In the semi-natural catchment of Leśny Potok, all chemical parameters depended solely upon the flow rate.

Table 4. Correlation between water chemistry and river flow

Parameter	Kubaleniec	Leśny Potok	Stara Rzeka
SC	–0.88	–0.66	–0.68
pH	–0.47	–0.66	–
Ca^{2+}	–0.83	–0.75	–0.65
Mg^{2+}	–0.87	–0.65	–0.62
Na^+	–0.89	–0.62	–0.75
K^+	–	–	–0.49
HCO_3^-	–0.62	–0.71	–0.71
SO_4^{2-}	–0.63	–	–
Cl^-	–0.87	–	–
NH_4^+	–	–	–
NO_2^-	–0.62	0.61	–
NO_3^-	–0.78	0.58	0.51
PO_4^{3-}	–0.47	–	–0.40

– statistically insignificant; SC – specific conductance

Table 5. Flow-adjusted trend analysis of chemical parameters in the Stara Rzeka and Kubaleniec streamwater according to Seasonal Kendall test (SC, pH: 1998–2004; main ions, nutrient compounds: 2002–2004)

Parameter	Kubaleniec	Stara Rzeka
SC	–	+6.902
pH	–	–
Ca^{2+}	–	–2.119
Mg^{2+}	–	–
Na^{+}	+2.711	+0.966
K^{+}	–	–
HCO_3^-	–	–11.880
SO_4^{2-}	+15.720	+5.080
Cl^-	–	+0.734
NH_4^+	–	+0.111
NO_2^-	–	–
NO_3^-	–	–
PO_4^{3-}	–	–

– statistically insignificant; SC – specific conductance

DISCUSSION

The increase in SC and concentration of several ions in the foothill catchments was primarily related to flow reduction (natural factor). This factor also caused an increase in the concentration of nutrients in streams suffering from anthropogenic impact, e.g. in Kubaleniec and Stara Rzeka. Flow reduction combined with a constant discharge of household sewage into the Kubaleniec and Stara Rzeka riverbeds (anthropogenic factor), led to the concentration (graduation) of these components in the stream waters. The leading role of flow in annual changes in the chemical composition of stream waters was also observed by Muscutt and Whithers (1996) in several dozen catchments in England and Wales as well as by Vuorenmaa *et al.* (2002) in several different size catchments in Finland.

It is worth paying attention to several cases, where an increase in ion concentrations was not only related to their graduation. An increase in nutrient concentration, e.g. NH_4^+ in Stara Rzeka, is an example of a change in the chemical composition irrespective of flow rate changes. This can be explained by an increase in household sewage discharged into the river. Owing to the construction of a water supply system there was an increase in water usage by farms and households, whereas the amount of sewage transported to the sewage treatment plant remained at the same level, mainly due to the lack of sewage system (Pietrzak 2005). The NH_4^+ concentration in Stara Rzeka has been gradually increasing since the end of 1980s (Anonymous 2003). This problem did not affect the semi-natural catchment, with only a slight anthropogenic impact (Leśny Potok).

From the end of 1980s, a gradual decrease in NH_4^+ concentration due to more efficient water management systems has been observed in well-developed countries (Sullivan 2000; Lehmann & Rode 2001). East European countries have lagged in this process (van Dijk *et al.* 1994); however, since the 1990s the process has been observed in large rivers (Pekarova *et al.* 1999; Dojlido *et al.* 2004). Stara Rzeka is an example of a small farmed catchment in the Carpathian Foothills still facing problems. Uncontrolled water management of arable lands is also responsible for poor quality of surface waters in other regions in Poland (Przedrzymirska & Błaszczyk 2003), as well as in other countries of the former Soviet block, like Estonia (Loigu & Iital 2003).

An increase in the concentration of Na^+ and Cl^- and a decrease in HCO_3^- and Ca^{2+} was caused by a natural factor related to gradually deeper and deeper water-circulation rather than the flow rate. A decrease in precipitation over several years, together with small retention capabilities and permeability of the superficial deposits in the Stara Rzeka catchment, have led to a gradual increase in deeper ground-water participation in the stream flow.

CONCLUSIONS

The major factor responsible for annual changes in the chemical composition of the foothill streamwaters has been the long-term fluctuation of the river flow (natural factor). The reduction of river flow has been a direct cause of the SC increase and the ion concentration.

The flow reduction has also caused an important increase in nutrient concentration in the Kubaleniec and Stara Rzeka catchments, where point sources of household sewage were found. This process has not occurred in the semi-natural catchment of Leśny Potok.

In the Stara Rzeka catchment, the NH_4^+ increase over several years was not caused only by the concentration (graduation) of this ion but also due to the increase in household sewage discharge into the river (anthropogenic factor). In case of the analysed catchments the economic changes after 1989 are not reflected in water quality improvement so far.

Another important factor that contributed to annual changes in the chemical composition of the foothill stream waters is gradually deeper and deeper water-circulation, responsible for an increase in the concentration of such ions as Na^+ and Cl^- and a decrease of HCO_3^- and Ca^{2+}.

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