Abstract: The aim of the studies was the recognition of natural and anthropogenic agents shaping changes of the chemical composition of mountain streams at flood discharge. Over 2002-2004 changes of the chemical composition of mountain stream waters were analysed during 10 flood discharges of rainfall origin and of 13 snowmelt and snowmelt-rainfall origin cases of at three differently managed catchments (forest, agricultural and of composite land use structure). Laboratory measurements of waters included the concentration of macroelements (Ca$^{2+}$, Mg$^{2+}$, K$^+$, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$), biogenic compounds (NH$_4^+$, NO$_2^-$, NO$_3^-$, PO$_4^{3-}$), specific electrical conductivity, reaction and suspended matter concentration.

Key words: flood discharges, water chemism, catchment land use, Carpathian Foothills

Introduction

Chemical composition of river waters provides much information on the mechanism of rainfall transformation into runoff and on the functioning of the catchment basin during high discharges. Each case of high discharge is characterized by an individual dependence of the chemical composition of waters on the rate of discharge. This is linked with the co-occurrence of many agents which shape the course of a flood wave; its size and duration, the length of time between successive floods, the wetting of a catchment and the ability of the substance for transport (Froelich 1975, 1982; Walling, Webb 1980). Various chemical properties of particular compounds, the share of part of them in biological circulation, in soil and geochemical processes bring about a diversification and sometimes even multidirectional changes of concentration of ions at high discharges (Gacek 2001, Kostrzewski et al. 1992, Siwek 2001).
The purpose of the investigations was to find out of the natural and anthropogenic agents shaping chemical composition changes of foothill stream waters at high discharges in catchments of various land use.

**Research area**

The research covered the catchment of the Stara Rzeka, situated in the escarpment part of the Wiśnicz Foothills, (down to the watergauge at Łazy) and two of its partial catchments that of the Kubaleniec and of the Leśny Potok (Fig. 1). The catchment of the Stara Rzeka (22 sq. km) is situated within the two nappe units; the Silesian and the Sub-Silesian ones with a salt series of Bochnia (Olewicz 1973). It is marked by a composite structure of land use – 41% of the surface is under forests, 38% - under arable land and 13.5% under meadows and pastures. The catchment of the Kubaleniec (1 sq. km) is situated within the Sub-Silesian unit built first of all of claystones and marl clays, covered by a thick layer of loess-like deposits. This is a typically agricultural catchment (arable land – 65%, meadows and pastures – 22%, rural buildings –12.5 % (Święchowicz 2002). It is marked by a dense network of roads and field terraces running parallel to the slopes. The catchment of the Leśny Potok (0,5 sq. km) lies within the Silesian unit which is built of Istebna sandstones covered by loess-like deposits. It is totally wooded. Both the catchment of the Kubaleniec and of the Leśny Potok are characterized by an oblong shape. It is therefore to be expected that the process of the formation of a flood wave will have a similar course in both streams.
The method and the scope

Over 2002-2004 chemical analyses of waters were carried out – of 10 summer half-year flood waves and of 13 snowmelt waves. At flood the water samples were taken with a frequency from a few minutes to a few hours – depending on the dynamics of flow rates. Water reaction, specific electrical conductivity (SEC), water temperature, and in some cases the concentration of oxygen were measured. Water was taken into polyethylene containers of 1 cubic dcm (for macro-element and suspension determination) and 0.25 cubic dcm (for biogenic compound determination). In the laboratory of the Institute of Geography and Spatial Management at Łazy the water was filtered (0.45 µm) and subject to of reaction, specific electrical conductivity, concentration of macroelements (calcium Ca$^{2+}$, magnesium Mg$^{2+}$, sodium Na$^{+}$, potassium K$^{+}$, carbohydrate HCO$_3^-$, sulfate SO$_4^{2-}$, chloride Cl$^-$), biogenic compounds (ammonium NH$_4^+$, nitrite NO$_2^-$, nitrate NO$_3^-$, orthophosphate PO$_4^{3-}$) and of suspension concentration measurements.

Results

A general regularity to be found at high discharges was a decrease of electrical conductivity and of the concentration of macroelements (Ca$^{2+}$, Mg$^{2+}$, Na$^{+}$, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$) except for potassium following an increase in the discharge rate (Fig. 2). This was due to the dissolution of waters from ground feeding by less mineralized waters of surface and midsoil flow and by rainfall waters directly feeding the stream. The most dynamic changes of the chemical composition were observed at the beginning of flood wave when the ground waters were enriched by midsoil and surface waters of varying proportions. At high discharges the chemical composition of waters did not reveal so great changes, this due to the dominant share in feeding of one source – surface flow.

Quite different was the behaviour of the ammonium, orthophosphate, potassium and nitrate ions whose concentration increased with a rise of stream discharge. In the case of poorly dissoluble and strongly suspension-sorbed ions (ammonium and orthophosphate) there were two peaks of the concentration of these ions – the first one associated with re-suspension of bottom deposits in the channel which appeared directly after the start of flood discharge and the other – associated with surface flow which appeared at a later stage of the formation of a flood wave (Fig. 3). In the case of poorly dissoluble potassium an increase in its concentration was chiefly linked with its washing out from the covers by infiltrating rainfall waters and midsoil flow to the channel. The concentration of nitrates at the initial phase of rainfall flood wave was vehemently decreasing (as were macro-elements) and then rose following the inflow into the channel of the waters of subsurface flow (as did potassium).

At snowmelt flood discharges and at snowmelt-rainfall ones an essential agent affecting the changes of the chemical composition of foothill stream waters was the state of covers in a catchment. In January 2003 within the catchments of the Kubaleniec, Stara Rzeka and Leśny Potok, with deeply frozen covers, midwinter snowmelt flood wave was observed. The streams were then fed chiefly by subsurface
and surface way, the frozen soil cover impeding the formation of midsoil flow. The chemical composition of fluvial waters was an effect of their dissolution by poorly mineralized waters coming from the melting snow cover. During a rise of a flood wave the delivery into the channel of poorly mineralized waters of surface flow rose and involved a clear drop of mineralization of waters in the stream. The fall of the input surface flow in to river runoff was followed by an increase in water mineralization of the stream. Changes of the chemograph were synchronous with changes of the hydrograph (Fig. 4A). Relationship between concentrations of ions and the rate of discharge revealed the character of narrow hystereses (Fig. 4B).

During flood discharges in January 2004, in the catchments of the Leśny Potok, Kubaleniec and Stara Rzeka, the ground was not frozen therefore snowmelt waters could freely infiltrate deep into the covers and get saturated with compounds present in them. The appearance of midsoil flow caused the conductivity and concentrations of the main ions the flood discharge to be higher than during snowmelt discharges with frozen soil cover (Fig. 5).

Midsoil flow played a very important role during summer rainfall floods by modifying the chemograph of a flow. The lowest mineralization of waters appeared after or before the culmination of a flood flow – the chemograph was asymmetrical as compared with the hydrograph. The more belated or more accelerated was chemism reaction to changes of flow, the wider became the loop of hysteresis.

During summertime rainfall floods a very important agent shaping the chemical composition of mountain stream waters was the moisture state of catchment before a flood. In July 2003 the flood discharge in the Leśny Potok took place accompanied by two culminations associated with variable rainfall rates during the passage of a cold atmospheric front. The first culmination occurred under the conditions of a strongly overdried catchment while the other of a well-wetted catchment. The conductivity and the concentrations

Fig. 2. Relationship between the specific electrical conductivity (SEC) and the rate of discharge (Q) during flood stages of snowmelt-rainfall and rainfall origin in the Leśny Potok, the Kubaleniec and the Stara Rzeka

Ryc. 2. Związek przewodnictwa elektrolitycznego właściwego (SEC) z natężeniem przepływu (Q) podczas wezbrań roztropowych, roztropowo-deszczowych i deszczowych w Leśnym Potoku, Kubaleńcu i Starej Rzece.
Fig. 3. Changes in the concentrations of ammonium, orthophosphate and potassium ions during two flood waves of torrential rain origin in the Kubaleniec (15-17 July 2002)

Ryc. 3. Zmiany stężenia jonu amonowego, azotanów, ortofosforanów i potasu w czasie dwóch wezbrań burzowych w Kubaleńcu (15-17 lipca 2002 r.)

Fig. 4. Changes in the specific electrical conductivity and of calcium concentrations during flood of snowmelt origin in the Kubaleniec (A) and their relationship to discharge rates (B)

Ryc. 4. Zmiany przewodnictwa elektrolitycznego właściwego i stężenia wapnia w czasie wezbrań roztopowego w Kubaleńcu (A) oraz ich związek z natężeniami przepływu (B)
During the first culmination, were higher than during the second culmination (Fig. 6). This was the result of washing out through the infiltrating rainfall waters of chemical compounds accumulated between flood periods in the soil covers. As the washing out of the covers continued the resources of accessible compounds decreased.

A very important agent, associated with human activities, shaping the changes of chemical composition of river water is land use pattern. This is linked with a different circulation of water in a forest and agricultural catchment. In a forest catchment, surface flow plays an inconsiderable part in feeding a watercourse and appears to be largely belated as compared with the culmination of a flood wave. In summer, during torrential rainfalls, the surface flow appeared along paths, while in winter – on the frozen ground. An increase in the rate of discharge in the Leśny Potok was first of all the result of the inflow of midsoil waters.
The chemical composition of waters reacted belatedly in response to changes of discharge intensity – maximum and minimum concentrations of ions occurred after the culmination of a bankful discharge wave (Fig. 6). The histereses of the conductivity of water and of ions, which decreased concentration with a rise of discharge (Ca$^{2+}$, Na$^{+}$, Mg$^{2+}$, SO$_4^{2-}$, HCO$_3^-$, Cl$^-$) adopted a clockwise turn (Fig. 7). In the case of ions which increased concentrations with a rise of discharge (K$^+$, NH$_4^+$, PO$_4^{3-}$) the turn of histereses was anticlockwise.

The reaction of the chemical composition of the Kubaleniec waters following an increase in discharge was different – extreme concentrations of ions were observed before the culmination of a discharge (Fig. 3). This was linked with a different circulation of waters in the agricultural catchment as compared to the forest one. A dense network of field roads and of furrows separating individual plots in the Kubaleniec catchment brought about a rapid surface flow. On the floor of a flat-bottomed alluvial valley furrows were dug to drain waters flowing down from the fields directly into the stream. The histereses of the conductivity and of ions which lowered concentrations with an increase in discharge rate (Ca$^{2+}$, Na$^{+}$, SO$_4^{2-}$, HCO$_3^-$, Cl$^-$) adopted
the anticlockwise turn. In the case of ions, which increased concentrations with a rise of discharge rate ($K^{+}$, $NH_4^+$, $PO_4^{3-}$), the turn of histereses was clockwise (Fig. 7).

Changes in the chemical concentrations in the waters of the Stara Rzeka, which drained a catchment of a composite management structure, were varying during floods of summer rainfall origin, either resembling the reaction of the Leśny Potok or that of the Kubaleniec (Fig. 7).

**Conclusions**

Changes in the chemical composition of waters of the Leśny Potok, the Kubaleniec and of the Stara Rzeka during flood discharges were dependent on composite processes of the transformation of rainfall into runoff. The mechanism of feeding the streams with water was conditioned by natural agents among which the most important appeared to be the state of covers (wetting, overfreezing) and anthropogenic agents such as agricultural use of land.

During summer flood discharges clear differences were found in the chemical composition of waters in the catchments of the Leśny Potok, the Kubaleniec and the Stara Rzeka. This was the effect of a different circulation of waters in catchments with different land use - agricultural or forest one. In a wooded catchment the delivery of waters into the channel was most affected by midsoil flow, surface flow playing a decisively lesser role. In an agricultural catchment surface flow was of very great importance.

At winter bankful discharge stages (snowmelt or snowmelt-rainfall stages) the frozen soil-wastemantle cover brought about the disappearance of differences in the functioning of differently used catchments which was expressed by similar changes in the chemical composition of waters. This was a consequence of the appearance of surface flow with a lack of midsoil flow.

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**Naturalne i antropogeniczne uwarunkowania zmian składu chemicznego wód potoków pogórskich w czasie wezbrań**

**Streszczenie**

Badania nad naturalnymi i antropogenicznymi uwarunkowaniami zmian składu chemicznego wód rzecznych w czasie wezbrań były prowadzone w trzech małych, różnie użytkowanych zlewniach (leśnej, rolniczej i o złożonej strukturze użytkowania) na Pogórzu Wiśnickim. W latach 2002-2004 przeanalizowano 10 fal wezbraniowych deszczowych i 13 fal roztopowych i roztopowo-deszczowych. Pomiary laboratoryjne wód obejmowały stężenia makroelementów (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻, Cl⁻), związków biogennych (NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻), przewodnictwo elektrolityczne właściwe, odczyn oraz koncentrację zawiesiny.

Wśród naturalnych uwarunkowań zmian składu chemicznego wód potoków w czasie wezbrań za najważniejsze uznano stan pokryw w zlewni w czasie bezpośrednio poprzedzającym wezbranie (nawilżenie, przemarznięcie), natomiast wśród uwarunkowań antropogenicznych bardzo ważnym okazało się użytkowanie ziemi w zlewni. Wpływ użytkowania ziemi na zmiany składu chemicznego wód w różnie użytkowanych zlewniach zanikał w czasie wezbrań roztopowych z głęboko przemarzniętą pokrywą glebowo-zwietrzelinową.

**Projekt finansowany ze środków KBN 3P04G 050 22**

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