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ROLE OF CHANNEL HEADS IN DETERMINING WATER CHEMISTRY OF 1ST-ORDER STREAMS IN POSTGLACIAL AREAS OF WEST POMERANIA

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Abstract: Detailed research studies on the physical and chemical properties of waters were conducted within the Żarnowo channel head in West Pomerania. Samples were collected at regular measuring sites, which represent groundwater of the footslope zone, interstitial waters and rivulets. In order to identify the origin of ionic components in channel headwaters, the collected hydrochemical data were subjected to factor analysis using the principal component method. The main factors shaping the chemistry of waters: geogenic, anthropogenic, biogenic, and redox were identified. The study was designed to identify the determinants of the water chemistry of 1st-order streams.

Keywords: channel head, 1st-order stream, chemistry of groundwater, factor analysis, West Pomerania

Introduction

Groundwater play the crucial role in shaping the runoff as well as the chemistry of water of 1st-order streams. The chemistry of water flowing out of channel head reflects not only the characteristics of groundwater feeding headwater zone (i.e. waters from the slope system) but also changes to which they are subjected within the channel head during the organisation of channel flow (Chapman *et al.* 1993). A lot of dispersed groundwater outflows (springs, leakages and seepages), most often located within amphitheatric headwater alcoves, are a characteristic feature of channel heads in the Polish Lowland region.

The chemical properties of waters flowing out of headwater alcoves are the result of mixing of exfiltrating waters, often with different physicochemical parameters (Michalska 2001; Stach 2003; Stolarska, Moniewski 2007; Ziułkiewicz 2007). The presence of ionic components in channel head waters is connected with the process of leaching of chemical weathering products of postglacial sediments. Anthropogenic inflows (domestic and agricultural wastes) can be a relevant sources of biogenic components.

Water-saturated sediments having a lot of organic elements can affect the chemical parameters of waters in headwater alcoves. Organic matter is subject to the process of decomposition and at the same time depletion of oxygen. The process of mineralization of organic matter under anaerobic conditions results in that microorganisms use oxygen coming from aerobic combinations of nitrogen and sulphur, which leads to a decline in the concentration of nitrates and sulphates in water by a reduction to gaseous nitrogen and hydrogen sulphide (Puchalski 1999). Moreover, the low redox potential favours the migration of reduced iron and manganese. These processes are characteristic of the hyporheic zone – ecotone being the contact zone of surface and groundwater (Puchalski 1999). Water of this zone (interstitial water) have different chemical properties both in relation to groundwater and surface waters (Michalska 2003; Jekatierynczuk-Rudczyk 2007, 2010).

The aim of the study is to identify the source of supplies of solutes and to identify the conditions of affecting ion outflows in the 1st-order stream based on the recognition of physicochemical properties and their variability of waters in headwater alcoves. The research study makes the grounds to assess the impact of groundwater onto the operation of channel heads of 1st-order streams within the postglacial zone of the West Pomerania.

Research area

The channel head Żarnowo located at the southern slope of the upper Parsęta valley (Drawskie Lake District, West Pomerania) was selected to be the research area (Fig. 1). Field studies were conducted at the headwater alcove consists of three niches, developing in the sand and gravel glaciofluvial plain and erosive-accumulative alluvial terrace made of river sands, gravels and silt.

Within each of the studied niches at the channel head Żarnowo the following three zones can be distinguished: exfiltration of groundwater in the footslope zones, hyporheic zone covering niche bottoms and rivulets draining individual niches and stream flowing out of the channel head (1st-order tributary of the Parsęta river). Within the footslope zones there are layer-erosive seepages fed by combined waters from the local near-surface aquifer of the glaciofluvial plain and

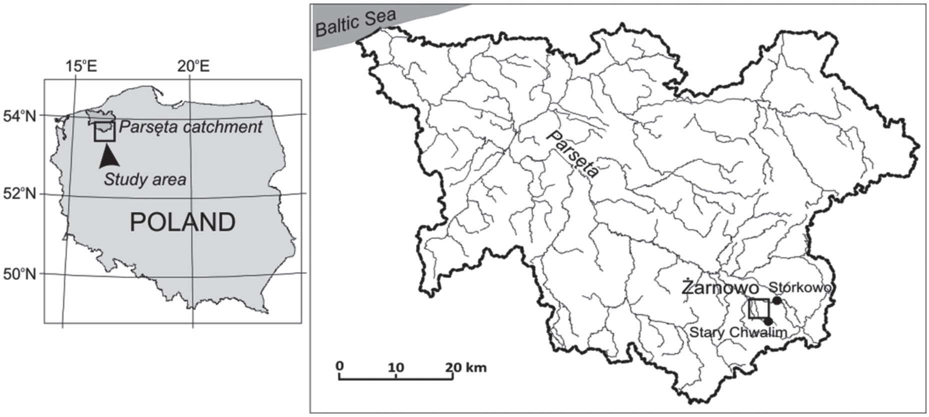

Fig. 1. Location of the research area with the Parsęta basin in the background

Source: authors' own study.

from the upper inter-morainic aquifer. The conducted preliminary measurements of groundwater level at the channel head bottom indicate that these waters are under hydrostatic pressure.

The level of waters has stabilised at several up to over 20 cm above the ground. Water flowing out in niches covers the entire bottom surface with a thin layer (its depth ranges from 3 cm up to over 10 cm). The studied niches are areas of intensive channel head erosion (seepage erosion) as evidenced by slope undercuts and erosional pavement at the bottom. Sand-gravel sediments are dominant within the bottom. Beyond these areas of erosion within the niche bottom there are patches of water-logged mineral and organic sediments containing organic matter up to 15%. Each of the niches is drained by rivulets – the largest ones reach discharge volumes ranging from several up to 45 $dm^3 \cdot s^{-1}$. The gradual concentration of rivulets leads to the formation of channel flow at the outlet of each of these 3 niches. Niches are connected by a common stream outflow with its length of 300 m. The discharge volume from the entire set of niches in 2000–2005 amounted to 72.3 $dm^3 \cdot s^{-1}$ (Mazurek 2010). A small area of the zero-order catchment (26.2 ha) with high levels of specific runoff indicates that the studied alcove can be fed from beyond the topographical catchment.

Within the studied set of niches developed various spring ecosystems conditioned by the following factors: lithology of bottom sediments, exfiltration rates of groundwater, dynamics of water outflows and intensity of seepage and channel erosion and accumulation. Within the channel head Żarnowo the largest area is covered by *Cardamino amarae-Beruletum* developed in broad strips along all the drainage lines, in three trophic forms: typical, related to rivulet banks and bottoms, with *Veronica beccabunga*, at places of footslope water outflows as well as with *Equisetum palustre* with boggy grounds being heavily saturated with exfiltrating water. They are accompanied by a pleuston group of *Lemnetum minoris*. The niche is surrounded by trees and shrubs, including: *Alnus glutinosa*, *Padus avium*, *Ribes nigrum* and *Salix fragilis*. In the western and eastern part, under tree overhangs developed nitrophilous, aquaphilous and ecotonal fringe herbaceous plants –*Stachyo sylvaticae-Impatientetum noli-tangere*. The channel head nature of the discussed habitat is highlighted by an association of *Pellio-Conocephaletum* with *Conocephalum salebrosum*, liverwort with its holarctic range. Its minor micro-phytocenoses occur at points in the immediate vicinity of all groundwater outflows.

The zero run-off catchment is dominated by arable lands in the land-use structure. Only in the immediate surroundings of the channel head, at the slope of the Parsęta valley, there is a line of mixed forest.

Research methods

Three hydrochemical mappings were conducted on the following dates: 22.06.2012, 11.09.2012 and 2.05.2013 within the channel head Żarnowo. Water samples were taken from the sites located at the places of outflow of groundwater at the footslope zone of the studied niches (9 sites), at the hyporheic zone (11 sites) and flows at individual niches and rivulet which drains the channel head (5 sites) (Fig. 2). In total 75 water samples were taken during these three mappings.

The range of measurements made directly in the field covered the following parameters: water temperature, pH and specific electrolytic conductivity. The SEC values were automatically corrected to a standard value of 25°C. In order to determine their chemical composition, water samples were taken from rivulets and from water exfiltration areas (down to a depth of 10 cm) by means of under-pressure probes (MacroRhizon). In laboratory conditions analytical methods were applied in line with the Polish Norms (Elbanowska *et al.* 1999; Markowicz, Pulina 1979; Witczak *et al.* 2013). Water samples were put through 0.45 µm Whatman's cellulose membrane filters. In filtered water samples, the concentration of bicarbonate ions were determined by titration and of sulphates, nitrates and chlorides – by ion chromatography (DX-120, Dionex Ion Chromatograph). A level of concentration of potassium and sodium was determined by emission spectrometry, of magnesium and iron and manganese – by flame atomic absorption spectrometry (SpectrAA 20 Plus, Varian Atomic Absorption Spectrometer). Water samples intended for the determination of iron and manganese were fixed with nitrate acid. The concentration of calcium was determined by titration. The concentration of ionised silica

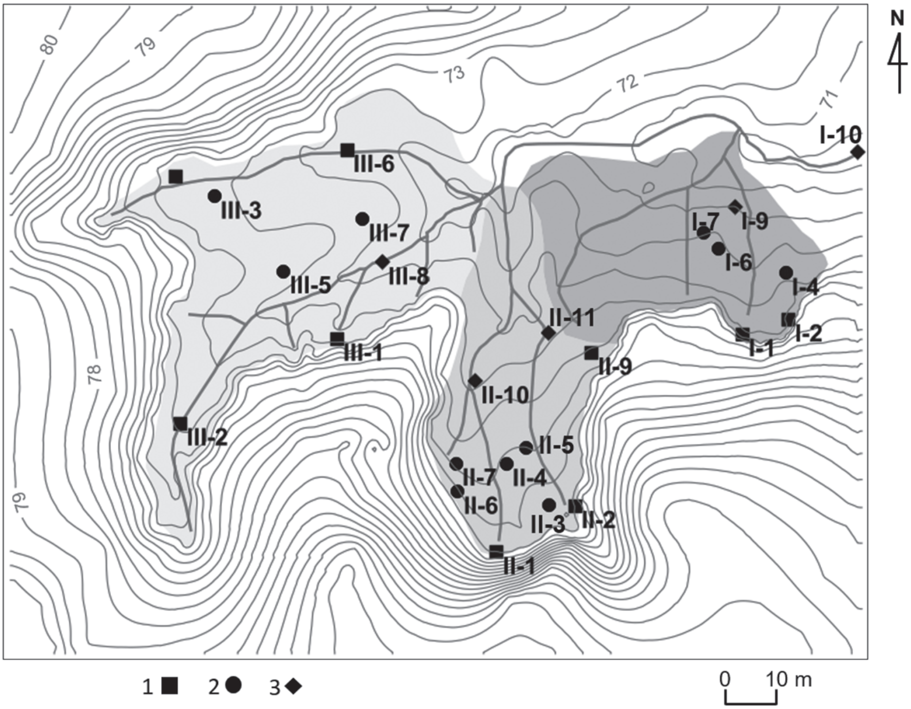

Fig. 2. Distribution of measurement sites within the Żarnowo channel head

1 – groundwater, 2 – interstitial water, 3 – surface water

Source: authors' own study.

and phosphate ions were determined by spectrophotometry (Spekol 1100, Zeiss). The analyses were conducted at the hydrochemical laboratory of the Geoecological Station of the Adam Mickiewicz University located in Storkowo.

The quality of the conducted analyses was verified on the ion balance. The calculated variance of aggregated anions and cations (in eq·dm^{-3}) in the analysed water samples did not exceed 5% of the total ionic components and was ranged within acceptable errors for this type of waters (Macioszczyk, Dobrzyński 2007).

The statistical analysis of the obtained results was made with the application of *Statistica* v.10. The presented statistics were calculated for individual niches taking into consideration the division into three supply zones. These figures are aggregated from the conducted three hydrochemical mappings.

In order to identify the process of supplies of chemical components the factor analysis (the principal components method) was applied (Varimax) (Siwek 2004;

Dragon 2008; Modelska, Buczyński 2007). Some normalised and standardised levels of concentrations of the analysed ingredients were taken as input variables. On the grounds of the Kaiser criterion it led to the singling-out of factors with their eigenvalues exceeding 1. To determine the relationship between and among ion distributions, the Spearman's Coefficient of Rank Correlation (r_s) was applied.

Results and discussion

Weather conditions in the study period

The observations conducted at the meteorological station in Storkowo (Fig. 1) show that the analysed hydrological years (2012 and 2013) according to the thermal and precipitation classification (Lorenc 1998) can be considered average in thermal terms. The average annual air temperature in 2012 was 8.1°C, while in 2013 it was 7.5°C (Szpikowski 2013, 2014). The total annual precipitation classifies year 2012 as standard (698.3 mm) and year 2013 as dry (579.9 mm). The hydrochemical mapping conducted on 22nd June 2012 was preceded by a wet period of time. Within ten years prior to the mapping, precipitation occurred daily, however it did not stand for higher levels of groundwater and rivulets within the analysed period. It was caused by a lack of precipitation in May which was one of the months with the lowest monthly total rainfall (26 mm). The mapping conducted on 11th September 2012 was preceded by a period of time with no precipitation and the measurements were conducted at low water levels. The most recent mapping on 5th February 2013 was conducted with no snow cover, in a wet period with some rain- and snow-fall.

Diversity of physico-chemical properties of waters in the channel head niches

The analysed waters in the channel head were characterised by specific electrolytic conductivity ranging from 393 $\mu S \cdot cm^{-1}$ (Niche II, hyporheic zone) up to 436 $\mu S \cdot cm^{-1}$ (Niche III, rivulet). These are averagely mineralised waters with neutral or alkaline reaction (pH from 7.40 to 8.84) (Tab. 1). In the system: the footslope zone – hyporheic zone – stream runoff, interstitial waters were characterised by the lowest mineralization. This regularity is perceived in each of the analysed niches.

According to the hydrogeochemical classification by Szczukariev-Prikłoński (Macioszczyk, Dobrzyński 2007) the studied waters belong to regular bicarbonate-calcium waters (apart from one site (III-1) with a high level of sulphates). A share of bicarbonates was at a level of 75% (Niche III) up to 94% (Niche I) of the anion equivalent total, then a share of calcium accounted for 75% (Niche I) up to 79%

Table 1. Statistical characteristics of the physical and chemical properties of waters in the Żarnowo channel head

Niche /Zone		N	Statistic	SEC	pH*	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	Fe^{2+}	Mn^{2+}
				[μS·cm^{-1}]		[mg·dm^{-3}]								[μg·dm^{-3}]	
Niche I	groundwater	6	avg±SD	423±40	7.80	66.9±6.7	8.5±0.5	7.5±0.8	2.3±1.2	252.2±20.3	4.7±1.5	6.3±4.1	2.5±1.9	63±87	158±298
			min-max	364–470	7.49–8.13	57.1–78.8	7.8–9.1	6.8–8.6	0.4–4.0	213.6–276.0	2.4–6.8	1.8–13.0	0.2–5.5	0–213	0–819
	interstitial water	9	avg±SD	399±48	7.93	66.9±8.8	8.5±0.5	7.7±1.3	2.2±1.1	247.9±18.0	5.9±2.9	8.6±6.9	1.1±1.5	579±709	303±277
			min-max	350–473	7.71–8.16	56.1–86.8	8.0–9.5	6.6–10.1	1.1–4.1	221.1–277.6	3.3–11.2	2.4–20.4	0.0–4.7	0–1799	4–790
	surface water	3	avg±SD	425±27	7.71	70.3±2.2	8.5±0.1	7.8±0.2	4.6±1.5	268.9±4.9	6.2±0.4	8.9±1.9	3.5±0.8	2±2	35±34
			min-maks	394–445	7.59–7.93	67.7–71.9	8.4–8.6	7.6–7.9	3.0–5.9	265.4–274.5	5.8–6.7	6.8-–10.4	2.6–4.3	1–4	13–74
Niche II	groundwater	9	avg±SD	433±38	7.65	78.0±7.3	7.8±1.0	7.4±0.7	3.7±1.8	254.8±18.1	8.6±1.8	20.4±8.9	19.4±8.4	22±30	70±116
			min-max	370–476	7.40–7.84	64.0–89.6	6.7–10.1	6.7–8.5	1.5–6.5	236.4–294.3	5.4–12.2	7.1–38.3	0.1-–28.5	0–91	0–356
	interstitial water	15	avg±SD	393±51	7.74	64.8±6.7	8.2±0.7	6.6±1.0	1.6±0.4	239.3±10.5	6.4±2.9	8.1±8.3	3.8±6.0	590±751	131±111
			min-max	320–512	7.55–7.99	55.7-–81.0	6.8–10.2	4.0–8.4	1.3–2.9	219.6–259.3	3.5–11.5	2.0–34.4	0.0–16.0	0–2065	0–324
	surface water	6	avg±SD	414±27	7.68	71.5±6.5	8.0±0.9	7.6±1.2	1.9±0.6	238.5±28.5	10.7±5.3	20.9±11.8	8.3±15.0	214±495	231±274
			min-maks	372–455	7.58–7.87	63.1–80.6	6. –8.9	5.5–8.8	1.1–2.9	198.3–284.3	5.7–19.0	9.4–40.7	0.0–38.4	0-–1224	1–766
Niche III	groundwater	12	avg±SD	427±48	7.87	74.1±7.2	7.6±1.0	7.1±0.8	1.4±0.5	230.6±16.3	10.8±5.1	20.9±11.2	19.9±10.8	37±59	66±125
			min-max	325–491	7.75–8.01	61.5–87.2	6.4–9.4	6.2–8.6	0.8–2.4	192.2–248.6	4.6–25.2	6.9–52.5	0.0–30.0	0-–171	0–399
	interstitial water	9	avg±SD	415±22	7.80	74.6±5.8	8.2±0.7	7.8±0.7	1.8±0.7	227.9±20.4	13.5±4.9	30.6±9.2	12.0±10.7	23±46	483±582
			min-max	389–456	7.56–8.30	69.7–86.2	6.5–9.1	6.7–8.8	1.1–3.7	183.0–259.3	6.2–22.5	14.4–45.0	0.0–28.0	0–151	0-1715
	surface water	3	avg±SD	436±84	7.73	67.6±3.9	8.0±0.5	7.2±0.7	1.7±0.4	230.3±17.6	10.7±3.1	20.6±7.8	12.9±11.2	82±110	568±710
			min-maks	341–498	7.54–8.04	63.1–70.3	7.6–8.5	6.4–7.8	1.4–2.2	210.5–244.0	8.0–14.1	13.2–28.7	0.0–20.0	0–207	0–1363
Outflow (I-10)		3	avg±SD	404±18	7.87	69.1±1.4	8.1±0.1	7.3±0.6	1.9±0.1	246.0±17.0	6.3±0.3	12.8±2.9	4.0±2.4	75±125	209±203
			min-maks	384–416	7.64–8.84	67.5–70.1	8.0-–8.2	6.9–7.9	1.8–1.9	234.9–265.4	6.0–6.5	11.1-–16.1	1.2–5.4	6–220	58–440
Niche I		18	avg±SD	411±45	7.84	67.4±7.7	8.5±0.5	7.7±1.1	2.7±1.5	252.8±19.5	5.5±2.4	7.8±5.7	1.9±1.9	311±588	210±288
Niche II		30		409±47	7.70	70.1±8.9	8.1±0.9	7.0±1.1	2.3±1.4	243.8±18.5	7.9±3.6	14.3±11.0	9.4±11.2	344±633	132±162
Niche III		24		423±44	7.82	73.5±6.7	7.8±0.9	7.4±0.8	1.6±0.6	229.6±17.8	11.8±4.9	24.5±11.0	16.0±11.3	38±62	285±484

* mean pH value calculated as follows pH = $-\log_{10}[H^+]$; avg±SD – average ± standard deviation, SEC – specific electrolytic conductivity, N –number of sample

Source: authors' own study.

(Niche I and III) of the cation total (Fig. 3). A level of concentration of bicarbonate and calcium ions was characterised by low spatial calcium not exceeding 15% (higher variability was observed for calcium). Concentrations of the two ions in the footslope zone, hyporheic zone and surface outflow zone were similar. Also among the niches differences in concentrations were minor.

The Spearman's rank correlation coefficient analysis for Ca^{2+}-HCO_3^- (Niche I: $r_s = 0.901$, $\alpha = 0.000$, $n = 18$, Niche II: $r_s = 0.641$, $\alpha = 0.000$, $n = 30$, Niche III: no correlation – $r_s = -0.135$, $\alpha = 0.540$, $n = 24$) (Fig. 4) allows to suggest that the establishment of the hydrogeochemical balance of the discussed waters is affected not only by the process of dissolution of carbonate minerals, but also by supplies from biogenic and / or anthropogenic sources.

The total share of other anions (sulphates, chlorides, nitrates and phosphates) in the channel head waters fluctuated between 5% and 29%. Compared to bicarbonates the spatial variability of concentrations of the specified anions, expressed through their coefficient of variation was significantly higher (sulphates 30–102%, nitrates 43.4–156.7%, chlorides 21.4–49.1%, phosphates 20.8– 59.2%). Generally, the highest concentration of sulphates and chlorides was observed within the exfiltration area of groundwater (apart from Niche I where the highest concentration was found in interstitial waters). In case of nitrates for each of the niches, the maximal concentrations (several tens of $mg \cdot dm^{-3}$) were found in the footslope zone and the lowest (almost undetectable at some places) in interstitial waters (the hyporheic

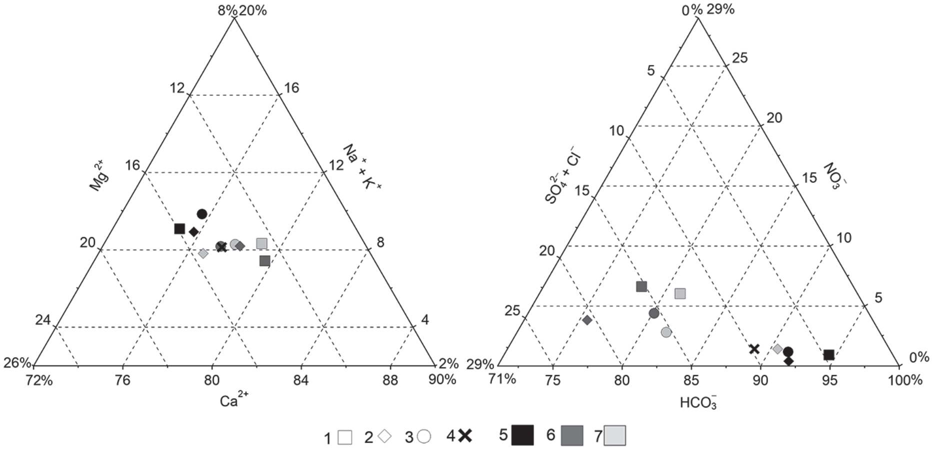

Fig. 3. Water chemistry of the Żarnowo channel head

1 – groundwater, 2 – interstitial water, 3 – rivulet, 4 – channel outflow, 5 – Niche I, 6 – Niche II, 7 – Niche III

Source: authors' own study.

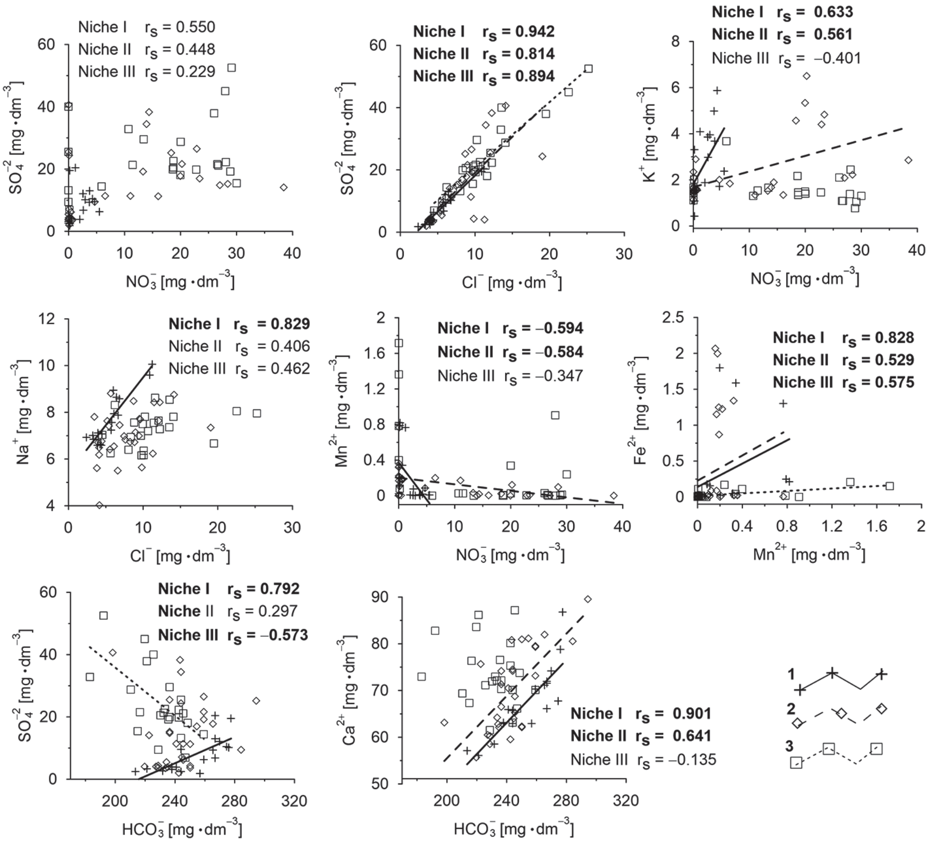

Fig. 4. Correlations between the concentrations of selected ions in the Żarnowo channel head

1 – Niche I, 2 – Niche II, 3 – Niche III, r_s – Spearman's rank correlation coefficient. Given in bold, r_s is statistically significant at $\alpha \leq 0.05$

Source: authors' own study.

zone). This regularity was observed on all the measurement dates. Waters discharged from across the channel head in the form of channel flow (site I–10) had their concentration of nitrates at 1.2 mg·dm^{-3}–5.4 mg·dm^{-3}. These values are higher than the ones in interstitial waters of the bottom hyporheic zone but significantly lower (in some cases up to 20 times) compared to exfiltrating waters in the footslope zone. The variation of concentrations of sulphate and nitrate ions occurs both for the individual zones and between the niches. The lowest concentrations of these anions were recorded in the Niche I. Within rivulets draining individual niches, their average concentrations of nitrates were as follows: 3.5 mg·dm^{-3} (Niche I), 8.3 mg·dm^{-3} (Niche II) and 12.9 mg·dm^{-3} (Niche III) and of sulphate, respectively: 8.9 mg·dm^{-3}, 20.9 mg·dm^{-3} and 20.6 mg·dm^{-3} (Tab. 1).

The Spearman's rank correlation coefficient analysis shows statistically significant dependencies between the spatial distribution of concentrations of Cl^- and SO_4^{2-} (respectively for the niches: $r_s = 0.942$, $\alpha = 0.000$, $n = 18$, II: $r_s = 0.814$, $\alpha = 0.000$, $n = 30$, III: $r_s = 0.894$, $\alpha = 0.000$, $n = 24$) (Fig. 4), which is likely due to the common origin of these ions (for example household or agricultural wastes from the zero run-off catchment). Similar dependencies did not occur in the case of a pair of anions: chlorides – nitrates. Beyond the Niche I where a statistically significant correlation between the concentration of chlorides and nitrates was found ($r_s = 0.554$, $\alpha = 0.018$, $n = 18$), for other niches the obtained coefficients of correlation were not statistically significant.

Phosphate ions were present in the channel head at low concentrations (their range: 0.03 mg·dm^{-3}–0.7 mg·dm^{-3}), which is typical of water sources in the Pomeranian region (Osadowski 2010). The spatial distribution of concentrations of phosphates in the channel head does not show any specific regularities and it is not seasonally variable. The reported concentrations in the individual zones in each of the studied niches studied were similar. A level of concentration of PO_4^{3-} in the stream draining the entire channel head area was at the level of 0.15 mg·dm^{-3} to 0.44 mg·dm^{-3}.

Within the studied channel head a minor level of the spatial variability of concentrations of calcium, magnesium and sodium was found. The coefficients of variation were as follows: 7.7%–13.2% for calcium, 5.5%–13.4% for magnesium and 8.7%–17.1% for sodium. Potassium was characterised by low concentrations with its highest coefficient of variation ranging within 24.6%–51.1%. On each of the measuring dates the lowest concentration of potassium ions was present in the Niche III. At most sites the concentration of potassium ranged from 0.4 mg·dm^{-3} to 6.5 mg·dm^{-3}. In the stream draining water from across the entire set of niches its concentration was kept at 1.9 mg·dm^{-3}. The spatial distribution of concentrations of potassium in the channel head shows no particular regularities and, as in the case of phosphates, there are no differences between successive mappings.

Iron and manganese belong to components of the channel head waters which are characterised by the largest range of the spatial variability of their concentration. The coefficient of variability Cv for iron ranged within 122%–197% and for manganese – 84%–189%. In the studied channel head waters the content of iron was 0 µg·dm^{-3}–2065 µg·dm^{-3} and of manganese – 0 µg·dm^{-3}–1715 µg·dm^{-3}. Concentrations of iron and manganese ions showed directly proportional significant correlations in all the niches due to the natural geochemical analogy of these metals (respectively: I: $r_s = 0.828$, $\alpha = 0.000$, $n = 18$, II: $r_s = 0.529$, $\alpha = 0.003$, $n = 30$, III: $r_s = 0.575$, $\alpha = 0.004$, $n = 24$) (Fig. 4). In general, the highest concentrations of iron (beyond the Niche I) and of manganese were present in the hyporheic zone. In extreme cases, the content of iron in interstitial waters was more than twenty times larger than the one observed in the footslope zone (Niche II). For manganese these disparities were smaller, the maximum concentration in interstitial waters exceeded the values recorded in the footslope zone seven times.

The presence of iron in groundwater feeding the analysed channel head was indicated by amorphous, rusty sediments at the place of groundwater outflows and also sometimes within the stream channel. Iron compounds precipitated in contact with air (mainly hydroxides Mazurek 2010) are the most abundant in the Niche II. In interstitial waters within the bottom zone there were present high and low concentrations of iron and manganese, which indicates the very local character of conditions in the niche hyporheic zone mainly due to the changes in the redox potential and the presence of organic matter. Rivulets leaving the channel head had the following concentrations on the specified measurement dates: for iron: 6; 220 and 1 $\mu g \cdot dm^{-3}$, and for manganese: 58; 440 and 129 $\mu g \cdot dm^{-3}$.

Identification of the sources of supply of solutes in the channel head niches

The recognition of processes affecting the chemical composition of waters within the channel head Żarnowo was conducted on the grounds of the factor analysis. Making use of 13 water components, separately for each of the niches, three (Niche I) or four (Niche II and Niche III) complementary components were singled out, which together explain respectively 83.1%, 77.4% and 79.8% of the variability of the chemical composition of water (Tab. 2). The analysis of the correlation matrix shows that the singled-out factors (factor 1 – Niche I and II, factor 2 – Niche II, factor 3 – Niche I and III, factor 4 – Niche III) are correlated, among others, with bicarbonate anions, calcium, magnesium, sodium, potassium cations and ionised silica. The presence of these ions is related to the process of chemical weathering of postglacial sediments, so these factors can be defined as geogenic. The mineral composition of Pleistocene and Holocene sediments within the Drawskie Lake District is dominated by quartz, plagioclases, potassium feldspars and muscovite. Within their fraction <2 µm, clay minerals, mainly from the group of illite, smectite and kaolinite as well as mixed-layer illite-smectite forms (Mazurek 2008). The mineral-petrographic composition of forms and a large area of the contact of loose sediments with infiltrating water favour the process of weathering of primary minerals (among others silicates) and ion exchange. These processes lead to the release of ions such as, among others,Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^- and ionised silica, which leached by infiltrating water, form the mineralization of groundwater. The presence of silica is related to the release of weathered silicate minerals and leached amorphous silica. The results of the research studies conducted within the Polish Lowland areas indicate that silica is present in trace amounts in rainfall waters and its concentration increases significantly during filtration in the aeration zone, reaching levels similar to or higher than the values recorded listed in the groundwater (Porowska 2007; Szpikowska 2007).

Calcium and bicarbonate ions being dominant in the chemical composition of waters are partly the result of leaching of calcium carbonate found in glacial sediments. Within the Drawskie Lake District tills contain from 2% to 14% $CaCO_3$, and sand and gravel inter-moraine sediments – 4% to 12.9% $CaCO_3$ (Popielski 2000). The results of the Spearman's Coefficient of Rank Correlation for $Ca^{2+}–HCO_3^-$ indicate that the establishment of the hydrogeochemical balance of the discussed waters is affected not only by dissolution of carbonate minerals but also by supplies from biogenic and/or anthropogenic sources. Ions with geogenic origin are characterised by their little diversified and stable distribution within the studied niches. Potassium is the exception – its presence is connected not only with geogenic processes (inclusion in the structure of clay minerals of 2:1 type, mainly illite, and sorption at the surface of soil colloids) but also with participation in the biological cycle.

The anthropogenic factor is represented by sulphates and chlorides – their joint presence in the channel head Żarnowo waters should be in principle combined with the inflow of household wastes from the nearby village of Stary Chwalim and/or pollution from lands used for agriculture situated in the zero-order catchment. This factor was singled out for the two niches: II and III. In the water of Niche I, their levels were found to be much lower than in the two adjacent niches (Tab. 1). As an explanation of this spatial distribution of the quality of groundwater, one can consider facial differences characteristic of Quaternary deposits and their different permeability caused by this fact. In effect, groundwater outflows in niches situated close to one another can have different physico-chemical properties reflecting not only the sources, but also the time and directions of groundwater flow.

At the factor load matrix (Tab. 2) attention should be turned to the negative correlation of nitrate ions with iron and manganese (the redox factor) – their migration in the aquatic environment is dependent on the redox potential and reaction (pH). Under reducing conditions comes a reduction of a degree of oxidation of iron and manganese in insoluble compounds, thus movable forms of these elements at the 2nd degree of oxidation appear in water. Under the same conditions comes a reduction of a degree of oxidation of nitrate nitrogen, which leads to the release of nitrogen in gaseous form and thereby decreased concentration of nitrates in water. Thus there are different dependencies between the redox agent and the analysed ions.

Table 2. Factor loadings obtained using on the basis of an analysis of the chemical composition of groundwater, interstitial water and surface water

Solute/Factor	FAC 1	FAC 2	FAC 3	FAC 1	FAC 2	FAC 3	FAC 4	FAC 1	FAC 2	FAC 3	FAC 4
	Niche I			Niche II				Niche III			
Ca^{2+}	**0.731**	-0.245	0.403	**0.869**	0.114	0.195	0.323	0.570	0.609	0.177	0.193
Mg^{2+}	**0.913**	0.206	0.028	-0.258	**0.841**	0.046	0.122	-0.103	-0.454	**-0.779**	0.138
Na^+	**0.947**	0.021	0.147	0.302	**0.808**	0.081	0.359	0.475	-0.086	**-0.722**	0.030
K^+	**0.737**	-0.447	0.063	**0.771**	-0.270	0.204	0.080	-0.254	0.182	**-0.798**	-0.117
HCO_3^-	0.680	-0.503	0.391	**0.794**	0.403	0.031	-0.249	-0.590	0.274	-0.526	-0.179
Cl^-	**0.874**	0.226	0.231	0.072	0.121	0.000	**0.929**	**0.960**	0.002	0.001	0.106
SO_4^{2-}	**0.875**	0.094	0.284	0.260	0.259	0.252	**0.847**	**0.976**	0.028	0.019	0.029
NO_3^-	-0.030	**-0.818**	0.312	**0.740**	0.023	0.179	0.252	0.194	0.642	0.115	0.654
PO_4^{3-}	0.178	0.159	**0.861**	0.233	-0.255	**-0.779**	-0.096	-0.396	0.044	-0.164	-0.564
Fe^{2+}	0.206	**0.918**	0.156	-0.253	-0.029	**-0.855**	-0.138	-0.022	**-0.820**	0.092	-0.007
Mn^{2+}	-0.081	**0.926**	0.033	-0.468	0.276	**-0.662**	0.029	0.233	**-0.886**	-0.065	-0.069
SiO_2	-0.329	0.321	**-0.729**	-0.611	0.100	0.115	-0.082	0.064	-0.095	0.125	**-0.949**
% variance explained	41.6	25.9	15.6	28.9	15.4	16.5	16.6	25.8	21.4	17.9	14.7

Given in bold are factor loads < -0.7 or > 0.7

Source: authors' own study.

Conditions of the physicochemical properties of 1^{st}-order stream in the postglacial zone

The research studies on the physico-chemical properties of groundwater conducted within the channel head Żarnowo indicate that there are groundwater with various parameters which blend together within the niche bottom. The chemical composition of waters within the emerging 1^{st}-order stream depends on the performance of individual sources of niche supplies. The presence of geogenic ingredients such as bicarbonates, calcium, magnesium, sodium and potassium in the rivulet waters is the result of chemical weathering and leaching of its products. The intensity and nature of these natural processes depend on the environmental parameters of the zero-order catchment, water migration rates and lithological variability of the niche aquifer and bottom.

Geogenic ions are dominant in the chemical composition of the channel head waters and are characterised by minor spatial variability and concentration stability over time. The differences in the facies characteristic of Quaternary deposits and the resulting differences in their permeability and filtration coefficients influence the direction and time of groundwater flow in the aquifers supplying channel head niches. As a result, groundwater flowing out in neighbouring niches can have different physical and chemical properties reflecting its flow conditions. Those differences can be wider in areas where man-made pollution exerts its direct impact.

The largest disparities of ion concentrations in waters of the individual niches were found for sulphates, chlorides and nitrates, representing the anthropogenic factor. The uncovered aquifer made by fluvioglacial sediments with favourable filtration conditions is characterised by high susceptibility to contamination. As no pollution sources were found in the direct neighbourhood of the channel head, their elevated levels can be due to the contamination of the water-bearing horizon with fertiliser components from the agricultural part of the headwater catchment, and to a lesser extent, from household waste coming from the village of Stary Chwalim (Fig. 1).

The highest concentrations of these ions were observed in the place of exfiltration of groundwater within the footslope zones in the studied niches. These can be outflows of anthropogenically contaminated waters which did not transform within the niche itself. A similar lack of favourable conditions for the transformation of waters (as a result of de-nitrification and reduction of sulphates) was observed for outflows under pressure located in the niche bottoms filled with mineral sediments (Michalska 2003; Angier *et al.* 2005; Shabaga, Hill 2010).

Nitrates belong to the group of components with the highest spatial variability of concentrations in the studied niches. Their concentration is significantly reduced in the hyporheic zone. This regularity is perceived in each of the analysed niches. This is the effect on biogeochemical processes connected with a change in the degree of oxidation of nitrogen in interstitial waters. The channel head bottom permanently water-logged is fed by waters with an average temperature of approx. 8.8°C (Mazurek 2010). As a result even in winter periods there is a green community of *Cardamino amarae-Beruletum erecti* Turmanova 1985. Dead vegetation is a source of organic matter. After the decay of organic matter follow aerobic deficits which determine the growth of microorganisms taking oxygen from aerobic combinations of nitrogen (Puchalski *et al.* 1997). These are the conditions which favour the process of reduction of nitrates to free nitrogen (denitrification), which is equivalent to decreasing the concentration of nitrate ions in the water. A factor reducing the content of nitrates in the channel-head floor can also be its abundant vegetation which promotes NO_3^- removal not only via denitrification, but also via vegetative uptake.

Within the niche waters a minor level of spatial variability was found in the concentration of chloride ions connected with the anthropogenic factor. This is a conservative component which does not participate in biogeochemical transformations. Its concentration is regulated by a volume of water flowing through the processes of concentration or dilution (Małecki 1998).

The chemical composition of waters in the emerging 1st-order stream also depends on shares and performance of individual supply components within the channel head area. In rainfall and melting periods surface-exfiltrating waters in the niche bottom may be subject to dilution, which causes changes in the chemical composition of waters, while during growing periods the channel head vegetation through evapotranspiration may lead to increased water mineralization. Atmospheric inflows as a source of ions in the outflow from the studied niches are of little importance. The monitoring of atmospheric precipitation at the Geoecological Station in Storkowo (Fig. 1) located 4 km from the channel head Żarnowo indicates that the today's share of atmospheric deposition in the load of components discharged from the catchment geoecosystems (the upper Parsęta catchment) is at a few percent (Szpikowska 2006).

Conclusion

The research conducted made it possible to identify determinants and processes common to the niches examined that affect the physico-chemical properties of their water. They include:

- the lithology of substratum deposits, especially those rich in calcium carbonate,
- the inflow of groundwater with a temperature stable throughout the year, and
- water- and moisture-loving types of plant communities and their seasonal variability affecting the uptake and release of dissolved substances.

In turn, the differences in the chemical composition of water in neighbouring niches can be put down to:

- differences in hydrodynamic conditions determining groundwater flow routes (residency time) and drainage conditions,
- the land-use pattern and management in areas of alimentation of groundwater outflows and the impact of various kinds of pollutants originating from point or dispersed sources,
- differences in the conditions of groundwater exfiltration: the rate of water seepage, its discharge, and type of outflow,
- the microtopography and mosaic of biogenic deposits resulting from hydrogeomorphological processes, and
- variations in the hydrogeochemical environment, e.g. resulting from changes in water temperature and redox conditions.

The channel head niche constitutes a point of contact of the slope and streambed subsystem; the physicochemical properties of waters of these two subsystems reflect various conditions and processes which eventually shape the chemistry of waters in the 1st-order stream. The conducted factor analysis indicates several major conditions affecting the chemical composition of waters within the channel head Żarnowo. They include the following factors: (1) geogenic – covering the properties of the aquifer system in the postglacial area, (2) anthropogenic – locally relevant, (3) biogenic and (4) redox – representing the direction of changes taking place in the hydrogeochemical environment within the hyporheic zone. These conditions with different intensities affect the quality of waters present in the adjacent channel head niches, as evidenced by a number of the singled-out factors and their relationships with individual ions.

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