# SPATIOTEMPORAL VARIABILITY IN HEADWATER STREAM CHEMISTRY IN THE YOUNG-GLACIAL LANDSCAPE OF THE SOUTHERN BALTIC COASTAL ZONE

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**Abstract:** A study investigating the spatial and temporal variation of physiochemical parameters in headwater streams was performed over a period of 12 months in the catchment of the Kamienna Creek (northern Poland). Water samples were collected in monthly cycles along three streams (in their upper, middle and lower sections) flowing through the riparian forest, as well as from the Kamienna Creek. In the collected samples, parameters including temperature, pH, electrolytic conductivity, concentration of dissolved oxygen and $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$, $HCO_3^-$, $Cl^-$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$ ions were determined. The collected water samples were characterised by a neutral or slightly basic pH (6.6-8.9), as well as considerable variation in average electrolytic conductivity, with values ranging between 213 and 544 $\mu S^.cm^{-3}$ in streams and between 114 and 366 $\mu S^.cm^{-3}$ in the creek. In general, waters were characterised by low concentrations of dissolved compounds, with a predominance of $HCO_3^-$ and $Ca^{2+}$. The waters in both the streams and the creek are calcium-bicarbonate type and are characterised by low seasonal variability, with season having no influence on concentrations of $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$, nor on conductivity, hardness and mineralisation. However, spatial variation in the chemical composition of waters was observed. Based on data analysis it was found that whereas the waters of the Kamienna Creek were dominated by $Ca^{2+}/Mg^{2+}$ and $HCO_3^-$, those the water of streams were characterised by moderate and low concentrations of calcium, magnesium and hydrocarbonate ions.

**Keywords**: Forest, riparian zone, headwater stream, groundwater chemistry, transformation processes

## 1. INTRODUCTION

As unique objects in the landscape of river valleys, springs represent an important element of the water network and play an essential function in the circulation of water and water balance, even shaping water equilibrium and habitat quality at far distant locations. Springs also play an important role in the functioning of river basin ecosystems, acting as a base or river supply and the stage for water chemistry transformation (Hill 2000; Butturini et al., 2002; Jekatieryńczuk-Rudczyk; 2005; Mazurek; 2006; Astel et al., 2008; Ranalli et al., 2010; Jonczak 2011). Headwater areas create habitats characterised by considerable phytocoenotic, floristic and faunal diversity (Osadowski, 2006, 2010; Dosskey et al., 2010), with the specific structure, properties and

dynamics of the processes occurring in these niches making such ecosystems extremely sensitive to human activities (Mazurek, 2008).

The outflow sites of spring waters represent transition zones between the underground and surface parts of water circulation in the catchment (Mazurek et al., 2014). According to local geomorphological, pedological and hydrological characteristics, as well as weather conditions, spring outflows are characterised by both a specific capacity and temporal variability of discharge (Gold et al., 2001; Hill et al., 2004; Mazurek, 2006, 2008; Gupta et al., 2011; Hindshaw et al., 2011). Water overflow and its constant flow; in particular, creates unique conditions for the development of soils in reference to other habitats (Stutter et al., 2006; Jonczak, 2010; Jonczak & Cysewska, 2010). On the one hand, outflow introduces to the ecosystem a given

amount of ions, while on the other, some compounds can be selectively leached from the soil (Janisch et al., 2012). The flow of ground water streams is responsible for heavy erosion at the site of outflow. In turn, development of flora not adapted to such conditions becomes difficult. Indeed, the presence of constantly flowing fresh water originating from depth does not allow organic matter deposition in the immediate vicinity of the source. The direction and extent of the transformation of spring water chemical composition, and subsequently the quality of river water, is determined primarily by the properties of the soils occurring within the area (Tabacchi et al., 2000, Temnerud & Bishop 2005, Jekatierinczuk-Rudczyk 2007), as well as by the nature of plant communities, seasons and the severity of anthropopression (Ohte et al., 2001; Welsch et al., 2001; Uhlenbrook & Hoeg 2003; Mayer et al., 2005; Temnerud & Bishop 2005; Helliwell et al., 2007; Buffam et al., 2008; Zhang et al., 2008; Dosskey et al., 2010). In recent years, increasing attention has been paid to the influence of tree species composition in the catchment and its role in shaping the quality of groundwater and surface water (Davies et al., 2005; Astel et al., 2008; Małek et al., 2010; Parzych et al., 2017). However, the physiochemical transformation of waters in the upper part of the stream network is often neglected, despite it having a significant impact on the assessment of water quality in lower courses (Bishop et al., 2008). Small streams with catchment areas $<2$ km$^2$ are of great ecological importance, with surveys of first and second order streams revealing considerable spatial and temporal variability in the water chemistry of these headwaters. The accurate diagnosis of hydrological processes occurring in areas of limited human pressure should form the basis for any evaluation of objects under the influence of anthropogenic transformation and represents an important element in the management of protection strategies. Despite the publication of numerous studies examining springs, transformation processes of the physicochemical parameters of water flowing through headwaters remain insufficiently recognised. The aim of the present study was thus to analyse the spatiotemporal transformation of the physiochemical parameters of spring water located in the central part of the Kamienna Creek valley (northern Poland), as well as its impact on the quality of river water.

## 2. MATERIALS AND METHODS

### 2.1. Study site

The study was conducted in the middle section of the Kamienna Creek valley, a left-hand tributary of the Słupia River located in northern Poland (54°19'N; 17°10'E) (Fig. 1). Sampling took place in the "Słupia Valley" landscape park, which is surrounded by forest and far from economic and industrial activities. The average annual aboveground temperature in 2012 measured within in riparian forest was 7.7°C (maximum 32°C in July, minimum -13.5°C in February), while total precipitation was 770 mm (Jonczak et al., 2015b). The catchment of the Kamienna Creek is almost entirely covered by forest with a diverse species composition, dominated by beech, pine and spruce on the plateau and by black alder in the valley bottom. Underground waters flowing in the niche are surrounded by riparian ash-alder, identified as *Fraxino-Alnetum cardaminetosum amarae*. The ribbons of trees found along streams are composed of 40-86 year old stands of black alder (*Alnus glutinosa* Gaertn.). Within the riparian forest, a high proportion of species generally considered as characteristic for this ecosystem are found, such as *Galium palustre* L., *Lycopus europaeus* L., *Lythrum salicaria* L., *Lysimachia vulgaris* L. and *Solanum dulcamara* L. Locally coexisting species include *Cardamine amara* L., *Chrysosplenium alternifolium* L., *Carex paniculata* L. and *Scirpus sylvaticus* L., as well as the protected plant species *Dactylorhiza majalis* (Rchb.) P.F. Hunt & Summerh. and *Polypodium vulgare* L. Forest stands lie on an overgrown bog dome built of alder peat with interbeds of alder-sedge peat. Histosols are characterised by a spatially varied thickness not exceeding 1 metre, with a slightly acidic or acidic pH. These soils are rich in nitrogen and calcium, and relatively poor in phosphorus, potassium and magnesium (Jonczak et al., 2015a). Soil and stream waters are continuously enriched in macro- and micronutrients supplied via organic deposition (3482.5 - 4106.9 kg/ha, Jonczak et al., 2016), although due to favourable conditions this is quickly decomposed (Jonczak et al., 2015b).

### 2.2. Water sampling and analysis

For physiochemical analysis, water samples were collected at monthly intervals (from January to December 2012) along three headwater springs in their upper (a), middle (b) and lower (c) sections flowing through a riparian forest, as well as from the Kamienna Creek directly up- and downstream of the niche. Samples were collected in 0.5 dm$^3$ polyethylene (PET) containers. Temperature, pH (CPI 551 Elmetron, Poland), electrolytic conductivity (CC 315, Elmetron, Poland) and dissolved oxygen O$_2$ (HI 9146, Poland) were measured in the field.
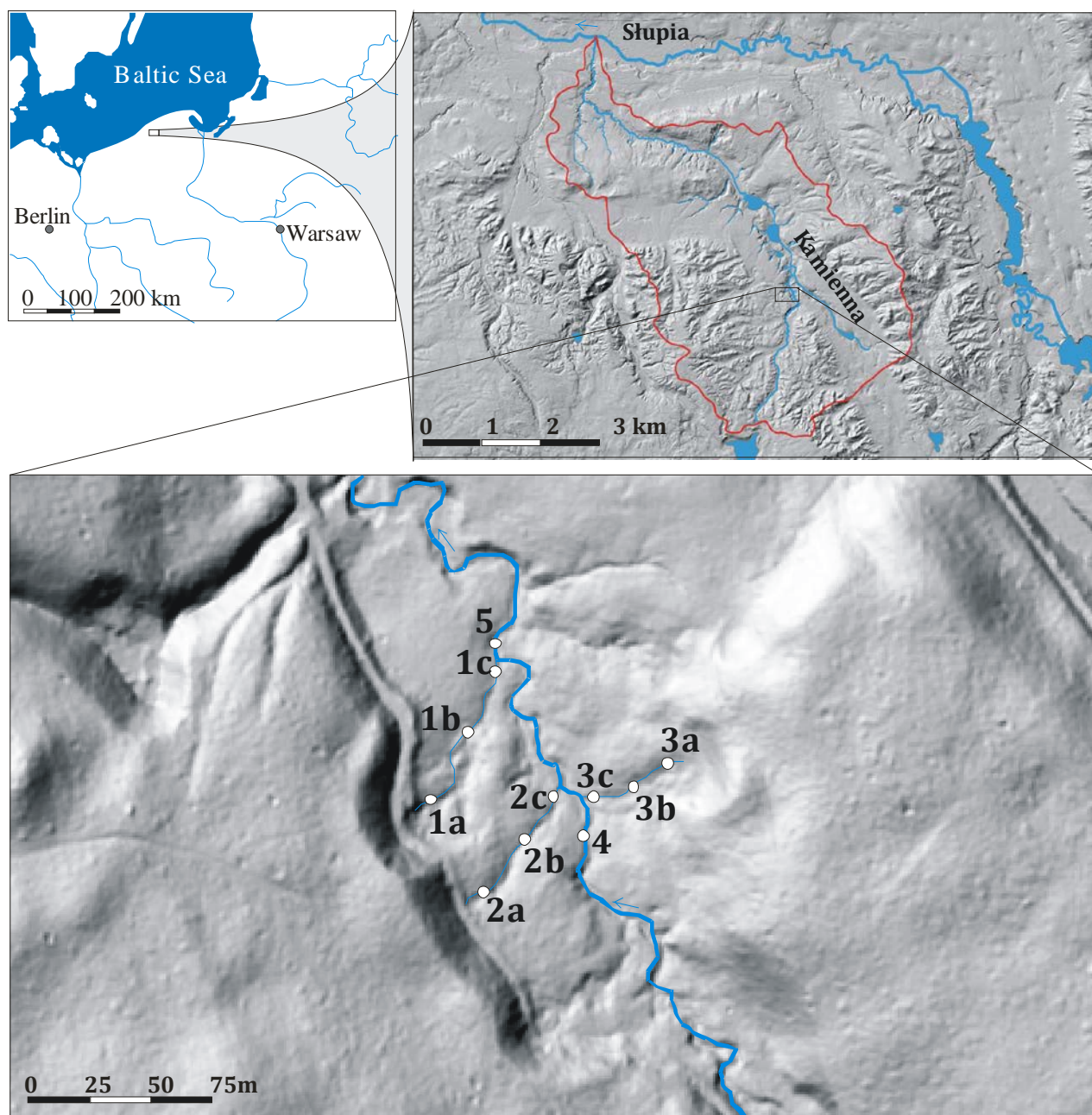
Figure 1. Sampling points distribution within the investigated spring niche on the background of airborne LIDAR based digital elevation model (DEM).

In the laboratory, concentrations of $HCO_3^-$ were determined via acid-base titration, and levels of $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$, $Cl^-$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$ using ion chromatography (881 Compact IC pro, Metrohm, Switzerland). Water samples were filtered through a 0.20 μm sterile syringe filter and diluted with demineralised water in a ratio of 1:4. The aforesaid determinations were carried out in Metrosep C4 250/4.0 and Metrosep A Supp 5 250/4.0 analytical columns equipped with Metrosep C4 Guard/4.0 and Metrosep A Supp 4/5 Guard 4.0 precolumns, respectively. The accuracy of the output and QA/QC were based on certified reference material (Multi-element Ion Chromatography Anion Standard, Certified 89 866-50ML-F, Fluka, France).

### 2.3. Statistical analysis

Based on the above results, the overall mineralisation as the sum of all anions and cations ($mg \cdot dm^{-3}$) was calculated, as well as water hardness (Hard) (sum of $Mg^{2+}$ and $Ca^{2+}$, $mval \cdot dm^{-3}$). Data distribution was checked using the Shapiro-Wilk's test ($p=0.05$), while the overall exploration of the analytical data was accomplished via Factor Analysis (FA) with Principal Component Analysis (PCA) as a method of latent factors extraction. A rotated PCA solution was then interpreted via the

use of a normalised varimax rotation algorithm. Factor scores were presented as a series of plots categorised according to season, month and stand. All calculations were performed using the software package STATISTICA 10.0 (Statsoft Inc., USA).

## 3. RESULTS

The mean temperature of headwater streams ranged between 7.6 and 7.8°C during the research period, with a value of 7.7°C recorded for the Kamienna Creek. Temperatures in the latter also exhibited much greater seasonal variation than the analysed stream waters (Table 1). The collected water samples were characterised by a neutral or slightly basic pH (6.6-8.9), as well as considerable variation in average electrolytic conductivity, with values ranging between 213 and 544 $\mu S \cdot cm^{-3}$ in streams and between 114 and 366 $\mu S \cdot cm^{-3}$ in the creek, corresponding to coefficients of variation of 20.5% and 32.7-35.3%, respectively. The concentration of dissolved oxygen varied depending on the sampling location, with values ranging between 3.4 and 12.4 $mg \cdot dm^{-3}$ in headwater stream waters, and between 7.4 and 12.3 $mg \cdot dm^{-3}$ in the Kamienna Creek (Table 1). Together with water flow along the watercourses, a 34% increase in oxygenation was observed.

Sodium concentrations ranged between 3.9 and 9.5 $mg \cdot dm^{-3}$ in headwater stream water and between 4.2 and 6.6 $mg \cdot dm^{-3}$ in the Kamienna Creek, average potassium ion concentrations from 1.4-1.6 $mg \cdot dm^{-3}$ in

stream water and 1.9 $mg \cdot dm^{-3}$ in the Kamienna Creek, while average concentrations of $NH_4^+$ varied up to 0.2 $mg \cdot dm^{-3}$ across all samples, with values of the coefficient of variation ranging between 88 and 103%. Among those investigated, calcium ions were the most abundant (Table 1), with concentrations ranging between 26.0 and 73.1 $mg \cdot dm^{-3}$ in streams and between 15.8 and 52.8 $mg \cdot dm^{-3}$ in Kamienna Creek surface water samples. In contrast, concentrations of magnesium ions were much lower, at between 2.6 and 2.9 $mg \cdot dm^{-3}$ in the streams and 1.6 $mg \cdot dm^{-3}$ in the Kamienna Creek. Average chloride levels varied between 6.5 and 7.3 $mg \cdot dm^{-3}$ (headwater streams) and 7.6 $mg \cdot dm^{-3}$ (Kamienna Creek), while the mean content of $HCO_3^-$ ranged between 140 and 183 $mg \cdot dm^{-3}$ (headwater streams) and between 73 and 153 $mg \cdot dm^{-3}$ (Kamienna Creek) (Table 1).

Outflows of groundwater were characterised by a smaller coefficient of variation for $HCO_3^-$ concentrations (3-4%) in comparison to that of Kamienna Creek waters (22%). Concentrations of nitrates in streams ranged from values lower than the detection limit (LOD) (0.05 $mg \cdot dm^{-3}$) to 5.8 $mg \cdot dm^{-3}$, and from <LOD to 2.9 $mg \cdot dm^{-3}$ for Kamienna Creek water, presenting seasonal variation of up to 66%. Mean content of $SO_4^{2-}$ varied from 18.1 to 22.0 $mg \cdot dm^{-3}$ (headwater streams) and 15.8 $mg \cdot dm^{-3}$ (Kamienna Creek), while phosphate levels were recorded at 0.9-1.4 $mg \cdot dm^{-3}$ and 1.2 $mg \cdot dm^{-3}$ for stream and river samples, respectively, presenting 59% variation over the research period depending on

Table 1. Physicochemical properties of water (mean ± standard deviation) of headwater streams and Kamienna Creek.

| Parameter | Headwater stream 1 | | Headwater stream 2 | | Headwater stream 3 | | Kamienna Creek | |
|---|---|---|---|---|---|---|---|---|
| | mean±SD | range | mean±SD | range | mean±SD | range | mean±SD | range |
| Temp.[$^o$C] | 7.7±2.6 | 2.3-12.0 | 7.6±3.1 | 0.8-12.0 | 7.8±3.1 | 1.1-12.0 | 7.7±3.6 | 0.9-13.0 |
| pH* | 7.8±0.5 | 6.7-8.8 | 7.7±0.5 | 6.9-8.9 | 7.7±0.5 | 6.6-8.9 | 7.7±0.5 | 6.7-8.6 |
| EC [$\mu S \cdot cm^{-3}$] | 336±87 | 226-544 | 316±81 | 228-435 | 293±74 | 213-393 | 238±79 | 114-366 |
| O$_2$ [$mg \cdot dm^{-3}$] | 9.0±1.5 | 4.4-12.2 | 8.9±1.6 | 3.4-12.4 | 8.9±1.2 | 5.1-11.4 | 9.9±1.3 | 7.4-12.3 |
| Na$^+$ [$mg \cdot dm^{-3}$] | 5.7±0.9 | 4.5-8.4 | 6.1±1.1 | 4.5-9.5 | 5.3±0.9 | 3.9-8.0 | 5.5±0.7 | 4.2-6.6 |
| K$^+$ [$mg \cdot dm^{-3}$] | 1.5±0.5 | 0.7-3.1 | 1.6±0.5 | 0.9-2.8 | 1.4±0.4 | 0.9-3.1 | 1.9±0.5 | 0.9-3.2 |
| NH$_4^+$ [$mg \cdot dm^{-3}$] | 0.2±0.2 | 0.0-1.2 | 0.2±0.2 | 0.0-0.7 | 0.2±0.2 | 0.0-0.7 | 0.2±0.2 | 0.0-0.7 |
| Ca$^{2+}$ [$mg \cdot dm^{-3}$] | 50.8±11.9 | 28.8-73.1 | 49.1±9.5 | 29.2-66.8 | 45.3±9.6 | 26.0-64.0 | 32.8±10.8 | 15.8-52.8 |
| Mg$^{2+}$ [$mg \cdot dm^{-3}$] | 2.9±1.6 | 0.1-5.5 | 2.7±1.7 | 0.0-5.0 | 2.6±1.6 | 0.0-5.0 | 1.6±1.3 | 0.3-3.8 |
| Cl$^-$ [$mg \cdot dm^{-3}$] | 7.3±1.6 | 5.3-15.0 | 6.9±1.4 | 4.8-13.6 | 6.5±1.0 | 4.3-8.9 | 7.6±2.7 | 5.4-19.8 |
| HCO$_3^-$ [$mg \cdot dm^{-3}$] | 165±5.8 | 152-183 | 163±6.4 | 152-183 | 156±5.9 | 140-170 | 114±24.4 | 73-153 |
| NO$_3^-$ [$mg \cdot dm^{-3}$] | 1.8±0.5 | 0.0-4.6 | 2.6±0.7 | 0.0-5.8 | 0.8±0.5 | 0.0-2.2 | 1.8±0.7 | 0.0-2.9 |
| SO$_4^{2-}$ [$mg \cdot dm^{-3}$] | 21.3±1.0 | 19.7-24.5 | 22.0±2.5 | 17.6-35.1 | 18.1±2.5 | 14.5-31.01 | 15.8±6.6 | 10.1-45.4 |
| PO$_4^{3-}$ [$mg \cdot dm^{-3}$] | 1.0±0.5 | 0.1-2.6 | 1.4±0.6 | 0.3-3.1 | 0.9±0.5 | 0.2-2.6 | 1.2±0.6 | 0.4-2.8 |
| Hard [$mval \cdot dm^{-3}$] | 2.8±0.6 | 1.6-4.1 | 2.7±0.5 | 1.6-3.4 | 2.5±0.5 | 1.4-3.6 | 1.7±0.6 | 0.8-2.9 |
| Total mineralization [$mg \cdot dm^{-3}$] | 258±13.5 | 233-292 | 255±11.4 | 233-285 | 237±13.5 | 215-264 | 182±36 | 119-237 |

Note: *mean pH value calculated as follows pH = -log$_{10}$[H$^+$], EC – electrolytic conductivity, SD – standard deviation

sampling location and date. The hardness of the tested waters also varied and was dependent primarily on levels of $Ca^{2+}$ and $Mg^{2+}$ ions, with stream waters characterised by slightly higher hardness (2.5-2.8 mval·$dm^{-3}$) than Kamienna Creek waters (1.7 mval·$dm^{-3}$) (Table 1). The share of ionic components in the analysed waters corresponded with their respective mineralisation; outflows of groundwater were richer in ionic compounds (237-258 mg·$dm^{-3}$) than river waters (182 mg·$dm^{-3}$).

## 4. DISCUSSION

### 4.1. Physicochemical properties of water

The temperature of the investigated waters was shaped by both meteorological conditions and season (Horska-Schwarz and Spałek 2010, Janisch et al. 2012, Garner et al. 2014). Stream waters were characterised by low temperature variation (8.6–8.7°C), which has a beneficial effect on the intensity of organic matter mineralisation (Jonczak et al., 2015b). Water temperatures were also negligibly higher than the average annual air temperature, measured within a niche, of 7.6°C. The obtained results lie within the half-year temperature range for the period 2000-2009 and are characteristic of groundwater at a depth of about 5 m b.s.l. Temperatures in the upper groundwater aquifer were close to the average annual air temperature and correlate with values found elsewhere in the literature (Bloomfield et al., 2013; Garner et al., 2013).

Although the temperature variation of Kamienna Creek water was slightly higher (10.6-12.1°C) than that of stream water, the differences were similarly rather small due to the location of the headwater area in a floodplain forest with a specific microclimate (Garner et al., 2014). According to the classification of Pazdro & Kozerski (1990), stream waters exhibited a neutral to slightly alkaline pH (6.6-8.9) (Table 1), a finding that is unsurprising as groundwater in young glacial areas often has an alkaline pH due to the prevalence of $CaCO_3$ (Mazurek et al., 2014). Similar results of alkaline pH of stream waters in northern Poland obtained Mazurek (2006), Jekatierynczuk-Rudczyk (2005, 2007) and Parzych et al., (2016). A slight pH decrease observed in May at all locations was the result of the beginning of the vegetation period and the associated increased demand for alkaline cations (Osadowski, 2010).

### 4.2. Chemical properties of water

The negligible values obtained regarding water electrolytic conductivity reflect a lack of anthropogenic impact, together with the shallow circulation and most likely a short residence time in the ground. The periodic decrease in electrolytic conductivity recorded in March reflects the inflow of snowmelt, with greater flow and reduced infiltration of the frozen soil (Jonczak, 2010). Water in the initial stream stages exhibited higher electrolytic conductivity and lower dissolved oxygen content than river water. The obtained electrolytic conductivity values are indicative of low or medium mineralisation of waters, which underwent modification along the course of the streams due to contact with the diverse riparian vegetation (Pielech et al., 2015). The recorded dissolved oxygen levels were derived almost exclusively from the atmosphere, with the contact surface between water and atmosphere increasing together with gradual oxygenation as a result of water mixing (Joshi & Kothyari 2003).

The chemistry of groundwater is usually modified by precipitation, which washes out the chemical components of soil via rainwater infiltration. Among those investigated in the present study, calcium cations were the most abundant (Table 1). The concentration of $Ca^{2+}$ in groundwater effusion depends on carbonates equilibrium. According to its physico-chemical characteristics, calcium may be either precipitated or pass to solution from sediments (Bukowska-Jania, 2003). In young glacial sediments an average concentration of calcium carbonate is usually lower that 10% in subsurface layers and reaches 10-20% in deeper ones (Bukowska-Jania 2003; Mazurek 2008). The chemical composition of such sediments and their contact with infiltrating waters leads to the release of $Ca^{2+}$ and $Mg^{2+}$, which after being washed out increase water mineralisation. Along the course of the streams from point (a) to (c), a slight decrease in cation levels was observed due to their uptake by vegetation, with the lowest concentrations of $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ observed in April and July. As nitrogen is absorbed by plants in the form of $NH_4^+$, or after oxidation as $NO_3^-$, the significant decrease in ammonium ions recorded in the middle (b) and lower (c) parts of the courses reflects intensive nitrification taking place during water oxygenation, as well as the sorption of both forms of mineral nitrogen by plants. $NO_3^-$ ions easily migrate in waters and to a small extent are subject to sorption (Bernot & Dodds 2005). Nitrates are intensively taken up by plants during the vegetation period and as a result their concentration in water decreases (Sickman et al., 2003; Rafałowska, 2008; Osadowski, 2010; Parzych, 2011). Indeed, many plant species more often assimilate $NO_3^-$ than $NH_4^+$ due to the slightly alkaline or neutral pH of waters (Britto & Kronzucke 2002; Parzych, 2010; Parzych et al., 2010).

Among the tested anions, bicarbonates dominated, with their primary source being the dissolution of carbon dioxide in water and the leaching of carbonate rocks under the influence of dissolved $CO_2$. The presence of carbonates may be also related to the weathering of silicates and aluminium silicates. Various forms of inorganic carbon play an important role in regulating the pH of natural waters (Jekatierynczuk-Rudczyk, 2007; Jonczak, 2010). The analysed outflowing underground waters exhibited a gradual decrease in $CO_2$ between points (a) and (c), associated with a reduction in $HCO_3^-$ with water flow.

Sulphate ions were found at slightly lower levels in the investigated waters and were characterised by little annual variation. Their origin in groundwater is usually related to biogeochemical processes, as well the impact of precipitation (Mazurek et al., 2014). Similarly, the source of phosphorus was likely decaying organic matter deposited along the stream length (McNeish et al., 2012). As phosphate ions are among the nutrients necessary for plants to produce biomass (Kelly et al., 2007, Parzych & Sobisz 2010), the decreased concentration of $PO_4^{3-}$ recorded in summer was caused by the increased biological activity of plants and the associated growth of biomass. A reduction in phosphate was also observed from stream points (a) to (c). This lower concentration of ions might be related to the presence of significant amounts of precipitation, with outflows of groundwater supplied with shallow circulation waters (Michalczyk et al., 2004).

### 4.3. Factors determining the physicochemical and chemical composition of water

Principal components analysis (PCA) revealed the presence of five independent factors explaining 76% of variability in the chemical composition of the investigated stream waters (Table 2). Factor 1 (F1) explained 28% of variability and included concentrations of $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$ and $SO_4^{2-}$, electrolytic conductivity, hardness and total mineralisation, all characterised by large positive factor loadings. Calcium, magnesium and bicarbonates considerably influenced electrolytic conductivity, hardness and total mineralisation. The second factor (F2), which explained 15% of variability, comprised the ions $Na^+$, $Cl^-$ and $SO_4^{2-}$, as well as water temperature. Increases in chloride, sulphate and sodium ions were observed together with decreases in water temperature. A decrease in water temperature during winter and spring often causes an increase in the concentrations of certain components, which then decrease with the beginning of the growing season (Sickman et al., 2003). The high value of the factorial load for $Na^+$ (0.5) indicates that this component refers mainly to the presence in water of salts, including NaCl and $Na_2SO_4$ (Table 2). The third factor was conditioned by dissolved oxygen, which was negatively correlated with water pH. This factor reflects the relationship between oxidative-reductive conditions and changes in the pH of the studied waters, with a higher pH resulting in a lower oxygen content and vice versa. The fourth factor (F4) explained 9% of variability in the chemical composition of the studied waters and was conditioned by a directly proportional correlation between $NO_3^-$ and $PO_4^{3-}$ ions. A biogenic origin of both nitrates and phosphates is the result of organic matter decomposition processes (Jonczak & Parzych 2014), which are favoured by a high moisture content, temperatures above 0°C and high levels of biological activity in topsoil. Elements and chemical components leached during this process likely influenced the chemical composition of the analysed spring waters, although a part of this load is bound by the soil sorptive complex (Jonczak, 2010) or taken up by plant roots (Mayer et al., 2005; Parzych et al., 2016). The fifth factor (F5), explaining 10% of total variability, was conditioned by electrolytic conductivity and was inversely proportionally correlated with concentrations of $Na^+$, $K^+$ and $NH_4^+$ (Table 2).

Factor values of the analysed objects were then represented in the form of categorised scattering charts, with the first example shown in figure 2 based on season of the year as the categorical variable, i.e. winter (December, January and February), spring (March, April and May), summer (June, July and August) and autumn (September, October and November).

Analysis of this figure reveals that season had no significant effect on concentrations of $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$, conductivity, hardness and mineralisation, with the variability of factorial values in relation to factor 1 ranging from -1 to 1 for most objects and with a parallel dispersion of points. Furthermore, the projection of values on the axis of factor 1 reveals the existence of several objects (in the form of a dispersed cloud on the left-hand side) representing waters characterised by low levels of $Ca^{2+}/Mg^{2+}$ and $HCO_3^-$ (soft water with low conductivity and total mineralisation). These samples represent river waters collected before and after the studied spring niche (locations 4 and 5). Such reasoning is confirmed by the second categorised graph of factorial values, in which stand location was used as the categorical variable (Fig. 3). From this figure it can be concluded that the geological parameters of the waters (F1) are spatially varied.

Table 2. Factor loading obtained from the principal components analysis (PCA) method on the basis of the physicochemical properties of headwater streams and Kamienna Creek

| | F1 geological | F2 seasonal | F3 redox | F4 biogenic (anionic) | F5 biogenic (cationic) |
|---|---|---|---|---|---|
| Temp.[$^{\circ}$C] | 0.3 | **-0.8** | 0.1 | 0.2 | 0.1 |
| pH | -0.2 | 0.1 | **0.8** | -0.0 | 0.1 |
| EC [$\mu S \cdot cm^{-3}$] | **0.6** | 0.1 | -0.3 | 0.1 | **0.6** |
| $O_2$ [$mg \cdot dm^{-3}$] | -0.0 | 0.1 | **-0.8** | -0.3 | 0.1 |
| $Na^+$ [$mg \cdot dm^{-3}$] | 0.3 | **0.5** | -0.3 | 0.3 | **-0.5** |
| $K^+$ [$mg \cdot dm^{-3}$] | -0.2 | 0.3 | -0.4 | 0.0 | **-0.5** |
| $NH_4^+$ [$mg \cdot dm^{-3}$] | -0.2 | 0.4 | 0.2 | -0.1 | **-0.7** |
| $Ca^{2+}$ [$mg \cdot dm^{-3}$] | **0.9** | -0.1 | -0.3 | 0.1 | 0.1 |
| $Mg^{2+}$ [$mg \cdot dm^{-3}$] | **0.6** | -0.3 | -0.3 | -0.1 | -0.4 |
| $Cl^-$ [$mg \cdot dm^{-3}$] | -0.0 | **0.8** | 0.1 | 0.0 | -0.2 |
| $HCO_3^-$ [$mg \cdot dm^{-3}$] | **0.9** | -0.1 | 0.4 | -0.0 | 0.0 |
| $NO_3^-$ [$mg \cdot dm^{-3}$] | 0.2 | 0.4 | 0.3 | **0.6** | -0.1 |
| $SO_4^{2-}$ [$mg \cdot dm^{-3}$] | **0.5** | **0.5** | 0.2 | 0.1 | 0.1 |
| $PO_4^{3-}$ [$mg \cdot dm^{-3}$] | 0.0 | -0.2 | 0.1 | **0.8** | 0.1 |
| Hardness [$mval \cdot dm^{-3}$] | **0.9** | -0.1 | -0.3 | 0.0 | 0.0 |
| Mineralization [$mg \cdot dm^{-3}$] | **1.0** | 0.0 | 0.1 | 0.1 | 0.0 |
| *Eigenvalues* | 4.56 | 2.40 | 2.28 | 1.40 | 1.59 |
| *Explained variance* [%] | 28 | 15 | 14 | 9 | 10 |

In general, the waters in headwater streams 1 and 2 are characterised by an increased content of $Ca^{2+}/Mg^{2+}$ and $HCO_3^-$, location 3 by moderate levels, and the water in the main channel by low amounts of these components.

An analysis of the spatio-temporal variability of variables forming other factors was performed in the next phase of data treatment, since the division of the year into two general seasons (cold and warm) and further into four seasons provided no satisfactory results regarding any seasonal variability in oxidative-reductive conditions. A similar blurring of seasonality in the concentration of biogenic components in headwater areas was also previously reported by Mazurek et al., (2014). Therefore, in the present study, month was used as the categorical variable (Fig. 4).

Based on an analysis of the categorised scatter chart of factorial values for factor 2 in relation to factor 3, it can be established that oxidative conditions (oxidative/reductive) were relatively stable over time, forming consistent groups of points that correspond to the month of sampling. It is worth emphasising that with the exception of December, January, February and September 2012, oxidising conditions were comparable in all waters of the studied spring niche (based on the fact that the variability of object factorial values relative to factor 3 ranged from -1 to +1). In contrast, values higher than +1, indicating reduced concentrations of

oxygen and an alkaline pH, were noted for samples collected in December 2012, while increased oxygenation and an acidic pH were observed in September, January and February 2012. Low concentrations of $Cl^-$ and $SO_4^{2-}$ ions also accompanied the increased oxygenation and acidic pH of some samples. The slight acidification of waters in September can likely be explained by the intensive uptake of alkaline components by plants during the growing season (Buffam et al., 2008). Samples taken in February were also characterised by increased concentrations of $SO_4^{2-}$ and $Cl^-$ ions, as well as reduced water temperatures, which according to Sickman et al., (2003) is a common phenomenon since the concentration of these ions tends to decrease with an increase in temperature.

A similar analysis was performed in relation to the fourth principal component ($NO_3^-/PO_4^{3-}$), based on the categorical scatter chart of factorial values of factor 1 in relation to factor 4, with the location of sampling points used as the categorical variable (Fig. 5). Although the observed relationships are not clear (factor 4 explains only 9% of total data variance), it appears that whereas water samples taken at location 2 were generally characterised by a higher concentration of nutrients (as evidenced by the mostly positive values on the $NO_3^-/PO_4^{3-}$ axis), those collected from locations 3 and 1 contained lower concentrations (as evidenced by the negative values on the $NO_3^-/PO_4^{3-}$ axis). Despite the dispersion of

object tags, whereas the median concentrations of $NO_3^-$ and $PO_4^{3-}$ ions in streams 1, 2 and 3 were statistically different, water samples obtained from the Kamienna Creek before and after the niche contained comparable amounts of nutrients. Therefore, it can be concluded that waters of the Kamienna Creek are not significantly influenced by that supplied from the studied niche. This is likely due to the fact that the effect of the higher nutrient concentrations at location 2 is compensated by the lower concentrations at locations 1 and 3, as well as by the rapid flow of water in these streams. An analysis of factorial values between factor 4 and factors 2 and 3 revealed no clear relationship.

## 5. CONCLUSIONS

Waters in the investigated spring niche are generally characterised by low concentrations of dissolved substances, a finding typical of afforested catchments with a predominance of sandy deposits, although it can in this case also be considered as an indicator of limited anthropopressure.

The waters in both the streams and the creek are calcium- bicarbonate type ($Ca^{2+}$–$HCO_3^-$) and are characterised by low seasonal variability, with season having no influence on concentrations of $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$, nor on conductivity, hardness and mineralisation.

However, spatial variation in the chemical composition of waters was observed. Whereas levels of $Ca^{2+}/Mg^{2+}$ and $HCO_3^-$ in stream waters sampled at locations 1 and 2 were found to be increased, only mean values were recorded at location 3, while the lowest levels were found in the waters of the main channel (Kamienna Creek). An analysis of spatiotemporal variability in oxidative-reductive conditions and other factors within the studied spring niche revealed no seasonal variation.
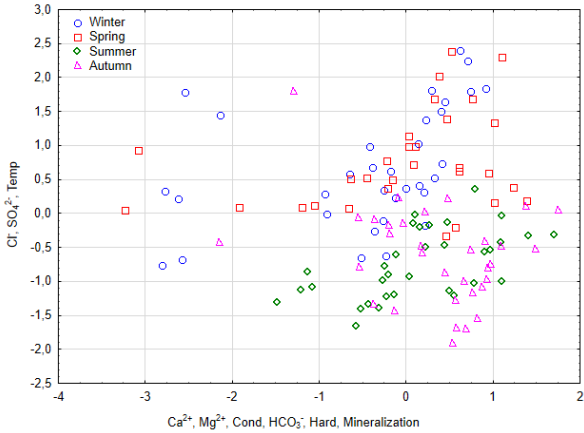


Figure 2. F1 ($Ca^{2+}$, $Mg^{2+}$, Cond, $HCO_3^-$, Hard, Mineralization) and F2 ($Cl^-$, $SO_4^{2-}$, Temp) relative to seasons scores according to headwater streams and Kamienna Creek
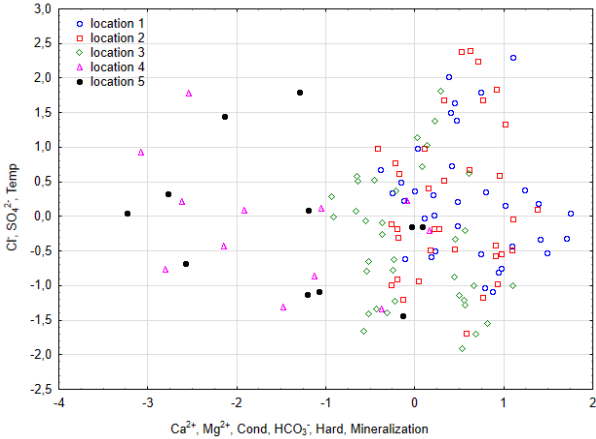


Figure 3. F1 ($Ca^{2+}$, $Mg^{2+}$, Cond, $HCO_3^-$, Hard, Mineralization) and F2 ($Cl^-$, $SO_4^{2-}$, Temp) relative to locations scores according to headwater streams and Kamienna Creek to locations
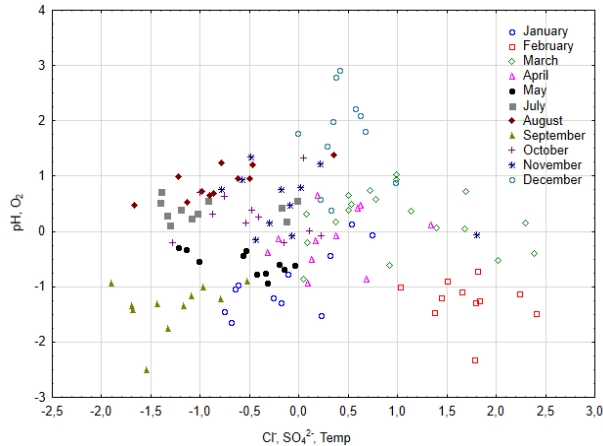


Figure 4. F2 ($Cl^-$, $SO_4^{2-}$, Temp) and F3 (pH, $O_2$) relative to moths scores according to headwater streams and Kamienna Creek
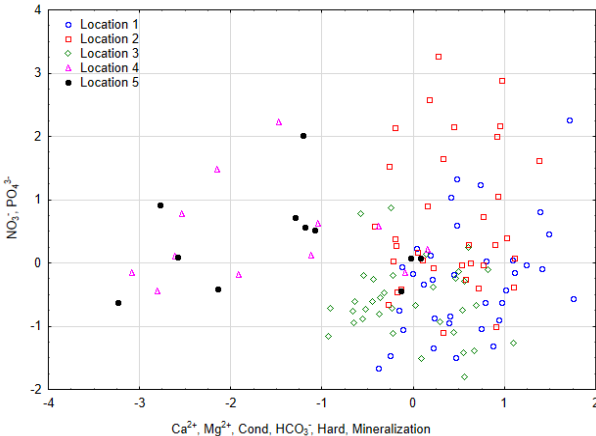


Figure 5. F1 ($Ca^{2+}$, $Mg^{2+}$, Cond, $HCO_3^-$, Hard, Mineralization) and F4 ($NO_3^-$, $PO_4^{3-}$) relative to the locations scores according to headwater streams and Kamienna Creek

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Furthermore, although stream waters at location 2 are characterised by generally higher levels of nutrients than locations 1 and 3, the waters from the investigated niche cause no significant changes to the chemistry of the main channel due to their small quantity.

## REFERENCES

**Astel, A., Małek, S. & Makowska, S.,** 2008. *Effect of environmental conditions on chemical profile of stream water in Sanctuary Forest Area.* Water, Air Soil Pollution 195, 137-149.

**Bernot, M.J. & Dodds, W.K.,** 2005. *Nitrogen retention, removal, and saturation in lotic ecosystems.* Ecosystems 8, 442–453.

**Bishop, K., Buffam, I., Erlandsson, M., Folster, J., Laudon, H., Seibert, J. & Temnerud J.,** 2008. *Aqua Incognita: the unknown headwaters.* Hydrological Processes 22, 1239-1242.

**Bloomfield, J.P, Jackson, C.R & Stuart, M.E.,** 2013. Changes in groundwater levels, temperature and quality in the UK over the 20th Century: an assessment. LWEC Working Paper.

**Britto, D.T. & Kronzucker, H.J.,** 2002. *$NH_4^+$ toxicity in higher plants: a critical review.* Journal of Plant Physiology 159, 567-584.

**Buffam, I, Laudon, H, Seibert, J, Mörth, C.M & Bishop K.,** 2008. *Spatial heterogeneity of the spring flood acid pulse in a boreal stream network.* Science of the Total Environment 407, 708–722.

**Bukowska-Jania, E.,** 2003. *The role of the system in the glacial cycle of calcium carbonate in the natural environment.* University of Silesia. Scientific Papers 2103, Katowice, pp. 247.

**Butturini, A., Bernal, S., Sabater, S. & Sabater, F.,** 2002. *The influence of riparian-hyporheic zone on the hydrological response in an intermittent stream.* Hydrology and Earth System Sciences Sc. 6, 3, 515-525.

**Davies, P.E., McIntosh, P.D., Wapstra, M., Bunce, S.E.H., Cook, L.S.J., French, B. & Munks, S.A.,** 2005. *Changes to headwater stream morphology, habitats and riparian vegetation recorded 15 years after pre-Forest Practices Code forest clearfelling in upland granite terrain, Tasmania, Australia.* Forest of Ecology and Management 217, 331–350.

**Dosskey, M.G., Vidon, P., Gurwick, N.P., Allan, J., Duval, T.P. & Lawrance, R.,** 2010. *The role of riparian vegetation in protecting and improving chemical water quality in streams.* Journal of the American Water Resources Association 1-18.

**Garner, G., Hannah D.M., Sadler, J.P.** & **Orr, H.G.,** 2013. *River temperature regimes of England and Wales: spatial patterns, inter-annual variability and climatic sensitivity.* Hydrological Processes 28, 22, 5583-5598.

**Garner, G., Malcolm, I.A., Sadler, J.P., Millar, C.P. & Hannah, D.M.,** 2014**.** *Inter-annual variability in the effects of riparian woodland on microclimate,*

*energy exchanges and water temperature of an upland Scottish stream.* Hydrological Processes 29, 6, 1080-1095

**Gold, A.J., Groffman, P.M., Addy, K., Kellogg, D.Q., Stolt, M. & Rosenblatt, A.E.,** 2001. *Landscape attributes as controls on groundwater nitrate removal capacity of riparian zones.* Journal of the American Water Resources Association 37, 6, 1457-1464.

**Gupta, H., Chakrapani, G.J., Selvaraj, K. & Kao, S.J.,** 2011. *The fluvial geochemistry, contributions of silicate, carbonate and saline-alkaline components to chemical weathering flux and controlling parameters: Narmada River (Deccan Traps), India.* Geochimica et Cosmochimica Acta 75, 800–824.

**Helliwell, R.C., Davies, J.J.L., Evans, C.D., Jenkins, A., Coull, M.C., Reynolds, B., Norris, D. & Ferrier, R.C.,** 2007. *Spatial and seasonal variations in nitrogen leaching and acidity across four acid-impacted regions of the UK.* Water, Air Soil Pollution 185, 3-19.

**Hill A.R., 2000.** *Stream chemistry and riparian zones.* Journal Environmental Quality 25, 743-755.

**Hill, A.R., Vidon, G.F. & Langat, J.,** 2004. *Denitrification potential in relation to lithology infive headwater riparian zones.* Journal of Environmental Quality 33, 911–919.

**Hindshaw, R.S., Tipper, E.T., Reynolds, B.C., Lemarchand, E., Wiederhold, J.G., Magnusson, J., Bernasconi, S.M., Kretzschmar, R. & Bourdon B.,** 2011. *Hydrological control of stream water chemistry in a glacial catchment (Damma Glacier, Switzerland),* Chemical Geology 285, 215–230.

**Horska-Schwarz, S. & Spałek, K.,** 2010. *The evolution of the Oder Valley in terms of fluvial processes and anthropogenic changes.* The Problems of Landscape Ecology 28, 229-240.

**Janisch, J.E., Wondzell, S.M. & Ehinger, W.J.,** 2012. *Headwater stream temperature: Interpreting response after logging, with and without riparian buffers*, Washington, USA. Forest of Ecology and Management 270, 302-313.

**Jekaterynczuk-Rudczyk, E.,** 2005. *The transformation of the chemical composition of the water in the area of lowland springs. State and anthropogenic changes of water quality in Poland.* Publishing University of Łódź, Łódź 3, 259-268.

**Jekaterynczuk-Rudczyk, E.,** 2007. *The Hyporeic zone its functioning and meaning.* Kosmos 56, 1-2, 181-196. (in Polish)

**Jonczak J. & Cysewska, J.,** 2010. *Taxonomy and selected properties of soils of spring niches in the valley of Jarosławianka River (Sławieńska Plain).* Soil Science Annual 61, 2, 45-65.

**Jonczak, J. & Parzych, A.** 2014. *Changes in concentrations of Cu, Mn, Ni, Sr and Zn during decomposition of four leaf litters in headwater riparian forest.* Forest Research Papers 75, 2, 193–

200.

**Jonczak, J.,** 2010. *Sorption and buffer properties of soils of spring niches in the Jarosławianka River Valley (Sławieńska Plain).* Soil Science Annual 61, 3, 45-51.

**Jonczak, J.,** 2011. *Pedological aspects in the functioning of spring niches as transition zones between underground and superficial parts of water in river basin.* Ecological Questions 15, 35-43.

**Jonczak, J., Olejniczak, M., Parzych, A. & Sobisz, Z.,** 2016. *Dynamics, structure and chemistry of litterfall in headwater riparian forest on the area of Middle Pomerania.* Journal of Elementology 21(2), 383-394.

**Jonczak, J., Parzych, A. & Sobisz Z.,** 2015a. *Distribution of carbon and nitrogen forms in the Histosols of headwater areas – a case study from the valley of the Kamienna Creek (Northern Poland).* Journal of Elementology 1, 95-105.

**Jonczak, J., Parzych, A. & Sobisz, Z.,** 2015b. *Decomposition of four leaf litters in headwater riparian forest.* Balt. Forest. 21(1), 133- 143.

**Joshi, B. K. & Kothyari, B.P.,** 2003. *Chemistry of perennial springs of Bhetagad watershed: a case study from central Himalayas, India.* Environmental Geology 44, 572-578.

**Kelly, J.M., Kovar, J.L., Sokolowsky, R. & Moorman, T.B.,** 2007. *Phosphorus uptake during four years by different vegetative cover types in a riparian buffer.* Nutrient Cycling in Agroecosystems 78, 239-251.

**Małek, S., Astel, A., Krakowian, K. & Opałacz, J.,** 2010. *Quality assessment of spring water from the area of Skrzyczne and Barania Góra mountains.* Sylwan 154, 7, 499-505. (in Polish)

**Mayer, P.M., Reynolds, Jr., S.K., Canfield, T.J. & McCutchen, M.D.,** 2005. *Riparian buffer width, vegetative cover, and nitrogen removal effectiveness: A Review of Current Science and Regulations.* EPA/600/R-05/118.

**Mazurek, M.,** 2006. *Outflows of groundwater in the southern part of the basin Parsęta.* Badania fizjograficzne nad Polska Zachodnią, Seria A – Geografia Fizyczna 57, 101-118. (in Polish)

**Mazurek, M.,** 2008. *Headwater areas as a link connecting slope and river channel systems, the Parsęta River basin.* Landform Analysis 9: 63-67. (in Polish)

**Mazurek, M., Kruszyk, R. & Szpakowska, G.,** 2014. *Transformation of the chemical composition of groundwater in headwater alcoves in postglacial areas (The Parsęta River basin).* Monografie Komitetu Gospodarki Wodnej PAN, 20, 355-369.

**McNeish, R.E., Benbow, M.E. & McEwan, R.W.,** 2012. *Riparian forest invasion by a terrestrial shrub (Lonicera maackii) impacts aquatic biota and organic matter processing in headwater streams.* Biological Invasions 14, 9, 1881-1893.

**Michalczyk, Z., Chmiel, S., Głowacki, S. & Zielińska, B.,** 2004. *Changes in productivity and water chemistry sources of Lublin Upland and Roztocze.* Annales Universitatis Mariae Curie-Sklodowska, Section B 59, 107-122.

**Ohte, N., Mitchell, M.J., Shibata, H., Tokuchi, N., Toda, H. & Iwatsubo, G.,** 2001. *Comparative evaluation on nitrogen-saturation of forest catchments in Japan and Northeastern United States.* Water, Air and Soil Pollution 130, 649–654.

**Osadowski, Z.,** 2006. *Threatened, protected and rate species of vascular plants in spring complexes in the central part of Polish Pomeranian.* Biodiversity: Research and Conservation 1-2, 174-180.

**Osadowski, Z.,** 2010. *The impact of hydrological and hydro-chemical conditions of the diversity ofvegetation springs in the upper glacial landscape of Pomerania.* Bogucki Scientific Publishing, Poznań-Słupsk. (in Polish)

**Parzych, A. & Sobisz, Z.,** 2010. *Biomass and net primary production of herbaceous plants in chosen forest associations in the Słowiński National Park.* Environmental Protection and Natural Research 42, 72-83.

**Parzych, A.,** 2010. *Nitrogen, phosphorus and carbon in forest plants in the Słowiński National Park in 2002-2005.* Environmental Protection and Natural Resources 43, 45-64.

**Parzych, A.,** 2011. *Contents of nitrogen and phosphorus compounds in groundwaters of selected forest associations in the Słowiński National Park.* Archives of Environmental Protection 37, 4, 95-105.

**Parzych, A., Sobisz, Z. & Trojanowski, J.,** 2010. *Variability of nitrogen and phosphorus concentration and the net primary production Vaccinium vitis-idaea L. and Vaccinium myrtillus L. in chosen woodland ecosystems of the Słowiński National Park.* Archives of Environmental Protection 36, 2, 91-104.

**Parzych, A., Jonczak, J. & Sobisz, Z., 2016.** *Changes of water chemistry in mid-forest headwater streamsin the valley of the Kamienna (Middle Pomerania).* Sylwan 160 (10), 871- 880.

**Parzych, A., Jonczak, J. & Sobisz, Z.,** 2017. *Bioaccumulation of macronutrients in the herbaceous plants of mid-forest spring niches.* Baltic Forestry 23(2), 384-393.

**Pazdro, Z. & Kozerski, B.,** 1990. *General hydrogeology.* Publishing Geological, Warszawa.

**Pielech, R., Anioł-Kwiatkowska, J. & Szczęśniak, E.,** 2015. *Landscape-scale factors driving plant species composition in mountain streamside and spring riparian forests.* Forest of Ecological Management 347, 217–227.

**Rafałowska, M.,** 2008. *Evaluation of the content of nitrates in surface area particularly threatened by pollution from agricultural sources.* Proceedings of ECOpole (2)2, 473-478.

**Ranalli A.J. & Macalady, D.L.,** 2010. *The*

*importancethe riparian zone and in – stream processes nitrate attenuation in undisturbed and watersheds – a review of the scientific literature.* Journal of Hydrology 389, 406-415.

**Sickman, J.O., Leydecker, A., Chang, C.C.Y., Kendall, C., Melack, J.M., Lucero, D.M. & Schimel, J.,** 2003. *Mechanisms underlying export of N from high-elevation catchments during seasonal transitions.* Biogeochemistry 64, 1–24.

**Stutter, M.I., Deeks, L.K., Low, D. & Billett, M.F.,** 2006. *Impact of soil and groundwater heterogeneity on surface water chemistry in an upland catchment.* Journal of Hydrology 318, 103–120.

**Tabacchi, E., Lambs, L., Guilloy, H., Planty-Tabacchi A.M., Muller E. & Décamps, H.,** 2000. *Impacts of riparian vegetation on hydrological processes.* Hydrological Processes 14, 2959-2976.

**Temnerud, J.** & **Bishop, K.,** 2005**.** *Spatial variation of streamwater chemistry in two swedish Boreal Catchments: Implications for Environmental Assessment.* Environmental Science & Technology 39, 1463-1469.

**Uhlenbrook, S. & Hoeg, S.,** 2003. *Quantifying uncertainties in tracerbased hydrograph separations: a case study for two-, three- and five-component hydrograph separations in a mountainous catchment.* Hydrological Processes 17,431–453.

**Welsch, D.L., Kroll, C.N., McDonnell, J.J. & Burns, D.A.,** 2001. *Topographic controls on the chemistry of subsurface stormflow.* Hydrological Processes 15 (10), 1925–1938.

**Zhang, Z., Fukushima, T., Shi, P., Tao, F., Onda, Y., Gomi, T., Mizugaki, S., Asano, Y., Kosugi, K., Hiramatsu, S., Kitahara, H., Kuraji, K., Terajima, T. &Matsushige, K.,** 2008. *Seasonal changes of nitrate concentrations in base flow headwaters of coniferous forests in Japan: A significant indicator for N saturation.* Catena 76, 63–69.

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