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SPATIAL VARIABILITY OF PHYSICAL AND CHEMICAL PROPERTIES OF RIVER WATER IN THE UPPER PARSĘTA CATCHMENT DURING RISING SPRING FLOWS

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Abstract: The paper discusses the spatial variability of the physical and chemical properties of river water in the upper Parsęta catchment (West Pomerania, Poland) during rising spring flows. Making use of data generated by 6 hydrochemical surveys, the studied waters were classified based on so-called fuzzy clustering methodology and attempts were made to interpret their spatial distribution. The obtained results show that during spring rising flows meteorological and hydrological conditions present in the period prior to sampling have a major impact on the water chemistry of the upper Parsęta catchment. These prior conditions significantly weaken the spatial variability of lithological and hydrogeological characteristics which is clearly perceptible in the case of low outflows.

Keywords: Upper Parsęta catchment, spatial variability of physical and chemical properties of river water, hydrochemical classification, fuzzy-k-means

Introduction

The chemical composition of surface waters results from mixing of genetically varied water: precipitation, surface run-off from rainfall or snow-melt, subsurface run-off and groundwater flow. Their properties and relative proportion depend on the geographical location of a given catchment (microclimatic conditions) and the system structure covering its geological structure, land formation and drainage network as well as land-cover and use. Also meteorological conditions which are varied in seasonal and short-period terms play a relevant role here. They significantly affect the volatility of water supplies to the riverbed and feeding of watercourses (streams) and consequently the physicochemical properties of surface waters. The complete determination of the spatial diversity and variability of physicochemical properties of waters calls for the detailed diagnosis of all the conditions within the river catchment geoecosystem and its operation as well as the identification of changes taking place at various stages of the water cycle in the catchment. It includes, among others: determination of supply areas of the riverbed, indication of supply sources of individual components as well as water circulation times and routes in the catchment. This kind of analysis (on these components / factors) is crucial to analyse the catchment system and its operation.

The issue of temporal variability and spatial diversity of physicochemical properties of waters has been discussed since the 50s of 20th century (cf.: Imeson 1973; Walling 1974). This issue has been considered in the literature from several perspectives. Walling (1974) – when reviewing the literature – emphasised four of them: (1) dependencies between flow volume and concentration of solutes under various weather conditions (including rising-water periods); (2) impacts of the quality and quantity of precipitation to explain the variability of solutes and their concentration levels; (3) seasonal variation of solutes in regard to interrelations between and among the biological, geochemical and hydrological systems; (4) human activities and their impact (expressed through the application of fertilisers and changes in land use) on the variability of physicochemical properties of waters. These issues have still been on-topic and are covered by numerous publications, among others: Walling (1974); Walling, Webb (1975, 1983); Webb, Walling (1983); Hakamata *et al.* (1992) and in Poland, among others, Froehlich (1975, 1982); Zwoliński (1989); Kostrzewski, Zwoliński (1992a, 1992b); Kostrzewski *et al.* (1994); Bukowska-Jania, Pulina (1997); Mazurek (1999, 2000) Stach *et al.* (2003a, 2003b) and others.

Within the upper Parsęta catchment such research studies have been conducted since the early 80s of the last century and covered, among others surface and ground waters and their hydrochemical diversity (Kostrzewski, Zwoliński 1985; Kostrzewski *et al.* 1994; Mazurek 2000), atmospheric-originated chemical components in the river flow, their quality, quantity and relevance (Kostrzewski, Zwoliński 1985; Szpikowska 2004), chemical and mechanical denudation in annual and seasonal circle, their course and intensity (Kostrzewski, Zwoliński 1990, 1992a, 1992b; Kostrzewski *et al.* 1993; Szpikowska, Tylkowski 2006), supply sources of solutes within the catchment and their diversification (Kostrzewski, Zwoliński 1992b; Kostrzewski *et al.* 1994, 1997; Mazurek 1999, 2000).

Hydrochemical mappings were the most commonly applied method to study the diversification of supply sources of solutes in the riverbed, water circulation routes in the catchment and riverbed supply areas (Hakamata *et al.* 1992; Kostrzewski, Pulina 1992; Kostrzewski *et al.* 1994, 1997; Mazurek 1998, 2000; Webb, Walling 1983). Most often they were run during low flow periods, which allowed to obtain fully comparable results and – above all – to identify relatively stable spatial relationships primarily connected with geological aspects and water circulation times. However, there are no similar analyses for high flow periods which are the most relevant in the catchment water-balance. The interpretation of such data is much more difficult due to fact that sampling is run at various phases of river flow in various sub-catchments depending on their sizes (volumes) and sampling times.

The aim of the present paper is to analyse the variability of physicochemical properties of river waters within the upper Parsęta catchment during spring rising-water flows against weather conditions. The paper includes the hydrochemical classification of these waters based on the fuzzy clustering methodology and attempts to interpret their spatial distribution.

Scope of the research studies

The upper Parsęta catchment (Fig. 1) – in regional terms – belongs to the West Pomeranian Lake District and is located within the mezo-region of the Drawskie Lake District. Within this area the diversity of land morphology and lithology of surface forms results from areal deglaciation derived from the Vistula glaciation. The catchment occupies the central part of the so-called Parsęta Lobe (Karczewski 1989) and is characterized by the presence of highly differentiated system of post-glacial forms (corrugated bottom moraine and out-wash plain are dominant - in total, more than 66% of the area) and the mosaic of surface formations, soils and land-uses (Kostrzewski *et al.* 1994; Dmowska 2012a).

The catchment area of the upper Parsęta closed by hydrometrical cross-section in Storkowo is 73.98 km^2 and its circumferential length is 58.3 km. The density of its river network is approx. 0.16 km/km^2. A length of the main watercourse from its springs to the hydrometrical cross-section in Storkowo is approx. 13.26 km. Altitude variances in the catchment reach a maximum of 120 m (83.35 m a.s.l.–202.84 m a.s.l.) with average relative land heights being within 10 m–20 m and average falls within 2.5 to 4% (Dmowska 2012a).

Most of the upper Parsęta catchment is covered with deposits of direct continental glacier accumulation – boulder clay (when close to the ground it is usually much sandy). There are also glaciofluvial and fluvial sands as well as Holocene organogenic sediments – lake peats and gyttjas. The soil cover is dominated by various subtypes of luvisols and podzolics. There are black, muck, peat-muck and muck soils within the land depressions.

The catchment of the upper Parsęta is made of agricultural and forest areas (respectively 58.9% and 38.7% of the area; Kostrzewski *et al.* 1994; Piotrowska 1994), with its low population density – compared to the average for the entire Poland (<20 people·km^{-2}). For the last 20 years this area has been affected by significant depopulation.

The average annual temperature for the catchment area can be estimated at approximately 7.7°C and the total annual precipitation at 670 mm. January was the coldest month (–0.5°C) and July – the warmest (17°C). Summer months – to a large extent – generate the annual precipitation. The upper Parsęta catchment is part of the area with a relatively high specific discharge (its long-term average value is 8.2 dm^3·s^{-1}·km^2). It results from higher precipitation (compared to the rest of the Polish Lowland), high retention capacity and considerable domination of groundwater alimentation. The upper Parsęta, river similarly to other streams in Lake Districts, is characterized by a levelled regime of low and very low absolute ratio (11.5) of its maximum flow / minimum flow.

Data and methods of the research studies

Hydrochemical mappings are one of the basis research methods applied in studying the hydrochemical diversity of waters (Hakamata *et al.* 1992; Kostrzewski, Pulina 1992; Kostrzewski *et al.* 1994, 1997; Mazurek 1998, 2000; Webb, Walling 1983). The present paper analyses the data collected during hydrochemical mappings made in the upper Parsęta catchments in spring periods of 1992–1994 and 2009–2010. During this season in the upper Parsęta catchment have been observed changes related to reduced pollution loads in precipitation, reduced aggressiveness of precipitation as well as qualitative and quantitative changes in land cover and land use. The research studies conducted in the upper Parsęta catchment mainly indicate a decline in the concentration of sulphate ions (Szpikowski 2011), which should be linked with their reduced supply with atmospheric precipitation, reduced supplies from anthropogenic sources such as sewage and agricultural activity. In-between these two periods a decrease in the concentration of chloride ions was also reported which, however, should be linked with changes in the methodology of analyses (Table 1).

The conducted comparative stand-to-stand analyses on physicochemical properties of waters did not show any significant differences for most of the stands between these two periods (Dmowska 2012b). The reported changes concerned just a couple of stands: the Suchy Stream catchment, Żegnica catchment, Dalęciński Stream (upper section), Parsęta (upper section). The changed physicochemical properties of waters at these stands were linked with a decrease in supplies from anthropo-

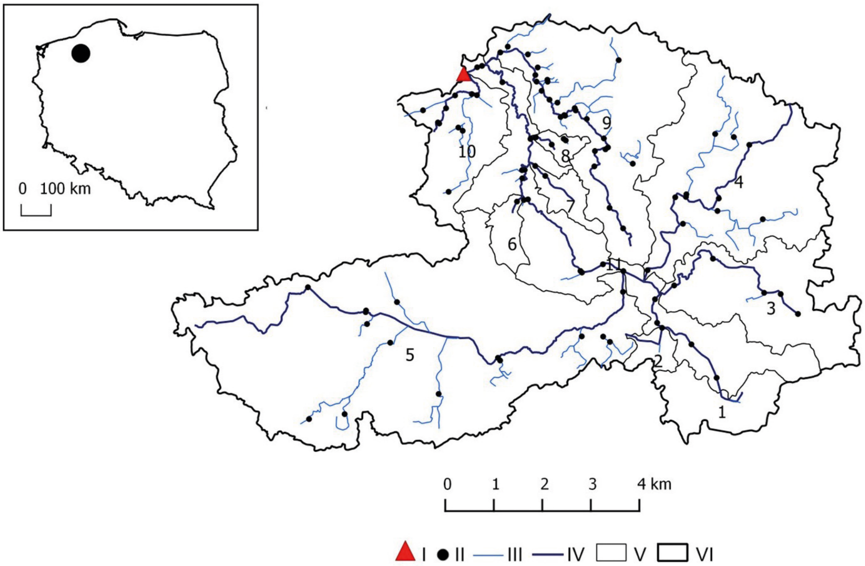

Fig. 1. Distribution of measuring stands during hydrochemical surveys in the upper Parsęta catchment

Explanations: I – meteorological station in Storkowo, II – measurement stands, III – hydrographical network, IV – main watercourses, V – full watershed of sub-catchments in the upper Parsęta catchment, VI – full watershed of the upper Parsęta catchment
Sub-catchments: 1 – Parsęta river springs, 2 – Drainage Ditch, 3 – Dalęciński Stream, 4 – Skalneński Stream, 5 – Żegnica, 6 – Leśny Stream, 7 – Suchy Stream, 8 – Krętacz, 9 – Kłuda, 10 – Młyński Stream

Source: authors' own study.

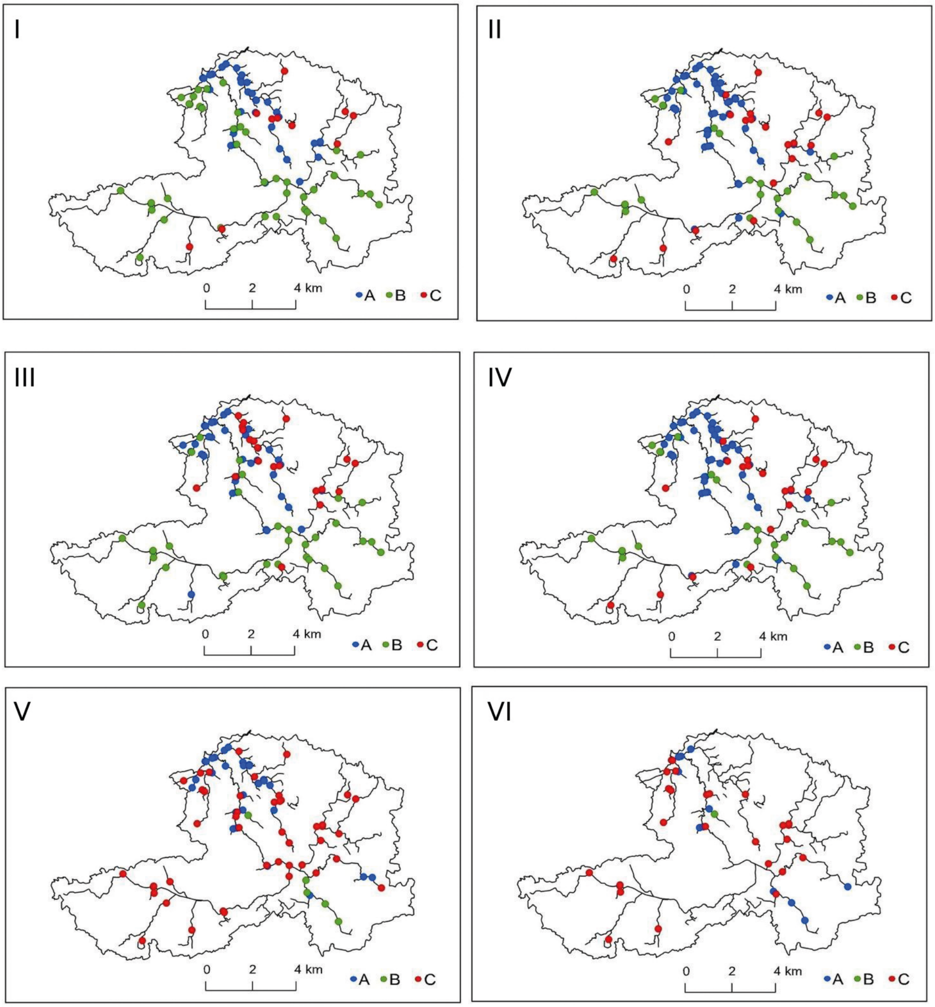

Fig. 6. Division of water sampling locations into hydro-chemical groups in the upper Parsęta catchment during subsequent hydro-chemical surveys
All the stands were assigned to the dominant group (i.e. with the highest membership level). Survey dates: I – April 1992, II – March 1993, III – March 1994, IV – April 1994, V – March 2009, VI – March 2010

Explanations: A – group of medium-mineral-content waters, B – group of high-mineral-content waters, C – group of low-mineral-content waters

Source: authors' own study.

Table 1. Laboratory analysis methods used in studied periods

Parameter	Analytical methods	
	1989–1998	2008–2010
specific electrolytic conductivity	conductometric	conductometric
pH	potentiometric	potentiometric
calcium Ca^{2+}	complexometric titration	complexometric titration or ion chromatography
magnesium Mg^{2+}	calculated from the variance between TOG and Ca^{2+} (in mV/l)	atomic absorption spectrometry via flame or ion chromatography
sodium, Na^{+}	flame photometry	atomic emission spectrometry via flame or ion chromatography
potassium K^{+}	flame photometry	atomic emission spectrometry via flame or ion chromatography
bicarbonate HCO_3^{-}	titration with methyl orange	titration with methyl orange
chloride Cl^{-}	argentometric titration	ion chromatography
sulphate SO_4^{2-}	Turbidimetric	ion chromatography
phosphate PO_4^{3-}	spectrophotometric, based on molybdate with stannous chloride	spectrophotometric, based on molybdate with stannous chloride
ionised silica SiO_2	spectrophotometric	spectrophotometric

Source: authors' own study.

genic sources (the Suchy Stream catchment, Żegnica catchment) and reduced or discontinued application of fertilisers (uppers sections of the Dalęciński Potok and Parsęta located in rural areas). Thus no changes for most of the stands indicate the strong dependence of physicochemical properties of waters primarily on lithologic and soil conditions which are not subject to any significant changes in a short time and high biogeochemical "inertia" in this type of hydrological systems. Therefore, the spatial variations of physicochemical properties of waters may be analysed on the base of measurements taken from two periods without consideration of additional factors in their interpretation.

94 stands located within watercourses of the upper Parsęta catchment were covered by seasonal hydrochemical mappings (Fig. 1). 76 up to 91 water samples were analysed during these mappings made in spring periods (23.04–28.04.1992, 26.03–1.04.1993, 2.03–7.03.1994, 22.04–26.04.1994, 29.03–1.04.2009). Only 38 stands were covered by hydrochemical mappings made on 18.03–22.03.2010. Other stands were not available due to high levels of ground waters and widespread wetlands.

The following parameters were laboratory determined and analysed in the collected water samples: specific electrolytic conductivity (SEC), pH (pH), concentration of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), concentration of anions (HCO_3^-, Cl^-, SO_4^{2-}; PO_4^{3-}), and ionised silica SiO_2. The applied analytical methods were based, among others, on the papers written by Krawczyk (1992), Markowicz, Pulina (1979) and Siepak (1992). Their specification is presented in Table 1. Water samples collected during the mappings were analysed at the Hydrochemical Laboratory / the Geoecological Station in Storkowo (supervised by the Adam Mickiewicz University) and the Geochemical Laboratory in Poznań. In-between the two measurement periods, i.e 1989–1998 and 2008–2010 in case of some ions the methods of their determination was changed (cf. Table 1). A series of comparative analyses conducted at the Hydrochemical Laboratory / the Geoecological Station in Storkowo proved that only in case of chlorides, changes in the methodology relevantly impacted the results (Szpikowska, oral information).

Meteorological and hydrological conditions

In spring periods, meteorological and hydrological conditions represent ones of the most important factors modifying the ionic composition of river waters; therefore their detailed diagnosis is relevant for further analysis. Hydrometeorological conditions were determined on the basis of measurements taken at the meteorological station in Storkowo.

The hydrochemical mapping made in-between 23.04–28.04.1992 was conducted after a rising-water period lasting from 13.03 to 20.04. The specific discharge ranged from 15.1 to 18.8 $dm^3 \cdot s^{-1} \cdot km^2$, 16.1 $dm^3 \cdot s^{-1} \cdot km^2$ on average.

The hydrochemical mapping made in-between 26.03–1.04.1993 was preceded by a several-day warming period with air temperatures exceeding 0°C, i.e. from 2°C to 9.3°C. It resulted in the following: melting of snow-cover (lying in-between 2.03–11.03), increased flows up to 23.0 $dm^3 \cdot s^{-1} \cdot km^2$ and 7-day rising-water period. The mapping in-between 26.03–1.04.1993 saw a decline in air temperature (from –1.1°C on 26 March to –2.8°C on 1 April) and snowfall. Soil freezing reached 5 cm. Snow-cover lay in-between 29.03–1.04 with its thickness of 7 cm. Another rise in temperature was initiated by a rising-level period lasting 13 days (from 1.04). Discharges at the water-gauge in Storkowo changed from 14.9 to 19.2 $dm^3 \cdot s^{-1}$ km^2 (16.4 $dm^3 \cdot s^{-1} \cdot km^2$ on average).

The mapping done in-between 2.03–7.03.1994 was conducted at lying snow-cover (up to 4 cm) and soil freezing from 41 cm to 36 cm. A rise in temperature from –2.3°C to 4.5°C found during the mapping caused snow-cover melting and ground thawing. Moreover, during the mapping, snowfall / rainfall was recorded (from 0.8 mm–2.6 mm). Such meteorological conditions triggered an increase in discharge from 12.7 dm^3 to 18.9 $dm^3 \cdot s^{-1} \cdot km^2$ and rising-water period lasting from 7.03 (i.e. the last mapping day) to 17.04.

The mapping done on 22.04–26.04.1994 was conducted after the rising-water period. During the mapping there was no precipitation reported. It resulted in discharge recession from 14.6 to 12.6 $dm^3 \cdot s^{-1} \cdot km^2$.

The first mapping (2009–2010) was made in two periods, i.e. 19.03–20.03 and 29.03–1.04.2009. The first period covered the stands in the Młyński Stream and Kłuda catchments; the second period – the remaining part of the upper Parsęta catchment. In the first part of the mapping, discharge within the Parsęta river amounted to about 9.6 $dm^3 \cdot s^{-1} \cdot km^2$ in the second part – 15.5 dm $3 \cdot s^{-1} \cdot km^2$. Increased water stage and discharge were caused by rainfall and snowfall as well as rising temperatures.

The mapping made in-between 18.03–22.03.2010 was conducted during the period of highest water levels within the Parsęta river in the specified hydrological year (2010). Due to the prevailing hydrological conditions, it covered only 38 measurement stands (the Parsęta river with larger tributaries). Till 19.03.2010 the upper Parsęta catchment was covered with snow, and till 21.03 its ground was frozen (down to 19 cm). Increased air temperatures caused snow-cover melting and ground thawing. As a result, in-between 20.03–23.03, rising waters were reported. On 21.03 the Parsęta discharge reached 28.5 $dm^3 \cdot s^{-1} \cdot km^2$.

The hydrochemical mappings made in spring periods of 1992–1994 and 2009–2010 were characterized by diverse meteorological and hydrological conditions (Fig. 2) Therefore, it allows for the analysis of physicalchemical properties of waters with the participation of diverse sources of supplies of dissolve substances solutes into watercourses.

Hydrochemical classification of surface waters

The classification of physicochemical properties of waters within the upper Parsęta catchment was made using the fuzzy k-means method. The classes, distinguished by fuzzy k-means method, are interpreted as hydrochemical groups. Because of this we use in this paper the term of a group instead of a class. The classic cluster analysis methods make sharp classifications, i.e. ‘in’ or ‘out’. However, the world is full of phenomena which change in a progressive, non-linear but not sharp manner. Therefore it is difficult to designate groups with clear boundaries. This problem also refers to the diversity of physicochemical properties of surface waters. Therefore the present paper makes use of the fuzzy k-means method in which a group membership is defined in terms of its probability. The theoretical concept of this method were developed by Bezdek (1981). Its specification is also included in the papers by McBratney, deGruijter (1992), Odeh *et al.* (1992), Burrough, McDonnell (1998), Burrough *et al.* (2000, 2001) (followed by Gorsevski *et al.* 2003; followed by Lagacherie *et al.* 1997). The fuzzy k-means method was applied in hydrochemical

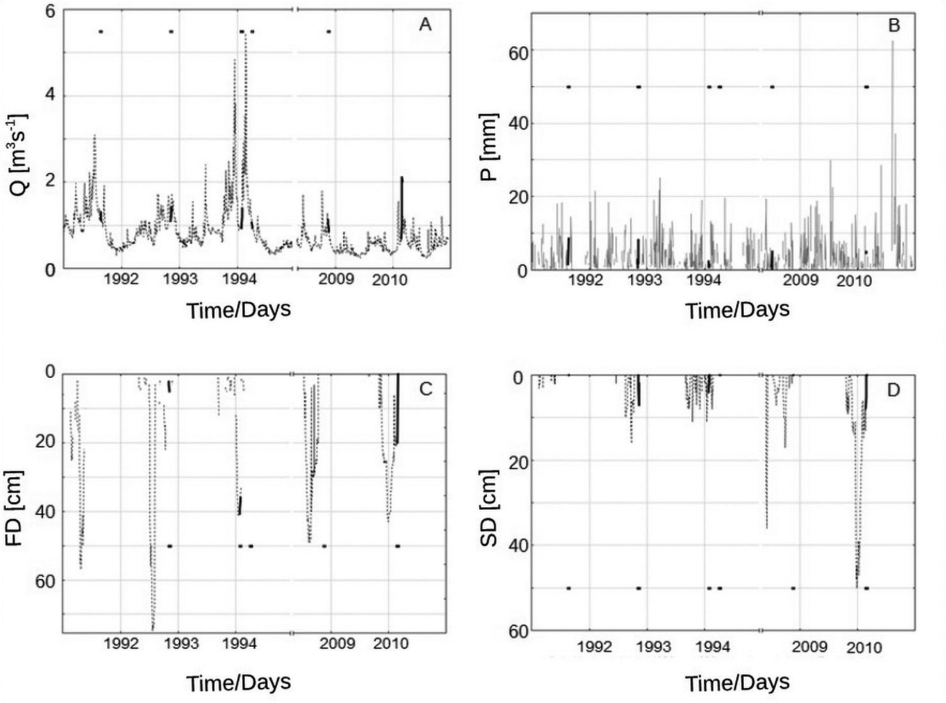

Fig. 2. Measurement dates (points on graphs) *vs.* meteorological and hydrological conditions in the observation periods (1992–1994 and 2009–2010) in the upper Parsęta catchment

Explanations: A – discharge, Q [m^3s^{-1}], B – precipitation, P [mm], C – depth (thickness) of freezing ground, FD [cm], D – depth (thickness) of snow, SD [cm]

Source: authors' own study.

research studies by Güler, Thyne (2004) who noted in their article that this method is very rarely applied for this type of issues.

The fuzzy k-means method, similarly to the classical method of k-means clustering, requires giving a number of groups. A selection of the optimal number of groups and *phi* fuzziness factor is referred to be a validation of classification (Lagacherie *et al.* 1997). Criteria applied to assess various classification results are called validity functions (performance measurements) (Gorsevski *et al.* 2003; Minasny, McBratney 2002; Odeh *et al.* 1992).

The optimum value of phi fuzziness factor is determined on the grounds of a measure defined as dj/d*phi* the value of which is derived from the OFV validation function (objective function value) introduced by McBratney and Moore (1985, followed by Gorsevski *et al.* 2003), where $phi = -[(dj/dphi) \cdot \text{sqrt(number of groups)}]$ (sqrt stands for square root).The optimum value of *phi* fuzziness factor for a given number of classes is determined by the maximum function after plotting – $[(dj/dphi) \cdot \text{sqrt(number of groups)}]$ *vs. phi* (Minasny, McBratney 2002).

The optimum number of groups can be determined through the minimisation of FPI (*Fuzziness Performance Index*) and MPE (*Modified Partition Entropy*) validity functions. Also S (*Separate Distance*) validity function can be applied. The optimum number of groups is determined for the minimum value of the S validation function (Minasny, McBratney 2002).

This paper presents the classification based on standardized values of 12 parameters: water temperature (Tw), water pH (pH), specific electrolytic conductivity (SEC), concentration of the following ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-} and SiO_2 identified for a total of 455 water samples. All the calculations were made on the base of FuzMe 3.5b software (Minasny, McBratney 2002) for *phi* fuzziness factor in the range of 1.00–2.00 and for a number of groups ranging from 2 to 10. The Euclidean distance was applied in all of the calculations. In the analyses of validation function values, *phi* fuzziness factor at 1.6 and division into 3 groups (Fig. 3A, 3B) were finally accepted as optimal.

As a result of the application of the fuzzy k-means method, 3 types of information is obtained: (1) membership to singled-out groups at a scale from 0 to 1; (2) assignment to the dominant group; (3) designated groups and defined confusion index CI indicating the differences between the dominant and sub-dominant groups. Confusion index is defined as (Gorsevski *et al.* 2005):

$$CI = 1 - (MFmax - MFmax_2),$$

where: CI – Confusion index, MFmax – membership to the dominant group, $MFmax_2$ – membership to the sub-dominant group.

The singled-out groups are interpreted as hydrochemical groups which reflect water circulation routes and rates within the catchment. The present article, when interpreting the results, assumes the assignment of stands to the dominant groups. The designated hydrochemical groups differ in numbers: group A – 176 measurements, group B – 152 measurements, group C – 127 measurements.

The singled-out groups correspond the following types of waters: low-mineralised (C hydrochemical group), medium-mineralised (A hydrochemical group) and high-mineralised (B hydrochemical group) (tab. 2).

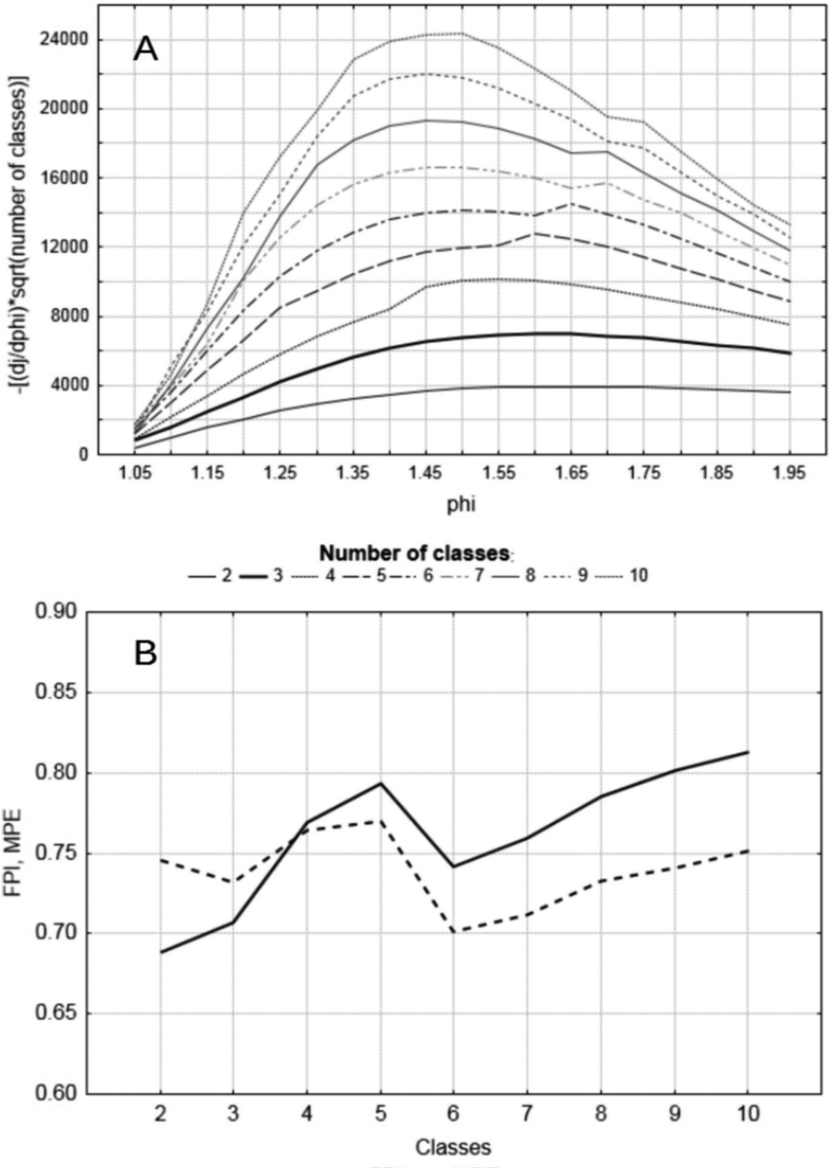

Fig. 3. Selection of calculation parameters in the fuzzy classification. A. Fuzziness factor. B. Selection of the number of groups (detailed explanation in the text)

Source: authors' own study.

Table 2. Water chemistry of selected hydro-chemical groups (A–C) for spring surveys in-between the periods 1992–1994 and 2009–2010

Parameter	Tw	pH	SEC	HCO_3^-	SO_4^{2-}	PO_4^{3-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	SiO_2
	°C	[-]	µS·cm^{-1}	mg·dm^{-3}								
Hydro-chemical group A												
MIN	-0.10	6.55	241.00	76.27	5.80	0.00	4.25	34.47	1.70	1.07	0.62	5.19
MAX	20.20	8.47	556.00	296.54	81.60	0.49	43.96	116.23	9.72	13.00	8.26	18.26
MEAN	7.21	7.76	383.75	174.51	38.10	0.14	13.10	66.96	4.78	7.00	2.23	10.40
SD	3.96	0.37	44.37	31.04	14.08	0.09	4.48	10.27	1.20	2.16	1.41	2.58
Hydro-chemical group B												
MIN	-0.20	5.62	329.00	45.76	31.50	0.00	11.57	43.69	0.24	4.24	0.60	0.99
MAX	18.60	8.57	814.00	293.49	170.60	0.70	49.63	147.49	10.21	19.90	23.80	12.81
MEAN	5.97	7.59	513.74	166.38	64.50	0.11	22.21	87.88	5.13	9.88	5.12	7.24
SD	3.30	0.49	110.73	50.53	19.50	0.09	5.80	23.13	1.63	3.20	3.64	1.92
Hydro-chemical group C												
MIN	-0.40	5.01	58.00	6.10	2.33	0.00	3ą.39	6.06	0.81	2.20	0.36	0.22
MAX	17.10	8.10	408.00	226.98	89.25	0.47	20.56	75.73	6.08	12.90	7.56	12.12
MEAN	5.66	6.99	243.67	96.51	33.09	0.09	9.41	41.88	2.95	4.77	2.08	6.89
SD	3.64	0.66	81.73	45.10	17.51	0.10	3.71	16.28	1.00	1.64	1.21	2.52

Source: authors' own study.

The distribution of group membership and confusion index is shown in Figure 4. When analysing the distribution of group membership to the singled-out hydro-chemical groups, attention should be turned to that all the three groups are dominated by their mean values. The 'A' hydrochemical group is characterised by a bimodal distribution with outstanding dominant mean (approx. 0.5) and higher (0.7–0.8) membership values. The 'B' hydrochemical group is dominated by membership values in the range of 0.6–0.7, while the 'C' hydrochemical group – apart from mean membership values – figures above 0.8 are at a higher percentage.

The confusion index for all the groups takes the full range of its variation. In case of assignment to the 'A' group (referred to as medium-mineralised waters) in most cases the 'B' group constitutes the sub-dominant group (referred to as high-mineralised waters). The ionic composition of waters in the 'A' hydrochemical group, apart from the environmental conditions, is a result of the supply of low-mineralisation surface

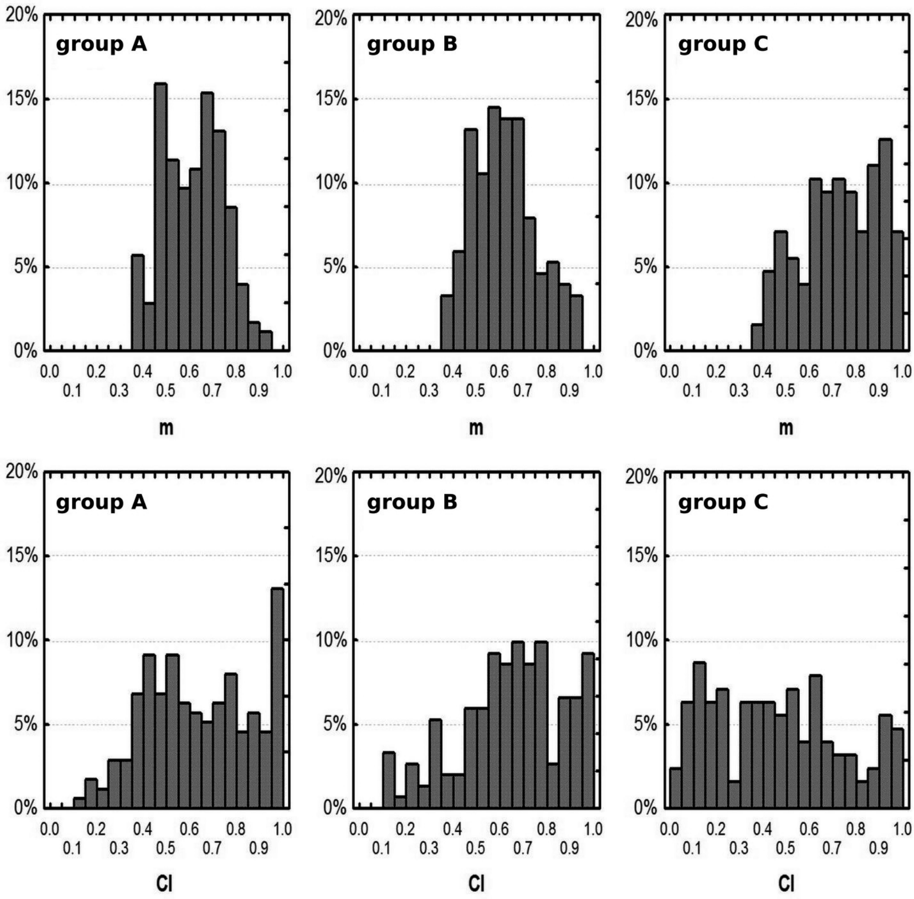

Fig. 4. Distribution of group membership values (m) and confusion index (CI) values given for individual hydro-chemical groups

Source: authors' own study.

run-off waters, which leads to water dilution with an increase in water flows. In case of other hydrochemical groups (B and C) the sub-dominant group is subject to changes for individual stands. The data presented in Figure 4 shows that under rising-water conditions the upper Parsęta catchment is a mixture of waters derived from various origins and with various circulation times, so it is possible to assess differences in their proportions only. It is not justified to single out acute hydro-chemical classes because it is not possible to determine clear boundaries between and among them.

Temporal variability of the hydro-chemical groups

The results of the water hydrochemical classification are relevantly varied for individual mappings (Fig. 5, 6). Attention should be turned above all to proportional changes between the hydrochemical mappings made in-between 1992–1994 and

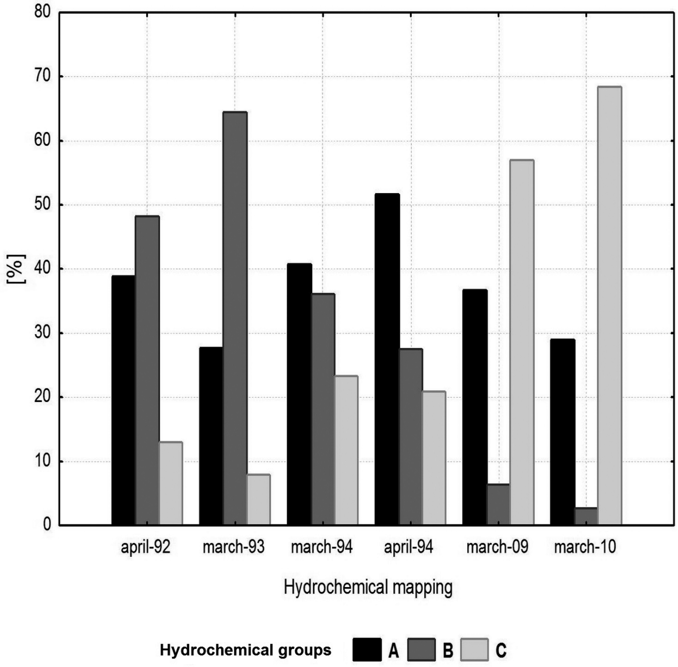

Fig. 5. Shares of hydro-chemical groups for surveys in the upper Parsęta catchment in spring periods in-between the periods 1992–1994 and 2009–2010

Explanations: A – group of medium-mineral-content waters, B – group of high-mineral-content waters, C – group of low-mineral-content waters

Source: authors' own study.

2009–2010. Taking into consideration the mappings made in March 2009 and March 2010, the dominance of stands classified in the 'C' hydrochemical group (i.e. with low-mineralised waters) stands out clearly, while in the period from 1992 to 1994, this group had the lowest number of stands.

Between the period of 1992–1994 and 2009–2010 a transition of some stands is reported from the 'A' hydrochemical group to the 'C' group or from the 'B' group to the 'C' group. The clearly increased share of the 'C' group (low-mineralised waters) with the decreased share of the 'B' hydrochemical group (high-mineralised waters) is caused by meteorological and hydrological conditions in this period. Also, for some measurement sites the share of anthropogenic sources was decreased. This article assumes that, apart from chloride ions, changes in the methodology of laboratory analyses had no impact on the results.

The higher share of stands assigned to the 'C' group in the hydrochemical mapping made in March 2010 is also an effect of meteorological and hydrological conditions. This mapping was made during the highest flows in the 2010 hydrological year resulted from intense thawing. Increased flows and supplies of surface run-off waters lead to the dilution of Ca^{2+}, HCO_3^- and a drop of water mineralisation. And this is the most likely cause of the high share of the 'C' group in March 1994.

The share of waters classified in the 'A' hydrochemical group (medium-mineralised waters) does not show any significant changes between the period of 1992–1994 and 2009–2010. Changes in the share of this group in the hydrochemical mappings should be linked with diverse hydrological conditions during the period of the research studies.

Spatial diversity of the hydro-chemical groups

The 'A' hydrochemical group corresponds to medium-mineralised waters with their specific electrolytic conductivity ranging 241 $\mu S \cdot cm^{-1}$-556 $\mu S \cdot cm^{-1}$ and averaging 384 $\mu S \cdot cm^{-1}$. It covers mainly the lower section of the upper Parsęta, Kłuda, Leśny Stream and Krętacz. This group includes both streams alimented by capacious groundwater reservoirs with low pace of resources recession (the Leśny Stream, Krętacz, the lower Kłuda) as well as the stands with their ionic composition of waters being the result of the moraine upland area drainage to upper stream channel sections (the lower and middle Parsęta river, the lower Młyński Stream). These both types of highly-mineralised groundwater supply are effectively diluted during spring high-flows.

The 'B' hydrochemical group corresponds to highly-mineralised waters with their specific electrolytic conductivity ranging 329 $\mu S \cdot cm^{-1}$-814 $\mu S \cdot cm^{-1}$ and averaging 514 $\mu S \cdot cm^{-1}$. It covers mainly the upper section of the upper Parsęta, the upper section of the Dalęciński Stream and Suchy Stream as well as several tributaries of the Żegnica river in the village of Chwalimki. In case of the Dalęciński Stream and upper Parsęta, higher concentration levels of individual ions are conditioned by the lithology of surface formations (presence of carbonate organic deposits in the ground). The Parsęta springs are located within anarea formed at the place of a former lake artificially drained in the 19th century (Piotrowska 1994) and filled with gyttia and lacustrine chalk sediments containing – at most cases – above 90% calcium carbonate (Kostrzewski, Zwoliński 1992a). In case of the Suchy Stream and the Żegnica tributaries, higher concentration levels of specific ions is associated with anthropogenic sources. Both of the sources of flow components have enough high conductivity and concentration levels of the selected ions so even high spring water flows are not able to sufficiently dilute them within relatively short initial runs of these streams.

The 'C' hydrochemical group included the stands located at small streams with their alimentation areas limited to local groundwaters. These stands primarily represent waters with short circulation times (also indicated by low reaction (pH) values, i.e. 6.99 – slightly acidic) fed mainly by soil-through and precipitation waters. The stands in this group are characterized by their lowest specific electrolytic conductivity (58–408 $\mu S \cdot cm^{-1}$, average 244 $\mu S\ cm^{-1}$) and the lowest concentration levels of bicarbonate ions, calcium, magnesium, i.e. standard denudation-originated components (weathering). Also the lowest average temperature of the water samples in this group confirms this interpretation.

Conclusions

The classification of physicochemical properties of surface waters in the upper Parsęta catchment (developed by Kostrzewski *et al.* 1994), taking into account the hydrochemical mappings results made during summer low water levels as well as spring periods, led to distinguish 5 hydrochemical groups: Group A, B – high-mineralisation waters associated with the presence of carbonate organic deposits in the ground (Group A) and the presence of calcium carbonate sediments building the moraine upland in the southern and eastern part of the catchment (Group B), Group C, D – medium-mineralisation waters having different concentration levels of ionised silica (Group C and D differ in concentration of silica) and Group E – low-mineralisation waters. The hydrochemical groups singled out by these authors primarily reflect the impact of lithology and soil-cover onto the formation of the chemical composition of waters. The ionic composition of waters also results from varied supplies of streams from different aquifers which are characterized by different water routes and circulation times.

The results presented in this article indicate that during spring high flows also meteorological and hydrological conditions in the period prior to sampling have a high impact onto the chemical composition of river waters within the upper Parsęta catchment. These conditions – to a large extent – may have weakening effects onto the diversity of river waters resulted from lithological and soil conditions. It is reflected in the resultant fuzzy hydrochemical classification of these waters. In the division into 3 groups, the presence of carbonate organic deposits (higher concentrations of individual ions) and the share of surface and subsurface run-off waters in the alimentation of water courses (streams) are clearly perceptible. There is no differentiation within medium-mineralisation waters due to concentration levels of ionised silica. During the spring high-water flows the increased share of surface and subsurface run-off waters feeding water courses (streams) affects low concentration levels of Ca^{2+}, Na^{+}, HCO_3^-, SiO_2 (denudation-weathering ions). Through feeding the river network by low-mineralisation melting waters it results in the dilution of Ca^{2+}, HCO_3^- which translates into no differences within medium-mineralised waters.

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